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# Volatile compounds of dry-fermented sausages as affected by solid-phase microextraction (SPME)

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**Abstract**

The analysis of volatile compounds from the headspace of dry-fermented sausages was done by solid-phase microextraction (SPME). The effects of exposure time and fibre coating were investigated. A total of 90 different compounds were extracted by the two fibre coatings and these were identified. Sixty-six compounds were extracted by divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) coating and were identified, while 24 more were found with the carboxen/polydimethylsiloxane (CAR/PDMS) fibre. These 24 volatile compounds were mainly of low molecular weight. Four of the major compounds extracted: acetic acid, ethanol, hexanal and butanoic acid, were in high proportions in the two fibre coatings. However, the main differences were a higher affinity of DVB/CAR/PDMS for aldehydes while, for CAR/PDMS fibre, the higher affinity was for ester compounds. The extraction yields of dry fermented sausages volatile compounds varied according to the fibre coating used and the time of exposure, although competition effects were detected due to the high generation of lipid oxidation products, such as hexanal.


*Keywords:* Solid phase microextraction; Dry fermented sausage; Volatile compound; Sausage flavour

## 1. Introduction

The use of solid-phase microextraction (SPME) for the quantitative analysis of volatile compounds has been applied to a high variety of foods (Steffen & Pawliszyn, 1996). However, in meat samples, the use of SPME has been focussed on the analysis of lipid oxidation products (Brunton, Cronin, Monahan, & Durcan, 2000; Nielsen, Sorensen, Skibsted, & Bertelsen, 1997), cooked pork (Elmore, Mottram, & Hierro, 2000) and dry-cured ham (Gianelli, Flores, & Toldrá, 2002; Ruiz, Cava, Ventanas, & Jensen, 1998). Moreover, SPME has been evaluated for the analysis of volatile metabolites produced by *Staphylococci* used in dry sausage manufacture (Vergais, Masson, Montel, Berdagué, & Talon, 1998).

The study of volatile compounds in fermented sausages has been done mainly by dynamic headspace analysis using the purge and trap technique (Berdagué, Monteil, Montel, & Talon, 1993; Viallon et al., 1996; Stahnke, 1994, 1995; Bruna, Fernandez, Hierro, Ordoñez, & de la Hoz, 2000a, 2000b; Bruna, Hierro, de la Hoz, Mottram, Fernández, & Ordóñez, 2001; Edwards, Ordóñez, Dainty, Hierro, & de la Hoz, 1999). In these studies Tenax was used as adsorbent material for quantification of volatile compounds, although Stahnke (1994, 1995) also used charcoal tubes for their identification. Tenax TA is generally the porous polymer of choice for the analysis of volatile flavours in dynamic headspace analysis because of its high thermal stability, its relatively low water retention and its low bleed (Pillonel, Bosset, & Tabacchi, 2002). It is important to note that breakthrough volume of compounds in an adsorbent material is highly dependent on purging method and other experimental parameters. In this case, Tenax TA® has a low affinity for low-boiling compounds, meaning that compounds, such as ethanol, 2-propanol, 2-methyl-propanal, and other low-boiling types, break through the Tenax

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TA without being retained. Thus, the quantitative profile, obtained by the dynamic headspace analysis method, cannot be compared to quantitative profiles obtained under different circumstances, as Stahnke (1994) also indicated.

In comparison with dynamic headspace analysis (purge and trap technique), SPME offers the advantages of not requiring extended sample preparation, resulting in time saving; it is less expensive and its superiority over dynamic headspace analysis, with respect to repeatability, background and carry-over peaks has been demonstrated (Marsili, 1999). However, in SPME analysis, an equilibrium is reached between the matrix and the stationary phase coating the fibre (Zhang & Pawliszyn, 1993). Therefore, the choice of the stationary phase and the extraction conditions can affect SPME fibre performance. On the other hand, Elmore, Erbahadir, and Mottram (1997) did not recommend the use of SPME for trace analysis because they compared single coatings (PDMS and polyacrylate) of SPME fibres with the dynamic headspace method. In recent years, the use of bipolar coatings, including selective phases such as carboxen and divinylbenzene with polydimethylsiloxane (PDMS), has been studied for the analysis of low-molecular weight volatile compounds, with higher recoveries (Dufour, Delbecq, & Perez Albela, 2001; Elmore et al., 2000; Roberts, Pollien, & Milo, 2000).

The flavour of dry-fermented sausages has been widely studied in recent years, due to the importance of this meat product (Ordóñez, Hierro, Bruna, & de la Hoz, 1999). The studies have been focused on the mechanism involved in flavour generation (Ordóñez et al., 1999) and on the analysis of volatile components using mainly headspace techniques (Berdagué et al., 1993; Bruna et al., 2000a, 2000b, 2001; Edwards et al., 1999; Meynier, Novelli, Chizzolini, Zanardi, & Gandemer, 1999; Stahnke, 1994, 1995, 1999). In dry-fermented sausages, there are several potential precursors of substances responsible for the flavour and odour. Lipid hydrolysis and autooxidation, proteolysis and transformation of amino acids to aromatic compounds, after spices and other condiments by directly affecting flavour and odour and by the modulation of autooxidative reactions (Ordóñez et al., 1999). Therefore, in this study spices were not added to the fermented sausages in order to avoid their volatile components interfering with those generated during chemical or enzymatic processing. However, spices have a high impact on the final flavour of the sausage by adding characteristic notes (Stahnke, 1995). In this manuscript we focus on the optimisation process to analyse the compounds generated in a dry-fermented sausage.

Our objective was to develop and optimise a solid-phase microextraction sampling procedure, for qualitative and quantitative determination of volatile compounds present in the headspace of dry fermented sausages, using different fibre coatings.

## 2. Materials and methods

### 2.1. Samples

The dry-fermented sausage consisted of lean pork (80%) and pork back fat (20%) and the following additives added, in g/kg of meat mixture; sodium chloride (28), lactose (10), dextrin (15), sodium caseinate (20), glucose (7), sodium ascorbate (0.5), sodium nitrite (0.15) and potassium nitrate (0.20). The meat was ground through a plate of 6 mm hole diameter, vacuum-minced with the remaining ingredients and inoculated with a starter culture SP-318 (Rhodia Iberia, groupe Rhône-Poulenc) containing *Lactobacillus sakei*, *Pediococcus pentosaceus*, *Staphylococcus xylosus* and *St. carnosus* and also inoculated with 5. $10^6$ cfu/g of *Debaryomyces* spp. CECT 11815. The mixture was stuffed into collagen casings (75–80 mm diameter), the final mass of each sausage being 500 g. The sausages were kept at 3–5 °C during 24 h in a refrigeration chamber. The fermentation stage was done at 24 °C and 90–80% relative humidity (RH) for 12 h and then, the temperature was lowered to 20 °C and 90–80% RH for an additional 12 h. Finally, the sausages were dried at 10 °C and 90–75% RH until the end of the ripening process. The total time of the process was 35 days with weight losses of about 45%. Sausages were vacuum packaged and stored at −20 °C until the day of analysis.

### 2.2. SPME fibres

The extraction of headspace volatile compounds was done using a SPME device (Supelco, Bellefonte, PA), using fibres of 75 μm, carboxen/polydimethylsiloxane (CAR/PDMS) and 50/30 μm, divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). Before the analysis, the fibres were preconditioned in the injection port of the GC as indicated by the manufacturer.

### 2.3. Procedure

For each experiment 3 g of dry-fermented sausage were minced and weighed into a 10 ml headspace vial and sealed with a PTFE-faced silicone septum (Supelco, Bellefonte, PA, USA). The vial was left at 30 °C in a thermo block (J.P. Selecta, Barcelona, Spain) during 1 h to equilibrate its headspace. Then, a SPME fibre was exposed to the headspace while maintaining the sample at 30 °C during different times (30 min, 90 min, 3 h, 5 h, 21 h). The compounds absorbed by the fibres were identified and quantified by gas chromatographic analysis using MS detectors.

### 2.4. Identification and quantification of volatile compounds

The compounds adsorbed by the fibre were desorbed from the injection port of the gas chromatograph (GC HP 5890 series II) for 6 min at 220 °C with the purge

valve off (splitless mode). The compounds were separated in a DB-624 capillary column (J&W Scientific, 30 m, 0.25 mm i.d., film thickness 1.4 μm). The GC was equipped with an HP 5972 mass selective detector (Hewlett Packard, Palo Alto, CA). Helium was used as carrier gas with a linear velocity of 27.3 cm/s. The GC oven temperature programme began when the fibre was inserted and held at 38 °C for 13 min, ramped to 110 °C at 3 °C per min, then to 150 at 4 °C per min and to 210 °C at 10 °C per min and finally, held at 210 °C for 5 min. The total run time was 58 min and the GC-mass spectrometer interface was maintained at 240 °C. Mass spectra were obtained by electron impact at 70 eV, and data were acquired across the range 29–400 uma.

The compounds were identified by comparison with mass spectra from a library database (Nist'98), Kovats retention index (Kovats, 1965) and by comparison with authentic standards. Quantification was based on either a total or single ion chromatogram on an arbitrary scale (eV). The results are expressed as means of three replicates for each experimental point.

## 3. Results and discussion

The analysis of volatile compounds in fermented sausages through solid-phase micro-extraction has not been previously reported. However, the selection of an appropriate fibre depends on the compounds and the food to be analysed. In this case, many authors have characterised the volatile compounds present in the headspace of dry-fermented sausages (Berdagué, 1993; Bruna, 2000a, 2000b; 2001; Stahnke, 1994, 1995; Sunesen, Dorigoni, Zanardi, & Stahnke, 2001; Viallon, 1997). Due to previous experience (Gianelli et al., 2002), we selected bipolar coatings for the extraction of the volatiles present in the headspace of dry fermented sausages because of the low extraction recoveries found with single polarity coatings for other meat products, such as dry-cured ham. In this study, spices were not added in order to avoid their volatile components interfering with those generated by chemical and enzymatic processing and also to avoid interference by the different affinities of the fibre coatings used.

The volatile compounds extracted by CAR/PDMS and DVB/CAR/PDMS fibres are shown in Figs. 1 and 2, respectively. Both fibres have been used for several foods (Marsili, 1999; Roberts et al., 2000; Wyllie & Fellman, 2000); however, their application to meat and meat products has only been for the study of lipid oxidation in cooked turkey (Brunton et al., 2000) and volatile compounds present in the headspace of cooked pork (Elmore et al., 2000) and dry-cured ham (Gianelli et al., 2002; Ruiz et al., 1998). Both fibre coatings are useful in the study of volatile compounds present in the headspace of dry-fermented sausages, as seen by the high number of compounds detected. The identification and quantification of the volatile compounds extracted were done by GC–MS as shown in Table 1. Their Kovats indices and average quantities extracted by the two fibres, after 3 h of exposure, are presented.

The extraction of the volatile compounds from the headspace of dry-fermented sausages was followed at 30 °C during 21 h. During the first 5 h, the CAR/PDMS

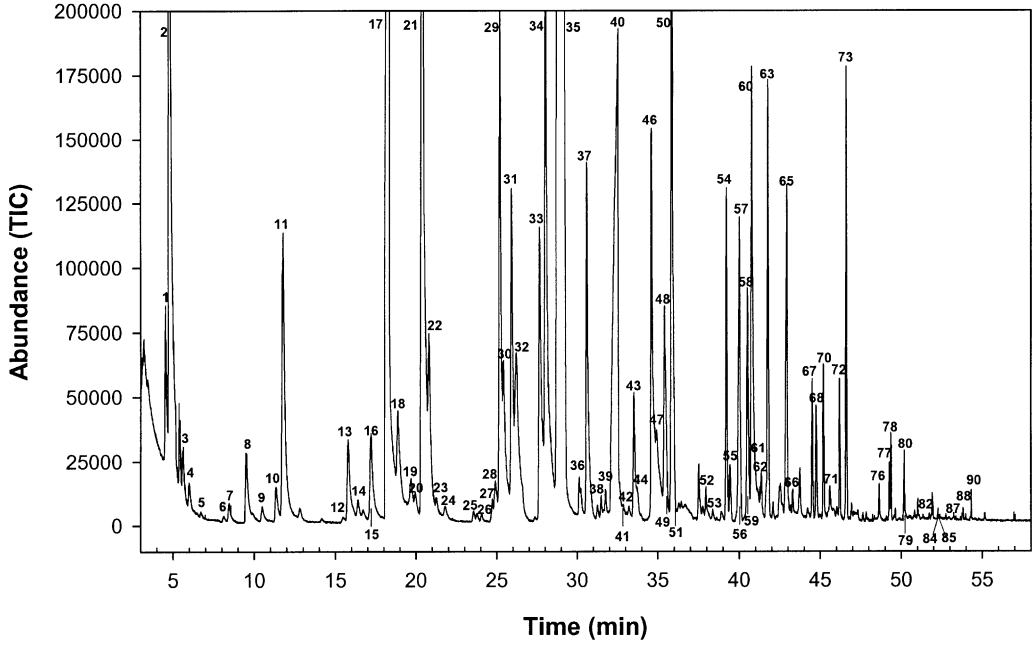


Fig. 1. Chromatograms obtained by SPME GC-MS after maintaining the SPME fibre (75 μm Carboxen/PDMS) for 3 h at 30° in the headspace of dry-fermented sausage. The numbers represent compounds identified and listed in Table 1.

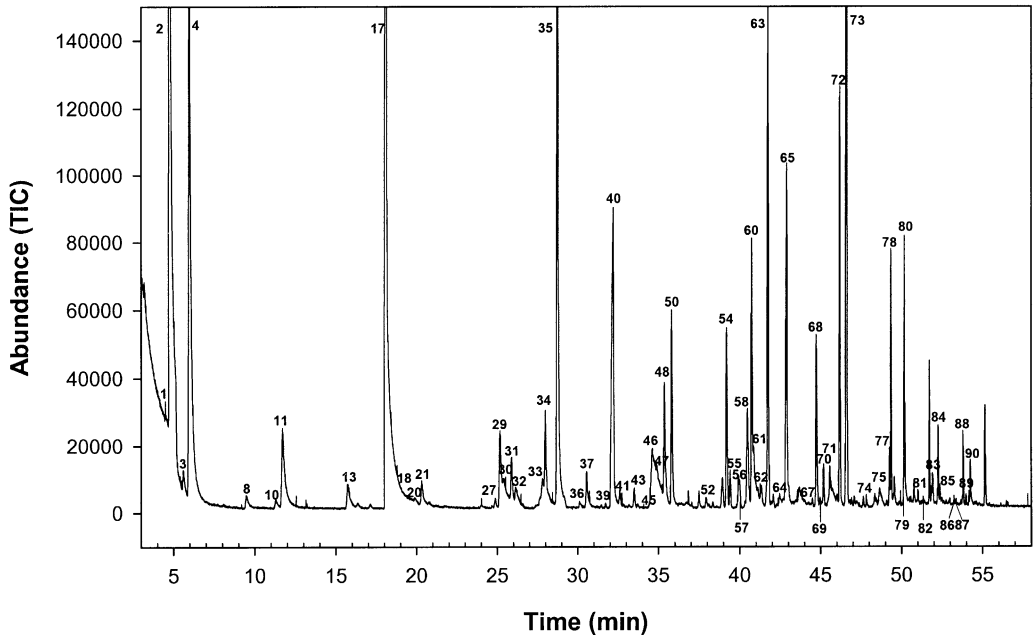


Fig. 2. Chromatograms obtained by SPME GC–MS after maintaining the SPME fibre (50/30 μm DVB/Carboxen/PDMS) for 3 h at 30° in the headspace of dry-fermented sausage. The numbers represent compounds identified and listed in Table 1.

fibre showed increasing volatile extraction, while DVB/CAR/PDMS showed a slight increase, maintaining its total concentration throughout exposure (Fig. 3). The graph of total area counts suggests that absorption reached equilibrium after 5 h of exposure to CAR/PDMS, while the equilibrium was reached in only 90 min with the DVB/CAR/PDMS fibre. However, in the DVB/CAR/PDMS coating, specific compounds extracted may still be increasing, as happens in the case of 2-nonanone, nonanal, ethyl octanoate and hexanoic acid (Figs. 4E and C, 5A and C, respectively).

The selectivity varied with the type of the fibre coating used, as can be seen in Table 1. In the headspace of fermented sausages, the DVB/CAR/PDMS fibre extracted, after 3 h of exposure; 10 alcohols (22.3%), 17 aldehydes (21.1%), 7 ketones (4.2%), 11 esters (7.0%), 9 hydrocarbons (5.1%), 9 acids (30.3%) and 2 furans and 1 sulphur compound (10%). This fibre extracted seven compounds in high quantities, constituting more than 70% of the total area. These compounds were acetic acid (20.5%), ethanol (17.2%), carbon disulphide (9.9%), nonanal (9.6%), hexanal (5.7%), butanoic acid (5.5%) and octanal (4.1%). On the other hand, the selectivity of CAR/PDMS fibre was different as seen by the extraction of 11 alcohols (32.6%), 14 aldehydes (11.5%), 9 ketones (2%), 17 esters (17.0%), 15 hydrocarbons (5.1%), 11 acids (31.3%) and 2 sulphur compounds and 2 furans (0.6%). In this case, seven compounds were also extracted by the fibre representing more than 70% of the total area. The compounds were acetic acid (22.4%), ethanol (17.3%), hexanal (7.9%), ethyl acetate (7.8%), 3-methyl-1-butanol (6.6%), butanoic acid (5.3%) and ethyl butanoate (4.6%). Four of the major compounds extracted by the two fibres (acetic acid, ethanol, hexanal and butanoic acid) were in similar percentages. However, the main differences were seen by a higher affinity of DVB/CAR/PDMS for aldehydes and a higher affinity of the CAR/PDMS coating for esters. The presence of ethyl esters in dry-fermented sausages is important due to their low sensory threshold values, imparting fruity notes to salami flavour (Stahnke, 1994).

In general, the compounds extracted by the two fibre coatings were basically the same as those extracted from dry-fermented sausages manufactured without the use of spices (Berdagué et al., 1993; Stahnke, 1994, 1995). The high recoveries of ethanol and acetic acid by CAR/PDMS and DVB/CAR/PDMS fibre coatings are characteristic of these coatings. Probably, they have not been recovered in high percentages by dynamic headspace analysis (Berdagué et al., 1993; Stahnke, 1994, 1995) due to the low affinity of Tenax for low-boiling compounds. On the other hand, hexanal has always been detected in the headspace of dry fermented sausages (Berdagué et al., 1993; Stahnke, 1994, 1995) because of its lipid oxidation origin. The volatile compounds extracted by the two fibre coatings appeared to be mainly formed by lipid oxidation, fermentation pathways, catabolism of branched amino acids and contamination. Lipid oxidation products are non-branched aliphatic compounds, such as alkanes, ketones, aldehydes, alcohols and furanic cycles (Frankel, 1984). Compounds of low molecular weight, released from fermentation pathways, are e.g. as 3-hydroxy-2-butanone, ethanol and acetic acid. Compounds from the catabolism of branched chain amino acids, such as

Table 1
Volatile compounds extracted from the headspace of fermented sausages by SPME after 3 h of extraction at 30 °C with different fibres (50/30μm DVB/CAR/PDMS and 75μm CAR/PDMS)

| N[a] | Compound | IK[b] | R[c] | DVB/CAR/PDMS | | CAR/PDMS | |
|---|---|---|---|---|---|---|---|
| | | | | Area[d] | %[e] | Area | % |
| 1 | pentane | 500 | a | 0.190 | 0.12 | 1.567 | 0.35 |
| 2 | ethanol | 506 | a | 26.489 | 17.17 | 76.920 | 17.30 |
| 3 | acetone | 527 | a | 0.359 | 0.23 | 1.145 | 0.26 |
| 4 | carbon disulphide | 536 | a | 15.400 | 9.98 | 2.069 | 0.47 |
| 5 | methyl acetate | 553 | a | – | | 0.025 | 0.01 |
| 6 | 2-methyl-propanal | 597 | a | – | | 0.293 | 0.07 |
| 7 | hexane | 600 | a | – | | 1.235 | 0.28 |
| 8 | 1-propanol | 612 | a | 0.507 | 0.33 | 2.629 | 0.59 |
| 9 | butanal | 629 | a | – | | 0.369 | 0.08 |
| 10 | 2-butanone | 637 | a | 0.246 | 0.16 | 1.422 | 0.32 |
| 11 | ethyl acetate | 640 | a | 3.268 | 2.12 | 34.581 | 7.78 |
| 12 | benzene | 677 | a | – | | 0.056 | 0.01 |
| 13 | 2-methyl-1-propanol | 688 | a | 1.112 | 0.72 | 13.493 | 3.03 |
| 14 | 3-methyl-butanal | 693 | a | – | | 2.639 | 0.59 |
| 15 | heptane (71) | 700 | a | – | | 0.099 | 0.02 |
| 16 | 2-methyl-butanal | 702 | a | – | | 3.538 | 0.80 |
| 17 | acetic acid | 720 | a | 31.618 | 20.49 | 99.569 | 22.39 |
| 18 | 2-ethyl furan (81) | 719 | a | tr[f] | | tr | |
| 19 | 1-butanol | 726 | a | – | | 2.034 | 0.46 |
| 20 | 2-pentanone | 733 | a | 0.630 | 0.41 | 2.334 | 0.52 |
| 21 | pentanal | 737 | a | 0.737 | 0.48 | 6.235 | 1.40 |
| 22 | ethyl propanoate | 743 | a | – | | 2.981 | 0.67 |
| 23 | propyl acetate | 748 | a | – | | 1.503 | 0.34 |
| 24 | 2-pentanol | 755 | a | – | | 1.630 | 0.37 |
| 25 | dimethyl-disulphide | 774 | a | – | | 0.408 | 0.09 |
| 26 | 3-hydroxy-2-butanone | 781 | a | – | | 0.667 | 0.15 |
| 27 | ethyl 2-methyl-propanoate | 786 | a | 0.330 | 0.21 | 0.976 | 0.22 |
| 28 | toluene | 790 | a | – | | 1.173 | 0.26 |
| 29 | 3-methyl-1-butanol | 793 | a | 2.086 | 1.35 | 29.540 | 6.64 |
| 30 | 2-methyl-1-butanol | 795 | a | 1.781 | 1.15 | 16.673 | 3.75 |
| 31 | octane | 800 | a | 1.548 | 1.00 | 7.376 | 1.66 |
| 32 | propanoic acid | 806 | a | 0.977 | 0.63 | 10.688 | 2.40 |
| 33 | 1-pentanol | 823 | a | 0.105 | 0.07 | 1.107 | 0.25 |
| 34 | ethyl butanoate | 829 | a | 2.285 | 1.48 | 20.439 | 4.60 |
| 35 | hexanal | 840 | a | 8.776 | 5.69 | 35.217 | 7.92 |
| 36 | 2-methyl-propanoic acid | 860 | a | 0.252 | 0.16 | 1.679 | 0.38 |
| 37 | ethyl 2-hydroxy-propanoate | 865 | a | 1.098 | 0.71 | 10.091 | 2.27 |
| 38 | ethyl 2-methyl-butanoate | 876 | a | – | | 0.902 | 0.20 |
| 39 | ethyl 3-methyl-butanoate | 880 | a | 0.099 | 0.06 | 1.150 | 0.26 |
| 40 | butanoic acid | 890 | a | 8.510 | 5.52 | 23.502 | 5.29 |
| 41 | p-xylene (91) | 891 | a | 0.634 | 0.41 | 0.762 | 0.17 |
| 42 | Nonane | 900 | a | – | | 0.485 | 0.11 |
| 43 | 3-methyl-1-butanol acetate | 905 | a | 0.398 | 0.26 | 1.010 | 0.23 |
| 44 | 2-methyl-1-butanol acetate | 908 | c | – | | 0.690 | 0.16 |
| 45 | styrene | 920 | a | 0.339 | 0.22 | – | |
| 46 | 1-hexanol (69) | 921 | a | tr | | 0.178 | 0.04 |
| 47 | ethyl pentanoate (85) | 928 | a | 0.019 | 0.01 | 0.049 | 0.01 |
| 48 | 2-heptanone (58) | 936 | a | 0.662 | 0.43 | 0.778 | 0.17 |
| 49 | 3-methyl-butanoic acid (60) | 936 | a | – | | 0.209 | 0.05 |
| 50 | heptanal (70) | 942 | a | 0.306 | 0.20 | 0.179 | 0.04 |
| 51 | 2-methyl-butanoic acid (74) | 943 | a | – | | 0.122 | 0.03 |
| 52 | pentanoic acid | 975 | a | 0.173 | 0.11 | 0.337 | 0.08 |
| 53 | 2-methyl-propyl 2-methyl-propanoate | 983 | c | – | | 0.160 | 0.04 |
| 54 | BCH[g] | 996 | c | 3.792 | 2.46 | 8.092 | 1.82 |
| 55 | decane | 999 | a | 0.925 | 0.60 | 0.480 | 0.11 |
| 56 | 2-pentyl-furan (81) | 1009 | c | 0.110 | 0.07 | 0.064 | 0.01 |
| 57 | 2-heptenal (Z) (41) | 1011 | a | 0.056 | 0.04 | tr | |
| 58 | benzaldehyde (77) | 1020 | a | 0.167 | 0.11 | 0.084 | 0.02 |
| 59 | butyrolactone (42) | 1025 | a | – | | 0.148 | 0.03 |

(*continued on next page*)

Table 1 (*continued*)

| N[a] | Compound | IK[b] | R[c] | DVB/CAR/PDMS | | CAR/PDMS | |
|---|---|---|---|---|---|---|---|
| | | | | Area[d] | %[e] | Area | % |
| 60 | ethyl hexanoate (88) | 1025 | a | 0.424 | 0.27 | 0.348 | 0.08 |
| 61 | 1-octen-3-ol (57) | 1027 | a | 0.322 | 0.21 | 0.092 | 0.02 |
| 62 | 2-octanone | 1037 | a | 0.544 | 0.35 | 0.697 | 0.16 |
| 63 | octanal | 1044 | a | 6.396 | 4.14 | 1.461 | 0.33 |
| 64 | 2,4-heptadienal (E,E) | 1061 | c | tr | | – | |
| 65 | hexanoic acid | 1068 | a | 4.418 | 2.86 | 2.877 | 0.65 |
| 66 | BCH | 1074 | c | – | | 0.164 | 0.04 |
| 67 | undecane | 1100 | a | 0.220 | 0.14 | 0.855 | 0.19 |
| 68 | phenol | 1104 | a | 1.559 | 1.01 | 0.856 | 0.19 |
| 69 | benzene acetaldehyde | 1110 | c | 0.094 | 0.06 | – | |
| 70 | 2-octenal (E) | 1116 | c | 0.297 | 0.19 | 0.120 | 0.03 |
| 71 | ethyl heptanoate | 1125 | a | 0.933 | 0.60 | 0.221 | 0.05 |
| 72 | 2-nonanone | 1142 | a | 3.549 | 2.30 | 0.964 | 0.22 |
| 73 | nonanal | 1152 | a | 14.867 | 9.63 | 0.957 | 0.22 |
| 74 | 2,4-Octadienal | 1180 | c | 0.114 | 0.07 | – | |
| 75 | phenylethyl alcohol | 1200 | c | 0.396 | 0.26 | – | |
| 76 | dodecane | 1200 | a | – | | 0.218 | 0.05 |
| 77 | 2-nonenal | 1215 | c | tr | | tr | |
| 78 | ethyl octanoate | 1226 | a | 1.569 | 1.02 | 0.397 | 0.09 |
| 79 | decanal (70) | 1255 | a | tr | | tr | |
| 80 | octanoic acid (60) | 1257 | a | 0.275 | 0.18 | 0.048 | 0.01 |
| 81 | 2,4-nonadienal | 1287 | c | 0.221 | 0.14 | – | |
| 82 | tridecane | 1300 | a | 0.194 | 0.13 | tr | |
| 83 | 2-decenal (E) | 1327 | a | 0.398 | 0.26 | – | |
| 84 | 2-undecanone | 1346 | a | 0.512 | 0.33 | 0.202 | 0.05 |
| 85 | nonanoic acid | 1351 | a | 0.120 | 0.08 | tr | |
| 86 | 2,4-decadienal (E,E) | 1392 | c | 0.079 | 0.05 | – | |
| 87 | tetradecane | 1399 | a | 0.058 | 0.04 | 0.064 | 0.01 |
| 88 | ethyl decanoate | 1421 | a | 0.330 | 0.21 | 0.174 | 0.04 |
| 89 | 2-undecenal | 1428 | c | 0.082 | 0.05 | – | |
| 90 | decanoic acid | 1442 | a | 0.356 | 0.23 | 0.139 | 0.03 |

[a] Number of peaks as in Figs. 1 and 2.
[b] KI: Kovats index calculated for DB-624 capillary column (J&W Scientific: 30 m, 0.25 mm id, 1.4 μm film tickness) installed on a gas chromatograph equipped with a mass-selective detector.
[c] R: Reliability of identification: a, mass spectrum and retention time identical with an authentic sample; b, mass spectrum and Kovats index from literature in accordance; c, tentative identification by mass spectrum.
[d] Results expressed as means of three replicates of total ion current (TIC) area by GC/MS except those compounds where the ion utilised in the quantification is indicated in parentheses.
[e] Percentage of total area.
[f] tr: compound detected as traces.
[g] BCH: branched chain hydrocarbon.

branched chain aldehydes (2-methyl-propanal, 2- and 3-methyl-butanal) were found in low percentages, while the branched chain alcohols were present in higher quantities (Table 1). However, the nature of the starters employed in dry-fermented sausages has a great influence on the volatile composition and, finally, on the sensory characteristics (Berdagué et al., 1993); but also, very important are the effects of processing parameters (Stahnke, 1994, 1995).

The absorption-time profiles of different groups of volatile compounds (alcohols, aldehydes, ketones, esters and acids) obtained through the usage of both fibre coatings are shown in Figs. 4 and 5. Two main factors affecting the extraction process were: the fibre coating and the extraction time, although the effect of the time of exposure was more marked for the CAR/PDMS fibre

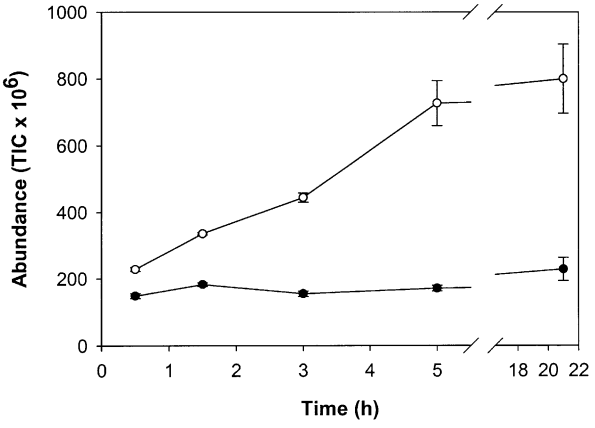


Fig. 3. Absorption-time profiles for total dry-fermented sausage volatiles using different fibre coatings. (●) DVB/Carboxen/PDMS and (○) Carboxen/PDMS coatings.

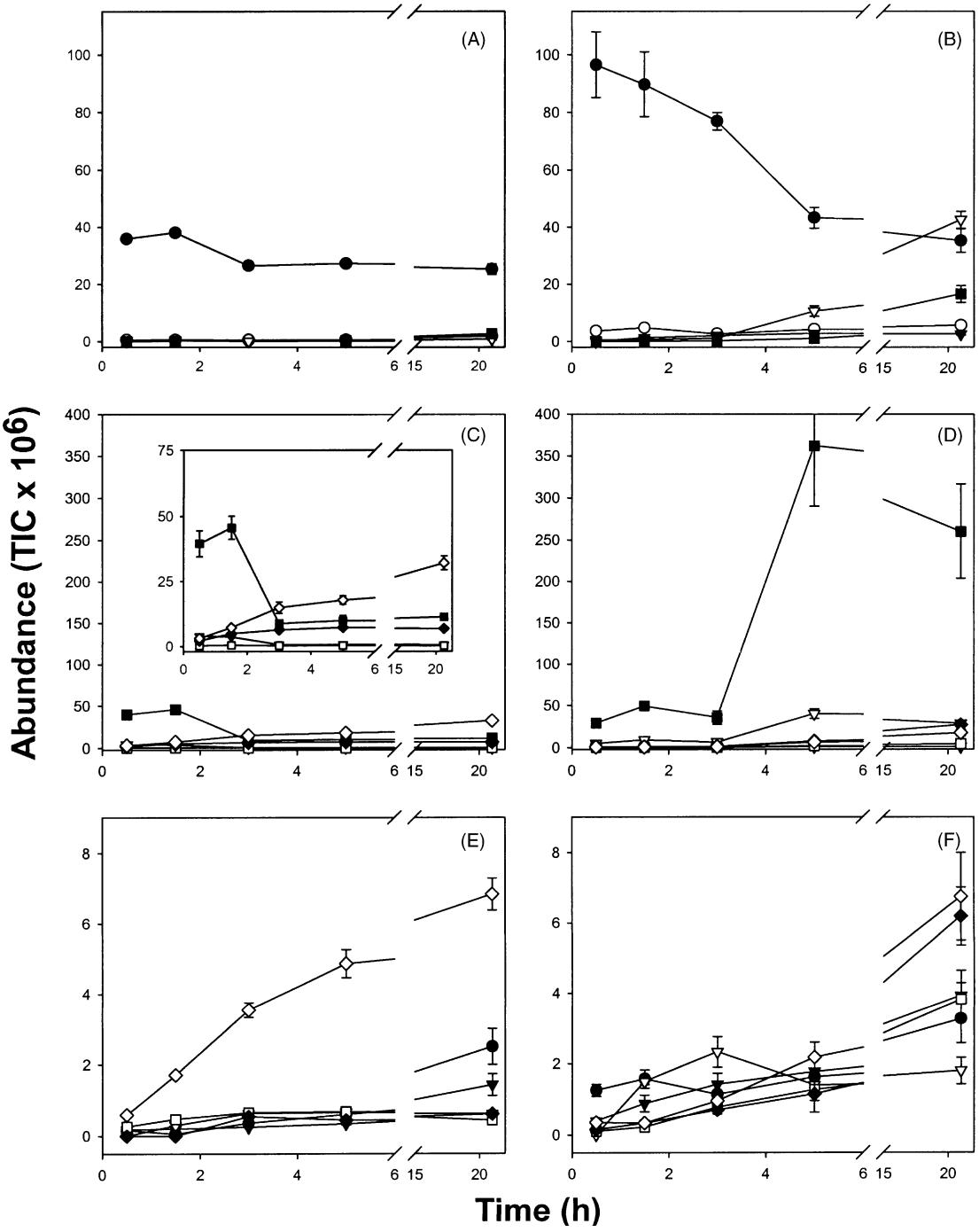


Fig. 4. Absorption-time profiles of volatile compounds using different fibres coatings of SPME: (A) alcohols by DVB/Carboxen/PDMS, (B) alcohols by Carboxen/PDMS, (C) aldehydes by DVB/Carboxen/PDMS, (D) aldehydes by Carboxen/PDMS, (E) ketones by DVB/Carboxen/PDMS and (F) ketones by Carboxen/PDMS. The symbols represent carbon number of compound C2 (●), C3 (○), C4 (▼), C5 (▽), C6 (■), C7 (□), C8 (◆), C9 (◇) and C10 (▲).

than for the DVB/CAR/PDMS fibre (Gianelli et al., 2002), because the peak areas of many compounds increased with increasing time of exposure. This is the case for the ketones, ethyl propanoate and ethyl butanoate, and butanoic acid (Figs. 4F, 5B, 5D) in CAR/PDMS fibre. However, the time of exposure only showed an important effect on the extraction of 2-nonanone by DVB/CAR/PDMS fibre (Fig. 4E). On the other hand, four compounds (hexanal, ethanol, ethyl acetate and acetic acid) showed surprising behaviour during the time of exposure using the CAR/PDMS fibre. Ethanol showed a decrease in peak area while increasing the time of exposure (Fig. 4B). On the other hand, hexanal showed a slight increase until 3 h of

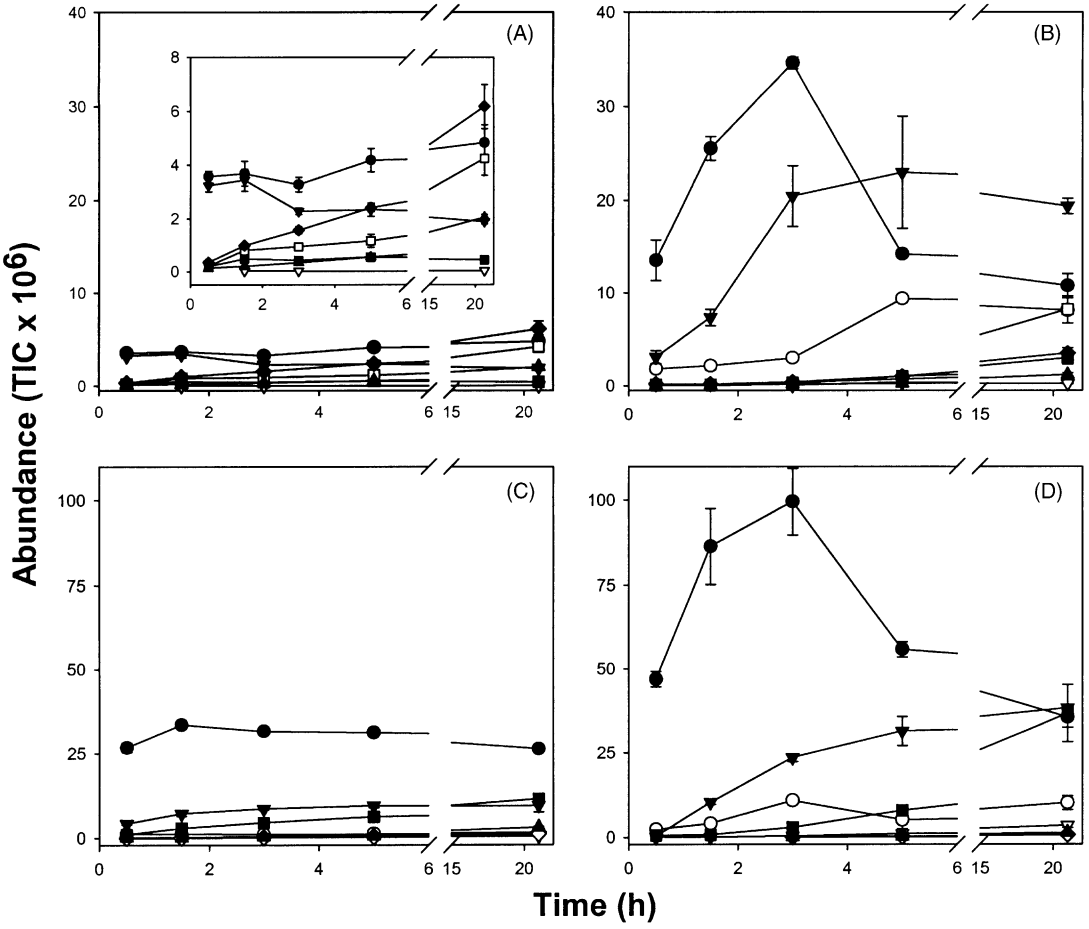


Fig. 5. Absorption-time profiles of volatile compounds using different fibres coatings of SPME: (A) ethyl esters by DVB/Carboxen/PDMS, (B) ethyl esters by Carboxen/PDMS, (C) acids by DVB/Carboxen/PDMS and (D) acids by Carboxen/PDMS. The symbols represent carbon number of compound C2 (●), C3 (○), C4 (▼), C5 (▽), C6 (■), C7 (□), C8 (◆), C9 (◇) and C10 (▲).

exposure and, after 5 h of exposure, its peak area increased seven times (Fig. 4D); at the same time, ethyl acetate (Fig. 5B) and acetic acid (Fig. 5D) showed decreases of one half of their peak areas. The reason for this behaviour could be the existence of competitive effects between hexanal and ethyl acetate and acetic acid (Roberts et al., 2000). The high generation of hexanal, due to the lipid oxidation phenomenon, could be due to the long exposure time (5 h). Therefore, a shorter time of sampling could help avoid this competition effect.

In conclusion, the optimal time of extraction should be the time to reach equilibrium, avoiding the presence of lipid oxidation processes favoured by a long time of exposure. In this case, all the compounds extracted by the DVB/CAR/PDMS fibre except for 2-nonanone reached equilibrium in 90 min, whilst the compounds extracted by the CAR/PDMS coating needed at least 3 h to reach equilibrium, longer times being inappropriate due to oxidation phenomena that can produce competitive effects between compounds. SPME is an appropriate tool for qualitative and quantitative analysis of volatile compounds in the headspace of dry-fermented sausage. However, the extraction yields of dry-fermented sausages volatile compounds varied according to the fibre coating used. Therefore, it is necessary to carefully select the extraction conditions, depending on the objective of the study.

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