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Headspace solid-phase microextraction–gas chromatography–mass spectrometry applied to quality control in multilayer-packaging manufacture[☆]

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Abstract

A method based on headspace solid-phase microextraction–gas chromatography–mass spectrometry is proposed for the quality control of multilayer packaging and its manufacturing process. Volatile organic compounds (VOCs) are produced in the manufacturing process of the packaging. They can cause organoleptic problems or modify the properties of the packaging depending on the nature and the amount of the VOCs formed. The quantification using packaging samples with a known VOC concentration for the calibration is proposed in order to reduce the analysis time, and the method is validated using a statistical test. Finally, the method is applied to the determination of odour-responsible compounds in multilayer packaging samples obtained under different extrusion-coating conditions, i.e. type of extruder, type of polymer and extrusion speed.
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Keywords: Packaging materials; Headspace analysis; Volatile organic compounds

1. Introduction

The physical properties of a material are directly linked to the nature and amount of chemicals that compose it. In the case of the polymers used to manufacture packaging materials, these chemicals affect properties such as the flexibility, stability, strength, adhesion, or organoleptic features of the product. Therefore, the analysis of these packaging materials is very useful to control their quality and study and optimise the manufacturing conditions.

The packaging material studied was formed by four layers: cellulose, polyethylene, aluminium, and polyethylene. In order to obtain a good adhesion between the polyethylene and the solid surface (cellulose or aluminium), the polymer is melted and placed on the solid surface. This process is called extrusion-coating. It is well-known that volatile organic compounds (VOCs) are formed during this process due to the presence of oxygen, high temperatures (approximately 300 °C) and extreme stress conditions [1]. Extrusion parameters such as the temperature, speed, type of extruder and type of polyethylene have an impact on the nature and

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amount of the VOCs formed and, therefore, on the physical properties of the product.

Solid-phase microextraction (SPME) is a free-solvent and direct technique [2] that had already been used to analyse VOCs in solid samples of sugar [3], tobacco [4], strawberries [5], coffee [6], cheese [7] or soils [8]. Therefore, this technique was chosen to analyse the VOCs present in our packaging samples. In previous studies, our group had studied VOCs related to bad odour/flavour problems [9]. They were mainly oxygenated compounds such as aldehydes, ketones, and carboxylic acids. External standard calibration, standard addition and multiple headspace (HS)-SPME were studied as quantification methods [10], multiple HS-SPME [11] being the method that provided the most reliable results, as the matrix effect was avoided, although it had a drawback, the long analysis time required (approximately 5 h per sample). This technique allowed us to know the levels of VOCs present in packaging samples.

In this work, the quantification of other packaging samples manufactured under different conditions was carried out using as reference a sample with a known VOC concentration in order to reduce the analysis time. The results obtained can be used to study the influence of the extrusion parameters on the amount of VOCs and control the quality of the packaging samples. This method was validated using a statistical test.

2. Experimental

2.1. Samples

The samples were flexible packaging materials consisting of a layer of cellulose, a layer of polyethylene, a layer of aluminium, and a layer of polyethylene, manufactured under different conditions and provided by Amcor Flexibles Tobepal (Logroño, Spain).

Four different samples were analyzed. Samples A and B were obtained under extrusion conditions E_1 (type of extruder and polyethylene) different from those used for samples C and D (extrusion conditions E_2). In addition, the extrusion speed used for samples A and C was higher than that used for samples B and D. All four samples were obtained at the same

extrusion temperature. The adhesion of the polyethylene film was good in samples A and B and bad in samples C and D.

2.2. Chemicals

The following chemicals were used to prepare the standard solutions: 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. Hexadecane (≥98%) from Fluka was used as solvent.

Stock solutions of pure compounds were made in hexadecane. Table 1 shows the concentration for each compound. 400-, 540-, 833-, 1250-, 2500-, 6666-, and 12 500-fold dilutions were used for the

Table 1
Concentrations (µg/ml) in VOC stock solution in hexadecane

Compound	Concentration (µg/ml)
Acetone	1856
Acetic acid	3232
Butanal	3783
3-Methylbutanal	3636
Pentanal	3793
Toluene	3802
2,4-Pentanedione	3831
Hexanal	3724
Pentanoic acid	5059
3-Heptanone	3582
Cyclohexanone	4408
Heptanal	4199
2-Ethylhexanal	4792
Hexanoic acid	4338
Decane	3831
Octanal	4018
Undecane	4663
Nonanal	3783
Dodecane	4069
Decanal	3754
Undecanal	3783
Dodecanal	1150

quantification of the packaging by multiple HS-SPME–GC–MS.

2.3. Instruments and materials

A Varian 3900 gas chromatograph with a Varian Saturn 2100T MS detector was used. SPME was performed manually with a SPME holder from Supelco, together with a hot plate from Corning. Each chromatographic peak was assigned using a GC–MS mass spectral library (US National Institute of Standards and Technology, NIST).

2.4. Sampling procedure

2.4.1. Area comparison with a packaging with a known VOC concentration

The samples (4.0 cm^2 of flexible multilayer packaging in a 15-ml sealed vial) were incubated at 100 °C for 5 min to speed up the VOC diffusion to the headspace, and then equilibrated with a 75-μm Carboxen–poly(dimethylsiloxane) (CAR–PDMS) fibre immersed in the headspace for 60 min. The equilibration time of the system [9] was selected as extraction time, but the extraction time could be shorter to reduce the analysis time. The desorption of the extracted compounds was performed in the injection port of the GC for 10 min.

The time needed to analyze a sample was 85 min (calibration not included): 5 min for incubation, 60 min for absorption and 20 min for chromatographic separation. But, after desorption (10 min), the fiber was ready for a new sample. Therefore, the final analysis time to process a batch of samples was 75 min/sample.

2.4.2. Multiple HS-SPME

First, 4.0 cm^2 of flexible multilayer packaging were placed into a 15-ml sealed vial and sampled four times at equal time intervals (60 min). The samples were pre-incubated at 100 °C for 5 min, and then equilibrated with a 75-μm CAR–PDMS fibre immersed in the headspace for 60 min. The desorption of the extracted compounds was performed in the injection port of the GC for 10 min. The analysis time for multiple HS-SPME was 5 h (calibration not included).

The calibration was performed by external stan-

dard using 10 μl of VOCs standard solutions in hexadecane with different concentrations (Table 1) sampled in the same way.

2.5. Chromatographic conditions

The GC–MS 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 a rate of 1.0 ml/min. The injector was maintained at 280 °C, with a 1:20 split ratio during an initial time of 0.5 min, followed by a 1:50 split ratio. The mass spectrometer was scanned from m/z 40 to 150 at one cycle per second; the ionization was performed by electronic impact; the ion trap temperature was 200 °C; and the electron multiplier voltage was 1600 V. A typical chromatogram is shown in Figure 1.

3. Results and discussion

3.1. Quantification of the packaging used as reference

Pentanal, toluene, 2,4-pentanedione, hexanal, pentanoic acid, 3-heptanone, heptanal, hexanoic acid, octanal, nonanal, and decanal were determined by multiple HS-SPME and external standard calibration using VOC standard solutions in hexadecane [11]. This method avoids the matrix effect, but not all the analytes could be quantified. Butanal, cyclohexanone, 2-ethylhexanal, undecane, dodecane and undecanal were determined by standard addition [10], and 3-methylbutanal and dodecanal were determined by external standard using VOC standard solutions in hexadecane [10]. Acetone, acetic acid and decane could not be determined with any method, since they showed a non-linear behaviour. Table 2 shows the VOC concentrations in the packaging sample used to quantify other samples by peak area comparison. Hexadecane was used for the blank.
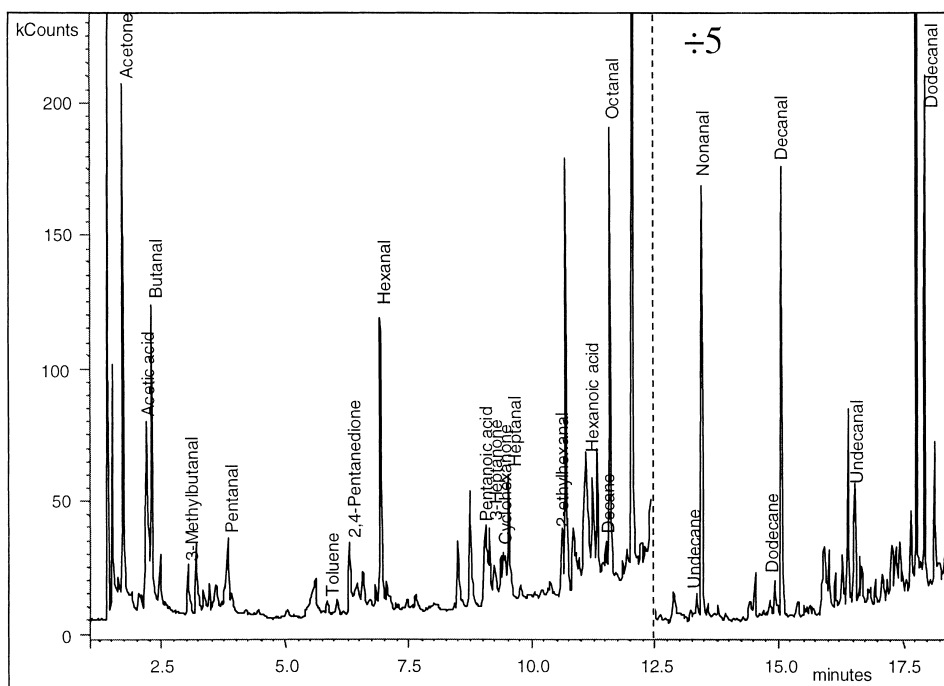
Fig. 1. HS-SPME–GC–MS chromatogram of 4.0 cm^2 of a packaging sample.

Table 2
VOC concentrations (μg/m^2) in the packaging sample used to quantify other packaging samples by peak area comparison

Compound	Concentration[a] (μg/m^2)
Butanal	48±28
3-Methylbutanal	5.4±0.5
Pentanal	57±7
Toluene	2.9±0.5
2,4-Pentanedione	65±9
Hexanal	106±17
Pentanoic acid	184±42
3-Heptanone	15±3
Cyclohexanone	67±37
Heptanal	25±4
2-Ethylhexanal	2.2±2.1
Hexanoic acid	302±48
Octanal	76±6
Undecane	23±9
Nonanal	255±28
Dodecane	31±5
Decanal	317±37
Undecanal	47±4
Dodecanal	196±31

[a] Mean value±standard deviation (three replicates).

3.2. Validation of the method

In order to validate the method, three packaging samples were analysed by multiple HS-SPME (method 1) and by area comparison with the packaging with a known VOC concentration (method 2). The results are shown in Table 3 (mean values of VOC concentrations expressed as μg of VOC per m^2 of packaging and standard deviation).

The first step of the validation was to determine whether the two methods provided the same variances ($s_1^2 = s_2^2$) Thus, a test of homogeneity of variances was applied; the variances obtained were equal for $\alpha_C = 0.05$. Variances are considered as homogeneous when $F_0 < F_C$. In our particular case, $F_C = 39.00$ for $\alpha_C = 0.05$. The second step was to determine whether the mean values of the methods were equal ($\bar{x}_1 = \bar{x}_2$), and a statistical test for homogeneous samples was applied. Mean values are considered as equal when $t_0 < t_C$. In our particular case, $t_C = 2.776$ for $\alpha_C = 0.05$. Table 4 shows the values of t_0 and F_0 calculated for each VOC and packaging sample. It can be seen that the two

Table 3
VOC Concentrations[a] (μg/m^2) in three packaging samples obtained by multiple HS-SPME and using a packaging with a known VOC concentration as reference

Compound	Sample 1		Sample 2		Sample 3	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
Pentanal	24±8	26±2	42±2	43±7	35±10	34±6
Toluene	2.8±0.4	2.9±0.1	8.1±0.8	7.7±2.2	7.9±1.9	6.1±1.8
2,4-Pentanedione	5.1±0.6	1.7±4.0	5.7±2.1	3.7±1.5	7.9±1.9	1.1±0.4
Hexanal	102±16	96±4	163±14	164±33	165±8	142±26
Pentanoic acid	73±38	75±25	163±46	149±73	97±1	87±43
3-Heptanone	4.6±1.2	5.2±1.5	9.3±1.0	8.8±1.8	14±6	6±1.7
Heptanal	23±8	22±2	25±3	29±11	26±6	21±8
Hexanoic acid	182±47	174±12	186±33	202±43	220±29	163±39
Octanal	53±6	58±1	89±18	82±13	63±6	58±9
Nonanal	198±18	191±7	222±55	250±54	181±7	164±40
Decanal	331±36	314±10	315±67	345±67	266±11	258±55

[a] Mean value±standard deviation (three replicates). Method 1: multiple HS-SPME. Method 2: area comparison with the reference packaging.

methods provided the same mean values except for 2,4-pentanedione in sample 3.

The validation was only made for the VOCs quantified by multiple HS-SPME.

3.3. Application to the analysis of multilayer packaging materials

The method developed was applied to the quantification of four samples obtained under different extrusion-coating conditions and with different polyethylene–aluminium adhesion. Table 5 shows the mean values of VOC concentration (three replicates)

expressed as μg of VOC per m^2 of packaging and their standard deviation. Samples A and B showed a good adhesion, whereas samples C and D showed a bad adhesion. The samples with a bad adhesion showed higher levels of butanal, 2,4-pentanedione, pentanoic acid and hexanoic acid, and lower levels of nonanal, decanal and dodecanal. Therefore, the degradation was higher in the packaging samples obtained under the extruder conditions E_2 and besides, these samples had a bad adhesion. A decrease in the amount of most of VOCs was identified when the extrusion-coating speed was reduced.

Table 4
t_0 and F_0 values calculated for each VOC and three packaging samples

Compound	Sample 1		Sample 2		Sample 3	
	F_0	t_0	F_0	t_0	F_0	t_0
Pentanal	10.43	0.278	0.06	0.158	2.28	0.069
Toluene	9.36	0.656	0.12	0.344	1.08	1.175
2,4-Pentanedione	0.02	1.444	2.00	1.388	20.18	6.001
Hexanal	19.67	0.630	0.18	0.053	0.10	1.474
Pentanoic acid	2.26	0.080	0.41	0.285	0.00	0.372
3-Heptanone	0.64	0.471	0.30	0.452	10.94	2.425
Heptanal	19.55	0.360	0.06	0.616	0.62	0.801
Hexanoic acid	14.44	0.299	0.61	0.508	0.54	2.053
Octanal	24.99	1.256	1.94	0.559	0.39	0.705
Nonanal	6.65	0.581	1.04	0.641	0.03	0.727
Decanal	14.45	0.809	0.98	0.559	0.04	0.243

Critical values ($n=3$, $\alpha_C=0.05$): $t_C=2.776$, $F_C=39.00$.

Table 5
VOC concentrations[a] (μg/m^2) found in four packaging materials manufactured under different extrusion-coating conditions

Compound	Sample A	Sample B	Sample C	Sample D
Butanal	52±32	67±50	145±93	131±84
3-Methylbutanal	3.4±0.7	2.0±0.6	2.3±0.5	1.6±0.4
Pentanal	30±5	23±5	31±9	25±6
Toluene	3.1±0.9	2.8±0.8	3.0±0.9	3.3±1.0
2,4-Pentanedione	0.7±0.4	0.5±0.2	1.6±0.9	1.4±0.6
Hexanal	110±23	103±18	110±23	101±18
Pentanoic acid	39±20	23±11	48±23	36±18
3-Heptanone	2.2±0.7	2.2±0.7	3.2±0.7	1.5±0.4
Cyclohexanone	2.9±2.0	1.9±1.3	1.1±0.7	0.5±0.3
Heptanal	25±10	16±6	17±7	11±4
2-Ethylhexanal	0.4±0.4	0.2±0.2	0.4±0.4	0.3±0.3
Hexanoic acid	51±13	47±12	101±26	55±12
Octanal	82±17	82±12	92±16	72±13
Undecane	28±12	47±19	44±19	46±20
Nonanal	283±72	258±57	168±38	105±31
Dodecane	38±9	33±8	31±8	32±10
Decanal	490±122	455±91	309±77	231±50
Undecanal	33±8	179±33	120±22	176±42
Dodecanal	59±14	63±14	40±9	28±7

[a] Mean value±standard deviation (three replicates). Sample A: speed V_1 and extruder conditions E_1. Sample B: speed V_2 and extruder conditions E_1. Sample C: speed V_1 and extruder conditions E_2. Sample D: speed V_2 and extruder conditions E_2. Speed value V_1 is higher than V_2.

4. Conclusions

The method presented is simple, quick, and reliable to quantify the VOCs present in packaging material samples and, thus, to control the quality of the process. The analysis time is reduced from 5 h/sample (multiple HS-SPME) to 1.25 h/sample, thus improving the quality control.

After the validation of the calibration procedure, the method was used to analyse four samples to control a manufacturing process. An improved adhesion was obtained with a lower degradation of the polyethylene. In this particular case, there were less VOCs in the sample and the compounds were mainly high molecular mass ones.

Under the extruder conditions E_1, an improved adhesion (lower degradation) was obtained. Besides, a reduction in the extrusion speed provided lower VOC levels.

Acknowledgements

The authors thank Amcor Flexibles Tobepal S.A.

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