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Development of a headspace solid-phase microextraction–gas chromatography–mass spectrometry method for the identification of odour-causing volatile compounds in packaging materials

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Abstract

A method for the identification of volatile organic compounds in packaging materials is presented in this study. These compounds are formed by thermooxidative degradation during the extrusion coating process in the manufacture of packaging. Headspace solid-phase microextraction (HS-SPME) was used as sample preparation technique prior to the determination of the volatile organic compounds by gas chromatography–mass spectrometry (GC–MS). The effects of extraction variables, such as the type of fibre, the incubation temperature, the pre-incubation time, the size of the vial and the extraction time on the amounts of the extracted volatile compounds were studied. The optimal conditions were found to be: carboxen–polydimethylsiloxane 75 μm fibre, 5 min of pre-incubation time, 100 °C of incubation temperature, 20-ml vial, and 15 min of extraction time. The chromatograms obtained by HS-SPME and static headspace extraction were compared in order to show that the HS-SPME method surpasses the static headspace method in terms of sensitivity. Twenty-five compounds were identified including carbonyl compounds (such as 3-methyl-butanal, 3-heptanone or octanal), carboxylic acids (such as pentanoic acid or hexanoic acid) known as odour causing compounds and hydrocarbons (such as decane, undecane or dodecane). Finally, the method was applied to different packaging samples (one odour-unacceptable, two odour-acceptable, and three odourless samples) and to the raw materials in order to find out the odour-responsible volatile organic compounds and their source.

Keywords: Headspace analysis; Solid-phase microextraction; Packaging materials; Off-flavor compounds; Volatile organic compounds

1. Introduction

Flexible multilayer packaging materials obtained by extrusion coating process are widely used to contain food, cosmetics or medicines. The presence of low molecular mass compounds can impart undesirable odours and tastes to the content of the packaging. The majority of the identified compounds are hydrocarbons, but odour-responsible compounds are mainly carbonyl compounds such as aldehydes, ketones and carboxylic acids [1–3]. Odour can be produced by a single chemical compound or by a mixture of several compounds, depending on their threshold odour concentration (TOC, the lower concentration of a compound in the air which can be smelt). The TOC values of hydrocarbons are usually much higher than those of carbonyl compounds (e.g. ethane 6.47×10^5 mg/m^3 and ethanal 0.70 mg/m^3 [4]).

Volatile organic compounds (VOCs) in packaging

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materials are mostly produced by thermooxidative degradation of polyolefins in the extrusion coating process. This process is necessary to achieve good adhesion properties, and entails depositing melting polymers on solid surfaces. The combination of high temperatures, often extreme shear stress and the presence of oxygen lead to the formation of organic radicals, and the combination of these radicals produces oxygenated compounds [5].

The parameters of the extrusion coating process may influence the nature and the amount of VOCs in the packaging materials. Since the TOC of odour-responsible VOCs is usually very low (e.g. below 10 $\mu g/m^3$ in fumes and 10 $\mu g/l$ in leachates), a very sensitive method is necessary in order to control the quality of the process.

The determination of VOCs in polymers by gas chromatography has been usually carried out by purge and trap [1,2,6–10], and direct thermal desorption techniques [11]. Bravo and Hotchkiss [12] reported a purge and trap method in which the trap was cooled in liquid N_2 and VOCs were extracted from the traps by washing with ultrapure Freon-113. The analysis of the fumes formed during the extrusion coating process using a solid adsorbent (Tenax GR) and a thermal desorption device has also been reported [3]. Gas chromatography–mass spectrometry with simultaneous sniffing [1–3] has been demonstrated to be a suitable method to identify the off-odour compounds formed during the extrusion coating process of low-density polyethylene. Besides, Fales et al. [13] reported a methodology for the correlation of the objective GC–MS analytical data with the odour panel results. The compounds that cause the off-flavors were identified by Villberg et al. [1–3] mainly as carbonyl compounds, and by Hodgson et al. [7,8] as aldehydes, while alkanes and alkenes rarely impart odour.

In this work, a method for the identification of VOCs in flexible packaging based on headspace solid-phase microextraction (HS-SPME)–GC–MS is presented. Solid-phase microextraction (SPME) [14,15] is a solvent-free technique for sample preparation, which allows a direct, simple and rapid analysis of solid samples, particularly recommended for volatile analytes. This is the first time that HS-SPME has been used for the direct analysis of this kind of sample; up to now, the only application of SPME reported in this field has been the determination of residual acetaldehyde in polyethylene terephthalate bottles [16]. VOCs are extracted by HS-SPME, separated and identified by GC–MS.

The experiments started from a real packaging sample with an odour problem. In order to select the SPME conditions to extract VOCs from the packaging, the influence of SPME variables on the amount of compound extracted was studied. A gas chromatograph with a flame ionisation detector and an automated injector, allowing static headspace and SPME injection, was used. Then, the reproducibility was determined under optimal conditions and the chromatogram was compared with that obtained by static headspace injection. In order to identify the compounds involved in the analytical signals obtained for the packaging with an unacceptable odour, GC–MS analysis was performed after manual SPME. The reproducibility was determined and, finally, the SPME–GC–MS method was applied to the analysis of several packaging samples and raw materials.

2. Experimental

2.1. Samples

The samples were flexible packaging materials consisting of a layer of cellulose (Cel), clay-coated paper (CCP) or satin cellulose (Sat), a layer of polyethylene (PE), a layer of aluminium, and another layer of polyethylene, copolymer (Cp) or ionomer (Ion), and were provided by Tobepal (Logroño, Spain).

The samples were classified as odourless, odour acceptable and odour unacceptable by an odour panel composed of laboratory staff from Tobepal and following the procedure described in Ref. [13]. The raw materials used in the manufacture of the multilayer packaging: cellulose, aluminium and polyethylene were also provided by Tobepal. The raw materials were all classified as odourless by the odour panel.

2.2. Chemicals

The following chemicals were used to identify the volatile compounds: pentanoic acid (≥99.0%),

butanal (≥97.0%), pentanal (≥98%), 2,4-pentanedione (≥99.5%), 3-methylbutanal (≥98%), cyclohexanone (≥99.5%), hexanal (≥98%), heptanal (≥95%), 3-heptanone (≥99.5%), 2-ethylhexanal (≥97%), octanal (≥98%), nonanal (~97%), decanal (~97%), undecanal (~97%), and dodecanal (~97%) from Fluka, hexanoic acid (+99.5%), decane (+99%), undecane (+99%), and dodecane (+99%) from Aldrich, acetone (99.8%) and toluene (99.8%) from Carlo Erba, and acetic acid (80%) from Panreac.

Stock solutions of pure compounds were made in methanol; dilutions of 1–10 μg/ml in water were used to identify the compounds. A volume (1 ml) of the diluted solution of the pure compounds was placed in a headspace glass sealed vial and analysed by SPME–GC as described below for packaging samples.

2.3. Instruments and materials

A Varian 3900 gas chromatograph with a Varian Saturn 2100T MS detector was used for the identification of volatile compounds and for the analysis of packaging samples and raw materials. The extraction of compounds was performed manually with an SPME holder from Supelco, together with a hot plate from Corning and a metal support for eight vials of 15-ml. The assignment of each chromatographic peak was determined using a GC–MS mass spectral library (US National Institute of Standards and Technology, NIST). Once the peaks were identified, individual standard solutions of the compounds were injected in order to make quite sure of the assignment by retention time.

A Varian 3800 gas chromatograph with a flame ionization detector (FID) and a Combipal autosampler (CTC Analytics), which allows automated static headspace and SPME injections using 10- and 20-ml vials, were used to optimise the SPME conditions and to compare the HS-SPME–GC and the static HS-GC methods.

2.4. Sampling procedure

Sixty cm^2 of flexible multilayer packaging material was bent to provide freer surface and placed in a 15-ml sealed vial with screw top (manual HS-SPME) or 20-ml headspace glass sealed vial (automatic HS-SPME). The sample was incubated at 100 °C for 5 min to speed up the release of off-odour-responsible volatile compounds from the packaging, and then equilibrated with a 75-μm carboxen–polydimethylsiloxane (CAR–PDMS) fibre immersed in the headspace above the packaging for 15 min. The VOCs were thermally desorbed in the injector port of the chromatograph for 15 min and transferred to the chromatograph column where they were separated, and finally the VOCs were carried to the mass spectrometer for their identification.

Sixty cm^2 of cellulose, 60 cm^2 of aluminium (30-μm thick), and a polyethylene pellet (32.4 mg) were processed following the manual HS-SPME procedure described for packaging samples.

2.5. Chromatographic conditions

The GC–MS system was equipped with a CP5860 wall-coated open tubular (WCOT) fused-silica column (30 m×0.25 mm I.D. with a 0.25 μm CP-SIL8 CB low-bleed/MS phase, Varian). An initial oven temperature of 35 °C for 5 min was used, followed by an increase in the temperature at a rate of 10 °C/min to 230 °C. A 0.8 mm I.D. insert was used, and the carrier gas was helium, at 1 ml/min. The injector was maintained at 280 °C, with a 1:20 split ratio at initial time, followed by a 1:50 split ratio at 0.5 min. Although the splitless injection is recommended in SPME–GC [14], a split injection was used since the splitless injection gave rise to poor resolution and tailing peaks in GC–MS chromatograms. The mass spectrometer was scanned from m/z 33 to 650 at a cycle of 1 s, the fragmentation was made by electronic impact, and the ion trap temperature was 200 °C.

The GC–FID system was equipped with a CP-Select 624 column (30 m×0.32 mm I.D. with 1.8 μm phase). An initial GC temperature of 35 °C for 5 min was used, followed by an increase in the temperature at a rate of 10 °C/min to 200 °C and to a final hold at 200 °C for 5 min. The carrier gas was helium, at 1.7 ml/min. The detector temperature was 300 °C, with a make up flow of 25 ml/min, a H_2 flow of 30 ml/min and an air flow of 300 ml/min. The conditions in the SPME injections were an injector temperature of 280 °C and a splitless mode

at the initial time, followed by a 1:50 split ratio at 0.5 min. A 0.8 mm I.D. insert was used. The conditions in the static headspace injections were as follows: an incubation step at 100 °C for 10 min, an agitation speed of 500 rev./min, a syringe temperature of 110 °C, an injection volume of 500 μl, an injector temperature of 250 °C and a 1:20 split ratio at initial time, followed by a 1:50 split ratio at 1.0 min. A 3.4 mm I.D. insert was used.

2.6. HS-SPME–GC signal reproducibility

On the one hand, 10 replicates were analysed by HS-SPME–GC–FID under the following conditions: the samples were placed in 20-ml headspace glass sealed vials, the incubation temperature was 100 °C, the pre-incubation time was 5 min, and the compounds were extracted with a CAR–PDMS 75 μm fibre for 30 min. The SPME was performed automatically. On the other hand, five replicates were analysed by HS-SPME–GC–MS using 15-ml vials with screw top, the incubation temperature was 100 °C, the pre-incubation time was 5 min, and the compounds were extracted with a CAR–PDMS 75 μm fibre for 15 min. The SPME was performed manually.

3. Results and discussion

3.1. Optimisation of HS-SPME variables

The influence of variables such as the type of fibre, the incubation temperature, the extraction time, the pre-incubation time or the size of the vial on the amount of VOCs extracted were studied using the univariate method. The aim of the study was to find out the optimal values providing the maximal amount extracted and a good reproducibility.

3.1.1. Type of fibre

The polarity of the fibre depends on the coating material. Several fibres with different polarity and thickness were tested including: 85 μm polyacrylate (PA 85), 100 μm polydimethylsiloxane (PDMS 100), 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB 65), 50/30 μm divinylbenzene–carboxen–PDMS (DVB–CAR–PDMS 50/30), 75 μm carboxen–polydimethylsiloxane (CAR–PDMS 75) and 85 μm carboxen–polydimethylsiloxane (CAR–PDMS 85) fibres.

Samples were placed in 20-ml headspace glass sealed vials, and the extraction was made at room temperature for 15 min. Duplicate extractions were performed. Table 1 shows the relative area values obtained with the different types of fibres for several selected compounds. The worst results were obtained using the most polar fibre (PA) and the most non-polar fibre (PDMS). As expected from the nature of the analytes, CAR–PDMS and DVB–CAR–PDMS fibres provided the best results in terms of amount of compound extracted; CAR–PDMS fibre provided the best results for low molecular mass compounds and DVB–CAR–PDMS fibre for high molecular mass compounds. As a compromise, CAR–PDMS 75 was selected for further experiments.

Table 1
Influence of the type of fibre on the HS-SPME of VOCs in packaging materials[a]

Compound	PA 85	PDMS 100	PDMS–DVB 65	DVB–CAR–PDMS 50/30	CAR–PDMS 75	CAR–PDMS 85
Acetone	–	–	2	51	100	15
Butanal	69	–	–	80	99	100
Pentanal	13	–	15	48	68	100
Toluene	4	2	47	95	100	42
Hexanal	5	–	47	65	59	100
Heptanal	–	–	80	100	54	53
Cyclohexanone	3	12	62	100	77	27
Octanal	–	23	86	100	41	39
Nonanal	24	62	87	100	25	53

[a] Relative area values are the mean of two replicates. For HS-SPME and GC–FID conditions, see the text.

3.1.2. Incubation temperature

This is one of the most important variables in the extraction of VOCs. On the one hand, the temperature affects the distribution constants of the equilibrium fibre–gas and sample–gas, therefore it determines the amounts of analyte extracted from the fibre; an increase in the temperature resulted in an increase in the concentration of VOCs in the gas phase. On the other hand, the temperature affects the kinetics of the process since the diffusion rates of VOCs in the polymer matrix and the fibre coating increase with the increase of temperature. Wyatt [6] reported on the headspace extraction of VOCs from polymers that low molecular mass compounds with significant vapour pressure can be extracted at room temperature, but when increasing temperature higher-molecular-mass compounds can also be extracted.

In this study, the samples were placed in 20-ml headspace glass sealed vials, preheated for 5 min, and the headspace was equilibrated with a CAR–PDMS 75 μm fibre for 15 min. The incubation temperatures were studied within the range of 40–120 °C. The experiments were performed in duplicate. Fig. 1 shows the relative areas obtained between 40 and 120 °C for several selected compounds. As expected, the amount of compound extracted increased by increasing the temperature. The effect of temperature on the extracted amount depended on each compound, while the amount of aldehydes still increased at 120 °C, other compounds such as acetic acid, toluene, or acetone achieved a plateau at 80 or 100 °C. However, an incubation temperature of 100 °C was selected for further experiments because some polymer melting was observed at 120 °C.

3.1.3. Pre-incubation time

The time during which the samples were preheated to volatilise the VOCs from the sample matrix before extraction was also optimised. Samples were placed in 20-ml headspace glass sealed vials, heated at 100 °C and the extraction was made with a CAR–PDMS 75 μm fibre for 15 min. Three pre-incubation times were studied: 5, 10 and 15 min. The experiments were performed in duplicate. The relative areas obtained for several selected compounds at these three pre-incubation time values are shown in Table 2. The pre-incubation time was not a significant variable, there was no tendency, and the signals

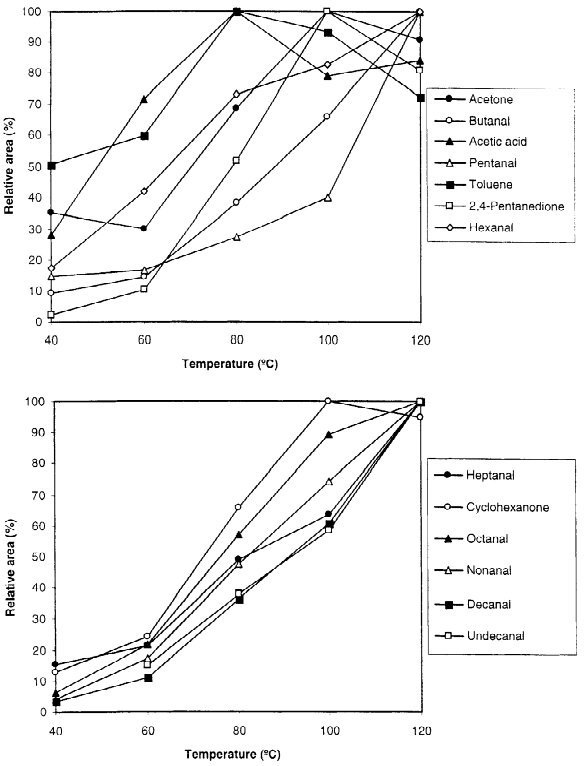

Fig. 1. Influence of the incubation temperature on the HS-SPME of VOCs in packaging materials. For HS-SPME and GC–FID conditions, see the text.

Table 2
Influence of pre-incubation time on the area of several identified VOCs[a]

Compound	5 min	10 min	15 min
Acetone	100	74	77
Butanal	100	78	98
Acetic acid	84	100	88
Pentanal	85	89	100
Toluene	100	50	45
2,4-Pentanedione	100	71	82
Hexanal	80	91	100
Heptanal	76	87	100
Cyclohexanone	93	80	100
Octanal	87	89	100
Nonanal	69	94	100
Decanal	70	95	100
Undecanal	78	90	100

[a] Relative area values are the mean of two replicates.

were similar within the experimental error. Therefore, 5 min of pre-incubation was chosen as a condition for further experiments.

3.1.4. Vial size

The size of the vial determines the volume of the headspace, so it affects the sensitivity of SPME. Headspace glass sealed vials of 10 ml and 20 ml were tested. Before the extraction, the samples were preheated for 5 min at 100 °C, and then the extraction was carried out using a CAR–PDMS 75 μm fibre for 15 min at 100 °C. Duplicate extractions were performed. Table 3 shows the relative areas obtained with 10-ml and 20-ml vials for several selected compounds. The amount extracted increased using 20-ml vials for the lower molecular mass compounds, whereas 10-ml vials provided better results for higher molecular mass compounds (less volatile compounds).

3.1.5. Extraction time

The measurements when the equilibrium is reached are more reproducible than non-equilibrium measurements. Therefore, the time the fibre was exposed to the headspace gas was optimised in order to determine the equilibrium time.

The samples were placed in 20-ml headspace glass sealed vials, a 5 min pre-incubation time was used, and the extraction was carried out using a CAR–PDMS 75 μm fibre at 100 °C. The extraction time varied from 1 to 60 min, and duplicate extractions were performed. The relative areas of identified peaks versus the extraction time are shown in Fig. 2. The extraction time needed to reach the distribution equilibrium depends on the compound. Thus, 15–25 min were enough for the smaller compounds, such as acetic acid, acetone, toluene or cyclohexanone, while the equilibrium was not reached in 60 min for volatile compounds with an increased number of carbon atoms, such as octanal, nonanal, decanal or undecanal. An extraction time of 15 min was selected for further experiments as a compromise between sensitivity and analysis time.

Table 3
Influence of size of vial on the area of several identified VOCs[a]

Compound	10 ml vial	20 ml vial
Acetone	96	100
Butanal	76	100
Acetic acid	100	98
Pentanal	89	100
Toluene	23	100
2,4-Pentanedione	100	99
Hexanal	100	96
Heptanal	100	87
Cyclohexanone	65	100
Octanal	87	100
Nonanal	100	62
Decanal	100	62
Undecanal	100	69

[a] Relative area values are the mean of two replicates.

3.2. Comparison of HS-SPME–GC–FID and static HS-GC–FID methods

In order to compare the sensitivity of the HS-SPME–GC–FID and the HS-GC–FID methods, 60

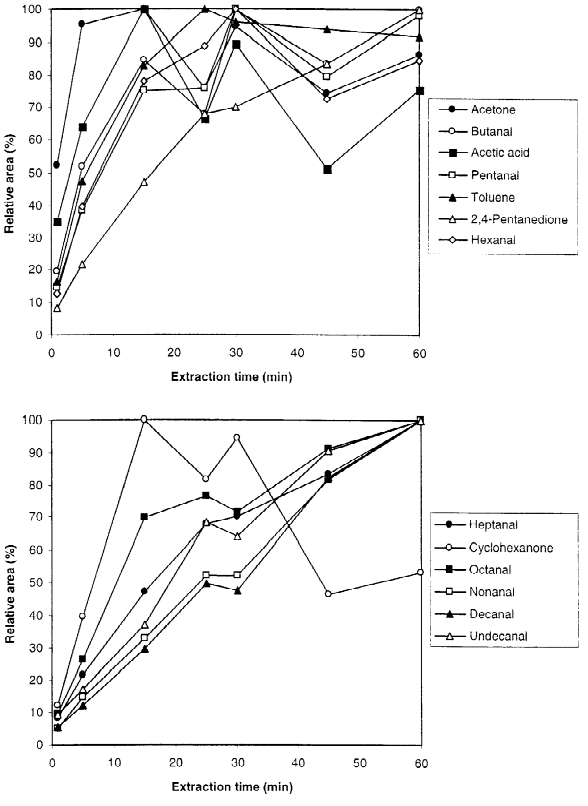

Fig. 2. Influence of the extraction time on the HS-SPME of VOCs in packaging materials. For HS-SPME and GC–FID conditions, see the text.

cm^2 of an odour unacceptable sample were processed in 20-ml vials. In the HS-SPME–GC method the compounds were extracted using a CAR–PDMS 75 μm fibre for 15 min at room temperature. The HS-GC conditions are described in the Experimental section. Fig. 3 shows the HS-SPME–GC and the HS-GC chromatograms obtained for the sample. Only four compounds provided significant signals using the static headspace method: acetone, toluene, hexanal and cyclohexanone. The HS-SPME–GC signal was 24, 430, 58 and 47 times higher for acetone, toluene, hexanal, and cyclohexanone, respectively. Consequently, the HS-SPME method is more sensitive than the static headspace method.

3.3. HS-SPME–GC signal reproducibility

After the optimisation of the HS-SPME variables,

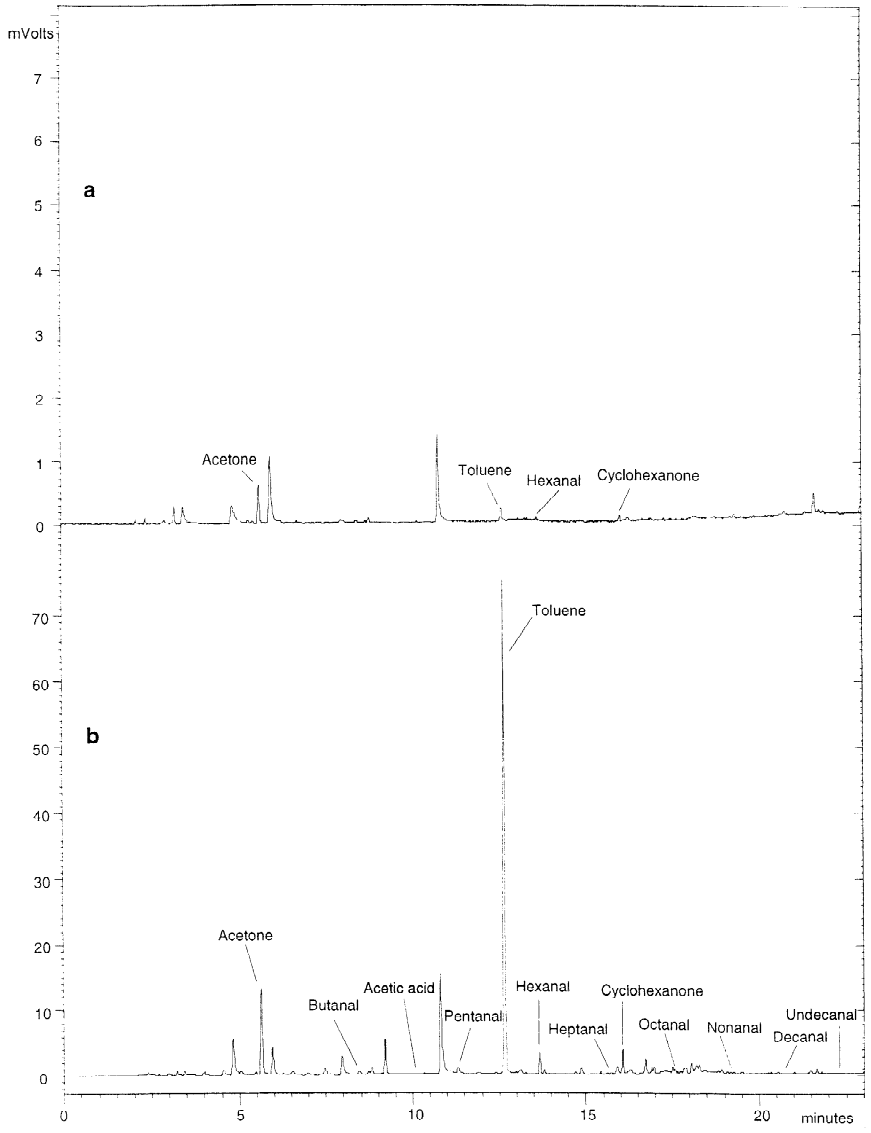

Fig. 3. Chromatograms obtained for an odour unacceptable packaging by (a) the HS-GC–FID and (b) HS-SPME–GC–FID method. For HS-GC–FID and HS-SPME–GC–FID conditions, see the text.

Table 4
Relative standard deviation (%) of the areas in compounds identified by the HS-SPME–GC–FID and the HS-SPME–GC–MS method

Compound	RSD %	
	HS-SPME–GC–MS ($n=5$) (manual)	HS-SPME–GC–FID ($n=10$) (automated)
Acetone	11.6	11.3
Acetic acid	11.0	32.1
Butanal	33.1	12.8
3-Methylbutanal	17.2	
Pentanal	8.8	8.7
Toluene	8.8	11.8
2,4-Pentanedione	9.9	11.3
Hexanal	4.0	7.1
Pentanoic acid	23.9	
3-Heptanone	13.2	
Cyclohexanone	15.0	30.5
Heptanal	8.0	5.4
2-Ethylhexanal	15.9	
Hexanoic acid	26.4	
Decane	13.9	
Octanal	7.6	7.5
Undecane	11.9	
Nonanal	8.0	13.8
Dodecane	7.7	
Decanal	12.5	14.5
Undecanal	9.3	8.2
Dodecanal	9.0	

a study of reproducibility was carried out. The relative standard deviations of the areas for the identified peaks are shown in Table 4. The results obtained were between 4 and 15%, except for acetic acid, butanal, 3-methylbutanal, pentanoic acid and hexanoic acid, which showed very low concentration levels.

3.4. Identification of volatile compounds

Two types of packaging materials with the same multilayer composition but obtained under different extrusion coating conditions, one of them with an unacceptable odour and the other with an acceptable odour, were analysed by HS-SPME–GC–MS. The odour-responsible volatile compounds must show higher signals in the unacceptable odour packaging material chromatogram. Fig. 4 shows the chromatograms of these two packaging materials and a blank. The assignment of each chromatographic peak was done using a GC–MS mass spectral library (NIST), and the identification of the volatile compounds was checked by HS-SPME injection of water–methanol solutions of the pure compounds. Table 5 shows the compounds identified, their retention time, and the area of the compound obtained for the odour unacceptable sample divided by the area of the compound obtained for the odourless sample. Twenty-five compounds, including hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids, were identified. The levels of VOCs, particularly of compounds such as 3-methylbutanal, toluene, 2,4-pentanedione, 3-heptanone, hexanoic acid, and undecanal were higher in the unacceptable odour sample than in the odourless sample. Also, the amount of azulenes was higher.

3.5. Analysis of the raw materials

The raw materials used in the manufacture of the multilayer packaging: cellulose, aluminium and polyethylene were analysed by HS-SPME–GC–MS in order to determine the presence of VOCs in these materials. Fig. 5 shows the chromatograms obtained.

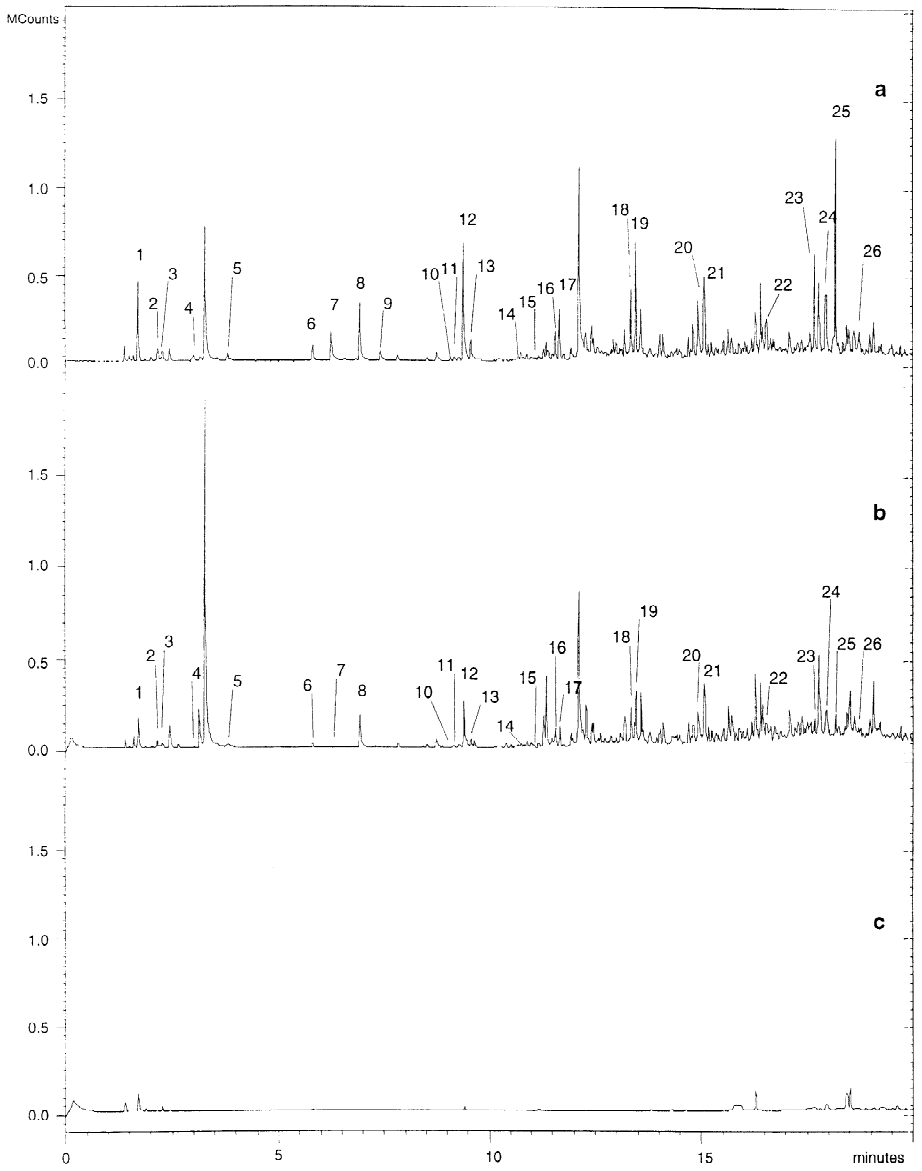

Fig. 4. Chromatograms of (a) an odour unacceptable packaging, (b) an odour acceptable packaging and (c) a blank. For HS-SMPE and GC–MS conditions, see the text. Peak assignment as in Table 5.

Azulenes were found in the cellulose samples, these compounds are used to get whiter cellulose and are not responsible for odour problems. Octanal, nonanal and decanal were found in aluminium, and they might have been formed by the oxidation of the oils used to get good aluminium properties [6]. Odour-responsible compounds were not found in polyethylene or had very low concentrations.

3.6. Analysis of multilayer packaging materials

Six packaging materials with different composition were analysed by HS-SPME–GC–MS in order to compare their levels of volatile organic compounds.

Table 6 shows the area percentage of each volatile organic compound in the packaging material related

Table 5
Compounds in an odour unacceptable packaging identified by HS-SPME–GC–MS

Peak number	Compound	Retention time (min.)	Odour/odourless level ratio
1	Acetone	1.71	2.7
2	Acetic acid	2.18	2.3
3	Butanal	2.27	3
4	3-Methylbutanal	3.02	8.8
5	Pentanal	3.81	2.6
6	Toluene	5.82	3.6
7	2,4-Pentanedione[a]	6.26	43.1
8	Hexanal	6.93	1.7
9	2,4-Pentanedione[a]	7.42	–
10	Pentanoic acid	9.09	2.7
11	3-Heptanone	9.17	3.6
12	Cyclohexanone	9.39	2.5
13	Heptanal	9.57	3.3
14	2-Ethylhexanal	10.69	2.7
15	Hexanoic acid	11.09	3.7
16	Decane	11.57	1.9
17	Octanal	11.66	2.7
18	Undecane	13.35	1.8
19	Nonanal	13.46	1.7
20	Dodecane	14.94	1.8
21	Decanal	15.08	1.4
22	Undecanal	16.56	3.2
23[b]	1,2,4-Methenoazulene, decahydro-1,5,5,8a-tetramethyl, [1S-(1α,2α,3aβ,4α,8aβ,9R)]-	17.68	9.2
24	Dodecanal	17.95	1.4
25[b]	1,4-Methanoazulene, decahydro-4,8,8-trimethyl-9-methylene-, [1S-(1α,3aβ,4α,8aβ)]-	18.17	11.3
26[b]	1H-Cycloprop[e]azulene, 1a,2,3,5,6,7,7a,7b-octahydro-1,1,4,7-tetramethyl-, [1aα,7α,7aβ,7bα)]-	18.72	19.3

[a] 2,4-Pentanedione gives rise to two tautomer peaks.
[b] Only identified by NIST library.

to the area of the compound in a sample with an unacceptable odour (sample 1). As it can be seen, the amounts of VOCs depend on the multilayer composition and the conditions of the extrusion coating process. The highest levels of VOCs were found in the sample with an unacceptable odour.

4. Conclusions

The HS-SPME–GC–MS method proposed is very useful for the identification of volatile compounds contained in packaging materials and formed during the extrusion coating process and can be used to control the quality of the raw materials. Also, the HS-SPME method surpasses the static headspace method in terms of sensitivity.

Regarding the optimisation of HS-SPME variables, the type of fibre, the extraction time and the temperature were the most influencing parameters for the amount of VOCs extracted.

Hydrocarbons and carbonyl compounds such as aldehydes, ketones and carboxylic acids were found

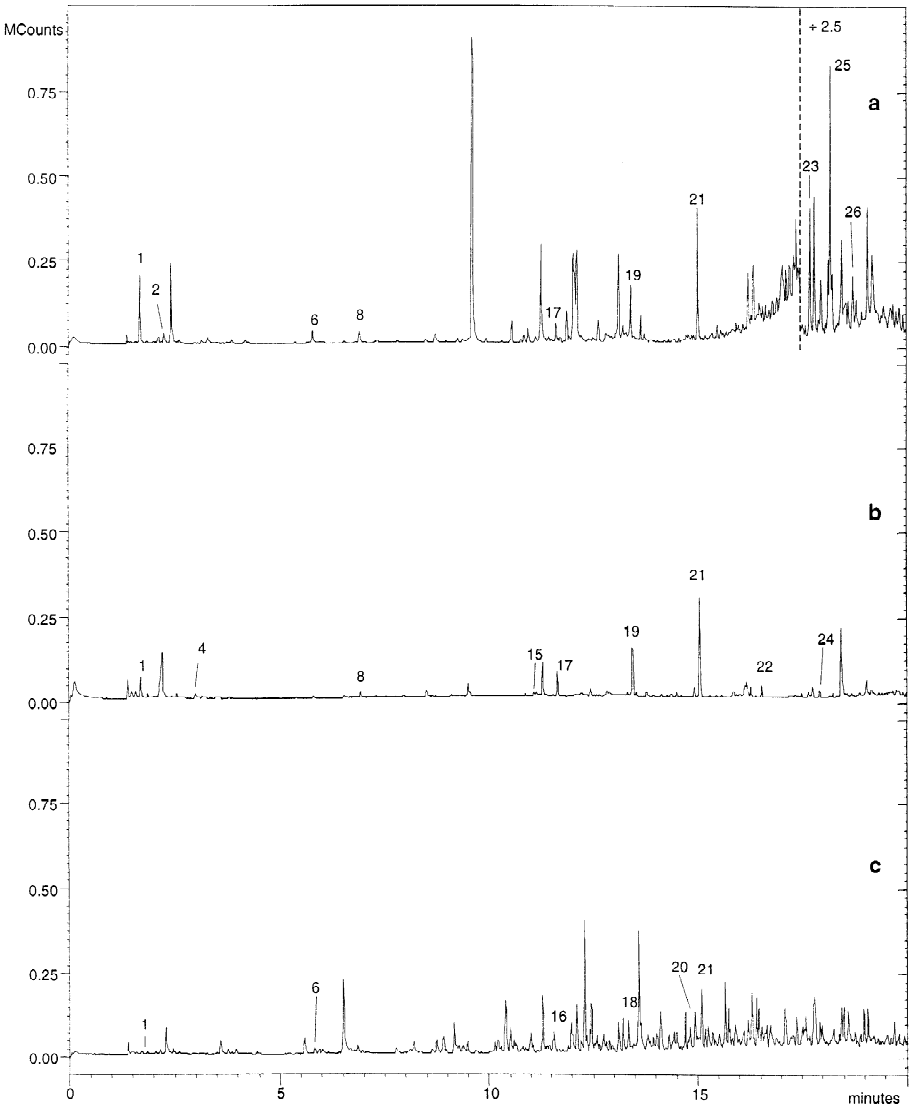

Fig. 5. Chromatograms of raw materials: (a) cellulose, (b) aluminium and (c) polyethylene. For HS-SMPE and GC–MS conditions, see the text. Peak assignment as in Table 5.

in packaging samples obtained by extrusion coating of polyethylene. No compounds with a significant odour were found in the raw materials used in the packaging manufacture.

The highest level of carbonyl compound was found in the packaging with an unacceptable odour. Carbonyl compounds, formed from hydrocarbons during the heating of polyethylene, are supposed to be the most probable reason for the organoleptic problems.

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Table 6
Comparison of the areas[a] of the volatile compounds in different packaging materials[b]

Compound	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Acetone	100	54	7	7	50	39
Acetic acid	100	14	14	10	15	34
Butanal	100	44	4	6	54	32
3-Methylbutanal	100	27	0	0	39	31
Pentanal	100	37	6	7	42	47
2,4-Pentanedione	100	2	7	7	74	0
Hexanal	100	65	10	12	79	90
3-Heptanone	100	31	8	16	41	15
Cyclohexanone	100	2	49	59	4	2
Heptanal	100	8	10	12	12	27
2-Ethylhexanal	100	29	0	0	70	10
Hexanoic acid	100	23	15	0	20	37
Octanal	100	85	16	16	105	119
Nonanal	100	29	35	33	41	70
Decanal	100	25	29	29	34	58
Undecanal	100	134	22	18	137	243
Dodecanal	100	23	13	12	19	44

[a] The results are the mean value of two replicates expressed as an area percentage related to the areas of sample 1.
[b] Sample 1, Cel–PE–Al–PE (odour unacceptable); sample 2, CCP–PE–Al–Ion (odour acceptable); sample 3, Sat–PE–Al–PE (odourless); sample 4, Sat–PE–Al–PE (odourless); sample 5, CCP–PE–Al–Cp (odourless); sample 6, CCP–PE–Al–PE (odour acceptable).

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References

[1] K. Villberg, A. Veijanen, I. Gustafsson, K. Wickström, J. Chromatogr. A 791 (1997) 213.
[2] K. Villberg, A. Veijanen, I. Gustafsson, Polym. Eng. Sci. 38 (1998) 922.
[3] K. Villberg, A. Veijanen, Anal. Chem. 73 (2001) 971.
[4] M. Meilgaard, G.V. Civille, B.T. Carr, Sensory Evaluation Techniques, CRC Press, New York, 1991.
[5] W. Voigt, R. Todesco, in: Proceedings of the 1st International Conference on Polymer Modification Degradation and Stabilisation, Palermo, September, 2000.
[6] D.M. Wyatt, J. Plast. Film Sheet 2 (1986) 144.
[7] S.C. Hodgson, M.J. O'Connor, R.J. Casey, S. Bigger, J. Agric. Food Chem. 46 (1998) 1397.
[8] S.C. Hodgson, R.J. Casey, J.D. Orbell, S.W. Bigger, J. Chem. Educ. 77 (2000) 1631.
[9] S. Jacobsson, J. High Resolut. Chromatogr. Chromatogr. Commun. 7 (1984) 185.
[10] A. Hagman, S. Jacobsson, J. Chromatogr. 395 (1987) 271.
[11] W.V. Ligon Jr., M.C. George, J. Polym. Sci. Polym. Chem. Ed. 16 (1978) 2703.
[12] A. Bravo, J.H. Hotchkiss, J. Appl. Polym. Sci. 47 (1993) 1741.
[13] N.J. Fales, L.C. Stover, J.D. Lamm, Polym.-Plast. Technol. Eng. 21 (1983) 111.
[14] J. Pawliszyn, Solid Phase Microextraction, Theory and Practice, Wiley–VCH, New York, 1997.
[15] J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, Cambridge, 1999.
[16] H. Cizkova, M. Voldrich, J. Dobias, Czech J. Food Sci. 16 (1998) 81.