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Direct quantitation of volatile organic compounds in packaging materials by headspace solid-phase microextraction–gas chromatography–mass spectrometry

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Abstract

The quantification of volatile organic compounds (VOCs) in flexible multilayer packaging materials using headspace solid-phase microextraction–gas chromatography–mass spectrometry (HS-SPME–GC–MS) was studied. The analytes include 22 compounds such as aldehydes, ketones, carboxylic acids and hydrocarbons formed by thermooxidative degradation of polyethylene during the extrusion coating process in the manufacture of the packaging, and many of them are involved in the unpleasant and undesirable odour of these materials. External standard calibration using a solution of the analytes in an appropriate solvent was the first approach studied. Aqueous solutions of the analytes provided low reproducibility and the reduction of aldehydes to alcohols under the HS-SPME conditions. Hexadecane was chosen as the solvent since its polarity is similar to that of polyethylene and its volatility is lower than that of the analytes. However, hexadecane should be added to the sample before the analysis as it modifies the absorption capacity of the fibre. A 75-μm Carboxen–poly(dimethylsiloxane) fibre was used to extract the VOCs from the headspace above the packaging in a 15-ml sealed vial at 100 °C after 5 min of preincubation. The influence of the extraction time on the amount extracted was studied for a standard solution of the analytes in hexadecane, together with the influence of the volume of the standard solution and the amount of the sample placed in the vial. Standard addition and multiple HS-SPME were also studied as calibration methods and the results obtained in the quantitative analysis of a packaging material were compared.

Keywords: Packaging materials; Headspace analysis; Volatile organic compounds

1. Introduction

Polyethylene is a polymer widely used as a packaging material due to its properties (strength, low cost, flexibility, inert character, stability, easy processing and chemical resistance). The packaged products are mainly foods, as well as medicines, cosmetic products and farming products. Frequently, the packaging materials are composed of several layers of different materials, i.e. cellulose–polyethylene–aluminium–polyethylene. In order to produce these multilayer packaging materials it is necessary to deposit the melted polymer on a solid surface such as cellulose or aluminium; this process is called extrusion-coating process.

The combination in the extruder of high temperatures, frequent extreme mechanical stresses and the presence of oxygen causes the degradation of polymers [1,2]. The mechanism of thermooxidative degradation highlights the presence of alkyl radicals that

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combined with oxygen produce alkoxy and peroxy radicals [2,3], and the combinations of these radicals produces volatile organic compounds (VOCs) such as hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids [4–6]. The VOCs formed during extrusion-coating process can migrate to the materials contained in the packaging and change their organoleptic properties imparting undesirable odours and flavours. The factors that determine the migration are mainly the temperature, the contact time, the equilibrium constant, the concentration, the solubility and the diffusion coefficient [7]. It is necessary to identify and quantify the VOCs formed in order to establish whether they can be toxic or modify the quality of the products.

The purge and trap technique is usually reported as the method to determinate VOCs in polymers [1,4,5,8–11]. Bravo and Hotchkiss [3] reported a purge and trap method in which the trap was cooled in liquid nitrogen and VOCs were extracted by washing with ultrapure Freon-113. Ligon and George [12] used a direct thermal desorption technique, and Villberg et al. [5] proposed a technique that uses a solid adsorbent (Tenax GR) and a thermal desorption device. Gas chromatography–mass spectrometry with simultaneous sniffing [4–6] or odours panels [13] has also been reported for the identification of off-odour compounds.

In this work, the determination of VOCs has been carried out by headspace solid-phase microextraction–gas chromatography–mass spectrometry (HS-SPME–GC–MS). SPME [14] is a technique that allows direct analysis of the volatile compounds in solid samples, thus avoiding the use of solvents. HS-SPME variables such as the type of fibre, the incubation temperature, the pre-incubation time, the size of vial and the extraction time were previously studied to identify the optimal analysis conditions [15].

Usually, quantitative analysis by SPME does not require any treatment of the samples. The calibration is carried out using external standards of exactly known concentration, or by standard addition to avoid the matrix effect. These procedures are easy for liquid samples, but are complex or impossible to apply to solid samples since there are no certificated reference materials for most of analytes in these solid samples at different ranges of concentration.

There are few applications to quantify VOCs in solid samples by SPME. The analysis of solid samples by SPME has been reported using some solid–liquid extraction techniques such as: lixiviation with solvents [16], extraction using ultrasound [17], microwave-assisted extraction [18], or pressurised solvents extraction [19] before the SPME, and the quantitative determination by SPME is carried out in the liquid extract. Besides, the direct analysis of solid samples by SPME has been carried out by suspending the soil in a solvent (usually water) in sealed vials, and by SPME performed in the vial headspace [20–24]. However, there are no described direct SPME quantitative methods for other kinds of solid samples such as polymers.

Multiple extraction allows calculation of the total area count of the analytes that corresponds to an exhaustive extraction, and, in this way, the matrix effect is avoided. The procedure involves sampling repeatedly the same sample at equal time intervals to obtain the exponential decay of the concentration of analytes. Some applications of this technique have been reported for headspace [25] and for SPME [26].

In this article, the quantitative analysis of VOCs in a multilayer packaging sample with an odour problem was carried out by three different methods: external standard calibration, standard addition and multiple headspace solid-phase microextraction.

2. Experimental

2.1. Sample

The sample was a flexible packaging material consisting of a layer of cellulose, a layer of polyethylene, a layer of aluminium, and another layer of polyethylene, and was provided by Tobepal (Logroño, Spain).

2.2. Chemicals

The following chemicals were used to prepare 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%), oc-

tanal (≥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, and dilutions from 25 ng/ml to 40 μg/ml in hexadecane were used in the different studies. Stock solutions of pure compounds were also made in methanol, and dilutions of 270–1700 ng/ml in water were used.

2.3. Instruments and materials

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

2.4. Sampling procedure

The sampling procedure depended on the quantification method.

In the external calibration method, 1.0 ml of hexadecane and 120 cm^2 of flexible multilayer packaging material were placed in a 15-ml sealed vial with a screw top.

In the standard addition method, 120 cm^2 of flexible multilayer packaging material were placed in a 15-ml sealed vial, and two standard additions of 1.0 ml of hexadecane solution with different concentrations of VOCs were performed.

In the multiple HS-SPME method, 4.0 cm^2 of flexible multilayer packaging material were placed in a 15-ml sealed vial and sampled five times at equal time intervals (60 min). The calibration was made using 10 μl of a VOC standard solution in hexadecane sampled in the same way.

The SPME conditions were the same for all the calibration methods. The samples were incubated at 100 °C for 5 min to speed up the volatile compounds, and then equilibrated with a 75-μm Carboxen–poly-(dimethylsiloxane) fibre immersed in the headspace for 60 min. The VOCs were thermally desorpted in the injector port of the chromatograph for 15 min and transferred to the chromatograph column where they were separated. Finally, the VOCs were taken to the mass spectrometer for their identification and quantification.

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 (99.996%), at a rate of 1 ml/min. The injector was maintained at 280 °C, with a 1:20 split ratio at the initial time, followed by a 1:50 split ratio at 0.5 min. The mass spectrometer was scanned from m/z 40 to 230 at one cycle per second, the fragmentation was made by electronic impact, the ion trap temperature was 200 °C and the electron multiplier voltage was 1550 V.

3. Results and discussion

3.1. Selection of a solvent for the standard solutions

Water and hexadecane were tested as solvents for standard solutions. Water could not be used as solvent since it provided a low reproducibility and a reduction of the aldehydes to alcohols was observed. Hexadecane is a long-chain non-polar solvent with a high boiling point (283–286 °C), a volatility lower than the analytes and a polarity similar to that of the polyethylene matrix. Consequently, hexadecane was selected as solvent.

The analytes studied were acetone, acetic acid, butanal, 3-methylbutanal, pentanal, toluene, 2,4-pentanedione, hexanal, 3-heptanone, pentanoic acid, cyclohexanone, heptanal, hexanoic acid, 2-ethylhexanal, decane, octanal, undecane, nonanal, dodecane, decanal, undecanal, and dodecanal.

3.2. Optimisation of HS-SPME variables

Some of the HS-SPME variables, such as the type of fibre, the incubation temperature, the extraction time, the pre-incubation time or the size of the vial had been already studied for the packaging material [15]. The following studies complete the optimisation of the HS-SPME variables.

3.2.1. Extraction time with VOC standard solution in hexadecane

The amount of analyte extracted was modified by increasing the extraction time (the exposition time of the fibre to the headspace gas) until the equilibrium time was reached.

A 1-ml aliquot of hexadecane solution was placed in a 15-ml sealed vial; the concentration of VOCs in the solution ranged from 27 ng/ml (pentanoic acid) to 4 μg/ml (cyclohexanone). The extraction time varied from 1 to 90 min, and triplicate extractions were performed. The relative areas of the chromatographic peaks versus the extraction time are shown in Fig. 1.

The influence of the extraction time depends on the compound. The signals of the smaller compounds, such as acetone, 3-methylbutanal, butanal, cyclohexanone, or 2-ethylhexanal, decreased after reaching a peak at 10–20 min, by increasing the extraction time, whereas the signal increased for the volatile compounds with an increased number of carbon atoms, such as nonanal, decanal, or undecanal. This suggests that semi-volatile compounds displace to the most volatile compounds from the fibre when the extraction time is higher.

An extraction time of 60 min was selected for further experiments because the variation of the signals between 60 and 90 min was small, within the standard deviation, for most of the analytes.

3.2.2. Solution volume with VOC standard solution in hexadecane

The amount of analyte extracted increased by increasing the VOCs solution volume until reaching a value at which the amount extracted remained approximately constant.

The volume varied from 50 to 1500 μl and the concentration of VOCs in the solution ranged from 460 ng/ml (dodecanal) to 770 ng/ml (2,4-pentanedione). The solution was placed in a 15-ml sealed vial and sampled as described in the Experimental section. Triplicate extractions were performed. The relative areas of the chromatographic peaks versus the solution volume are shown in Fig. 2.

Most of the VOCs showed a plateau from 500 to 1000 μl onwards, whereas the compounds with a higher molecular mass showed a peak using 300 μl. A solution volume of 1000 μl was selected for further experiments.

3.2.3. Packaging amount

The influence of the packaging amount was also studied. The sample amount ranged from 30 to 200 cm^2. The samples were bent in order to introduce them into a 15-ml sealed vial and expose the maximum polyethylene surface in the headspace. Triplicate extractions were performed. The relative areas of chromatographic peaks versus the packaging surface are shown in Fig. 3.

The signals increased by increasing the packaging amount from 30 to 120 cm^2, most of the analytes reached a peak at 120 cm^2, and then the signals decreased with increasing packaging amount due to problems introducing this amount of packaging in the vial with enough free surface for the mass transport. A packaging amount of 120 cm^2 was selected for further experiments. The thickness of the packaging material was 85 μm, therefore the packaging amount for 120 cm^2 was 1.02 ml, which is approximately equal to the optimised volume of hexadecane.

3.3. Linearity study with VOC solutions in hexadecane

After optimisation of the HS-SPME variables, a linearity study was carried out. A 1-ml sample of VOC standard solution in hexadecane was placed in a 15-ml sealed vial and processed as described in the Experimental section.

Table 1 shows the ranges of the VOC concentrations studied, the linear ranges, the limits of detection (LODs), the correlation coefficients (R) and the relative standard deviations (RSDs) found. A linear behaviour was observed when the concentrations were low, together with a curved trend at

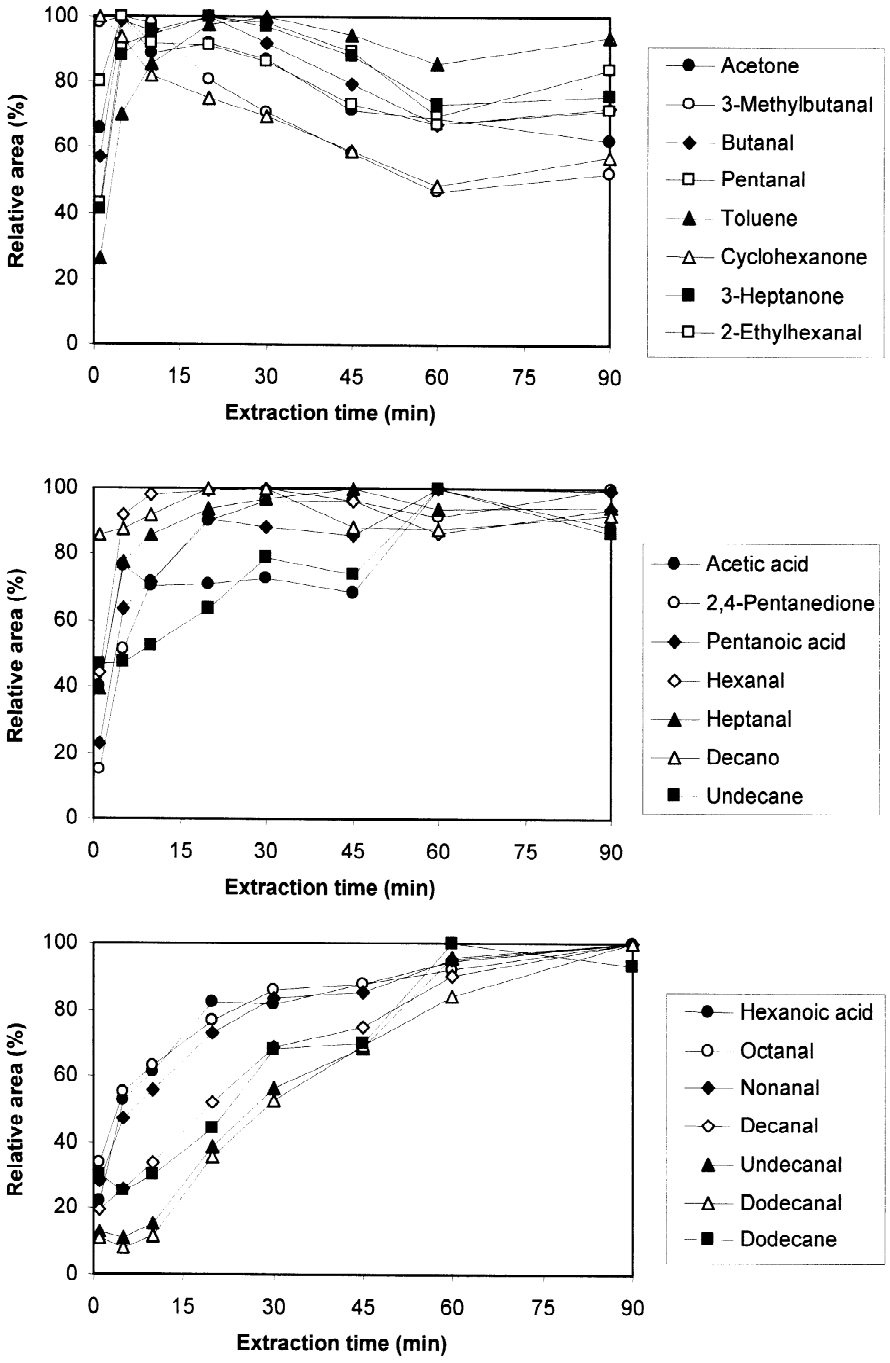

Fig. 1. Influence of the extraction time on the HS-SPME of VOCs from hexadecane solutions. For HS-SPME and GC–MS conditions, see the text.

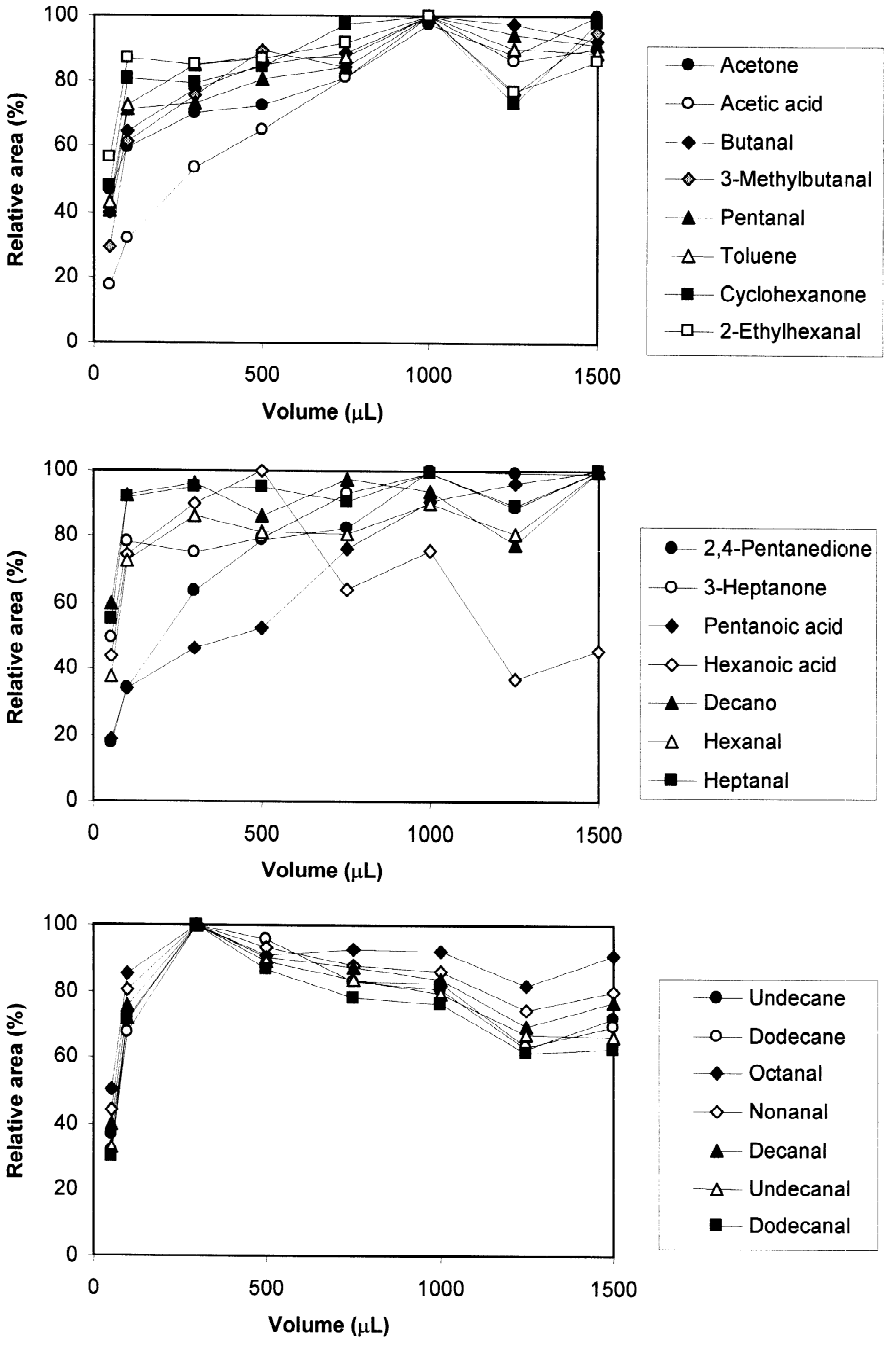

Fig. 2. Influence of the solution volume on the HS-SPME of VOCs from hexadecane solutions. For HS-SPME and GC–MS conditions, see the text.

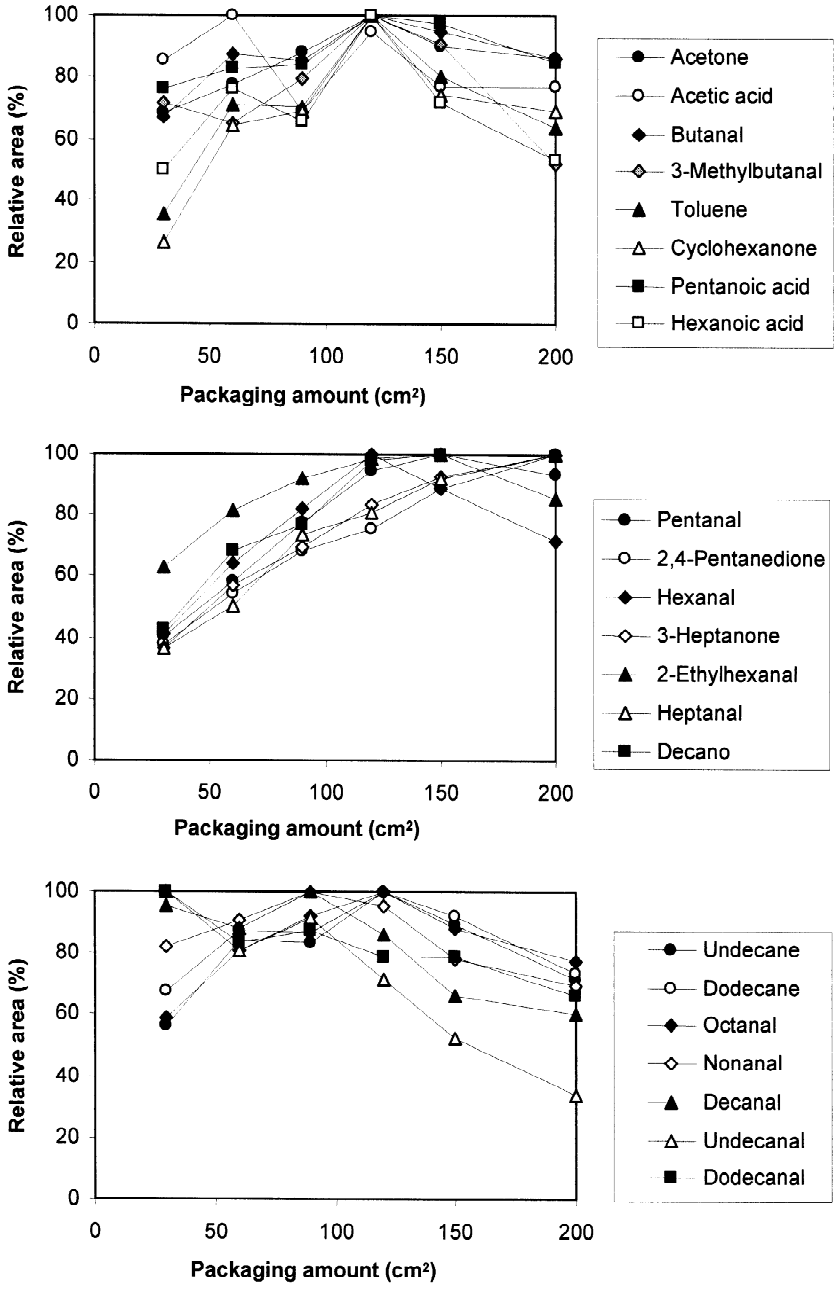

Fig. 3. Influence of the packaging amount on the HS-SPME of VOCs from packaging materials. For HS-SPME and GC–MS conditions, see the text.

higher concentrations. Acetone did not show linearity within the range studied. The relative standard deviations were between 5 and 14%, except for acetic acid, pentanoic acid and undecanal, whose RSDs were ~17%.

3.4. Quantitative analysis of a sample of packaging material

The concentration of VOCs in a sample of packaging material was estimated by three different meth-

Table 1
Linearity study with VOC standard solutions in hexadecane

Peak number	Compound	Studied range (ng/ml)	Linear range (ng/ml)	LOD (ng/ml)	*R*	RSD (%)
1	Acetone	0–4000	No linear	–	–	12.8
2	Acetic acid	0–2600	590–1300	237	0.993	17.1
3	Butanal	0–14 500	80–1500	24	0.986	8.3
4	3-Methylbutanal	0–16 000	55–1700	30	0.993	13.9
5	Pentanal	0–1200	20–600	3	0.991	10.9
6	Toluene	0–1500	55–625	16	0.992	8.1
7	2,4-Pentanedione	0–2700	19–2700	17	0.982	13.9
8	Hexanal	0–11 000	38–1300	11	0.990	13
9	Pentanoic acid	0–1300	20–1300	4	0.995	16.9
10	3-Heptanone	0–1300	18–625	3	0.995	11.2
11	Cyclohexanone	0–39 000	15–2800	9	0.995	12
12	Heptanal	0–1000	38–600	11	0.995	11.2
13	2-Ethylhexanal	0–2200	19–600	11	0.995	10.5
14	Hexanoic acid	0–1300	26–1300	5	0.996	14.1
15	Decane	0–7200	115–1000	83	0.994	9.9
16	Octanal	0–7800	160–1850	56	0.995	4.7
17	Undecane	0–11 000	140–2700	56	0.992	11
18	Nonanal	0–11 700	330–2300	156	0.993	10.1
19	Dodecane	0–7000	150–1600	98	0.996	8.8
20	Decanal	0–9700	110–2400	13	0.995	12.4
21	Undecanal	0–3300	64–1600	46	0.991	16.3
22	Dodecanal	0–4600	930–2250	375	0.998	8.8

ods: external standard calibration, standard addition and multiple HS-SPME.

3.4.1. External standard calibration

The first approach studied was to interpolate the area values of VOCs of a packaging material in the calibration graphs obtained for the VOC standard solutions in hexadecane, but an influence of the hexadecane on the absorption capacity was observed. Fig. 4 shows the chromatograms obtained for 120 cm^2 of packaging material without hexadecane, and with 1.0 ml of hexadecane added. Therefore, the interpolation was made with the area values obtained from a mixture consisting of 120 cm^2 of packaging material and 1.0 ml of hexadecane. Triplicate extractions were performed. The concentration mean values found are listed in Table 2.

The presence of hexadecane reduced the sensitivity of the method. The concentrations obtained by processing the sample without adding hexadecane were influenced by a positive error due to the differences in the distribution constants in presence (calibration solutions) and in absence of hexadecane (sample). Acetic acid, toluene, 3-heptanone, 2-ethylhexanal, decane, undecane and dodecane could not be measured by external standard calibration since their concentrations were below the detection limits.

3.4.2. Standard addition calibration

Two additions of standard solution were performed: one addition of 1.0 ml of VOC standard solution in hexadecane containing between 21 ng/ml and 3.9 μg/ml of analytes (depending on the compound) to 120 cm^2 of the packaging sample; and 1.0 ml of VOC standard solution in hexadecane containing between 42 ng/ml and 7.8 μg/ml of VOCs to the same amount of sample. The sample was also processed without standard addition, and only 1.0 ml of pure hexadecane was added.

The analyses were performed in triplicate and the mean concentration values obtained are shown in Table 2. Acetic acid, 2,4-pentadione, pentanoic acid, hexanoic acid and dodecanal could not be quantified by standard addition since they provide a non-linear response, and 3-methylbutanal and decane could not be quantified either as their concentrations were below the detection limit. The level of VOCs in the

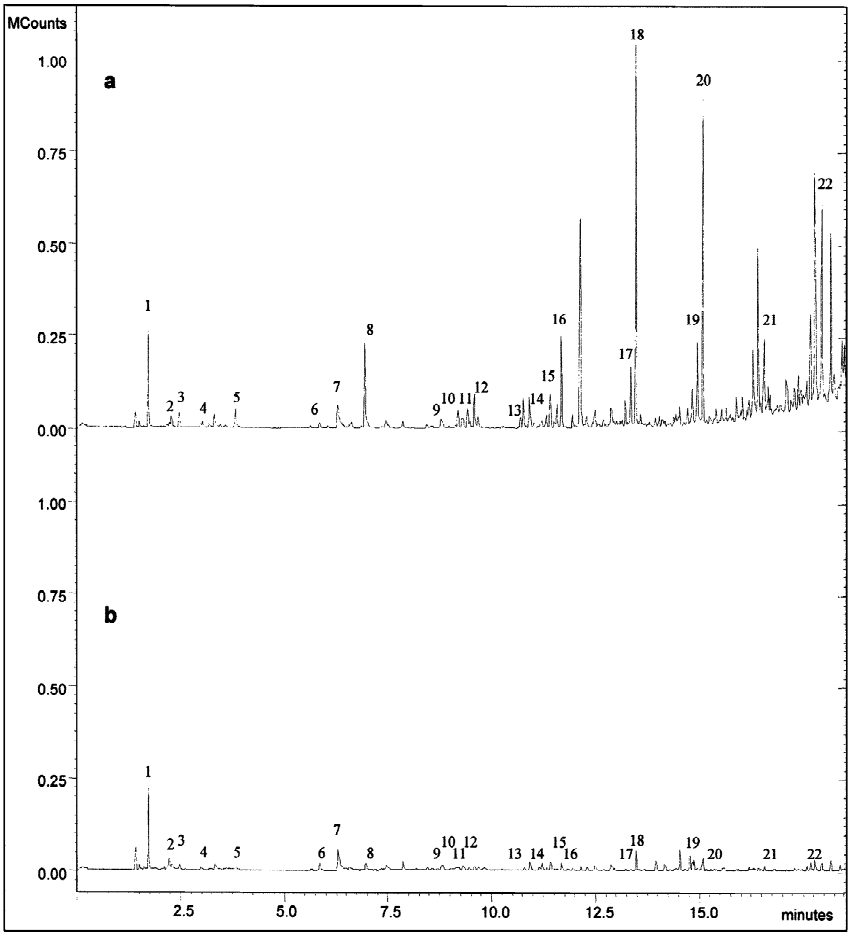

Fig. 4. Chromatograms of (a) 120 cm^2 of packaging material without hexadecane and (b) 120 cm^2 of packaging material with 1.0 ml of hexadecane added. For HS-SPME and GC–MS conditions, see the text. Peak assignment as in Table 1.

packaging obtained by the external standard method with hexadecane and the standard addition method were similar (within the standard error) for most of the analytes. The differences in the fibre absorption capacity and the phase volumes (packaging, hexadecane and headspace) can be overcome by the standard addition method, although some differences in the behaviour of the spiked and the native analytes remain.

3.4.3. Multiple HS-SPME

The 4.0 cm^2 of packaging sample were processed as described in the Experimental section to obtain the total area count of analyte per m^2. A 10-μl volume of a VOC standard solution in hexadecane containing between 0.3 and 1.8 μg/ml of VOCs (depending on the compound) were processed in the same way to obtain the total area count of analyte per μg.

The concentration of VOCs in the packaging sample was calculated combining the values obtained from the packaging and the standard. The analyses were performed in triplicate and mean concentrations found are shown in Table 2. Acetone, acetic acid, butanal, 3-methylbutanal, decane, undecane, and dodecane could not be quantified by multiple HS-SPME since they caused a non-exponential decay of the concentration in the packaging and/or in the standard. In general terms, the results obtained by multiple HS-SPME are higher than the standard additions calibration ones (except for toluene, hexa-

Table 2
Concentrations[a] of VOCs in a packaging material (expressed as μg of VOC per m^2 of packaging material) found by HS-SPME with different calibration methods

Compound	External standard without hexadecane	External standard with hexadecane	Standard addition	Multiple HS-SPME
Butanal	132 (15)	55 (28)	48 (58)	
3-Methylbutanal	214 (9)	5.4 (10)		
Pentanal	119 (15)	10 (8)	7.1 (19)	17 (9)
Toluene			6.2 (14)	5.0 (18)
2,4-Pentanedione	74 (20)	74 (1)		46 (13)
Hexanal	615 (12)	48 (15)	29 (16)	23 (9)
Pentanoic acid		2.0 (25)		59 (2)
3-Heptanone	63 (22)		1.7 (63)	14 (26)
Cyclohexanone	926 (13)	61 (3)	67 (54)	10 (27)
Heptanal	199 (16)	7.2 (50)	3.6 (13)	8.7 (33)
2-Ethylhexanal	194 (17)		2.2 (95)	9.6 (39)
Hexanoic acid	7 (15)	8.4 (34)		55 (1)
Decane	401 (4)			
Octanal	774 (12)	28 (27)	31 (28)	42 (8)
Undecane	1217 (3)		23 (41)	
Nonanal	2370 (5)	67 (31)	79 (16)	97 (2)
Dodecane	1931 (8)		31 (17)	
Decanal	2493 (5)	66 (23)	93 (26)	168 (2)
Undecanal	985 (3)	13 (42)	47 (8)	34 (7)
Dodecanal	5864 (10)	196 (16)		144 (2)

[a] Mean of three replicates. RSD (%) in parentheses.

nal and cyclohexanone). This suggests that the native analytes are more difficult to extract than the spiked analytes, and this difference causes a default error in the quantification by standard addition. By multiple HS-SPME, these differences are eliminated because the results are extrapolated to an exhaustive extraction with no errors.

A study of the linearity and the influence of the type of fibre will be done in further experiments to analyse VOCs in packaging materials by multiple HS-SPME.

4. Conclusions

Hexadecane is a solvent valid for the preparation of standards and the quantification of VOCs, but its presence reduces the sensitivity of the method and therefore hexadecane has to be added to the packaging to estimate the concentration of VOCs by external standard calibration.

Multiple HS-SPME removes the differences between the extraction of the native and the spiked analytes since the analyte amounts extracted are extrapolated to an exhaustive extraction. The concentration estimated by multiple HS-SPME is higher than that obtained by the other calibration methods, thus suggesting that there are default errors in the quantitative analysis by external standard and standard addition calibration.

HS-SPME is a technique that simplifies the quantitative analysis of volatile organic compounds in solid samples and avoids the use of organic solvents to prepare the samples.

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