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Multiple headspace solid-phase microextraction for the quantitative determination of volatile organic compounds in multilayer packagings

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Abstract

The theory of multiple headspace solid-phase microextraction (HS-SPME) and a method based on multiple HS-SPME for the quantitative determination of volatile organic compounds (VOCs) in packaging materials is presented. The method allows the direct analysis of solid samples without using organic solvents to extract analytes. Multiple headspace solid-phase microextraction is a stepwise method proposed to eliminate the influence of the sample matrix on the quantitative analysis of solid samples by HS-SPME. Different amounts of packaging and different volumes of standard solution were studied in order to remove a substantial quantity of analytes from the headspace at each extraction and obtain the theoretical exponential decay of the peak area of the four successive extractions and, thus, the total area was calculated from these four extractions. In addition, two fibres were compared: carboxen–polydimethylsiloxane (CAR–PDMS) and divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS), as they showed differences in the linearity of the exponential decay with the number of extractions depending on the compound. The CAR–PDMS fibre was better for the VOCs with a low molecular mass, whereas the DVB–CAR–PDMS fibre was better for the VOCs with a high molecular mass. Finally, the method was characterised in terms of linearity, detection limit and reproducibility and applied to analyse four multilayer packaging samples with different VOCs contents.

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1. Introduction

The quantitative analysis of volatile organic compounds in solid samples is difficult due to the lack of certified reference materials to be used as standards for the calibration of the direct analysis methods. Analytes are usually extracted from solid samples using a solid–liquid extraction technique such as

leaching with solvents [1], and with ultrasound [2], microwave-assisted extraction [3] or pressurised solvents extraction [4], and then this liquid extract is analysed by solid-phase microextraction (SPME)–GC. However, analyte losses by evaporation can occur if the analytes have a high volatility.

Multiple headspace extraction (MHE) was developed to analyse volatiles in solid samples [5,6]. This technique implies performing several extractions from a single sample. In this way, the concentration of the analyte decays exponentially and the total peak area corresponding to an exhaustive

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extraction of the analyte can be calculated as the sum of the areas of each individual extraction. Therefore, the matrix effect is completely removed.

SPME is a free-solvent and direct technique [7] which provides more sensitivity and selectivity than headspace for the analysis of volatiles. Multiple HS-SPME has the same aim as MHE. The amount of analyte extracted by the fibre is proportional to the initial amount, and it can be proved that the peak area decays exponentially with the number of extractions. The total peak area can be estimated performing a few (three or four) successive extractions by HS-SPME. Multiple HS-SPME applied to the quantitative determination of vinyl chloride in poly(vinyl chloride) has already been reported [8].

In this paper, the theory of multiple HS-SPME is presented for the first time and applied to the analysis of volatile organic compounds (VOCs) in multilayer packaging materials. The analytes studied are developed by the thermooxidative degradation of polymers during the extrusion-coating process when these packaging materials are manufactured [9]. These analytes, previously identified by HS-SPME–GC–MS [10], are carbonyl compounds and carboxylic acids, as well as hydrocarbons. Most of these analytes impart off-taste and/or flavours to the content of the packaging and affect the quality of the product. Therefore, it is very important to know the amounts of these VOCs in the packaging materials [11] in order to control the quality of the products and select the optimum manufacturing conditions.

In addition, different aspects of multiple HS-SPME such as the influence of the amount of the packaging, the amount of standard, and the type of fibre are studied. Finally, the multiple HS-SPME method is characterised and applied to the quantitative analysis of packaging samples with different VOC contents.

1.1. Theory of multiple HS-SPME

The multiple HS-SPME technique is an absolute quantitative method whereby the determination becomes independent of the sample matrix. It is a stepwise HS-SPME method. Each step consists of two substeps: partitioning of the analyte in a three-phase system (fibre coating/headspace/sample ma-

trix) and desorption of the analyte concentrated in the coating into a gas chromatograph.

There are three conditions that must be fulfilled to carry out a proper multiple HS-SPME:

(1) The relationship between the peak area and the amount of analyte in the fibre coating (amount of analyte introduced in the GC) must be linear over the whole amount range studied.

(2) The distribution constants of the analyte between the fibre and the sample, and between the headspace and the sample, and the volume of the three phases (fibre coating, headspace and sample) must be constant during all the extraction steps.

(3) The overall equilibrium of the analyte in the three-phase system must be established for each extraction step.

The mass of the analyte extracted by the fibre coating (m_f) is related to the overall equilibrium of the analyte in the three-phase system, and can be expressed once the equilibrium is reached as:

$$m_f = \frac{K_{fs}V_f}{K_{fs}V_f + K_{hs}V_h + V_s} \cdot m_0 \quad (1)$$

where m_0 is the initial mass of analyte in the three-phase system, K_{fs} and K_{hs} are the coating/sample-matrix and the gas/sample-matrix distribution constants, and V_f , V_h and V_s are the coating, gas phase and sample volumes, respectively. It has been assumed that the concentration and the activity are approximately equal as the analyte is at trace levels in the phases.

If the distribution constants and the phase volumes are constant, the mass of analyte absorbed by the coating is proportional to the initial mass of analyte, and Eq. (1) can be rewritten as:

$$m_f = \alpha m_0 \quad (2)$$

where α ($0 < \alpha \leq 1$) is the constant that gathers these constants:

$$\alpha = \frac{K_{fs}V_f}{K_{fs}V_f + K_{hs}V_h + V_s} \quad (3)$$

Considering a HS-SPME procedure carried out in a sequential number of extractions (N) on the same sample until the whole analyte is removed from the system, that is $m_{fN} = 0$, the mass of analyte in the coating at the end of the first extraction when the

equilibrium is already established in the system will be:

$$m_{f1} = \alpha m_0 \quad (4)$$

after the second and third extraction:

$$m_{f2} = m_{f1}(1 - \alpha) \quad (5)$$

$$m_{f3} = m_{f1}(1 - \alpha)^2 \quad (6)$$

and after the *i*th extraction:

$$m_{fi} = m_{f1}(1 - \alpha)^{i-1} \quad (7)$$

Since the peak area is related to the amount of analyte introduced into the gas chromatograph, that is, the mass of analyte absorbed by the fibre coating, according to an instrumental constant, *k*:

$$A_i = km_{fi} \quad (8)$$

and Eq. (8) can be rewritten as:

$$A_i = km_{f1}(1 - \alpha)^{i-1} = A_1(1 - \alpha)^{i-1} = A_1\beta^{i-1} \quad (9)$$

where β is $(1 - \alpha)$ and $0 \leq \beta < 1$, and the sum of all the partial peak areas can be calculated as:

$$A_T = A_1 + A_2 + A_3 + \dots + A_N \quad (10)$$

$$A_T = A_1[1 + \beta + \beta^2 + \dots + \beta^{N-1}] \quad (11)$$

Eq. (11) is a geometric progression whose sum is:

$$A_T = \sum_{i=1}^N A_i = \frac{A_1}{1 - \beta} \quad (12)$$

According to Eq. (12), the total peak area can be calculated from only two values: the first peak area, A_1 , and the constant β . The former is a measured value, whereas the latter can be obtained from the linear regression analysis of the following equation:

$$\ln A_i = (i - 1)\ln \beta + \ln A_1 \quad (13)$$

which is the logarithmic form of Eq. (9). The β value can be calculated from the slope of the linear plot $\ln A_i$ versus $(i - 1)$ obtained from a few (three or four) HS-SPME-GC determinations. Fig. 1 shows the chromatographic peaks obtained from four HS-SPME-GC determinations of nonanal in hexadecane and the linear plot $\ln A_i$ versus $(i - 1)$.

Finally, the initial mass of analyte in the sample,

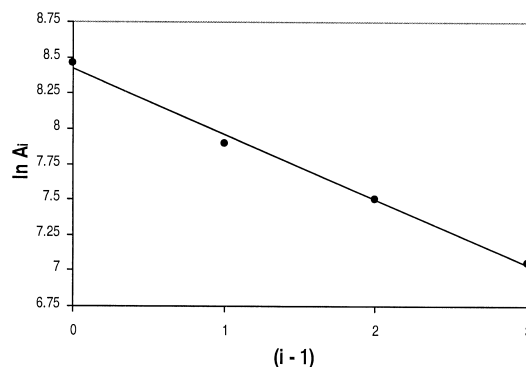
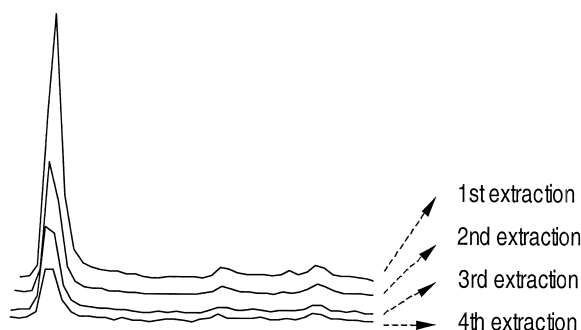


Fig. 1. Chromatographic peaks obtained in four successive HS-SPME-GC determinations of nonanal in a single hexadecane solution and linear plot $\ln A_i$ versus $(i - 1)$.

m_0 , can be calculated from the total peak area, A_T , and the calibration factor, *k*, which can be determined using a standard solution of the analyte.

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 another layer of polyethylene, manufactured under different conditions and provided by Tobepal (Logroño, Spain).

2.2. Chemicals

The following chemicals were used to prepare the standard solutions: pentanoic acid ($\geq 99.0\%$), butanal ($\geq 97.0\%$), pentanal ($\geq 98\%$), 2,4-pentanedione

($\geq 99.5\%$), 3-methylbutanal ($\geq 98\%$), cyclohexanone ($\geq 99.5\%$), hexanal ($\geq 98\%$), heptanal ($\geq 95\%$), 3-heptanone ($\geq 99.5\%$), 2-ethylhexanal ($\geq 97\%$), octanal ($\geq 98\%$), nonanal ($\sim 97\%$), decanal ($\sim 97\%$), undecanal ($\sim 97\%$), and dodecanal ($\sim 97\%$) 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 Pan-reac. Hexadecane ($\geq 98\%$) from Fluka was used as solvent.

Stock solutions of pure compounds were made in hexadecane, and dilutions from 0.20 to 12 $\mu\text{g}/\text{ml}$ in hexadecane were used in the different studies.

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

Flexible multilayer packaging (4.0 cm^2) was placed in a 15-ml sealed vial and sampled four times for equal time intervals (60 min). The samples were pre-incubated at 100°C for 5 min to speed up the diffusion of the volatile compounds to the headspace, and then equilibrated with a $75\text{-}\mu\text{m}$ carboxen–polydimethylsiloxane (CAR–PDMS) fibre immersed in the headspace for 60 min. The VOCs were thermally desorbed in the injector port of the chromatograph for 10 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. The calibration was performed by external standard using $10 \mu\text{l}$ of VOCs standard solutions in hexadecane with different concentrations sampled in the same way.

2.5. Chromatographic conditions

The GC–MS system was equipped with a CP5860 wall-coated open tubular (WCOT) fused-silica col-

umn ($30 \text{ m} \times 0.25 \text{ mm}$ I.D. with a $0.25\text{-}\mu\text{m}$ 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 $10^\circ\text{C}/\text{min}$ to 230°C . A 0.8-mm I.D. insert was used, and the carrier gas was helium, at a rate of $1 \text{ ml}/\text{min}$. The injector was maintained at 280°C for CAR–PDMS and at 270°C for divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS), 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 fragmentation was made by electronic impact, the ion trap temperature was 200°C , and the electron multiplier voltage was 1750 V.

3. Results and discussion

3.1. Optimisation of HS-SPME variables

3.1.1. Standard and packaging amount

A substantial amount of analyte must be removed from the system at each extraction to obtain the exponential decay of the peak areas. In order to determine this amount, 10, 20 and $50 \mu\text{l}$ of a VOC standard solution in hexadecane containing between 0.3 and $1.8 \mu\text{g}/\text{ml}$ of VOCs (depending on the compound) were processed as described Section 2. Also, 1, 2, 3 and 4 cm^2 of flexible multilayer packaging material were processed to choose the packaging amount that provided the best results.

The optimal values were selected bearing in mind, firstly, the linearity of the $\ln A_i$ versus $(i-1)$ plots and then the sensitivity. Linearity was evaluated by the number of compounds with an exponential decay of the peak areas and by the correlation coefficient of the linear plot $\ln A_i$ versus $(i-1)$ obtained. Sensitivity was compared by using the mean of the normalised peak areas. For each compound, a normalised area value of 100 was assigned to the experiment providing the highest peak area ($50 \mu\text{l}$ and 4 cm^2 for standard volume and packaging amount, respectively). The normalised area values for the rest of experiments were calculated as the percentage of the highest area: dividing the corresponding area by the highest area and multiplying by 100. Table 1 shows, the number of compounds with an exponential decay

Table 1
Optimisation of the standard solution volume and sample amount

| | Number of compounds with exponential decay | Correlation coefficient (R) ^a | Mean of normalised areas (%) ^a |
|------------------------------------|--|--|---|
| Solution volume (μl) | | | |
| 10 | 15 | 0.991 ± 0.007 | 31.4 ± 14.6 |
| 20 | 12 | 0.990 ± 0.008 | 37.7 ± 10.9 |
| 50 | 11 | 0.988 ± 0.008 | 100.0 |
| Packaging amount (cm^2) | | | |
| 1 | 14 | 0.987 ± 0.010 | 47.6 ± 20.5 |
| 2 | 13 | 0.989 ± 0.011 | 54.0 ± 17.0 |
| 3 | 13 | 0.989 ± 0.008 | 91.5 ± 34.5 |
| 4 | 13 | 0.993 ± 0.010 | 100.0 |

^a Mean value \pm standard deviation.

the mean correlation coefficients (R), and the mean of normalised signals for the different values of standard and packaging amount studied. Ten μl provided the highest number of compounds with an exponential decay of the peak area and the best correlation coefficients (R), and 4 cm^2 was selected since it provided the highest peak areas and best

correlation coefficients (R) of linear exponential decay of the peak area.

3.1.2. Type of fibre

The influence of the type of coating on the extraction of the analytes by multiple HS-SPME was studied using a CAR–PDMS fibre and a DVB–

Table 2
Correlation coefficient (R) of the exponential decay of the peak areas obtained by multiple HS-SPME of VOCs from a packaging sample and a standard using CAR–PDMS and DVB–CAR–PDMS fibres

| Peak no. | Compound | CAR–PDMS | | DVB–CAR–PDMS | |
|----------|-----------------|------------|------------|--------------|------------|
| | | Packaging | Standard | Packaging | Standard |
| 1 | Acetone | Non linear | Non linear | Non linear | Non linear |
| 2 | Acetic acid | Non linear | Non linear | Non linear | Non linear |
| 3 | Butanal | Non linear | Non linear | Non linear | Non linear |
| 4 | 3-Methylbutanal | 0.999 | Non linear | Non linear | Non linear |
| 5 | Pentanal | 0.995 | 0.998 | Non linear | 0.993 |
| 6 | Toluene | 0.991 | 0.994 | 0.993 | 0.996 |
| 7 | 2,4-Pentadione | 0.997 | 0.993 | 0.973 | 0.996 |
| 8 | Hexanal | 0.992 | 0.986 | 0.996 | 1.000 |
| 9 | Pentanoic acid | 0.996 | 0.985 | 0.997 | 0.998 |
| 10 | 3-Heptanone | 0.999 | 0.999 | Non linear | 0.995 |
| 11 | Cyclohexanone | 0.995 | 0.999 | Non linear | Non linear |
| 12 | Heptanal | 0.992 | 0.992 | 0.995 | 0.996 |
| 13 | 2-Ethylhexanal | 0.994 | 0.988 | Non linear | 0.995 |
| 14 | Hexanoic acid | 0.994 | 0.999 | 0.938 | 0.999 |
| 15 | Decane | Non linear | Non linear | 0.995 | 0.981 |
| 16 | Octanal | 0.994 | 0.990 | 1.000 | 0.992 |
| 17 | Undecane | Non linear | Non linear | 0.984 | 0.996 |
| 18 | Nonanal | 0.988 | 0.992 | 0.992 | 0.991 |
| 19 | Dodecane | Non linear | Non linear | 0.990 | 1.000 |
| 20 | Decanal | 0.985 | 0.995 | 0.999 | 0.996 |
| 21 | Undecanal | 0.973 | 0.960 | 0.993 | 0.996 |
| 22 | Dodecanal | 0.983 | 0.983 | 0.990 | 0.990 |

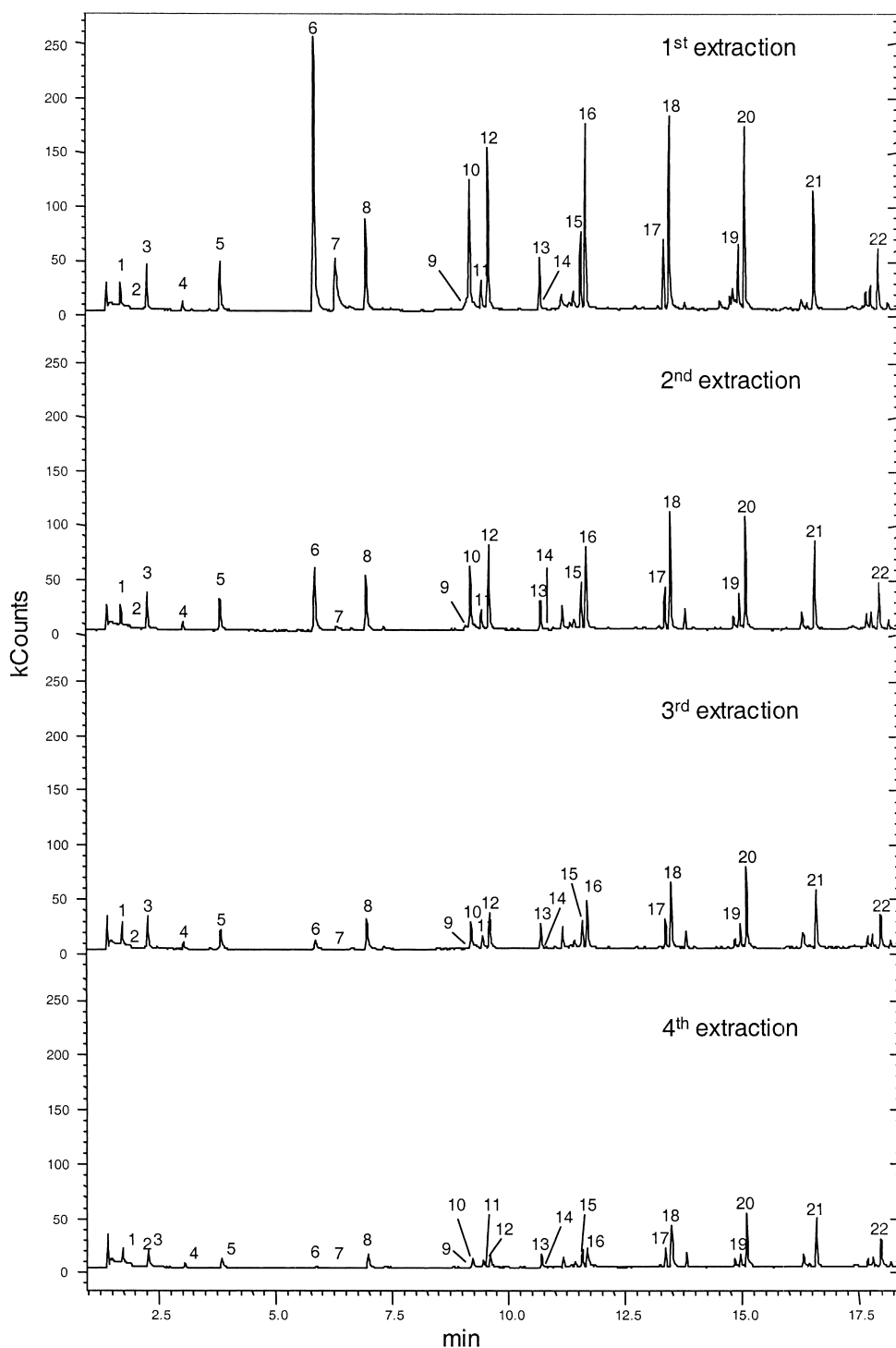


Fig. 2. Chromatograms of four successive HS-SPME extractions from 10 μ l of a VOC standard solution in hexadecane. Peak assignment as in Table 2.

CAR–PDMS fibre. Since an exponential decay of the peak areas with the number of extractions is necessary to quantify the analytes, the linearity of the plots was studied for sample and standard solutions using both fibres. Table 2 shows the correlation coefficient (R) for the exponential decay of the peak area. As it can be seen, the behaviour of CAR–PDMS was better for the VOCs with lower molecular masses, whereas the DVB–CAR–PDMS fibre behaved better for the VOCs with higher molecular masses. The compounds classified as non-linear (acetone, acetic acid, etc.) showed an increase of the value of $\ln A_i$ increasing $(i-1)$ or a correlation coefficient less than 0.925, therefore they cannot be quantified by multiple HS-SPME.

3.2. Features of the method

The linearity of the total peak area versus the mass of VOCs was studied for standard solutions in hexadecane using a CAR–PDMS fibre. Ten μl of VOC standard solution in hexadecane were placed in a 15-ml sealed vial and processed as described Section 2. Fig. 2 shows the chromatograms obtained from four successive HS-SPME–GC extractions using the same standard solution in hexadecane containing between 2.2 and 6.1 $\mu\text{g}/\text{ml}$ of VOCs (depending on the compound).

Table 3 shows the ranges of the VOC masses studied, the linear ranges, the limits of detection (LODs), the correlation coefficients (R) and the relative standard deviation identified. The total peak

area was linear with the amount of VOCs in the vial for the following compounds: pentanal, toluene, 2,4-pentanedione, hexanal, pentanoic acid, 3-heptanone, heptanal, hexanoic acid, octanal, nonanal, and decanal. On the other hand, cyclohexanone, 2-ethylhexanal, undecanal and dodecanal, which showed an exponential decay of the peak area, did not produce reproducible results. The extrapolation to obtain the total peak area was reproducible enough, with relative standard deviations ranging from 5 to 15%. The limits of detection were calculated from the area of the first extraction of a blank since the total area of the blank could not be obtained as the peak areas from the successive extractions did not show exponential decay.

3.3. Analysis of multilayer packaging materials

Four multilayer packaging samples manufactured under different conditions were analysed by multiple HS-SPME using a CAR–PDMS fibre. Fig. 3 shows the chromatograms obtained in four successive HS-SPME–GC extractions from the same packaging material sample.

The concentrations of VOCs in the packaging samples were estimated by interpolating the total peak area values obtained in the calibration graphs. Table 4 shows the concentration in the packaging samples expressed as μg of VOCs per m^2 of packaging material. Toluene could not be measured in samples 1 and 2 since their concentration were below the detection limit. The highest levels of

Table 3
Features of the multiple HS-SPME method for VOCs in hexadecane

| Compound | Studied range (ng) | Linear range (ng) | LOD (ng) | R | RSD (%) ^a |
|------------------|--------------------|-------------------|----------|-------|----------------------|
| Pentanal | 0–95 | 1.2–95 | 1.0 | 0.997 | 12 (30) |
| Toluene | 0–95 | 1.6–95 | 0.3 | 1.000 | 5 (6) |
| 2,4-Pentanedione | 0–96 | 1.6–96 | 0.7 | 0.995 | 12 (96) |
| Hexanal | 0–93 | 7.4–93 | 1.3 | 0.998 | 8 (15) |
| Pentanoic acid | 0–126 | 4.8–126 | 2.7 | 0.984 | 9 (8) |
| 3-Heptanone | 0–90 | 0.4–90 | 0.2 | 0.998 | 5 (66) |
| Heptanal | 0–105 | 3.9–105 | 1.5 | 0.991 | 7 (34) |
| Hexanoic acid | 0–109 | 3.0–80 | 2.5 | 0.987 | 15 (35) |
| Octanal | 0–100 | 4.3–100 | 0.2 | 0.990 | 9 (74) |
| Nonanal | 0–95 | 7.4–95 | 2.0 | 0.995 | 8 (70) |
| Decanal | 0–94 | 6.3–94 | 1.0 | 0.982 | 13 (70) |

^a RSD calculated from three replicates. Mass (ng) in brackets.

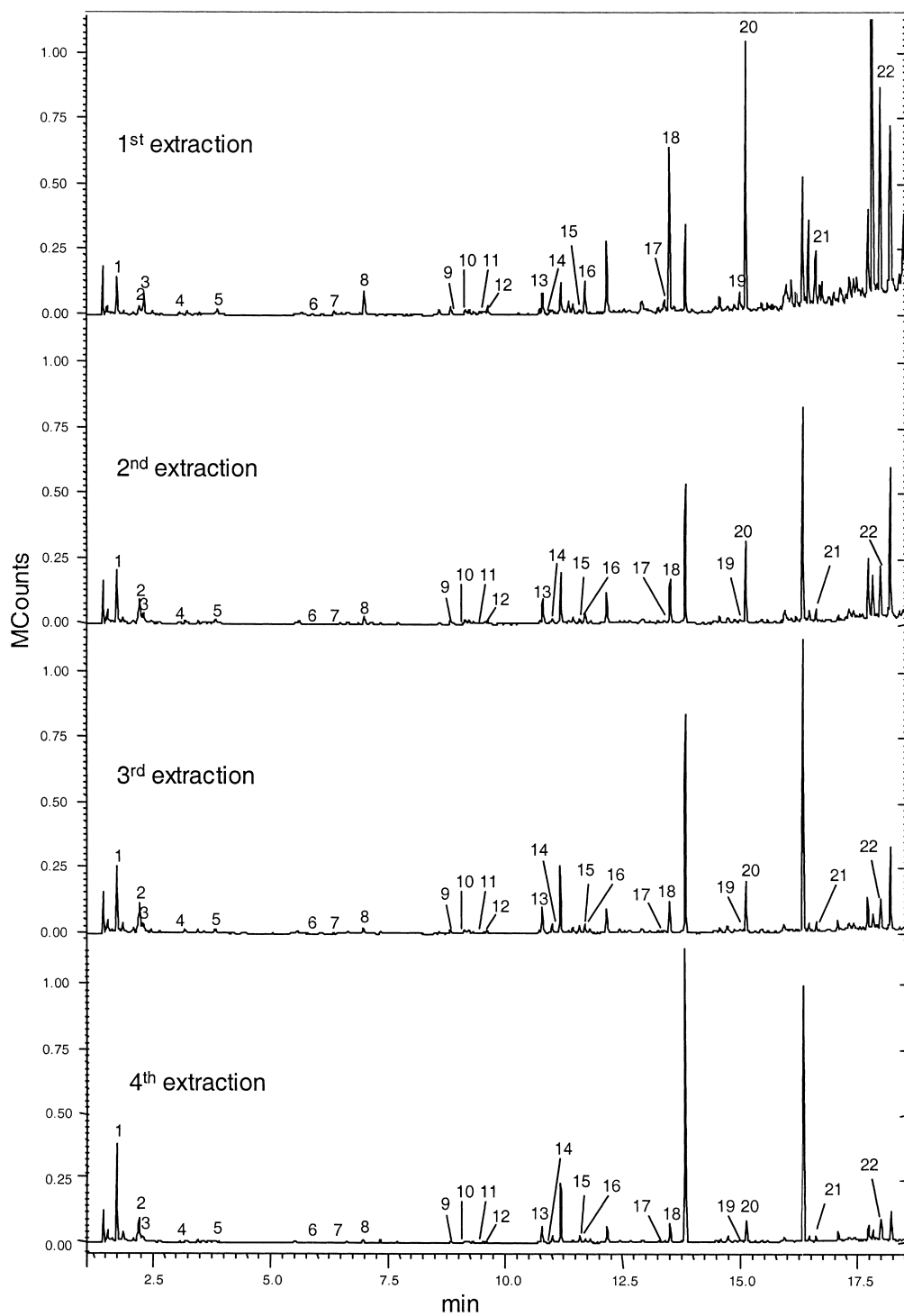


Fig. 3. Chromatograms of four successive HS-SPME extractions from 4 cm² of a packaging sample. Peak assignment as in Table 2.

Table 4
Concentrations^a of VOCs in different packaging samples (µg/m²) found by multiple HS-SPME

| Compound | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|------------------|----------|----------|----------|----------|
| Pentanal | 57±7 | 24±8 | 42±2 | 51±1 |
| Toluene | – | – | 8±1 | 10±2 |
| 2,4-Pentanedione | 65±9 | 10±2 | 6±2 | 9±2 |
| Hexanal | 106±17 | 102±16 | 163±14 | 169±4 |
| Pentanoic acid | 184±42 | 73±38 | 163±46 | 106±17 |
| 3-Heptanone | 15±3 | 5±1 | 9±1 | 15±9 |
| Heptanal | 25±4 | 23±8 | 25±3 | 26±6 |
| Hexanoic acid | 302±48 | 182±47 | 186±33 | 250±66 |
| Octanal | 76±6 | 53±6 | 89±17 | 83±7 |
| Nonanal | 255±28 | 198±18 | 222±55 | 254±55 |
| Decanal | 317±45 | 331±36 | 282±101 | 297±9 |

^a Mean value±standard deviation (three replicates).

VOCs were found in the sample 1 whose odour was more intense than that of the other samples.

4. Conclusions

The theory of multiple HS-SPME has been presented for the first time.

The total peak area is calculated from a few individual areas, and this value corresponds to an exhaustive extraction of analyte. Therefore, multiple HS-SPME removes the influence of the matrix.

This method allows the direct quantification of VOCs in solid samples such as multilayer packaging samples in a simple way, and avoids the use of organic solvents and tedious extraction procedures.

5. Nomenclature

| | |
|----------|--|
| A_1 | peak area obtained in the first step |
| A_2 | peak area obtained in the second step |
| A_3 | peak area obtained in the third step |
| A_i | peak area obtained in the i th step |
| A_N | peak area obtained in the N th step |
| A_T | total peak area, sum of the peak areas of the N extractions. |
| α | constant |
| β | constant |
| k | instrumental constant of the GC method |
| K_{fs} | coating/sample-matrix distribution constant |

| | |
|----------|---|
| K_{hs} | gas/sample-matrix distribution constant |
| m_0 | initial mass of analyte in the three-phase system |
| m_f | mass of analyte absorbed by the coating after the equilibrium is reached |
| m_{f1} | mass of analyte absorbed by the coating and desorbed into the gas chromatograph in the first step |
| m_{f2} | mass of analyte absorbed by the coating and desorbed into the gas chromatograph in the second step |
| m_{f3} | mass of analyte absorbed by the coating and desorbed into the gas chromatograph in the third step |
| m_{fi} | mass of analyte absorbed by the coating and desorbed into the gas chromatograph in the i th step |
| m_{fN} | mass of analyte absorbed by the coating and desorbed into the gas chromatograph in the N th step. |
| N | total number of extractions |
| V_f | volume of the fibre coating |
| V_h | volume of the headspace in the vial |
| V_s | volume of the sample in the vial |

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