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Analysis of odour and taste problems in high-density polyethylene

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Abstract

The compounds that cause off-flavours in plastics, have been recognized mainly as carbonyl compounds (aldehydes, ketones and esters). They occur in low concentrations, and due to their low-threshold odour concentrations, their typical odours were identified. Most of these off-flavour compounds are volatile. Chemical analysis of smelling compounds requires a very sensitive method with a high-resolution capability. The analysis of volatile organic compounds (VOCs) in high density polyethylene (HD-PE) granules and waters in which the granules have been shaken for 4 h, were carried out by gas chromatography–mass spectrometry–sniffing system (GC–MS–SNIFF) and by gas chromatography–fourier transform infrared spectroscopy–sniffing system (GC–FTIR–SNIFF). A purge-and-trap technique was used to introduce the VOCs from samples into the gas chromatograph. Leaching waters of HD-PE granules were also evaluated by panel. This panel agreed upon six descriptive attributes for odour: sweet, chemical, stale, dusty, foul and floor-cloth. The attributes for taste were: sweet, metallic, stony, pungent, dusty, plastic, foul, stink bug and candle grease. © 1997 Elsevier Science B.V.

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1. Introduction

Plastics are used in an overwhelming variety of applications. There are many types of polyethylene, each with a specific property and use. When more heat-tolerant, inflexible and compact products are needed, high density polyethylene (HD-PE) is used [1]. Pipes made of HD-PE are also generally preferred for buried sections. Because water should be odourless/tasteless, the pipes must be free of off-flavours. The majority of public complaints likely to be faced by a water utility concern taste and odour problems in drinking water. For many reasons it is

important to know the identity and levels at which contaminants are present [2].

The additives (antioxidants, plasticizers, solvents and cross-linking agents) that are used to improve the plastic quality and confirm the process, can cause off-flavours [3]. In addition, synthetic polymers often contain small amounts of residual volatile monomers (styrene, vinyl acetate, acrylates) derived from PE process. These monomers and solvents can be transferred from the inner surface of the plastic pipe to the water after water has been standing for some time. When polymer is heated, it may release into the water volatile compounds that cause tainting and smelling [4–6]. Also some off-flavours are transferred by contamination through the plastic pipe wall from the surrounding earth [7].

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The smell of polyethylene is often described as unpleasant plastic. In general, the threshold odour concentrations (TOCs) of carbon and hydrogen compounds are not very low. However, many terpenes and unsaturated and branched hydrocarbons are more odorous than linear hydrocarbons [4,5]. Atoms such as oxygen, nitrogen and sulphur in certain functional groups in alcohols, aldehydes, amines, esters, ketones etc., make up what have been called odour-bearing groups [8]. An off-odour can be produced by a single chemical compound or by a mixture of several substances. The relative concentrations of the mixture components make a description of the odour impression difficult [9].

Taste and odour of polymers are difficult to measure. It is important to identify chemicals causing odours and tastes in plastics. Sniffing with the human nose is an effective way to find out the sensory active trace compounds [10,11]. The use of a one-column system, when sample is injected twice, is one of the sniffing techniques, and the another is simultaneous sniffing, where the column system is divided into two identical columns [12–14]. Most of the analytical methods for plastics involve headspace sampling to introduce compounds into the gas chromatography–mass spectrometry (GC–MS) system [15]. Headspace gas chromatography (HSGC) is divided into two categories: static HSGC and dynamic HSGC (purge and trap). The analytical method requires high sensitivity; the recovery of the volatile compounds depends on e.g., desorption temperature and sampling temperature [16,17]. All things considered, the headspace method is very useful when analysing plastics: non-volatile compounds do not occur and solvent extractions can be avoided [18–22]. In addition, the essence of the purge-and-trap method is its ability to transfer odorous volatile analytes from plastics into the gas phase, so that they can be analysed by GC–MS [23]. Fourier transform-infrared spectroscopy (FTIR) spectra confirmed the structures of compounds containing functional groups [10].

The purpose of the present study was to investigate the off-flavour compounds in high-density polyethylene (HD-PE) used for pipe manufacture. In addition, the oxidation of the internal surface of the pipe during extrusion and dissolution of additives can cause organoleptic changes [24]. The volatile

organic compounds of polyethylene granules were identified using GC–MS. In addition, water soluble compounds were tested by leaching the granules with odour-free water and then analysing water by smelling and tasting it. Based on the sniffing technique, using the human nose as a detector, the MS spectra of bad smelling compounds were further interpreted and discussed.

2. Experimental

2.1. Sample preparation

The samples were black high-density polyethylene (HD-PE) solid granules (4 mm in diameter and 2 mm thick), which are encoded in Table 1. Samples were received from Neste Polyeten, Stenungsund, Sweden (at present: Borealis). Polyethylene granules (18 g) were placed into a 25 ml sample tube (Tekmar purge and trap sample tube) and purged with helium (40 ml/min) for 12 min and analysed under the optimized conditions shown in Table 2. Water removable compounds of granulates were analysed by placing granules (32 g) into 250 ml odour-free water (Ultra High Quality ELGA-water) and the mixture was shaken for 4 h at room temperature. After 24 h, 5 ml of leaching water was analysed under the same conditions as the granule samples.

2.2. Instrumental analysis

A VG AutoSpec (Manchester, UK) high-resolution mass spectrometer connected to a HP 5890 Series II gas chromatograph was used in the mass spectrometric analysis of the polyethylene granules and their leaching waters. The mass spectrometer was scanned from m/z 39 to 350 at a cycle of 1 s. The ion source was kept at 250°C and the electron ionization potential (EI) was 70 eV. Purge-and-trap system Tekmar 2000 (Cincinnati, OH, USA) was used to introduce the samples into the GC–MS system. The purge gas was high purity (99.995%) helium. The purge gas flow was 40 ml/min. All the lines in the Tekmar 2000 were kept at 100°C and the temperature of the mount was 40°C. The trap material was Tenax GC (2,6-diphenylene oxide). The GC-column

Table 1
Encoded polyethylene samples and the results of odour and taste panels

Encoded as	Odour panel	Taste panel
Granule black 1	(good) ^a	(good) ^a
Granule black 2	(bad) ^a	(bad) ^a
Water 1 (water of black 1 granules)	Sweet ++ Chemical + Stale +++ Dirty ++ Foul ++	Sweet ++ Metallic +++ Stony ++ Pungent ++
Water 2 (water of black 2 granules)	Stale ++ Dirty ++ Foul +	Dusty ++ Stale +++ Plastic +++ Foul +++ Stink bug + Candle grease +

^a This result is based on the taste panel of the producer.

Relative odour/taste intensity: +=weak; ++=moderate; +++=strong.

was a Noribond SE 54 25 m×0.25 mm I.D. (1 μm phase) and there were two identical columns. The carrier gas flow-rate was 1.5 ml/min. The eluted compounds from one column were sniffed with the nose at the same time as the peak of the same compound appeared on the total ion chromatogram (TIC). In the sniff port the column is lead through the open wall inside a copper tube to the sniffing funnel [13]. Use of a moist air stream prevented the nose from losing its sensitivity to flavours [14]. The temperature program of the GC oven was 40°C (5 min)–5°C/min–250°C (10 min).

IR-spectra were obtained by a HP FTIR detector

Table 2
Operating conditions of purge and trap equipment

Function	Time/temperature
Prepurge time	3 min
Preheat time	3 min
Sample temperature	75°C (waters) 100°C (granules)
Purge time	12 min
Dry purge time	6 min
MCM (moisture control module)	0°C
Cryo cooldown	–120°C
Desorb preheat	175°C
Desorb time/temperature	4 min/180°C
Inject time/temperature	0.85 min/250°C
Bake time/temperature	7 min/225°C

5965A connected to GC–FID (flame ionization detection) system. The GC column was a 30 m×0.53 mm I.D. wide bore HP-5 (phase 2.65 μm), the carrier gas flow-rate was 4 ml/min. A Tekmar 2000 Purge-and-Trap system was used to introduce the samples into the GC. An initial temperature for gas chromatogram oven of 40°C for 5 min was used, followed by increasing the temperature at a rate of 5°C/min to 250°C and a final hold for 10 min.

2.3. Sensory evaluation

To the panellists, students and staff of the Chemistry Department of University of Jyväskylä, 5 ml of both leaching waters (water 1 and water 2) were provided and they were asked to characterize the taste and odour of waters using their own expressions. The attributes of water are listed in Table 1.

2.4. Quantitative measurements

Quantitative measurements of off-flavour compounds were done by using the external standard-method. One μl of a standard solution containing aldehydes and ketones was analysed by GC–MS using the same operating conditions as described in Section 2.2. The sample run was repeated seven times to confirm the amount of volatile compounds

of the sample. The peak areas of off-flavour compounds of seven determinations were observed and compared with the peak areas of the standard solution and the concentrations of smelling compounds were calculated.

3. Results and discussion

3.1. Results of GC–MS–SNIFF

3.1.1. Granule samples

The shapes of TICs were very similar, with the majority of identified compounds being hydrocarbons with no odours. Differences between “good” and “bad” samples were noticed by comparing the perceived odours. There were more bad odours with stronger intensities in black “bad granule” samples (black 2) than in “good granule” samples (black 1). These latter samples were not further analysed by the panelists (Table 1). The amount of odour-causing compounds was small, but the odours were strong. Most of these off-flavour compounds were carbonyl compounds with one alkylbenzene (toluene with model-glue odour) and one hydrocarbon (2,2,4,6,6-pentamethylheptane with stony, dusty odour). The strongest odours were caused by 2-octenal (mushroom odour) and butylacrylate (glue-like odour) in black “bad granule” sample (black 2). These two compounds were not detected in black “good granule” sample (black 1). In addition, 2-propanal, the smell of which was glue-like, methylhexanal with pungent, green odour and some ketones (C_6 – C_8) with moderate odours did not appear in black “good granule” sample (black 1). The TICs of black granules with odours and corresponding compounds marked are shown in Fig. 1 and the amounts of smelling compounds are presented in Table 3.

3.1.2. Water samples

Two water samples where granules were shaken are encoded in Table 1. There were no carbonyl compounds (aldehydes, ketones) in the “good water” sample (water 1). The two main compounds were hydrocarbons: 2,2,4,6,6-pentamethylheptane (stony odour) and 1-dodecene which did not cause any odour. 1-Dodecene was present in much greater quantities than any of the other compounds. In “bad

water” sample (water 2) there were three carbonyl compounds: 2,4-heptadienal causing bad odour, nonanal with bad unpleasant aldehydic odour and undecadienal with weak pungent odour. The strongest odour (glue) in “bad water” (water 2) was caused by ethylpropanate. The amount of that compound was quite small (0.1 ng/sample/l). The amount of hydrocarbons was two-fold greater in “bad water” (water 2) than in “good water” (water 1). The amounts of smelling compounds are shown in Table 3 and the tainting compounds and corresponding odours and intensity of odours are presented in Table 4.

3.2. Results of GC–FTIR–SNIFF

To verify the GC–MS results by identifying the functional groups, the granulates were tested by GC–FTIR. Off-flavour compounds were present in very low concentrations, so the functional group analysis by IR was very useful in confirming the mass spectrometric results. FTIR is less sensitive than MS in obtaining reasonable IR-spectra as sample concentration was higher than with MS runs. Since the GC conditions in MS and FTIR runs were similar and the columns were of the same type (Noribond SE54 and HP-5), the chromatograms were easy to confirm.

3.3. Results of odour and taste panels

After shaking the granules (32 g) in odour-free water (1000 ml), samples were given to panellists for odour and taste description. The evaluations of odours were sweet, little bit dirty and stale when smelling the leaching water of black “good granules” and the odour descriptions were stale, dirty and foul when smelling the leaching water of black “bad granules”.

The taste of leaching water of black “bad granules” was described by some panellists as dusty, stale, plastic, foul, stink bug and candle grease. The leaching water of black “good granules” had weak sweet, metallic, stony and pungent taste and some panellists did not detect any taste at all. The results of odour and taste panels are shown in Table 1.

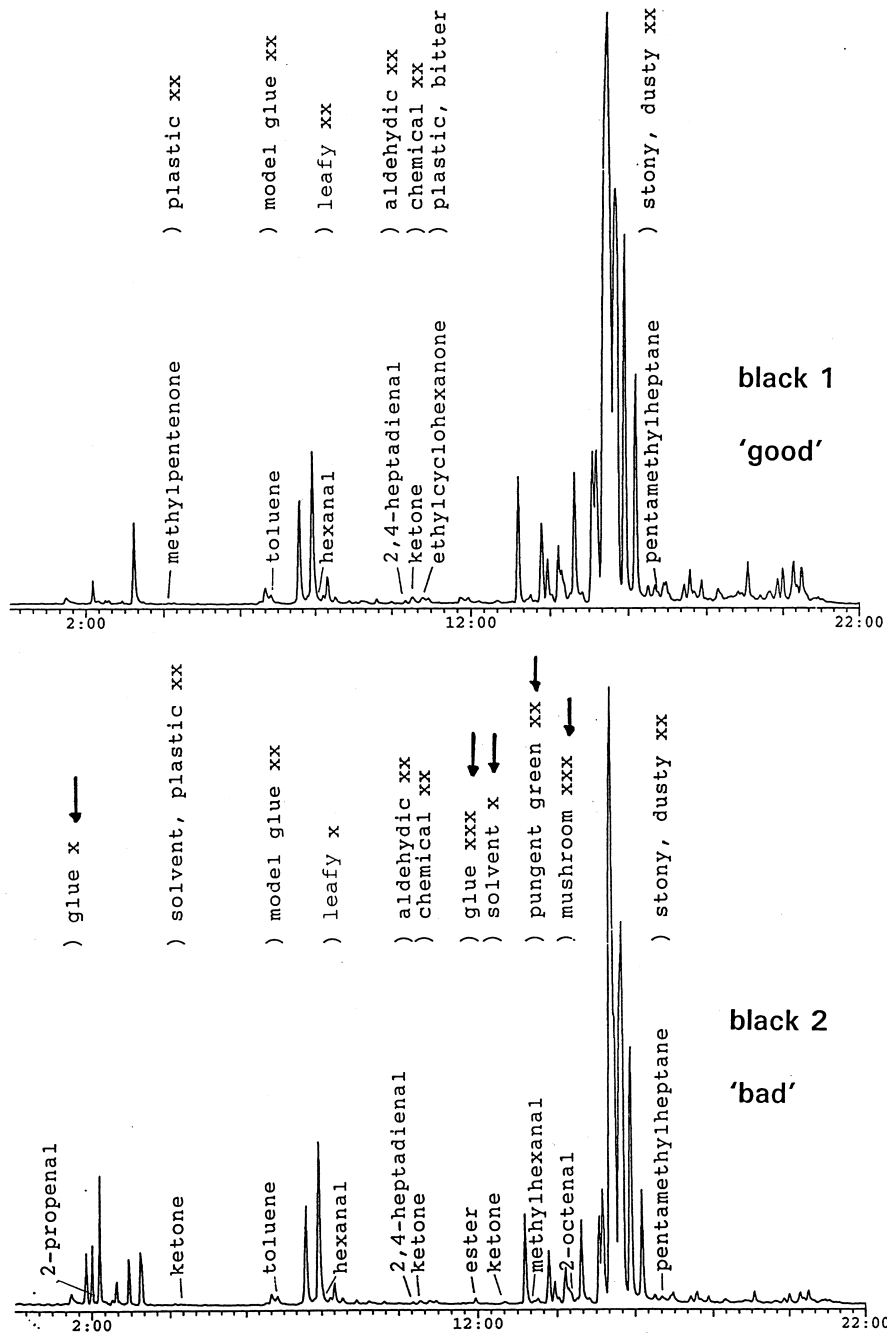


Fig. 1. TICs of granule samples with odours and corresponding compounds marked (differences in odours have been marked with arrows).

4. Conclusions

The compounds that caused the off-flavours in

plastic pipes have been mainly characterized as carbonyl compounds.

The purge-and-trap system connected to the GC-

Table 3
Calculated amounts of off-flavours (ng/sample/l) in samples

Compound	Calculated amounts of off-flavours			
	Black 1	Black 2	Water 1	Water 2
2-Propanal	–	34.2	–	–
Ethyl propanate	–	–	–	0.1
C ₆ -Ketone	0.5	–	–	–
Methylpentenone	–	2.0	–	–
Toluene	52.5	36.9	–	–
Hexanal	6.4	53.4	–	–
2,4-Heptadienal	9.0	29.4	–	0.1
C ₇ -Ketone	1.8	2.2	–	–
Ethylcyclohexanone	1.8	–	–	–
Butyl acrylate	–	65.6	–	–
C ₈ -Ketone	–	0.9	–	–
Methylhexanal	–	44.2	–	–
2-Octenal	–	50.2	–	–
Nonanal	–	–	–	0.2
Pentamethylheptane	33.5	8.7	0.1	0.2
1-Dodecene	–	–	25.5	52.5
Undecadienal	–	–	–	0.3

MS system with simultaneous sniffing is a very powerful technique for solving the off-flavour problems of HD-PE. Some of the odours were just detectable and because of the good sensitivity of this

equipment it has been possible to focus on those compounds that participate in tainting and smelling. Bad odours were chosen for more detailed study.

When comparing granulate samples the main

Table 4
Tainting compounds and corresponding flavours and intensity of odours in samples

Compound	Odour	Intensity of odour			
		Black 1	Black 2	Water 1	Water 2
2-Propanal	Putrid, glue	+			
Ethyl propanate	sweet, candy				+++
C ₆ -Ketone	Solvent, plastic		++		
Methylpentenone	Plastic	++			
Toluene	Model glue	++	++		
Hexanal	Leafy	++	+		
2,4-Heptadienal	Aldehydic	++	++		+++
C ₇ -Ketone	Chemical	++	++		
Ethylcyclohexanone	Bitter	+			
Butyl acrylate	Glue		+++		
C ₈ -Ketone	Solvent		+		
Methylhexanal	Pungent green		++		
2-Octenal	Mushroom		+++		
Pentamethylheptane	Stony, dusty	++	++	++	++
Nonanal	Bad, aldehydic				+++
Undecadienal	Pungent				+

Relative odour intensity: +=just noticeable odour; ++=moderate odour; +++=strong odour.

difference between “good” and “bad” granule samples were the larger amounts of aldehydes (2-propanal, methylhexanal and 2-octenal) in the “bad” one.

In leaching waters of granule samples (“good” and “bad” waters) there were no bad smells in “the good” one. In the “bad” one, an ester, one dienal and also a nonanal caused unpleasant odours.

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