Food Chemistry **46** (1993) 367–371

Combined gas chromatography and sniffing port analysis of volatile compounds of mineral water packed in polyethylene laminated packages

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(Received 12 May 1992; accepted 8 July 1992)

Commercial mineral waters packed in polyethylene-lined aluminium/cardboard packages were incubated at 40°C and sensorially evaluated for intensities of the descriptors: synthetic, musty, sickly, metallic, astringent and dry. Tasting of these samples with the use of nose clips diminishes the intensities of the descriptors significantly, except for dry. Volatile compounds of this mineral water were analysed by sniffing the effluent of a gas chromatographic column, which provided similar descriptors as above. The components detected by sniffing were tentatively identified by combined gas chromatography and mass spectrometry as being mainly aromatic hydrocarbons and carbonyls. Semi-quantitative analysis showed that the concentrations of the compounds which migrated into the mineral water ranged between 10 and 15 ppb. Storage at elevated temperatures seems to involve flavour deterioration, because no taint was observed in mineral water samples, which were incubated at 20°C.

INTRODUCTION

The rapid substitution of relatively inert materials such as glass and metal with more interactive synthetic polymers for packaging materials has created new problems concerning interactions between foods and their packages. Migration of low molecular weight components from these polymers to a packed product can result in a change of flavour, and so affect the perceived quality of the product (Harte & Gray, 1987). Polyethylene (PE) packaging material is widely used by the food packaging industry, because of its low costs and outstanding service properties (Giacin, 1980). It is used in mono- and multilayer systems as well as in lined cardboard and aluminium packages. During the PE polymerisation process, oxygen and peroxides are added to initiate radical reactions and consequently it is possible to have carbonyl and carboxyl groups present in PE (Shorten, 1982). Additional oxidation products can be formed during high-temperature processing in the presence of oxygen, e.g. extrusion coating (Hoff & Jacobsson, 1981; Hoff *et al.*, 1982). Extrusion conditions of low-density polyethylene (LDPE) can affect the flavour of the packed product: higher melt temperatures were responsible for increased off-taste intensity of drinking water in contact with PE (Potts *et al.*, 1990).

There is hardly any information about the nature of taint of foods, originating from interactions between food and PE. Kiermeier and Stroh (1969) suggested an exchange of ions between the cations of milk-salts and the acidic proton of carboxyl groups of PE as responsible for a 'plastic flavour' sometimes found in milk. Bojkow *et al.* (1976) have not found significant changes in taint intensity of milk packed in PE-lined cardboard after one week of storage. Berg (1980) reported that products such as spring water, milk and fruit juices frequently have a taint after being stored in bottles of PE or PE-lined cartons. In PE granulate he found volatile compounds like saturated and unsaturated hydrocarbons, aromatic hydrocarbons and aromatic hydrocarbons with an unsaturated side chain. An 'intense plastic off-flavour' was ascribed to C_3- and C_4-alkyl benzenes. Also C_2–C_5 carbonyl and carboxyl compounds can influence taste and odour of a packed product (Bojkow, 1982). Carbonyls such as 2-nonenal and 1-hepten-3-one were identified as a source taint in water packed in LDPE-lined cardboard by Koszinowski and Piringer (1983). The taint was described as candle-grease, musty, rancid and soapy. Degradation products formed during extrusion lamination of an ionomer, in which PE was the major component, were studied by Fernandes *et al.* (1986). Mainly carbonyl compounds such as pentanal, 2-hexanone and 3-heptanone were identified. Performing combined gas chromatography and sniffing port analysis (GC-sniffing) the aldehyde was described as pungent

Food Chemistry 0308-8146/93/$06.00

and the ketones as acrid. In our former study, the taint of water packed in PE-lined aluminium test pouches was described as musty, sickly, astringent, synthetic, metallic and dry. Additional instrumental analysis showed that C_4–C_{11} carbonyls could be responsible for the taint (Linssen *et al.*, 1991).

The aim of the present study was to describe and identify volatile compounds in commercial mineral water packed in PE-lined aluminium/cardboard packages. Techniques used were GC-sniffing and gas chromatography combined with mass spectrometry (GC–MS).

MATERIALS AND METHODS

Sample preparation

Commercial mineral waters packed in 2 litre packages of LDPE-lined aluminium/cardboard (test samples) were bought at a local store in Wageningen (The Netherlands). Reference mineral water packed in glass bottles was kindly provided by the manufacturer and used as a control. Test samples were incubated at 20°C and 40°C for 24 h. These samples and the control were used for flavour intensity studies and for preparation of dynamic headspace samples for analysis by GC-sniffing and GC–MS. Dynamic headspace samples were prepared by purging 2 litres of water at 40°C for 1 h with purified nitrogen at a flow rate of 100 ml/min. A cold trap (−10°C) was used for retention of water vapour, and volatile compounds were trapped on Tenax TA (35/60 mesh; Alltech Nederland BV, Zwijndrecht, The Netherlands).

Sensory evaluation

In our former study the PE taint of water packed in LDPE-lined aluminium test pouches was described by 6 attributes: metallic, synthetic, dry, astringent, musty and sickly (Linssen *et al.*, 1991). These attributes were now used for a flavour intensity study of commercial mineral water packed in LDPE-lined aluminium/cardboard packages. A panel of 11 assessors was selected and trained. All of them were students of the Wageningen Agricultural University and aged 20–25 years. Part of the training was utilisation of a 180 mm visual analogue scale on a portable computer screen (Toshiba T1000; Toshiba America, Inc., Irvine, California, USA) for scoring perceived flavour intensities.

A computer interactive interviewing system for composing questionnaires was used to gather survey information (Ci2 system; Sawtooth Software Inc., Ketchum, Idaho, USA). The portable computers with field disks were placed in sensory evaluation booths. Each assessor entered his/her personal code, after which detailed information about evaluation of the samples was displayed on the screen. Data from the field disks were accumulated with the Ci2 program onto a hard disk (ES/12 computer; HP Vectra, Amstelveen, The Netherlands) and converted into an SPSS 'include file'. The SPSS program (MANOVA) was used for statistical evaluations. Samples were tasted at room temperature with and without the use of nose clips (Jaeger Nederland BV, Breda, The Netherlands).

Gas chromatography

GC-sniffing was performed with a Carlo Erba gas chromatograph, type 6000 VEGA series (Interscience BV, Breda, The Netherlands). A thermal desorption/cold trap device (Chrompack TCT injector 16200; Chrompack, Middelburg, The Netherlands) was used for transferring the volatile compounds from the Tenax onto a fused silica capillary column (DB 1; 30 m × 0·32 mm, film thickness 1·0 μm: J & W Scientific, Folsom, California, USA). An initial oven temperature of 60°C for 4 min was used, followed by a rate of 2°C/min to 140°C and 10°C/min to 250°C and a final hold for 5 min. The detector temperature was kept at 275°C. The gas chromatograph was equipped with a flame ionisation detector (FID) and 2 sniffing ports (SGE, Milton Keynes, UK), one at each side of the instrument. At the end of the capillary column the effluent was split 1 : 2 : 2 for FID, sniffing port 1 and sniffing port 2, respectively. Ten assessors, women aged 20–50 years, were selected on their availability, sensitivity, memory and ability to recognise odours. Prior to exit port sniffing of samples, the assessors were trained on the technique of sniffing with a standard mixture. The instrument was placed in a room made free from distracting odours and noise to create an ideal environment for the assessors. The maxima 820 system (Dynamic Solutions, Ventura, California, USA) recorded the FID chromatogram outside the room of the assessors. Supplementary air was bubbled through distilled water in a gas-scrubbing bottle, which runs through stainless steel tubing to the exit port in order to prevent drying out of assessors' nasal membranes during sniffing for approximately 40 min. Assessors used portable computers (Toshiba T1000) with a program in Pascal for data collection. They kept a button pushed on the keyboard during the time that they got an odour impression (Acree *et al.*, 1984). Using a Pascal program, the data were converted from the field disks into the Lotus 123 program for manipulation of the raw data.

A listing of 14 descriptors was obtained from a preliminary analysis by GC-sniffing of the volatile compounds obtained from water packed in LDPE-lined aluminium/cardboard packages (Table 1). Besides 'other', these descriptors had to be used for each component detected by the 10 assessors at the sniffing port. Tenax tubes without adsorbed volatile compounds were used as dummy samples for determining the signal-to-noise level of the group of assessors. FID calibration curves for pentanal, heptanal, decanal, 2-nonanone and ethylbenzene were prepared to estimate the concentrations of migrants in the mineral water.

Table 1. Odour descriptors used for sniffing port analysis

Dutch expression	English translation[a]
Champignon geur	Mushroom-like
Cacao	Cocoa-like
Fris	Fresh
Fruitig	Fruity
Gras	Green
Kunstmatig	Artificial
Lijm	Glue-like
Metaal	Metallic
Muf	Musty
Plastic	Plastic
Prikkelend	Astringent
Wee	Sickly
Zoetig	Sweet
Zuurtjes	Candy-like

[a] The English translation may not be an exact synonym of the terms used by the Dutch assessors.

The volatile compounds trapped on Tenax TA were identified by combined GC (Pye 204, Unicam Ltd, Cambridge, UK) and MS (VG MM 7070 F, Fisons Instruments, Weesp, The Netherlands), using the thermal desorption device, the capillary column and the temperature conditions described before. Mass spectra were recorded in the electron impact mode at an ionisation voltage of 70 eV and scanned from $m/z = 300$ to 25 with a cycle time of 1·8 s (Badings *et al.*, 1985; Olafsdottir *et al.*, 1985).

RESULTS AND DISCUSSION

The use of nose clips by the assessors in the flavour intensity studies diminishes significantly ($P < 0{\cdot}05$) the flavour intensities of the commercial sample incubated at 40°C for 24 h for each descriptor except for the descriptor 'dry'. The latter appears to be a kind of mouthfeel (Table 2). These findings indicate that most of the descriptors are related to volatile substances. Therefore, GC-sniffing is appropriate for further studies.

Figure 1A presents the average FID chromatograms ($n = 5$) of control (REF) and commercial LDPE-packed water samples, which were incubated at 20°C (BD 20) and 40°C (BD 40). Reconstructed chromatograms of the components detected at the sniffing port by more than four assessors at the same time, are shown in Fig. 1B. GC-sniffing of the dummy samples revealed that detection of a smell at the sniffing port by less than 5 out of 10 assessors, can be considered as 'noise'. Table 3 presents the compounds identified by

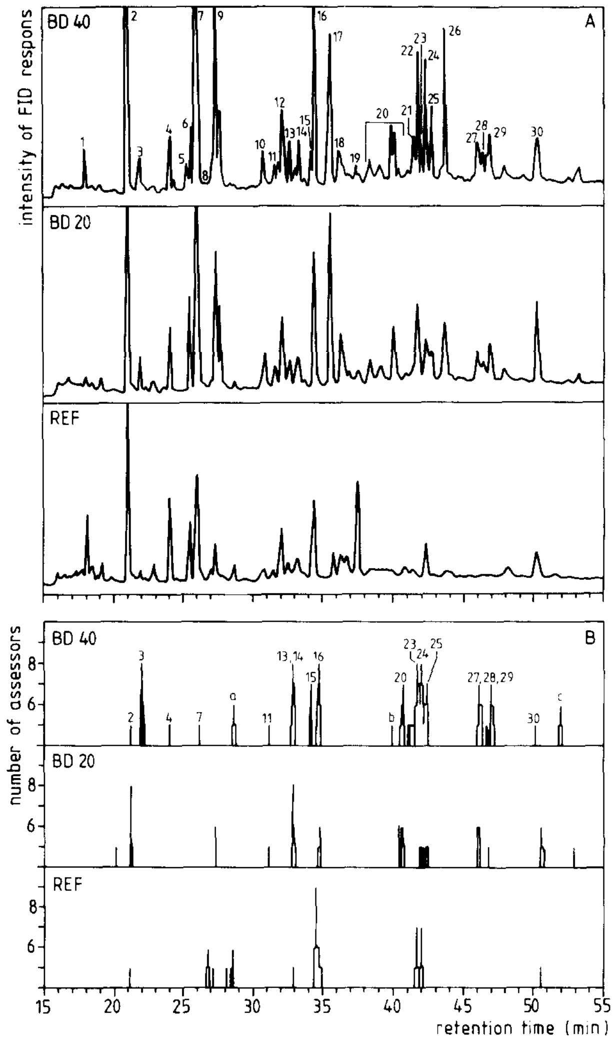

Fig. 1. Reconstructed chromatograms of dynamic headspace samples. Average of 5 replicates (A) and the number of assessors out of 10, who had a smell impression at the sniffing port at the same time (B). Corresponding responses have the same symbol. REF: control; BD 20 and BD 40: LDPE packed water samples incubated at 20°C and 40°C, respectively.

Table 2. Mean score (± SD) of intensity (%) obtained for each descriptor on a visual analogue scale of 180 mm with (N) and without (WN) the use of nose clips ($n = 11$)

Descriptors	Mineral water					
	Reference		20°C/24 h[a]		40°C/24 h[a]	
	N	WN	N	WN	N	WN
Metallic	28 ± 24	34 ± 25	20 ± 19	20 ± 18	23 ± 21	51 ± 23
Synthetic	20 ± 18	39 ± 32	15 ± 18	27 ± 23	18 ± 22	79 ± 21
Dry	41 ± 28	34 ± 22	45 ± 24	41 ± 22	35 ± 31	55 ± 26
Astringent	34 ± 25	31 ± 18	30 ± 23	28 ± 21	28 ± 25	48 ± 22
Musty	13 ± 10	30 ± 23	14 ± 11	31 ± 28	18 ± 16	58 ± 23
Sickly	21 ± 18	34 ± 24	18 ± 23	24 ± 17	23 ± 18	58 ± 20

[a] Temperature/time conditions for incubation of commercial mineral water samples 'as is'.

Table 3. Volatile compounds of mineral water incubated at 40°C in LDPE lined aluminium/cardboard packages and their odour description

Peak no.[a]	Compound	Odour description
1	Pentanal	
2	Toluene	Plastic, astringent, glue-like, ‘other’
3	Hexanal	Green, artificial, mushroom-like, fruity, musty, ‘other’
4	4-OH-4Me-2-Pentanone	Musty, fruity, ‘other’
5	Isopropyl acetate	
6	Ethylbenzene	
7	*p*-, *m*-Xylene	Plastic, musty, astringent, artificial,
a		Metallic, mushroom-like, ‘other’
8	Heptanal	
9	*o*-Xylene	
10	α-Pinene	
11	*n*-Propylbenzene	Fruity, sweet, ‘other’’
12	C$_3$-Alkyl benzene	
13	C$_3$-Alkyl benzene	Plastic, astringent, glue-like
14	C$_3$-Alkyl benzene	Musty, astringent, metallic
15	Octanal	Sickly, musty, candy-like, ‘other’
16	C$_3$-Alkyl benzene	Astringent, fresh, sweet, candy-like, fruity
b		Fresh, green, mushroom-like, sweet
17	2,2,4,6,6-Pentamethylheptane	
18	C$_3$-Alkyl benzene	
19	Limonene	
20	C$_4$-Alkyl benzene + branched alkanes	Artificial, musty, fresh, mushroom-like, musty, metallic, sweet, sickly
21	2-Nonanone	
22	Unknown	
23	Nonanal	Astringent, cocoa-like, mushroom-like, ‘other’
24	Unknown	Plastic, glue-like, metallic, artificial, musty
25	Unknown	Plastic, glue-like, metallic
26	Unknown	
27	Unknown	Plastic, astringent, sickly, metallic, artificial
28	Unknown	
29	Unknown	Plastic, glue-like, metallic, musty, artificial
30	Decanal	Artificial, plastic, metallic, plastic, sweet, glue-like, ‘other’
c		

[a] Peak no. corresponds to the peak symbols in Fig. 1.

GC–MS, and the odour described by the assessors at the sniffing port. ‘Glue-like’ is often mentioned as a new descriptor, while synthetic (plastic), metallic, musty, astringent and sickly were also generated in our previous study (Linssen *et al.*, 1991). The test pouches used then were made of aluminium and LDPE-coated at a relatively high temperature of 310°C, so they are not directly comparable with a commercial LDPE-lined package. Moreover, the pouches were immediately folded and sealed after LDPE lining to prevent evaporation of volatile compounds. In that case, carbonyls were identified to be responsible for the taint described. However, as can be seen in Table 3, mainly aromatic hydrocarbons such as toluene, xylenes, *n*-propylbenzene, C$_3$- and C$_4$-alkyl benzenes, and some unknowns, were found to be the compounds corresponding to the descriptors given by the assessors. Berg (1980) reported similar compounds in PE granulate and indicated that C$_3$- and C$_4$-alkyl benzenes have an ‘intense plastic smell’. In Fig. 1A, differences between test samples and control mineral water were notably found for three groups of compounds: isomers of C$_3$-alkyl benzenes with retention times 32–34 min (peaks 12–16) and two groups of unknown isomers with retention times 42–44 min (peaks 22–26) and 46–47 min (peaks 27–29). At the same retention times, sniffing port assessors agreed upon the detection of volatile compounds from the LDPE-packed water samples (Fig. 1B). The absence of a descriptor for 2,2,4,6,6-pentamethylheptane is remarkable, because this compound has been suggested for the taint sometimes found in LDPE-packed products (vom Bruck & Hammerschmidt, 1977). In Table 3, pentanal, hexanal, heptanal and octanal were found to be present in the LDPE-packed mineral water sample, which was incubated at 40°C. Also, the unknown compounds are (probably branched) carbonyl compounds. The latter are hardly present in the control sample, but appear as higher peaks in the FID chromatograms of the LDPE-packed mineral water samples after incubation.

Semi-quantitative analysis showed that the concentrations of the compounds identified by GC–MS are in the very low ppb range. Ethylbenzene, pentanal, heptanal, decanal and 2-nonanone are below a level of 2 ppb; none of the compounds will exceed a level of 10–15 ppb.

The results of this study indicate that the main descriptors for volatile compounds (separated by gas chromatography) in commercial mineral water packed in LDPE-lined aluminium/cardboard and incubated at 40°C are: plastic, astringent, musty, sickly, glue-like and metallic. Isomers of C$_3$-alkyl benzenes and isomers of unknown carbonyls appear to be responsible for these descriptors. The concentrations of these compounds are in the very low ppb range. Storage at higher temperatures for a longer time can imply flavour deterioration.

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