New Device for Direct Extraction of Volatiles in Solid Samples Using SPME

Jorge Ruiz,* Jesús Ventanas, and Ramón Cava

Tecnología y Bioquímica de los Alimentos, Facultad de Veterinaria, Universidad de Extremadura, Avda Universidad s/n, 10071 Cáceres, Spain

A new device that allows extraction of volatiles from solid materials by SPME, avoiding preparation of the sample, was designed and tested in two different food products. Volatiles from dry-cured ham and canned liver sausage were analyzed by headspace SPME (HS SPME) and by using a new device that protects the SPME fiber in the core of the solid material. Volatile profiles generated by using both methods of extraction were very similar in both products. Compounds that have been previously highlighted as quality markers, such as products from oxidative degradation of lipids, products from Strecker degradation of amino acids, or terpenes, were satisfactorily extracted by SPME coupled to the device for direct extraction. In addition, by using this method no laboratory contaminants were extracted, whereas some major laboratory solvents were presented in the chromatogram using the HS SPME method. However, coefficients of variation were higher when performing the direct sampling procedure. This new device appears to have potential as a simple method for extracting volatiles in solid materials while at the same time avoiding taking samples.

Keywords: *Direct extraction; solid-phase microextraction (SPME); volatiles; ham; meat products*

INTRODUCTION

A number of methods have been developed to analyze volatiles in food, biological materials, soil, chemicals, and other complex matrixes. New techniques have achieved a considerable reduction in the amount of sample required for analysis. However, when studying solid materials, all of them require a sampling step, which in many cases causes analytical and practical problems. When target compounds in the analysis are very volatile, sampling or preparation of the sample for analysis can lead to losses of such compounds. Moreover, procedures involved in the sampling step might produce artifacts, such as compounds derived from lipid oxidation (*1*, *2*). In some studies, it is necessary to keep the product intact while following the changes in volatile profile throughout a period of time, and sampling interferes with the experiment. Besides, in the industry, analytical methods for control of volatile profile or detection of some volatiles such as contaminants or quality markers may involve depreciation of the product, and thereby economical losses.

The absorption technique solid-phase microextraction (SPME) (*3*, *4*) has been used for a number of applications, such as to analyze volatile profiles in different foodstuffs, detect chemicals in biological and inorganic materials, and so on (reviewed by *5*). It has also been used to extract volatiles from liquids by introducing the fiber directly in the sample. In fact, direct extraction on-field has many advantages when compared to traditional sampling procedures (*6*). However, the latter cannot be performed in solid samples because the fiber is too weak to be pushed into the solid material.

In this study, a device that allows introduction of the SPME fiber into the core of the solid material and therefore, direct extraction of volatiles from the solid sample avoiding sample manipulation, has been designed and tested (*7*), and results have been compared with those obtained by headspace SPME.

* Corresponding author (phone 34 927 257169; fax 34 927 257110; e-mail jruiz@unex.es).

MATERIALS AND METHODS

Materials. Blocks (500 g each) of vacuum-packaged dry-cured ham and canned liver sausage were purchased from a local supermarket. Both products were divided into two parts, half for each method of analysis. Samples were kept under refrigeration storage until analyses, which were carried out within the next 3 days. Analysis of volatiles was carried out five times both by HS SPME and by SPME coupled to the direct extraction device (DED).

Sampling. For both HS SPME and SPME−DED, a SPME (Supelco Co., Bellefonte, PA) fiber (10 mm length) coated with Carboxen-poly(dimethylsiloxane) (75 μm thickness) was used to extract the volatiles of dry-cured ham and canned liver sausage. Prior to analysis the SPME fiber was preconditioned at 280 °C for 45 min in the GC injection port.

For HS SPME extraction, dry-cured ham was ground with a commercial grinder, whereas canned liver sausage was directly taken from the can. A 2.00-g portion of each material wase weighed into a 4-mL vial, and the vial was screw-capped with a laminated Teflon-rubber disk (Figure 1). The fiber was inserted into the sample vial through the septum and then exposed to headspace. The extractions were carried out in an oven to ensure a homogeneous temperature for sample and headspace. Extraction was performed at 25 °C for 30 min. Before extraction, samples were equilibrated for 15 min at the same temperature used for extraction.

To carry out the analysis by SPME using the new DED (Figure 1), the needle of the SPME holder was placed into the DED, and thereafter the DED was introduced into the core of either the dry-cured ham or the canned liver sausage by pressing on. Once inside the solid material, the fiber was exposed to the small space inside the DED, which has small holes that allow the volatiles from the sample to enter into the space in which the fiber is kept. Extraction was carried

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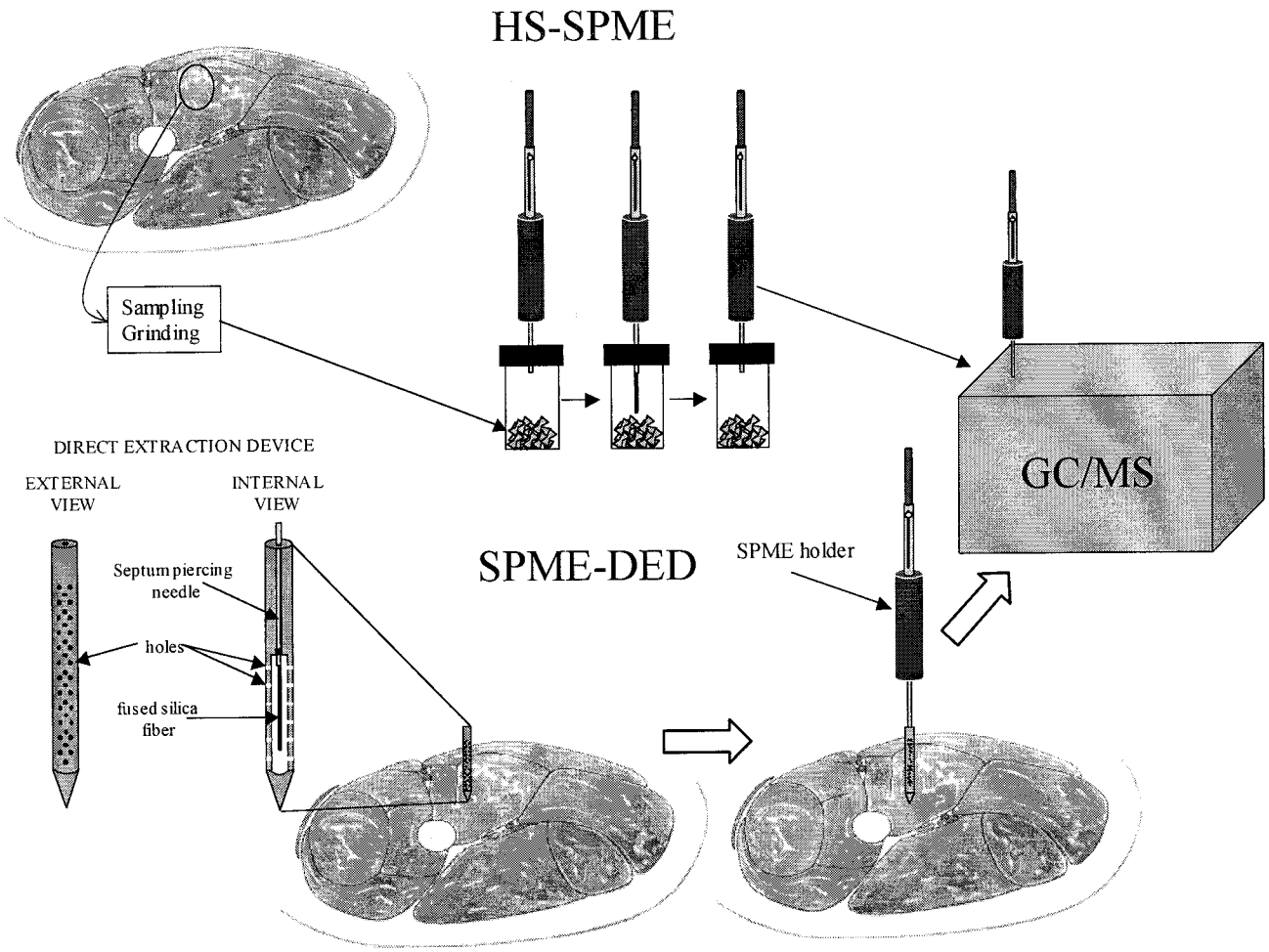

Figure 1. Diagram of the direct extraction device and its use (*7*), compared to headspace SPME.

out for 30 min at 25 °C. Previous to analysis, the samples were kept at extraction temperature until the internal temperature was constant. Analyses using both headspace SPME and SPME−DED were repeated five times.

Gas Chromatography−Mass Spectrometry. Analyses were performed using a Hewlett-Packard 5890 series II gas chromatograph coupled to a mass selective detector (Hewlett-Packard HP-5971 A). Volatiles were separated using a 5% phenyl-methyl silicone (HP-5) bonded-phase fused silica capillary column (Hewlett-Packard, 50 m × 0.32 mm i.d., film thickness 1.05 mm), operating at 6 psi of column head pressure, resulting in a flow of 1.3 mL min^{-1} at 40 °C. The SPME fiber was desorbed and maintained in the injection port at 280 °C during the whole chromatographic run. The injection port was in a splitless mode. The temperature program was isothermal for 10 min at 40 °C, raised to 200 °C at a rate of 5 °C min^{-1}, and then raised to 250 °C at a rate of 15 °C min^{-1}, and held for 5 min. *n*-Alkanes (Sigma R-8769) were run under the same conditions as the samples to calculate the Kovats index values of compounds.

The transfer line to the mass spectrometer (MS) was maintained at 280 °C. The mass spectra were obtained using a mass selective detector (Hewlett-Packard HP-5971 A) by electronic impact at 70 eV, a multiplier voltage of 1756V, and collecting data at a rate of 1 scan s^{-1} over the *m*/*z* range of 30 to 300. Compounds were tentatively identified by comparing their mass spectra with those contained in the NIST/EPA/NIH and Wiley libraries and by comparison of Kovats indexes with those reported in the literature (*8*, *9*). Results from volatile analyses are provided both in total area counts and area percentage of volatile compounds identified.

RESULTS AND DISCUSSION

More than 100 peaks were detected both in dry-cured ham and canned liver sausage using either method of analysis (Figure 2). The identified compounds are given in order of elution in Table 1. The number of compounds that were tentatively identified in dry-cured ham was 75 by HS SPME and 63 by SPME−DED, whereas in canned liver sausage was 82 and 78 compounds, respectively.

With regards to the group of compounds extracted from dry-cured ham, there was little variation between the two methods of extraction, as can be observed in Figure 2. Aldehydes constituted the major group using HS SPME, and the second one using SPME−DED, with a similar percentage of total area in both methods (28.9 and 26.1% of total area respectively). The other groups of compounds detected were the same using the two methods of analysis: aliphatic alcohols (12.3 and 12.2%, respectively), aliphatic ketones (16.3 and 13.2%), carboxylic acids (22.5 and 30.5%), aromatic and aliphatic hydrocarbons (8.8 and 13.1%), nitrogen compounds (1.1 and 1.7%), sulfur compounds (0 and 0.4%), aliphatic esters (4.0 and 1.0%), chloride compounds (4.7 and 0.0%), and furans (0.5 and 1.8%). This profile of volatile compounds is similar to previously reported results in different types of dry-cured hams, in which aldehydes has been shown as the group with the highest area percentage, and the group of compounds found have been basically the same as those in the present study using SPME−DED (*1*, *2*, *10*, *11*). However, in the

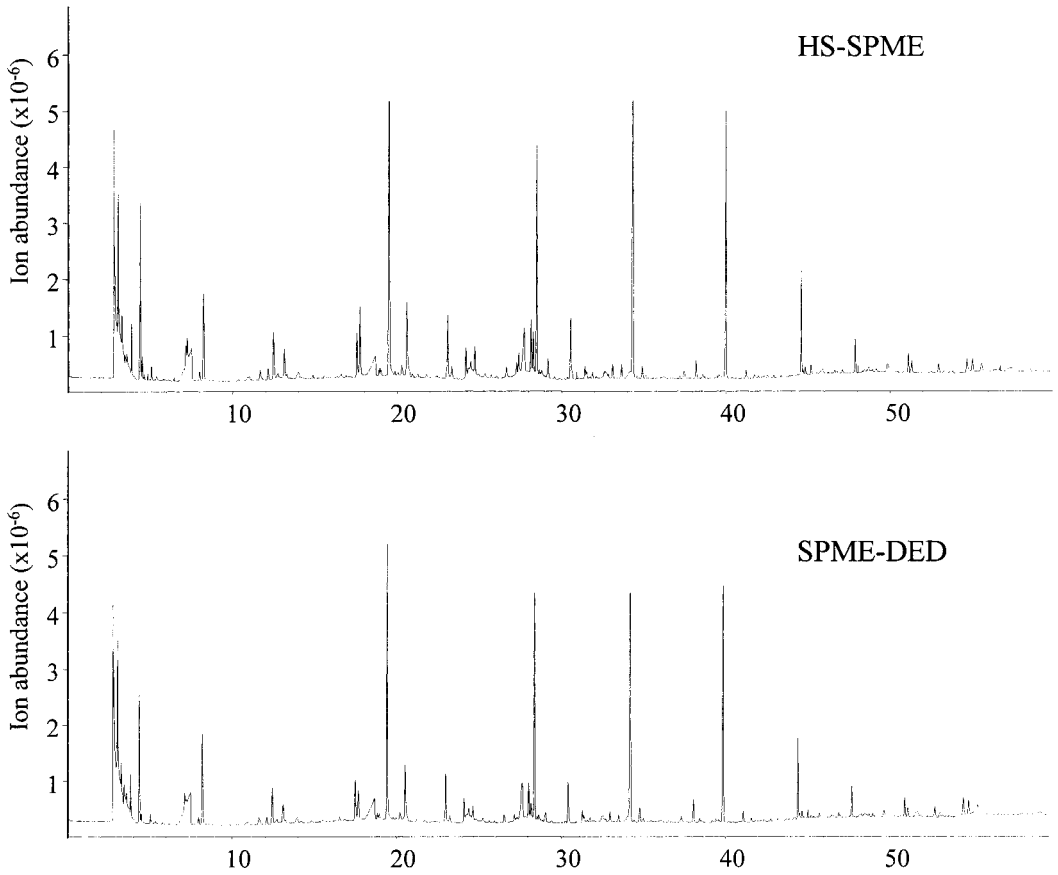

Figure 2. Comparative gas chromatograms of volatile profile from dry-cured ham using either headspace SPME (HS SPME) or SPME coupled to the direct extraction device (SPME−DED).

present study the area shown by short-chain acids, comprising acetic, butanoic, 2- and 3-methyl butanoic, hexanoic, heptanoic, octanoic, nonanoic, decanoic and dodecanoic acids (22.5−30.5% of total area using HS SPME and SPME−DED, respectively) was much higher than in previously published studies. Similarly, some aldehydes did not follow exactly the same pattern as in other publications. In fact, 3-methyl butanal, which has been shown to be one of the major compounds in dry-cured hams did not reach 1% of total area in the present study, neither by using HS SPME nor by SPME−DED. This is not strange, as the peak areas obtained by SPME−GC−MS method do not necessarily reflect the true proportion of the components in the sample, because individual compounds with different structures exhibit different volatilities and also different physical properties which can affect partition coefficients. In addition, differences with previously published results could also be due to the marked variations in area percentage of several compounds between different types of dry-cured hams.

In a previous study about HS SPME analysis of dry-cured Iberian ham volatiles the successful extraction of main compounds related to ham flavor was highlighted (*1*). In the present research such compounds were successfully extracted using the SPME−DED technique. Major compounds such as 2-propanone (7.0 and 7.2% of total area using either HS SPME or SPME−DED), acetic acid (10.0 and 11.3%), or hexanal (22.3 and 10.0%) were basically the same using both procedures of extraction, and similar to those described previously in dry-cured Iberian hams by SPME using a PDMS fiber (*1*). Most compounds found in dry-cured ham are derived from the autoxidation of unsaturated fatty acids, although some of them could also result from amino acids, having either a microbial or a Strecker degradation origin, and some others might also have an animal feed origin (*2*, *12*). Among the formers, some of the straight-chain aliphatic aldehydes found, such as pentanal, hexanal, heptanal, 2-heptenal, octanal, nonanal, 2-nonenal, decanal, 2-decenal, 2,4-decadienal, and 2-undecenal, have been commonly used to monitor lipid oxidation, not only in dry-cured ham (*13*) but in a number of meat products (reviewed by *14*), and in the present study were satisfactorily analyzed using SPME−DED. Some of these compounds, especially hexanal and 2,4-decadienal, have been related to rancid flavor in hams and other meat products (*13*, *15*). Hexanal has been shown as the major compound in other studies about dry-cured ham volatiles (*10*, *16*), and in the present study also showed the highest area using either HS SPME or SPME−DED.

Most of the hydrocarbons also have a lipid oxidation origin, although an animal feed origin has also been hypothesized for some of them, such as the branched alkanes (*2*, *17*). Hydrocarbons and other compounds from lipid oxidation with importance in dry-cured ham flavor, like 1-octen-3-ol, were also extracted using SPME−DED.

Compounds derived from amino acids, such as 2- and 3-methylbutanal, 2- and 3-methyl butanoic acids, 2-methylpropanal, or dimethyl disulfide, have been highlighted as important contributors to the flavor of dry-cured ham (*11*, *12*) and other fermented meat products (*18*). Moreover, 2- and 3-methylbutanal have been shown to increase during processing in dry-cured ham,

Table 1. Volatile Compound Areas and Percentages from Dry-Cured Ham and Canned Liver Sausage Using either Headspace SPME or SPME−DED

		canned liver sausage				dry-cured ham			
		HS SPME		SPME−DED		HS SPME		SPME−DED	
compound	rel[b]	area[a] (CV)	% area	area (CV)	% area	area (CV)	% area	area (CV)	% area
2-aminopropanol	MS	nd[c]	nd	nd	nd	15.3 (17)	0.9	5.2 (60)	0.6
acetaldehyde	MS	9.7 (17)	0.5	9.2 (36)	0.4	nd	nd	nd	nd
methanethiol	MS	4.2 (47)	0.2	9.4 (31)	0.4	4.4 (13)	0.2	8.1 (50)	0.9
ethanol	MS	7.8 (28)	0.4	5.9 (28)	0.2	25.4 (14)	1.4	54.8 (68)	5.8
2-propanone	MS	35.8 (30)	1.7	27.8 (67)	1.1	125.2 (13)	7.0	67 (48)	7.2
pentane	MS, KI	nd	nd	nd	nd	8.5 (45)	0.5	2.7 (63)	0.3
thiobismethane	MS	2.1 (53)	0.1	16 (40)	0.6	0.6 (15)	0	2.7 (45)	0.3
1,3-pentadiene	MS, KI	nd	nd	nd	nd	8.6 (16)	0.5	1.7 (66)	0.2
dichloromethane	MS, KI	4.4 (17)	0.2	nd	nd	nd	nd	nd	nd
1-propanol	MS, KI	nd	nd	nd	nd	1.3 (31)	0.1	2.2 (54)	0.2
2-methylpropanal	MS, KI	4.3 (38)	0.2	6.9 (57)	0.3	nd	nd	3.5 (64)	0.4
2,3-butanedione	MS, KI	2.6 (79)	0.1	nd	nd	nd	nd	nd	nd
2-butanone	MS, KI	12.4 (29)	0.6	6.1 (69)	0.2	14.7 (15)	0.8	6.3 (47)	0.7
hexane	MS, KI	nd	nd	nd	nd	9 (77)	0.5	nd	nd
1-propanethiol	MS	10 (37)	0.5	20.2 (36)	0.8	nd	nd	nd	nd
acetic acid	MS, KI	113.6 (40)	5.4	92.3 (32)	3.5	177.5 (6)	10	106 (24)	11.3
acetic acid ethyl ester	MS, KI	nd	nd	nd	nd	9 (11)	0.5	1.6 (23)	0.2
chloroform	MS, KI	11.7 (9)	0.6	nd	nd	83.5 (22)	4.7	nd	nd
3-methylbutanal	MS, KI	5.7 (72)	0.3	14 (52)	0.5	2.5 (71)	0.1	7.3 (78)	0.8
1-butanol	MS, KI	nd	nd	nd	nd	4.3 (17)	0.2	1.5 (27)	0.2
2-methylbutanal	MS, KI	4.9 (50)	0.2	9.1 (37)	0.3	7.1 (32)	0.4	10.5 (92)	1.1
1,2-propanediol	MS	46.8 (31)	2.2	53.4 (38)	2.0	15.6 (11)	0.9	7.3 (19)	0.8
2-propanone-1-hydroxy	MS	0.4 (36)	0.05	2.6 (57)	0.1	nd	nd	nd	nd
1-penten-3-ol	MS, KI	nd	nd	nd	nd	13.4 (27)	0.8	3.9 (57)	0.4
2-pentanone	MS, KI	nd	nd	nd	nd	57.4 (15)	3.2	23.8 (25)	2.5
pentanal	MS, KI	1.3 (63)	0.1	3.6 (29)	0.1	30.4 (19)	1.7	8.5 (26)	0.9
heptane	MS, KI	1.3 (17)	0.1	4.8 (62)	0.2	7.3 (24)	0.4	9.7 (25)	1.0
propanoic acid	MS, KI	1.4 (66)	0.1	nd	nd	nd	nd	nd	nd
2-ethyl furan	MS, KI	2.1 (39)	0.1	1.3 (42)	0.1	nd	nd	nd	nd
acetoin	MS, KI	nd	nd	nd	nd	14.7 (15)	0.8	7.9 (61)	0.8
2,4-dimethylfuran	MS	2.4 (26)	0.1	2.1 (44)	0.1	nd	nd	nd	nd
butanoic acid methyl ester	MS, KI	nd	nd	nd	nd	3.8 (19)	0.2	nd	nd
pyrazine	MS	15.2 (36)	0.7	9.6 (22)	0.4	nd	nd	nd	nd
dimethyl disulfide	MS, KI	2.4 (52)	0.1	4.7 (55)	0.2	nd	nd	3.4 (18)	0.4
3-ethoxy-1-propanol	MS, KI	nd	nd	nd	nd	3.8 (9)	0.2	nd	nd
1-(H)-pyrrole	MS, KI	4.5 (58)	0.2	10.5 (72)	0.4	nd	nd	nd	nd
1-pentanol	MS, KI	nd	nd	2.2 (32)	0.1	51.4 (9)	2.9	11.9 (45)	1.3
toluene	MS, KI	7.5 (45)	0.4	nd	nd	48.3 (31)	2.7	nd	nd
butanoic acid	MS, KI	4.7 (39)	0.2	2.3 (32)	0.1	75.6 (17)	4.2	34.1 (12)	3.6
2-hexanone	MS, KI	nd	nd	nd	nd	4.7 (7)	0.3	nd	nd
1-octene	MS, KI	nd	nd	nd	nd	5 (22)	0.3	nd	nd
hexanal	MS, KI	33.6 (36)	1.6	54.8 (30)	2.1	397 (28)	22.3	94 (31)	10.0
2-octene	MS, KI	nd	nd	nd	nd	3 (18)	0.2	nd	nd
branched alkene	MS	nd	nd	nd	nd	2.4 (37)	0.1	nd	nd
acetic acid butyl ester	MS, KI	nd	nd	nd	nd	11.6 (10)	0.6	nd	nd
2-methyl pyrazine	MS, KI	23.1 (29)	1.1	20.8 (19)	0.8	nd	nd	nd	nd
3-methyl butanoic acid	MS, KI	nd	nd	nd	nd	3.5 (21)	0.2	1.4 (58)	0.2
furfural	MS, KI	6.6 (28)	0.3	8.8 (20)	0.3	nd	nd	nd	nd
2-methyl butanoic acid	MS, KI	nd	nd	nd	nd	3.4 (31)	0.2	1.1 (79)	0.1
furfuryl alcohol	MS, KI	27.3 (34)	1.3	62.7 (26)	2.4	nd	nd	nd	nd
2-methyl 3-hexanol	MS	nd	nd	nd	nd	59.1 (5)	3.3	4.5 (61)	0.5
1-hexanol	MS, KI	1.5 (56)	0.1	1.7 (21)	0.1	nd	nd	nd	nd
m-xylene	MS, KI	3.6 (19)	0.2	9.3 (20)	0.4	nd	nd	nd	nd
4-heptanone	MS, KI	nd	nd	nd	nd	8.8 (34)	0.5	2 (93)	0.2
2-heptanone	MS, KI	4.9 (40)	0.2	4.8 (19)	0.2	25.9 (11)	1.5	8.9 (49)	1.0
styrene	MS, KI	nd	nd	nd	nd	10.8 (33)	0.6	nd	nd
heptanal	MS, KI	26.1 (29)	1.2	84.1 (65)	3.2	18.4 (27)	1.1	17.5 (71)	1.9
methional	MS, KI	15.7 (13)	0.7	18.9 (67)	0.7	nd	nd	nd	nd
2,6-dimethylpyrazine	MS, KI	47.2 (22)	2.3	40.4 (35)	1.5	nd	nd	nd	nd
dihydrofuranone	MS	nd	nd	nd	nd	4.5 (35)	0.3	4.3 (27)	0.5
hexanoic acid methyl ester	MS, KI	nd	nd	nd	nd	2.4 (20)	0.1	nd	nd
1-methylethylbenzene	MS, KI	nd	nd	nd	nd	2.1 (32)	0.1	0.7 (63)	0.1
α-thujene	MS, KI	20.6 (55)	1.0	34.3 (45)	1.3	nd	nd	nd	nd
methyl propyl disulfide	MS, KI	13.3 (52)	0.6	24.4 (49)	0.9	nd	nd	nd	nd
α-pinene	MS, KI	111.5 (19)	5.3	178.3 (15)	6.8	nd	nd	nd	nd
2-furancarboxylic acid	MS	11.3 (66)	0.5	11.7 (44)	0.4	nd	nd	nd	nd
2-heptenal	MS, KI	32.2 (50)	1.5	56.5 (52)	2.2	7.4 (37)	0.4	3.7 (44)	0.4
propylbenzene	MS, KI	nd	nd	nd	nd	9.5 (74)	0.5		
hexanoic acid	MS, KI	nd	nd	nd	nd	74.6 (11)	4.2	42.7 (45)	4.6
hexanoic acid + benzaldehyde	MS, KI	80.3 (24)	3.8	82.8 (18)	3.2	nd	nd	nd	nd
1-octen-3-ol	MS, KI	nd	nd	nd	nd	40.6 (13)	2.3	5.8 (35)	0.6
2,3-octanedione	MS, KI	nd	nd	nd	nd	25.3 (55)	1.4	7 (83)	0.7

Table 1. Continued

		canned liver sausage				dry-cured ham			
		HS SPME		SPME−DED		HS SPME		SPME−DED	
compound	rel[b]	area[a] (CV)	% area	area (CV)	% area	area (CV)	% area	area (CV)	% area
sabinene	MS, KI	93.4 (17)	4.5	145.1 (8)	5.5	nd	nd	nd	nd
β-pinene	MS, KI	85.1 (20)	4.1	158.7 (17)	6.1	nd	nd	nd	nd
2-octanone	MS, KI	nd	nd	nd	nd	2.9 (25)	0.2	1.1 (61)	0.1
β-myrcene	MS, KI	129.5 (17)	6.2	87 (19)	3.3	nd	nd	nd	nd
2-pentylfuran	MS, KI	nd	nd	nd	nd	4.1 (26)	0.2	12.7 (53)	1.4
octanal	MS, KI	33.1 (19)	1.6	49.9 (51)	1.9	17.8 (16)	1.0	14.2 (31)	1.5
trimethylpirazine	MS	3.5 (49)	0.2	5.3 (23)	0.2	nd	nd	nd	nd
α-phellandrene	MS, KI	10.1 (8)	0.5	20.5 (42)	0.8	nd	nd	nd	nd
3-carene	MS, KI	7.4 (16)	0.4	13.1 (9)	0.5	nd	nd	nd	nd
eucalyptol	MS, KI	15.9 (27)	0.8	22.9 (25)	0.9	nd	nd	nd	nd
β-*trans*-ocimene	MS, KI	5.2 (47)	0.2	2.2 (58)	0.1	nd	nd	nd	nd
benzeneacetaldehyde	MS, KI	10.4 (70)	0.5	17.1 (42)	0.7	nd	nd	nd	nd
heptanoic acid	MS, KI	nd	nd	nd	nd	13.9 (15)	0.8	17.9 (27)	1.9
2-octenal	MS, KI	13.8 (42)	0.7	25.9 (44)	1.0	nd	nd	nd	nd
γ-terpinene	MS, KI	68.3 (25)	3.3	67.6 (35)	2.6	nd	nd	nd	nd
1-octanol	MS, KI	7.3 (39)	0.3	8.3 (40)	0.3	2.8 (22)	0.2	3.5 (26)	0.4
p-cresol	MS, KI	nd	nd	nd	nd	5.2 (21)	0.3	nd	nd
2-nonanone	MS, KI	6.5 (52)	0.3	6.7 (31)	0.3	10.3 (50)	0.6	nd	nd
terpinolene	MS, KI	44.1 (23)	2.1	35 (22)	1.3	nd	nd	nd	nd
linalool	MS, KI	20.6 (19)	1.0	30.4 (12)	1.2	nd	nd	nd	nd
nonanal	MS, KI	97.4 (37)	4.7	69.4 (7)	2.7	17.7 (41)	1.0	22.5 (37)	2.4
dipropyl disulfide	MS, KI	24.5 (29)	1.2	23 (54)	0.9	nd	nd	nd	nd
maltol	MS, KI	2 (31)	0.1	7.3 (48)	0.3	nd	nd	nd	nd
octanoic acid	MS, KI	55.3 (42)	2.6	65 (51)	2.5	18.5 (25)	1.1	33.2 (46)	3.5
2-nonenal	MS, KI	nd	nd	nd	nd	4.3 (20)	0.2	9.3 (36)	1.0
endo-borneol	MS, KI	1.8 (52)	0.1	1.8 (44)	0.1	nd	nd	nd	nd
4-terpineol	MS, KI	56.7 (12)	2.7	75.8 (25)	2.9	nd	nd	nd	nd
decanal	MS, KI	nd	nd	nd	nd	2 (16)	0.1	6.2 (39)	0.7
α-terpineol	MS, KI	18.3 (25)	0.9	29 (50)	1.1	nd	nd	nd	nd
nonanoic acid	MS, KI	43.8 (59)	2.1	49.3 (58)	1.9	23.1 (54)	1.3	29.3 (26)	3.1
2-decenal	MS, KI	33.5 (11)	1.6	44 (33)	1.7	3.9 (39)	0.2	20.2 (43)	2.2
β-octalactone	MS, KI	3.9 (57)	0.2	5.2 (37)	0.2	1 (41)	0.1	2.8 (46)	0.3
isopropyl cresol	MS, KI	27.7 (13)	1.3	36.5 (28)	1.4	nd	nd	nd	nd
tridecane	MS, KI	nd	nd	nd	nd	nd	nd	5.9 (55)	0.6
1-H-indole	MS, KI	3 (55)	0.1	5.2 (41)	0.2	nd	nd	nd	nd
2,4-decadienal	MS, KI	8.7 (37)	0.4	16.8 (39)	0.6	1.8 (59)	0.1	6.4 (81)	0.7
decanoic acid	MS, KI	35.5 (61)	1.7	76 (48)	2.9	9.1 (39)	0.5	9.9 (35)	1.1
2-undecenal	MS, KI	42.6 (27)	2	60.5 (44)	2.3	5.2 (35)	0.3	20.5 (86)	2.2
heptylbenzene	MS	nd	nd	nd	nd	1.3 (44)	0.1	2.7 (50)	0.3
alkene	MS	nd	nd	nd	nd	1.3 (32)	0.1	4.6 (83)	0.5
tetradecane	MS, KI	3.9 (26)	0.2	2.6 (60)	0.1	2.1 (21)	0.1	6.6 (68)	0.7
trans-caryophyllene	MS	18.9 (20)	0.9	34.9 (61)	1.3	nd	nd	nd	nd
1-dodecanol	MS	nd	nd	nd	nd	1.8 (3)	0.1	19.4 (51)	2.1
alkene	MS	nd	nd	nd	nd	6.8 (71)	0.4	26.8 (102)	2.9
pentadecane	MS, KI	21.9 (60)	1.0	29.2 (72)	1.1	12.2 (60)	0.7	43 (83)	4.6
alkene	MS	nd	nd	nd	nd	9.6 (35)	0.5	8.8 (55)	0.9
BHT	MS, KI	3.4 (31)	0.2	7.6 (97)	0.3	nd	nd	nd	nd
myristicin	MS, KI	23.2 (21)	1.1	55.2 (44)	2.1	nd	nd	nd	nd
dodecanoic acid	MS, KI	7.8 (65)	0.4	3.4 (32)	0.1	2.8 (20)	0.2	10.6 (94)	1.1
nonylbenzene	MS	nd	nd	nd	nd	4.5 (60)	0.3	9.5 (81)	1.0

[a] Values are means (area counts × 1000) of five analyses with percentage coefficient of variation shown in parentheses. [b] MS, Mass spectrum tentatively identified using NIST, EPA, NDH library. KI, Kovats index in agreement with literature. [c] nd, not detected.

and have been proposed as ripening markers for this product (*2*). All these compounds were successfully analyzed by SPME−DED, and a study about the analysis of 2- and 3-methylbutanal using SPME−DED throughout the ripening of the hams to control the processing is currently being carrying out.

Quality control in the dry-cured ham industry is mainly focused on the aroma of the product, as it has been shown to be the key attribute affecting acceptability (*19*). It is carried out by either analytical or sensory methods. The formers involve sampling, and this is a potential problem, first, because in Spain and Italy most dry-cured hams are commercialized as whole pieces, and therefore, taking samples implies depreciation of the product; second, because the ham should be kept as a whole piece throughout the processing to allow a satisfactory dehydration and development of the chemical reactions leading to the proper aroma and flavor of the hams (*2*, *12*, *19*). On the other hand, the standard sensory method, known as "la cala" consists of introducing a tool made out of a piece of the *tibialis* bone from a cattle inside the core of the ham; thereafter, an expert sniffs the bone and perceives the aroma retained on it. This method is easier and does not spoil the ham, but it is subjective and extremely dependent on the expert. SPME−DED appears as an unbiased, repetitive, and nondestructive method for the quality control of hams, because it satisfactorily reflects the groups of volatile substances and the individual volatile compounds of dry-cured ham that are quality and ripening markers. Although some of the volatiles showed proportions very different from those found in other studies about dry-cured ham, this is most likely due to the use of SPME or perhaps the type of fiber used in

the present study, and not to the device for direct extraction, considering differences found between HS SPME and SPME−DED were scarce.

A remarkably high proportion and number of terpenes was found in the canned liver sausage (18 compounds representing 43.7 and 42.8% of the total area by HS SPME and SPME−DED, respectively). These compounds comprise most of the volatiles of many plant spices (*20*, *21*). Nevertheless, the high proportion of terpenes found in the present study using either HS SPME or SPME−DED could be due not only to the high amount of spices in the commercial canned liver sausage, but to the used of SPME, which could enhance the extraction of compounds with low polarity, such as hydrocarbons and terpenes, with respect to other techniques such as purge and trap or static headspace, in which the polarity does not influence extraction as much. At any rate, proportions found were very similar using either method, and therefore SPME−DED does not seem to interfere in the extraction of these or any other types of compounds. The satisfactory extraction of this kind of compounds using SPME−DED highlights the potential use of this procedure to carry out quality control of aroma in different types of food products in which spices are major ingredients. The other groups of compounds found in canned liver sausage were aliphatic and aromatic aldehydes (17.1 and 19.9% of total area using HS SPME and SPME−DED, respectively), aliphatic alcohols (4.0 and 3.9%), aliphatic ketones (3.0 and 1.8%), carboxylic acids (16.3 and 14.2%), aromatic and aliphatic hydrocarbons (4.6 and 5.7%), nitrogen compounds (4.8 and 4.6%), sulfur compounds (3.1 and 3.5%), chloride compounds (0.8 and 0.0%), and furans (2.4 and 3.3%).These are basically the same as those described in the literature for meat products with similar characteristics (*21*). Some of these compounds, such as straight-chain aliphatic aldehydes, alcohols, ketones, and some hydrocarbons, are most likely derived from the thermal oxidative decomposition of unsaturated fatty acids and lipids (*22*). Others, such as sulfur compounds, nitrogen compounds, and furans, are likely derived from Maillard reactions (*23*).

By using SPME−DED, extraction of several compounds that are most likely laboratory contamination (such as dichloromethane, chloroform, hexane, or toluene) was avoided in dry-cured ham and canned liver sausage. This might be due to the avoidance of sample preparation when using SPME−DED: for instance, the sample is not ground in the lab where ambient pollutants may be present. This procedure involves the placement of the fiber into the device, which is introduced directly into the solid material. Laboratory pollutants in the air probably are not extracted because they cannot directly interact with the fiber when it is in the device in the solid material.

SPME−DED extraction is also a headspace extraction method, but in this case the headspace is inside the device instead of in the vial. Both HS SPME and SPME−DED are equilibrium methods, and thus they are strongly influenced by experimental conditions, especially extraction temperature (*1*). We have chosen an extraction temperature of 25 °C because it is similar to the temperature of the last step of ham processing, and also near to room temperature. A higher temperature would increase the volatiles extracted (*1*), but could also negatively influence the quality of the product.

Variations in area found using HS SPME were of the same order as those found in a previous study about HS SPME in dry cured ham (*1*), in which the coefficients of variation (CV) ranged from less than 10% in some compounds to around 75% in some others. Using the SPME−DED method, CV were also of the same order, although higher than those found when using HS SPME. Thus, CV ranged from between 10 and 20% to around 100% in the less volatile compounds. Previously reported CV using HS SPME (*24*) were considerably lower. These high CV (both in HS SPME and SPME−DED) might be due to the complexity of the matrix (*1*, *25*) to some extent, but also may be due to the type of fiber selected for the analysis, as carboxen/PDMS has been shown to have a poorer linearity and repeatability of response than PDMS/DVB or Carbowax/DVB fibers (*26*). However, after testing different types of fibers we chose carboxen/PDMS for its sensitivity, which has been shown previously (*27*). For quantitative analysis carboxen/PDMS probably would not be the fiber of choice, but it seems hard to quantify using SPME−DED, because adding an internal standard to the sample is not possible.

The slightly higher variability found using SPME−DED might be produced by differences in the portion of sample exposed to the holes of the device, especially when analyzing dry-cured ham because the matrix materials are fat and lean which are heterogeneously distributed. Moreover, diverse muscles can be included in each analysis. Volatiles from each component are different, and even the volatile profile from each muscle is not exactly the same (*15*). Besides, the partition of analytes between matrix and headspace strongly depends on matrix material (*28*), with a lipid material markedly increasing the detection limits (*29*).

Although finding an alternative method for quality control of dry-cured hams was the main goal of our group when this device was designed, this is not the only possible application of SPME−DED: this new extraction procedure has a number of applications in other solid foodstuffs in which sampling might be a problem (for different reasons) such as cheeses, sausages, vegetables, fruits, etc. In fact, the current analysis of volatiles in the other meat product, canned liver sausage, showed that this technique does not interfere in volatile extraction when comparing with HS SPME. Moreover, SPME−DED could also be used for different applications in other solid materials, such as chemicals in soils, volatiles in live plants, etc.

CONCLUSIONS

The device for direct extraction of volatiles from solid material allowed the analysis of main volatiles in two products evaluated (dry-cured ham and canned liver sausage), without markedly interfering in the extraction with respect to HS SPME. Variability using SPME−DED was higher than that reported for other methods; nevertheless, using SPME−DED maintains the integrity of the product, and this makes SPME−DED a suitable method for quality control in the food industry and for research when the sampling step interferes with the analysis.

LITERATURE CITED

(1) Ruiz, J.; Cava, R.; Ventanas, J.; Jensen, M. T. Headspace solid-phase microextraction for the analysis of volatiles in a meat product: dry cured Iberian ham. *J. Agric. Food Chem*. **1998**, *46*, 4688−4694.

(2) Ruiz, J.; Ventanas, J.; Cava, R.; Andrés, A. I.; García, C. Volatile compounds of dry-cured Iberian ham as affected by the length of the curing process. *Meat Sci.* **1999**, *52*, 19−27.
(3) Arthur, C. L.; Pawliszyn, J. Solid-phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem.* **1990**, *62*, 2145−2148.
(4) Arthur, C. L.; Potter, D. W.; Buchholz, K. D.; Motlagh, S.; Pawliszyn, J. Solid-phase microextraction for the direct analysis of water: theory and practice. *LC-GC Int.* **1992**, *10*, 656−661.
(5) Pawliszyn, J. *Solid-Phase Microextraction: Theory and Practice.* Wiley-VCH: New York, 1997.
(6) Müller, L.; Górecki, T.; Pawliszyn, J. Optimization of the SPME device design for field applications. *Fresenius J. Anal. Chem.* **1999**, *364*, 610−616.
(7) Ruiz, J.; Ventanas, J.; Cava, R. Dispositivo para análisis de compuestos volátiles. Spain Patent 200.001.082, 2000.
(8) Kondjoyan N.; Berdagué, J. L. *A Compilation of Relative Retention Indices for the Analysis of Aromatic Compounds.* Laboratoire Flaveur, Station de recherches sur la Viande, INRA: Theix, France, 1996.
(9) Acree, T.; Arn, H. *Flavornet: Gas chromatography − olfactometry (GCO) of natural products*. Cornell University. 1997. http://www.nysaes.cornell.edu/flavornet/.
(10) Buscailhon, S.; Berdagué, J. L.; Monin, G. Time-related changes in volatile compounds of lean tissue during processing of French dry-cured ham. *J. Sci. Food Agric.* **1993**, *63*, 69−75.
(11) Hinrichsen, L. L.; Pedersen, S. B. Relationship among flavor, volatile compounds, chemical changes, and microflora in Italian-type dry-cured ham during processing. *J. Agric. Food Chem.* **1995**, *43*, 2932−2940.
(12) Ruiz, J.; García, C.; Díaz, M. C.; Cava, R.; Tejeda, J. F.; Ventanas, J. Dry cured Iberian ham nonvolatile components as affected by the length of the curing process. *Food Res. Int.* **1999**, *32*, 643−651.
(13) Cava, R.; Ruiz, J.; Ventanas, J.; Antequera, T. Effect of α-tocopheryl acetate supplementation and the extensive feeding of pigs on the volatile aldehydes during the maturation of Iberian ham. *Food Sci. Technol. Int.* **1999**, *5*, 235−241.
(14) Shahidi, F. Assesment of lipid oxidation and off-flavor development in meat, meat products and seafoods. In *Flavor of Meat, Meat Products and Seafoods*; Shahidi, F., Ed. Blackie Academic & Professional: London, 1998.
(15) Lai, S.; Gray, J. I.; Booren, A. M.; Crackel, R. L.; Gill, J. L. Assessment of off-flavor development in restructured chicken nuggets using hexanal and TBARS measurements and sensory evaluation. *J. Sci. Food Agric.* **1995**, *67*, 447−452.
(16) García, C.; Berdagué, J. J.; Antequera, T.; López-Bote, C.; Córdoba, J. J.; Ventanas, J. Volatile components of dry cured Iberian ham. *Food Chem.* **1991**, *41*, 23−32.
(17) Berdagué, J. L.; Denoyer, C.; Le Quere, J. L.; Semon, E. Volatile components of dry-cured ham. *J. Agric. Food Chem.* **1991**, *39*, 1257−1261.
(18) Stanhke, L. H. Dried sausages fermented with *Staphylococcus xylosus* at different temperatures and with different ingredient levels − Part II. Volatile components. *Meat Sci.* **1995**, *41*, 193−209.
(19) Ruiz, J.; Ventanas, J.; Cava, R.; Timón, M. L.; García, C. Sensory characteristics of Iberian ham: influence of processing time and slice location. *Food Res. Int.* **1998**, *31*, 53−58.
(20) Salzer, U. J. The analysis of essential oils and extracts (oleoresins) from seasonings − A critical review. *CRC Crit. Rev. Food Sci. Nutr.* **1977**, *9*, 345−373.
(21) Chevance, F. F. V.; Farmer, L. J. Identification of major volatile odor compounds in frankfurters. *J. Agric. Food Chem.* **1999**, *47*, 5151−5160.
(22) Forss, D. A. Odour and flavour compounds from lipids. *Prog. Chem. Fats Other Lipids* **1972**, *13*, 181−252.
(23) Shahidi, F.; Rubin, L. J.; D'Souza, L. A. Meat flavour volatiles: a review of the composition, techniques of analysis, and sensory evaluation. *CRC Crit. Rev. Food Sci. Nutr.* **1986**, *24*, 147−185.
(24) Elmore, J. S.; Erbahadir, M. A.; Mottram, D. S. Comparison of dynamic headspace concentration of tenax with solid-phase microextraction for the analysis of aroma volatiles. *J. Agric. Food Chem.* **1997**, *45*, 2638−2641.
(25) Steffen, A.; Pawliszyn, J. Analysis of flavor volatiles using headspace solid-phase microextraction. *J. Agric. Food Chem.* **1996**, *44*, 2187−2193.
(26) Brunton, N. P.; Cronin, D. A.; Monahan, F. J.; Durcan, R. A comparison of solid-phase microextraction (SPME) fibers for measurement of hexanal and pentanal in cooked turkey. *Food Chem.* **2000**, *68*, 339−345.
(27) Page, B. D.; Lacroix, G. Application of solid-phase microextraction to the headspace gas-chromatographic analysis of halogenated volatiles in selected foods. *J. Chromatogr. A* **1993**, *648*, 199−211.
(28) Keszler, A.; Héberger, K.; Gude, M. Quantitative analysis of aliphatic aldehydes by headspace SPME sampling and ion-trap GC-MS. *Chromatographia* **1998**, *48*, 127−132.
(29) Page, B. D.; Lacroix, G. Analysis of volatile contaminants in vegetable oils by headspace solid-phase microextraction with Carboxen-based fibres. *J. Chromatogr. A* **2000**, *873*, 79−94.

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