Available online at www.sciencedirect.com
SCIENCE DIRECT®
Food Chemistry 94 (2006) 151–156
Food Chemistry
www.elsevier.com/locate/foodchem

Analytical, Nutritional and Clinical Methods

Headspace volatile components of smoked swordfish (*Xiphias gladius*) and cod (*Gadus morhua*) detected by means of solid phase microextraction and gas chromatography–mass spectrometry

M.D. Guillén *, M.C. Errecalde, J. Salmerón, C. Casas

Tecnología de Alimentos, Nutrición y Bromatología, Facultad de Farmacia, Universidad del País Vasco, Paseo de la Universidad 7, 01006 Vitoria, Spain

Received 25 July 2004; received in revised form 14 January 2005; accepted 30 January 2005

Abstract

A study of the headspace of smoked swordfish and cod was carried out by means of Solid Phase Microextraction followed by gas chromatography–mass spectrometry. The headspace of both smoked fish species contains ketones, aldehydes, alcohols, acids, esters, hydrocarbons, ethers, nitrogen derivatives, phenol, guaiacol, and syringol derivatives, as well as some chlorinated contaminants. The differences found between the headspace of both smoked fish are basically due both to a higher proportion of smoke components in cod than in swordfish, and to specific fish components being present or absent in each fish sample. The high proportion of syringol in both fish samples indicates that smoking was carried out using hardwood. Some smoke components were not detected in the headspace of these smoked fish samples.

Keywords: Smoked swordfish and cod; Volatile components; Solid phase microextraction; Gas chromatography–mass spectrometry

1. Introduction

The smoking process was basically used in the past for preservative purposes, although the changes in colour, odour, flavor and texture which were provoked in foods by this process were also judged as desirable. Nowadays, due to the great advance of preservative techniques, smoking is used fundamentally for the development of sensory properties in food.

Fish is a food that is very often processed by smoking. Traditionally, in Europe, smoked fish has been produced and consumed, principally, in countries of the Centre and North, and in recent times, its production and consumption have also become more common in the South, where these products are, in some cases, considered delicacies. For this reason, the smoking technique has been contemplated as of great interest in order to obtain food products of high added value from undervalued fish species (Garcia, Perez-Villarreal, & Pozo, 1996).

In spite of the broadly recognized pleasant flavor of smoked fish, the responsible compounds have rarely been studied. To the best of our knowledge, only the headspace composition of a reduced number of smoked fish species has been studied (Cardinal, Berdagué, Dinel, Knockaert, & Vallet, 1997; Guillén & Errecalde, 2002; Kasahara & Nishibori, 1979a, 1979b, 1981a, 1981b, 1982, 1983).

In order to understand the smoking process in depth, in previous papers we have studied the composition of smoke produced from different woods (Guillén & Ibargoitia, 1996; Guillén, Manzanos, & Ibargoitia, 2001; Guillén & Manzanos, 1999), as well as the composition

* Corresponding author. Tel.: +34 945 013081; fax: +34 945 013014.
E-mail address: knpgulod@vf.ehu.es (M.D. Guillén).

0308-8146/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2005.01.014

of several commercial smoke flavorings (Guillén & Ibargoitia, 1998; Guillén, Manzanos, & Zabala, 1995; Guillén & Manzanos, 1997; Guillén, Sopelana, & Partearroyo, 2000). In this paper, a study of the headspace components of smoked swordfish (*Xiphias gladius*) and cod (*Gadus morhua*) is carried out. The purpose of this work is to study the constituent compounds of the headspace of these commodities. The study was accomplished by means of Solid Phase Microextraction (SPME) followed by gas chromatography–mass spectrometry.

2. Materials and methods

2.1. Samples

Commercial fillets of swordfish (*X. gladius*) and cod (*G. morhua*), from two different manufacturers, salted and smoked with natural smoke and vacuum-packaged, ready to eat as soft-cured products, were acquired in local supermarkets. These were stored frozen at −35 °C for no longer than two weeks until their study. For each type of smoked fish, four samples were studied, all of them from the same manufacturer. The day before the study the samples were transferred to the refrigerator, and after thawing they were chopped; samples of 1 g of the chopped meat were weighed into a 4-mL amber vial Screw Top (Supelco), and sealed with a perforated cap and a PTFE/silicone septum for the generation of headspace.

2.2. Headspace SPME

A Fibre of Polyacrylate (85 μm film thickness), acquired from Supelco, was used. Previous experiments carried out in our laboratory on the study of the headspace components of other smoked fish using fibres of Carboxen/Polydimethylsiloxane, Polydimethylsiloxane (100 μm film thickness) and Polyacrylate (85 μm film thickness) show that: Carboxen/Polydimethylsiloxane fibre basically retains the most volatile components of the headspace, in very high proportions, however Polyacrylate (85 μm film thickness) fibre retains components of a broader volatility range; and Polydimethylsiloxane (100 μm film thickness) fibre has less ability to retain smoke components than Polyacrylate (85 μm film thickness) fibre. For these reasons, the Polyacrylate fibre was selected. Vials containing 1 g of the fish muscle were held in a water bath at 50 °C. After a period of sample equilibration (15 min) the fibre was inserted into the headspace of the sample and held there for 60 min.

2.3. Gas chromatography–mass spectrometry

Fibres with the volatile compounds adsorbed on them were injected into a Hewlett–Packard gas chromatograph model HP 6890 Series II, equipped with a Mass Selective Detector 5973 and a Hewlett–Packard Vectra XM Series 4 computer operating with the ChemStation program. The column used was a fused-silica capillary column (60 m long × 0.25 mm inner diameter × 0.25 μm film thickness from Hewlett-Packard), coated with a non-polar stationary phase (HP-5MS, 5% phenyl methyl siloxane). The operating conditions were: oven temperature set initially at 45 °C (0.50 min hold), increased to 250 °C at 4 °C/min followed by 20 min hold; the temperatures of the ion source and the quadrupole mass analyzer were kept at 230 and 150 °C, respectively; helium was used as carrier gas at a pressure of 16.5 psi; injector and detector temperatures were held at 220 and 280 °C, respectively; splitless mode was used for injection with a purge time of 5 min. The fibre was maintained in the injection port for 10 min. Mass spectra were recorded at an ionization energy of 70 eV. After the first desorption, the fibre was routinely desorbed for a second time in order to determine if the first process was complete.

Some components were identified by using standards. So, asterisked compounds in Tables 1–3 were acquired commercially and used as standards for identification. Many other components were only tentatively identified. In this latter case, retention times, together with mass spectra, and matching with mass spectra of a commercial library higher than 85%, were taken as identification criteria (Wiley 138.L, Mass Spectral Database, Wiley 1990) as in previous studies (Guillén & Ibargoitia, 1996; Guillén et al., 1995). Semiquantification of the components was based on arbitrary units of total current ion peak area counts divided by 10^5.

The study of each one of the four samples of each kind of fish was carried out by duplicated and the average values obtained together with the standard deviations are given in Tables 1–3.

3. Results and discussion

Smoke and smoke flavorings contain a large number of components, derived from cellulose, hemicellulose and lignin pyrolysis, which have different functional groups, such as ketones, aldehydes, acids, ethers, hydrocarbons, carbohydrate derivatives, nitrogen derivatives, and phenol, guaiacol, syringol, and pyrocatechol derivatives (Guillén & Ibargoitia, 1996, 1998; Guillén et al., 1995, 2001; Guillén & Manzanos, 1997, 1999; Maga, 1988; Toth & Potthast, 1984). Among these components, carbonyl and carboxyl derivatives together with carbohydrate derivatives are the major smoke components, whereas phenolic derivatives are in smaller proportions (Maga, 1988).

In the smoking process the smoke components are adsorbed by the fish surface, and they react or establish

Table 1
Ketones, alcohols, aldehydes and acids detected in the headspace of smoked swordfish and cod and their concentrations in area counts divided by 10^5 together with the standard deviations

Compound	Swordfish	Cod
Ketones and diketones		
Propanone*	44.4(8.9)	12.1(1.6)
1-Hydroxy-2-propanone	–	5.8(1.2)
1-(2-Furanyl)ethanone*	tr[a]	4.0(1.6)
2(3H)-Dihydrofuranone	55.4(0.3)	18.4(1.5)
3-Methyl-2-cyclopenten-1-one*	–	5.5(1.3)
3-Methyl-2-hydroxy-2-cyclopenten-1-one (cyclotene)*	7.4(1.4)	16.5(2.6)
2,3-Dimethyl-2-cyclopenten-1-one (or isomer)	3.2(1.6)	6.1(2.2)
3-Hydroxy-2-methyl-4H-pyran-4-one (maltol)*	2.4(0.6)	8.7(1.5)
Ethylcyclopentenolone	5.1(1.9)	6.7(1.2)
2,3-Dihydro-1H-inden-1-one (indanone)*	5.5(0.8)	16.5(4.0)
Alcohols		
Ethanol*	61.4(12.9)	4.3(1.8)
3-Methyl-1-butanol	22.8(4.3)	–
2-Furanmethanol	13.5(1.6)	24.1(3.1)
Benzenemethanol*	0.9(0.1)	46.2(6.7)
Aldehydes		
2-Furancarboxaldehyde*	–	4.6(1.7)
Benzaldehyde*	2.5(0.5)	2.4(0.7)
5-Methyl-2-furancarboxaldehyde	–	6.3(2.1)
1H-pyrrole-2-carboxaldehyde	–	2.4(0.8)
Benzeneacetaldehyde*	3.1(1.5)	–
Nonanal*	2.0(0.5)	9.3(1.6)
Decanal*	1.0(0.3)	3.4(1.2)
2-Decenal*	–	4.8(1.5)
Dodecanal*	5.6(0.3)	5.6(1.7)
Tetradecanal*	2.6(0.6)	–
Hexadecanal*	7.4(0.7)	1.6(0.9)
Acids		
Acetic acid*	90.3(28.0)	16.9(2.8)
Propanoic acid*	–	5.8(1.3)
Butanoic acid*	–	2.3(1.0)
Pentanoic acid	40.2(5.7)	–
Hexanoic acid*	3.0(0.6)	–
Heptanoic acid*	1.4(0.6)	–
2-Ethyl hexanoic acid	9.9(6.1)	–
Octanoic acid*	nq[b]	–
Nonanoic acid*	15.1(1.7)	6.4(1.6)
Tetradecanoic acid*	6.3(2.3)	19.7(3.1)
Hexadecanoic acid*	9.2(5.0)	68.5(7.3)

[a] tr = traces
[b] nq = not quantified.
* Asterisked compounds were acquired commercially and used as standards for identification.

Table 2
Hydrocarbons, esters, nitrogenated derivatives and ethers detected in the headspace of smoked swordfish and cod and their concentrations in area counts divided by 10^5 together with the standard deviations

Compound	Swordfish	Cod
Hydrocarbons		
Styrene*	–	0.9(0.1)
Dimethylbenzene	tr[a]	–
Dimethylbenzene	3.3(1.8)	–
Dimethylbenzene	*r*	–
2,2,4,6,6-Pentamethylheptane(or isomer)	–	31.5(3.7)
Pentadecane*	7.5(0.6)	–
1-Heptadecene (or isomer)	6.4(1.7)	11.7(4.1)
Heptadecane*	1.8(0.1)	–
2,6,10,14-Tetramethyl pentadecane (pristane)*	33.8(2.1)	–
Esters		
Diethyl-1,2-benzenedicarboxylate	66.8(18.9)	1.2(0.3)
Ethyl-tetradecanoate	6.7(3.6)	–
Bis(2-methylpropyl)-benzenedicarboxylate (or isomer)	3.4(3.3)	–
Dibutyl-1,2-benzenedicarboxylate (or isomer)	6.4(2.0)	–
Ethyl-hexadecanoate	4.7(2.2)	–
Nitrogenated derivatives		
N,*N*-dimethylmethanamine	14.6(14.6)	nq[b]
Benzeneacetonitrile	–	1.5(0.5)
1H-indol	–	4.1(0.9)
3-Methyl-1H-indol	–	10.5(2.6)
Ethers		
2-Buthoxy-ethanol	tr	22.7(4.1)
1,4-Dimethoxybenzene (or isomer)	8.4(0.3)	8.4(2.2)
1,3-Dimethoxybenzene (or isomer)	5.3(1.9)	7.8(2.8)
Dihydrobenzofuran (isomer)	–	5.9(2.1)
Dihydrobenzofuran (isomer)	–	7.5(0.4)
Dimethoxytoluene (isomer)	1.2(0.3)	13.1(2.3)
Trimethoxybenzene (isomer)	2.0(0.3)	5.9(2.1)

[a] tr = traces.
[b] nq = not quantified.
* Asterisked compounds were acquired commercially and used as standards for identification.

interactions more or less strongly with fish components depending on the magnitude of the intermolecular forces existing between components of both systems. As consequence of this, the headspace of the smoked fish only will contain those smoke components, adsorbed on the fish surface, which have not reacted or interacted very strongly with fish components. That is to say the presence or absence of smoke components in the headspace of the smoked fish is governed by the interactions established between components of both systems.

In addition to smoke components the fish headspace will contain components coming from fish. Aldehydes, ketones and alcohols having six, eight and nine carbon atoms have been considered the major flavor impact compounds in fresh fish (Josephson, Lindsay, & Olafsdoitter, 1987; Lindsay, 1994). The origin of these compounds is considered to be the polyunsaturated fatty

Table 3
Phenol, methoxyphenol and dimethoxyphenol derivatives, and other compounds detected in the headspace of smoked swordfish and cod and their concentrations in area counts divided by 10^5 together with the standard deviations

Compound	Swordfish	Cod
Phenol derivatives		
Phenol*	51.4(6.5)	117.6(6.9)
2-Methylphenol*	29.4(4.0)	57.8(7.3)
4-Methylphenol and 3-methylphenol*	53.1(6.6)	149.6(10.4)
2,6-Dimethylphenol (or isomer)	2.9(0.5)	6.2(1.2)
2-Ethylphenol (or isomer)	2.5(0.7)	10.9(2.3)
2,4-Dimethylphenol (or isomer)	19.0(3.2)	44.9(3.1)
4-Ethylphenol (or isomer)	7.0(0.9)	19.5(3.8)
3,4-Dimethylphenol (or isomer)	nq[b]	34.1(1.2)
2,3-Ethylphenol (or isomer)	nq	9.6(1.8)
3,5-Dimethylphenol (or isomer)	1.0(0.5)	7.7(2.0)
4-Ethyl-3-methylphenol (or isomer)	2.4(0.3)	4.4(1.2)
2,3,5-Trimethylphenol (or isomer)	1.9(0.8)	7.9(1.8)
2,4,6-Trimethylphenol (or isomer)	3.3(1.3)	3.9(1.1)
2,6-Bis(1,1-dimethylethyl)-4-methylphenol (BHT)*	12.6(5.4)	19.5(3.7)
Methoxyphenol derivatives		
2-Methoxyphenol (guaiacol)*	74.1(3.1)	182.2(10.3)
4-Methyl-2-methoxyphenol (4-methylguaiacol)*	100.2(11.6)	117.6(7.6)
4-Ethyl-2-methoxyphenol (4-ethylguaiacol)*	54.7(12.7)	64.1(4.1)
4-Vinyl-2-methoxyphenol (4-vinylguaiacol)*	21.5(3.4)	56.9(5.3)
4-(2-Propenyl)-2-methoxyphenol (eugenol)*	24.5(7.9)	46.1(6.3)
ethyl-methyl-methoxyphenol (isomer)	6.3(1.9)	–
4-Propyl-2-methoxyphenol (4-propylguaiacol)*	12.6(4.7)	16.2(3.5)
4-(2-Propenyl)-2-methoxyphenol (isomer)	8.9(3.9)	35.4(3.2)
4-(1-Propenyl)-2-methoxyphenol	42.5(17.4)	151.4(11.4)
4-Hydroxy-3-methoxy-benzaldehyde(vanillin)*	tr[a]	–
4-Hydroxy-3-methoxy-benzoic acid	tr	–
Dimethoxyphenol derivatives		
Dimethoxyphenol (isomer)	tr	36.8(4.2)
2,6-Dimethoxyphenol (syringol)*	118.4(12.1)	323.9(15.5)
4-Methyl-2,6-dimethoxyphenol (4-methylsyringol)*	51.8(9.1)	94.5(10.2)
4-Ethyl-2,6-dimethoxyphenol (4-ethylsyringol)	13.7(4.5)	33.9(5.6)
2,6-Dimethoxy-4-(2-propenyl)-phenol (isomer)	tr	4.8(1.6)
2,6-Dimethoxy-4-(2-propenyl)-phenol (isomer)	–	7.6(2.1)
Others		
Trichloromethane (chloroform)*	26.3(3.8)	–
Dichlorobenzene	–	2.5(0.7)
Trichlorobenzene	–	3.9(0.9)

[a] tr = traces.
[b] nq = not quantified.
* Asterisked compounds were acquired commercially and used as standards for identification.

acids of fish lipids. In addition, volatile compounds of low molecular weight having alcohol, aldehyde, and ketone functional groups together with some nitrogen and sulphur derivatives, which may be brought about in the degradation process, can also be found in the headspace of fish (Human & Khayat, 1981; Miller, Scanlan, Lee, & Libbey, 1972).

Solid phase microextraction of the headspace of the smoked fish samples followed by gas chromatography–mass spectrometry allowed the detection of seventy-nine components in the headspace of smoked swordfish and of seventy-one in the headspace of smoked cod. They are given in Tables 1–3, together with their concentrations, expressed in arbitrary units, as well as their standard deviations; those compounds whose separation was not good enough to be quantified are indicated as nq. These compounds belong to a small number of groups such as ketones, alcohols, aldehydes, acids, esters, hydrocarbons, phenolic derivatives, nitrogenated and chlorinated derivatives.

Table 1 shows the detected ketones, alcohols, aldehydes and acids. All detected ketones are well known smoke components, however propanone can also come from fish degradation processes (Human & Khayat, 1981; Miller et al., 1972). Among the detected alcohols, 2-furanmethanol and benzenemethanol are also known as smoke components (Maga, 1988), however ethanol and 3-methylbutanol are fish components, also detected in other marine species such as raw shrimp (Sun Pan & Kuo, 1994) and associated with fish muscle degradation processes (Human & Khayat, 1981; Miller et al., 1972).

The aldehyde group contains not only those compounds known as smoke components, such as furancarboxaldehyde, 5-methyl-furancarboxaldehyde, benzeneacetaldehyde and benzaldehyde, but also those which are known as fish components, such as linear aldehydes from 9 to 16 carbon atoms, these latter probably derived from lipid autoxidation (Sakakibara, Yanai, & Hayashi, 1988). Some aldehydes from two to six carbon atoms have been related to fish muscle degradation proceses (Human & Khayat, 1981; Miller et al., 1972), but they were no detected in the headspace of these fishes. A group of acids, from 2 to 16 carbon atoms, were also present; those of low molecular weight, especially acetic acid, are also smoke components. It must be noticed that in swordfish headspace a higher number of acids was detected than in cod headspace. This fact could be due either to swordfish containing a slightly higher proportion of lipids (approx. 4%) than cod (approx. 1%) (Murray & Burt, 1979), or to the first fish being more affected by bacterial spoilage (Joffraud, Leroi, Roy, & Berdague, 2001; Sanceda, Suzuki, & Murata, 1999). It should be pointed out that although free fatty acids content is considered, in some cases, to be a misleading parameter for spoilage (De Koning, 2002), it is well accepted, in general, that bacterial spoilage can produce some acids (Joffraud et al., 2001; Sanceda et al., 1999).

Table 2 gives the detected hydrocarbons, esters, nitrogenated derivatives and ethers. In the hydrocarbons group, there are typical fish components such as 2,6,10,14-tetramethyl pentadecane or pristane (Ackman, 1971; Norio, Yuko, & Minoru, 1973), and others such as dimethylbenzene isomers which may have come from smoke, although some of these have been detected in fish tissue (Gases, Lloyd, Batista, & Zimba, 2000) and in boiled snow crab (Sung-Hee, Young-Man, & Sook-Kyung, 2001). It is worth noting the absence of polycyclic aromatic hydrocarbons, some of which have carcinogenic activity; these compounds are produced in wood pyrolysis, and can be deposited on the food if the smoking process is not carried out adequately (Guillen & Sopelana, 2003).

Some esters have also been detected in smoked swordfish, but they are absent in smoked cod; among these there are the ubiquitous benzenedicarboxylate derivatives and some fatty esters. Although some esters of low molecular weight have been associated with bacterial spoilage (Joffraud et al., 2001) those here detected are of high molecular weight.

Nitrogen derivatives are also present. In swordfish, only trimethylamine has been detected; this is a common fish component whose concentration has been taken as a measure of fish freshness (Regenstein, Schlosser, Samson, & Fey, 1982). In addition, the headspace of smoked cod contains: 1H-pyrrole-2-carboxaldehyde, a compound detected in fish sauce (Peralta, Shimoda, & Osajima, 1996); benzeneacetonitrile, and two indol derivatives with unpleasant notes, one of them also found in raw shrimp (Kubota, Shuimaya, & Kobayashi, 1986). The ether group contains basically ethers also present usually in smoke, except 2-butoxyethanol, which has been also detected in crayfish (Vejaphan, Hsieh, & Williams, 1988).

The most noticeable group of compounds detected in the headspace of both smoked fishes is that of phenolic derivatives including phenol, guaiacol, and syringol derivatives, which are given in Table 3. The phenol group contains 14 components; the guaiacol group 11 compounds, and the syringol group six components. All these compounds are smoke components, coming from wood pyrolysis and are most responsible for the smoky flavor (Maga, 1988). These are the major components detected in the headspace of these smoked fishes, and among them, syringol is the main component in both cases, showing that the wood used in the smoking process was hardwood. Pyrolysis of softwood produces higher proportions of guaiacol than of syringol and the opposite is true for hardwood (Baltes, Wittkoswki, Söchtig, Block, & Toth, 1981, chap. 1).

Finally, chlorinated derivatives (see Table 3) have also been detected in both fish samples. Swordfish contains chloroform, and cod chlorobenzene derivatives. The presence of these compounds can be attributed to contamination, and they have also been observed, in fish tissues, by other authors (Reinert, Hunter, & Sabatino, 1983).

In conclusion some smoke components have not been detected in the headspace of these smoked fishes, and other smoke components are present in these fish headspaces but in proportions very different to those usually found in smoke. So, groups of compounds such as carbohydrate derivatives (levoglucosane and others of similar nature) and pyrocatechol derivatives are generally present in smoke but they were not detected in the headspace of these smoked fishes. In addition, in the headspace of these smoked fishes have been detected proportions of carbonyl and carboxyl derivatives and of phenolic derivatives which are very different from those generally found in smoke. Carbonyl (ketones, diketones, aldehydes and furan and pyran derivatives) and carboxyl (basically acetic acid) derivatives are in much higher proportions, in relation to the other smoke components, in smoke than in the headspace of these smoked fishes. On the other hand, other smoke components such as phenol, guaiacol, and syringol derivatives are present in the headspace of both smoked fish species. Differences between headspaces of both smoked fish species are basically due to the different concentrations of smoke components, and to the specific components coming from fish. The differences found in the concentration of smoke components in both fishes could be due, among other causes, to them being submitted to different smoking conditions. Finally, it only remains to add that the absence of unsaturated aldehydes, compounds previously detected in the headspace of smoked rainbow trout and black bream (Guillén & Errecalde, 2002), could indicate that the present smoked fish samples have not suffered degradative oxidation processes.

Acknowledgements

This work has been supported by the Comisión Interministerial de Ciencia y Tecnología and Ministerio de Ciencia y Tecnología (MCYT, AGL2003-01838) and the Universidad del País Vasco (9/UPV 00101.125. 13667/2001). M.C. Errecalde thanks the Universidad del País Vasco for a predoctoral fellowship.

References

Ackman, RG. (1971). Pristane and other hydrocarbons in some fresh water and marine fish oils. *Lipids, 6*, 520–522.

Baltes, W., Wittkoswki, R., Söchtig, I., Block, H., & Toth, L. (1981). In G. Charalambous & G. Inglett (Eds.). *The quality of food and beverages* (Vol. 2). New York: Academic Press.

Cardinal, M., Berdagué, J. L., Dinel, V., Knockaert, C., & Vallet, J. L. (1997). Effet de différentes techniques de fumage sur la nature des composés volatils et les caractéristiques sensorielles de la chair de saumon. *Science des Aliments, 17*, 679–696.

De Koning, A. J. (2002). Quantitative quality tests for fish meal. II. An investigation of the quality of South African fish meals and the validity of a number of chemical quality indices. *International Journal of Food Properties, 5*, 495–507.

Garcia, I., Perez-Villarreal, B., & Pozo, R. (1996). Valorización de especies pesqueras infrautilizadas. *Alimentación Equipos y Tecnología*, 145–149.

Gases, G. C., Lloyd, S. W., Batista, R., & Zimba, P. V. (2000). Using microwave distillation-solid-phase microextraction-gas-chromatography–mass spectrometry for analyzing fish tissue. *Journal of Chromatographic Science, 38*, 289–296.

Guillén, M. D., & Errecalde, M. C. (2002). Volatile components of raw and smoked black bream (*Brama raii*) and rainbow trout (*Oncorhynchus mykiss*) studied by means of solid phase microextraction and gas chromatography/mass spectrometry. *Journal of the Science of Food and Agriculture, 82*, 945–952.

Guillén, M. D., & Ibargoitia, M. L. (1996). Aqueous liquid smoke flavoring preparations from vine shoots and beech wood. *Journal of the Science of Food and Agriculture, 72*, 104–110.

Guillén, M. D., & Ibargoitia, M. L. (1998). New components with potential antioxidant and organoleptic properties detected for the first time in liquid smoke flavoring preparations. *Journal of Agricultural and Food Chemistry, 46*, 1276–1285.

Guillén, M. D., Manzanos, M. J., & Ibargoitia, M. L. (2001). Carbohydrate and nitrogenated compounds in liquid smoke flavorings. *Journal of Agricultural and Food Chemistry, 49*, 463–468.

Guillén, M. D., Manzanos, M. J., & Zabala, L. (1995). Study of a commercial liquid smoke flavouring by means of GC/MS and FTIR. *Journal of Agricultural and Food Chemistry, 43*, 463–468.

Guillén, M. D., & Manzanos, M. J. (1997). Characterization of the components of a salty smoke flavouring preparation. *Food Chemistry, 58*, 97–102.

Guillén, M. D., & Manzanos, M. J. (1999). Extractable components of the aerial parts of Salvia lavandulifolia and the composition of the liquid smoke flavoring obtained from them. *Journal of Agricultural and Food Chemistry, 47*, 3016–3027.

Guillén, M. D., Sopelana, P., & Partearroyo, M. A. (2000). Determination of polycyclic aromatic hydrocarbons in commercial liquid smoke flavorings of different compositions by gas chromatography–mass spectrometry. *Journal of Agricultural and Food Chemistry, 48*, 126–131.

Guillen, M. D., & Sopelana, P. (2003). Polycyclic aromatic hydrocarbons in diverse foods. In J. P. F. D'Mello (Ed.), *Food safety. Contaminants and toxins* (pp. 175–198). Edinburgh: CABI Publishing.

Human, J., & Khayat, A. (1981). Quality evaluation of raw tuna by gas chromatography and sensory methods. *Journal of Food Science, 46*, 868–873, 879.

Joffraud, J. J., Leroi, F., Roy, C., & Berdague, J. L. (2001). Characterisation of volatile compounds produced by bacteria isolated from the spoilage flora of cold-smoked salmon. *International Journal of Food Microbiology, 66*, 175–184.

Josephson, D. B., Lindsay, R. C., & Olafsdoitter, G. (1987). Measurements of volatile aroma constituents as a means for following sensory deterioration of fresh fish and fishery products. In D. E. Kramer & J. Liston (Eds.), *Developments in food science. Seafood quality determination (Proceedings of the international symposium on seafood quality determination, Anchorage, Alaska, 10–14 November, 1986)* (Vol. 15, pp. 27–47). Amsterdam: Elsevier Science Publishing.

Kasahara, K., & Nishibori, K. (1979a). Volatile components of smoked salmon. *Nippon Suisan Gakkaishi, 45*, 1543–1545.

Kasahara, K., & Nishibori, K. (1979b). Volatile components of smoked salmon. II. The relationship between flavors of smoked salmon and smoke-tar. *Nippon Suisan Gakkaishi, 45*, 1547–1549.

Kasahara, K., & Nishibori, K. (1981a). Volatile components of smoked sardine. *Nippon Suisan Gakkaishi, 47*, 113–119.

Kasahara, K., & Nishibori, K. (1981b). Volatile components of smoked herring. *Nippon Suisan Gakkaishi, 47*, 783–786.

Kasahara, K., & Nishibori, K. (1982). Volatile components of smoked sardine. II. Volatile carbonyls and acids of smoked sardine. *Nippon Suisan Gakkaishi, 48*, 691–695.

Kasahara, K., & Nishibori, K. (1983). Volatile components of smoked cuttlefish and octopus. *Nippon Suisan Gakkaishi, 49*, 913–918.

Kubota, K., Shuimaya, H., & Kobayashi, A. (1986). Volatile components of roasted shrimp. *Agricultural and Biological Chemistry, 50*, 2867–2873.

Lindsay, R. C. (1994). Flavour of fish. In F. Shahidi & J. R. Botta (Eds.), *Seafoods: chemistry, processing technology and quality* (pp. 75–84). London, UK: Blackie Academic & Profesional.

Maga, JA. (1988). *Smoke in food processing*. Boca Ratón: CRC Press, pp. 49–86.

Miller, A., Scanlan, R. A., Lee, J. S., & Libbey, L. M. (1972). Volatile compounds produced in ground muscle tissue of canary rockfish (Sebastes pinniger) stored on ice. *Journal of the Fisheries Research Board of Canada, 29*, 1125–1129.

Murray, J., & Burt, J. R. (1979). *The composition of fish, Torry Advisory Note No. 38*. Edinburgh: Ministry of Agriculture Fisheries and Food.

Norio, I., Yuko, H., & Minoru, A. (1973). Pristane in salmon muscle lipid. *Suisan Gakubu kenkyu Iho, 23*, 209–214.

Peralta, R., Shimoda, M., & Osajima, Y. (1996). Further Identification of volatile compounds in fish sauce. *Journal of Agricultural and Food Chemistry, 44*, 3606–3610.

Regenstein, J. M., Schlosser, M. A., Samson, A., & Fey, M. (1982). Chemical changes of trimethylamine oxide during fresh and frozen storage of fish. In R. E. Martin, G. J. Flick, C. E. Hebard, & D. R. Ward (Eds.), *Chemistry and biochemistry of marine food Products* (pp. 137–149). Westport, CT: AVI Publishing Co..

Reinert, K. H., Hunter, J. V., & Sabatino, T. (1983). Dynamic heated headspace analyses of volatile organic compounds present in fish tissue samples. *Journal of Agricultural and Food Chemistry, 31*, 1057–1060.

Sakakibara, H., Yanai, I., & Hayashi, K. (1988). Changes in volatile flavor compounds of powdered dried bonito (Katsuobushi) during storage. *Agricultural and Biological Chemistry, 52*, 2731–2739.

Sanceda, N. G., Suzuki, E., & Murata, T. (1999). Formation of volatile acids during fermentation of fish sauce. In F. Shahidi & C. T. Ho (Eds.), *Flavor and chemistry of ethnic foods (Proceedings of a meeting held during the 5th chemical congress of North America, Cancun, November 11–15, 1997)* (pp. 41–53). New York: Kluwer Academic/Plenum Publishers.

Sun Pan, B., & Kuo, J. M. (1994). Flavour of shellfish and kamaboko flavorants. In F. Shahidi & J. R. Botta (Eds.), *Seafoods: chemistry, processing technology and quality* (pp. 85–114). London, UK: Blackie Academic & Profesional.

Sung-Hee, C., Young-Man, K., & Sook-Kyung, H. (2001). Volatile flavor components in boiled snow crab (*Chionocetes japonicus*) and its concentrated cooker effluent. *Journal of Food Science and Nutrition, 6*, 87–90.

Toth, L., & Potthast, K. (1984). Chemical aspects of the smoking of meat and meat products. *Advances in Food Research, 29*, 87–158.

Vejaphan, W., Hsieh, T. C.-Y., & Williams, S. S. (1988). Volatile flavor components from boiled crayfish (*Procambarus clarkii*) tail meat. *Journal of Food Science, 53*, 1666–1670.