Available online at www.sciencedirect.com
SCIENCE DIRECT®
Food Chemistry 87 (2004) 627–637
Food Chemistry
www.elsevier.com/locate/foodchem

Analytical, Nutritional and Clinical Methods

Characterisation of volatile compounds of fruit juices and nectars by HS/SPME and GC/MS

M. Riu-Aumatell [a], M. Castellari [b], E. López-Tamames [a], S. Galassi [c], S. Buxaderas [a,*]

[a] Facultat de Farmàcia, Departament de Nutrició i Bromatologia, Centre de Referència en Tecnologia dels Aliments (CeRTA), Universitat de Barcelona. Avda. Joan XXIII, s/n, 08028 Barcelona, Spain
[b] IRTA-Food Chemistry Unit, Granja Camps i Amet, s/n, 17121 Monells, Girona, Spain
[c] Universitá di Bologna – Facoltá di Agraria, Dipartimento di Scienze degli Alimenti, sede di Cesena, Via Ravennate 1020, 47023 Cesena, Italy

Received 4 June 2003; received in revised form 18 December 2003; accepted 18 December 2003

Abstract

Here we described a rapid evaluation of volatile profiles of several commercial fruit juices (pear, apricot and peach) by head-space-solid phase microextraction and gas chromatography/mass spectrometry (HS-SPME and GC/MS). This method allows to analyse a wide range of flavour compounds (97 esters, aldehydes, alcohols, terpenoids, lactones, and isoprene derivatives) and is a rapid, easy and inexpensive procedure. In addition, this is the first study to report the detection of several norisoprenoids (mainly naphthalenes) that characterised apricot and peach juices. Moreover, by means of volatile compounds it could be possible to distinguish between juices of organic and conventional production and juices with flavourings additioned.

Keywords: Pear; Peach and apricot nectar; HS-SPME; Aroma profile; Norisoprenoids; Organic agriculture

1. Introduction

Volatiles directly affect the sensorial quality of fresh and processed fruit products, the aroma of which is formed by a complex group of chemical substances (e.g., aldehydes, alcohols, ketones, esters, lactones, terpenes). The concentration of these volatile compounds is generally low (μg/L) and can be affected by a number of agronomic (variety, climatological conditions, ripening stage) (Douillard & Guichard, 1990; Rizzolo, Polesello, & Polesello, 1992; Vendramini & Trugo, 2000; Visai & Vanoli, 1997) and technological (harvest, post-harvest treatments, storage and processing conditions) factors (Botondi, DeSantis, Bellicontro, Vizovitis, & Mencarelli, 2003; Douillard & Guichard, 1990; Lambert, Demazeau, Largeteau, & Bouvier, 1999; Lin, Rouseff, Barros, & Naim, 2002; Mawele Shamaila, Powrie, & Skura, 1992; Rizzolo et al., 1992). Fruit juices are specifically defined in the council directive 2001/112/EC, which can be summarised as being 100% pure fruit juice without preservatives. Fruit nectar are fermentable but unfermented product obtained by adding water and sugars and/or honey to the fruit juices, fruit juices from concentrate, concentrated fruit juices, or fruit purée or to a mixture of those products. The addition of sugars and/or honey is permitted up to 20% of the total weight of the finished product. Moreover, organic food can be defined as the product of a farming system which avoids the use of man-made fertilisers, pesticides, growth regulators and livestock feed additives (Regulation (EEC) No. 2092/91). According to the Regulation (EEC) No. 223/2003 the feed materials from organic production method were comprised of organically-produced at least 95% of the product's dry matter.

Therefore the production–transformation chain of fruits and derivatives requires simple and high-throughput analytical procedures which allow the characterisation of volatile profiles. A rapid analysis of aroma constituents may improve the standardisation of quality and provide a relationship between sensorial and volatile contents. Various studies have evaluated the volatile compounds of fresh fruits (Derail, Hofmann, & Schieberle, 1999; Gomez & Ledbetter, 1997; Guichard,

* Corresponding author. Tel.: +34-93-4024510; fax: +34-93-4035931.
E-mail address: susana@farmacia.far.ub.es (S. Buxaderas).

0308-8146/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2003.12.033

1988; Horvat & Chapman, 1990; Narain, Hsieh, & Johnson, 1990; Suwanagul & Richardson, 1998a; Suwanagul & Richardson, 1998b; Visai & Vanoli, 1997); however, the analytical methods used are not practical for quality control purposes.

Solid phase microextraction (SPME) involves the adsorption of analytes onto a fused silica fibre coated with suitable stationary phases and their subsequent desorption immediately before chromatographic analysis (Arthur & Pawliszyn, 1990; Pawliszyn, 2000; Zhang & Pawliszyn, 1993). The target analytes can be adsorbed on the fibre by immersing it in the sample or by exposing it to the sample headspace (HS-SPME), in which case matrix interferences can be drastically reduced. HS-SPME is a promising technique for the evaluation of the aroma profile of apple (Matich, Rowan, & Banks, 1996; Song, Gardner, Holland, & Beaudry, 1997; Song, Fan, & Beaudry, 1998) and strawberries, raspberries, blackberries, mango and banana (Ibañez, López-Sebastián, Ramos, Tabera, & Reglero, 1998) and fruit juices such as orange (Jia, Zhang, & Min, 1998; Steffen & Pawliszyn, 1996) and tomato (Servili, Selvaggini, Taticchi, Begliomini, & Montedoro, 2000).

Here, we developed a rapid HS-SPME-GC method to measure the volatile compounds of several commercial nectars and fruit juices of peach, pear and apricot, in order to characterise their aroma profile. HS-SPME could be a particularly useful alternative to other tedious or expensive extraction methods, such as liquid–liquid extraction (Di Cesare, Nani, Mariani, & D'Angelo, 1996), solid phase extraction (SPE) (Polesello, Di Cesare, & Nani, 1989), vacuum distillation (Derail et al., 1999; Gomez & Ledbetter, 1997; Guichard, 1988; Guichard, Schlich, & Issanchou, 1990; Horvat & Chapman, 1990), and dynamic headspace (Narain et al., 1990; Suwanagul & Richardson, 1998a; Visai & Vanoli, 1997). The commercial samples used in this study were purchased from Italy and Spain (two of the largest producers of fruit and derivatives in Europe) and some were organically-produced in order to enlarge the data base on aroma composition of nectars and juices.

2. Experimental

2.1. Samples

Thirty-three samples of juice (5 apricot, 11 pear and 17 peach) were analysed. All samples of pear and peach juice were purchased from commercial establishments in Italy and Spain, while apricot juice was only from Italy. 40% of the samples were organic agricultural products. Table 1 showed the characteristics of the samples.

2.2. Chemicals

A model juice made up of 110 g/L of saccharose, 4 g/L of citric acid and 1 L of double distilled water was prepared.

An internal standard solution (IS) of nonanoic acid ethyl ester, 95% purity (Fluka, St. Louis, MO, USA) in methanol (SDS, Peypin, France) was prepared at a concentration of 100 mg/L.

Standard solutions of limonene, ethyl esters of octanoate, decanoate and dodecanoate, hexyl acetate, 2-octanol, benzaldehyde, linalool, α-terpineol, geraniol, and γ-butyrolactone (Sigma, St. Louis, MO, USA) and ethyl esters of hexanoate, nonanoate, tetradecanoate, 1-hexanol and 2-phenylethanal (Fluka, St. Louis, MO, USA) were prepared in methanol (SDS, Peypin, France).

2.3. Analytical procedure

An SPME device (Supelco, Bellefonte, PA, USA) with a 10 mm fibre coated with 100 μm polydimethylsiloxane was used for the extraction. A 5 ml juice sample, previously added to 5 μL of IS solution, was put in a 10 ml vial (Reference 27385, Supelco, Bellefonte, PA, USA) and extraction was performed by headspace mode (with a distance from the liquid surface of 20 mm) at 40 °C for 30 min with magnetic stirring (700*g*). After extraction, the SPME device was introduced in a Gas Chromatograph (GC) splitless injector and maintained at 250 °C for 5 min. Each day the fibre was activated by inserting it into the GC injector at 250 °C for 30 min.

Semiquantitative measurements were carried out using a Hewlett–Packard (Palo Alto, CA, USA) 5890A gas chromatograph equipped with flame ionisation detector (FID). The capillary column was a Supelcowax (Bellefonte, PA, USA) 10 with PEG 20M stationary phase (30 mm × 0.25 mm, 0.25 μm). Helium was used as a carrier gas. The injector and detector temperatures were 250 and 280 °C respectively. The temperature program was from 60 °C (held for 5 min) to 240 °C (held for 10 min) at 3 °C/min using splitless injection mode. The results were expressed as follows:

$$\frac{\text{Peak area}}{\text{Internal Standard (IS)area}} \times 1000.$$

Volatile compounds were identified with a HP5971A quadropole mass selective detector. Mass spectral ionisation was set at 180 °C. The mass spectrometer was operated in the electron ionisation mode at a voltage of 70 eV. The same temperature program as described above was used.

Volatile components were identified by comparing a private library spectra built with chemical standards and two spectral libraries (NIST/EPA/MSDC 49K Mass

Table 1
Code samples and chemical characteristics according to the label of the commercial fruit nectars and juices

	Fruit	pH	°Brix	Product type[A]	% Fruit	Production[B]	Ascorbic acid	Citric acid	Lemon juice	Grape juice	Agave juice	Apple juice	Flavourings	Sugar[C] additioned
A1	Apricot	3.43	15.3	n	40	c	+	−	−	−	−	−	−	g, s
A2	Apricot	3.49	16.2	n	45	c	+	−	−	−	−	−	+	s
A3	Apricot	3.48	15.2	n	45	c	+	−	−	−	−	−	−	g, s
A4	Apricot	3.42	15.3	n	40	o	+	−	−	−	−	−	−	g, s
A5	Apricot	3.40	16.2	n	45	o	+	−	−	−	−	−	−	s
R1	Pear	3.57	14.4	n	50	c	+	+	−	−	−	−	−	g, s
R2	Pear	3.68	15.1	n	50	c	+	+	−	−	−	−	−	g, s
R3	Pear	3.89	15.4	n	50	c	+	+	−	−	−	−	−	g, s
R4	Pear	3.58	13.8	n	55	c	+	+	−	−	−	−	+	s
R5	Pear	3.56	11.3	n	50	c	−	−	+	−	−	−	−	f
R6	Pear	3.60	11.3	j	100	c	−	−	−	−	−	−	−	−
R7	Pear	3.70	12.3	j	100	o	−	−	−	−	−	−	−	−
R8	Pear	3.77	14.8	n	50	o	+	+	−	−	−	−	−	s
R9	Pear	3.70	10.8	n	55	o	−	−	+	−	+	−	−	−
R10	Pear	3.69	14.8	n	>50	o	−	−	+	−	−	+	−	−
R11	Pear	3.91	15.2	n	50	o	+	+	−	−	−	−	−	s
P1	Peach	3.68	14.7	n	45	c	+	+	−	−	−	−	−	g, s
P2	Peach	3.65	15.9	n	45	c	+	+	−	−	−	−	−	g, s
P3	Peach	3.43	14.8	n	50	c	+	+	−	−	−	−	+	s
P4	Peach	3.80	15.4	n	45	c	+	+	−	−	−	−	−	g, s
P5	Peach	3.30	9.3	n	>50	c	−	−	+	−	−	−	−	f
P6	Peach	3.58	13.9	n	45	c	+	−	+	−	−	−	−	s
P7	Peach	3.49	5.8	n	50	c	+	+	−	−	−	−	−	a
P8	Peach	3.83	11.9	n	45	c	+	+	−	−	−	−	−	g, s
P9	Peach	4.04	15.3	n	45	c	+	+	−	−	−	−	−	a
P10	Peach	3.90	12.4	j	100	c	−	−	−	+	−	−	−	−
P11	Peach	3.63	12.4	j	100	c	−	−	−	+	−	−	−	−
P12	Peach	3.78	10.4	n	50	o	−	−	+	−	+	−	−	−
P13	Peach	3.75	15.4	n	45	o	+	+	−	−	−	−	−	s
P14	Peach	3.71	13.3	n	45	o	−	−	+	−	+	−	−	−
P15	Peach	3.71	13.8	n	>50	o	−	−	+	−	−	+	−	−
P16	Peach	3.70	13.8	n	>50	o	−	−	−	−	−	+	−	−
P17	Peach	3.79	15.7	n	45	o	+	+	−	−	−	−	−	s

+, the compound in the row was present in the sample; −, the compound in the row was not in the sample; A (n, fruit nectar; j, fruit juice); B (c, conventional production; o, organic production) C (g, glucose syrup; s, sucrose; f, fructose; a, artificial).

Spectral Database, Hewlett–Packard Co., Palo Alto, CA, USA and Registry of Mass Spectral Data with Structures, Wiley 6.l, NY, USA). When available, MS identifications were confirmed by comparing GC retention times with pure standards. We also used the injection of retention index standards (Sigma, St. Louis, MO, USA) of C_8 to C_{32} aliphatic hydrocarbons dissolved in methanol to calculate the Kovats-type gas chromatographic retention indices in Carbowax phase (PEG) and Silicone phase [using a SPB-1^{TM} column with Fused Silica stationary phase (30 m × 0.25 mm, 0.25 μm)] (Supelco, Bellefonte, PA, USA).

2.4. Absolute response factors

Five millilitre of model solution were spiked with three different quantities of the standard solutions (Table 2). Then these solutions were extracted three times by HS-SPME, as described above. The concentration range of these standard solutions was chosen to obtain area responses that included those obtained from fruit juices.

2.5. Detection and quantification limits

Detection and quantification limits were determined according to the method of U.S.P. XII (1989). Five millilitre of model solution spiked with 5 μL of IS was analysed seven times following the analytical procedure described. In each blank, 10 signal noises around the integration zone (corresponding to each standard used to calculate the absolute response factors) were studied. Peaks from the fibre were not taken into account (100 m/z). The mean of signal noises was transformed as concentration using the internal standard area value. For each compound the limit of detection (LD) was calculated as three times the concentration corresponding to signal noise ratio, and the limit of quantification (LQ) as 10 times the signal noise ratio (Table 2).

2.6. Repeatability

All juices were analysed three times following the procedure described above. Repeatability was expressed as the coefficient of variation of the three measurements. The precision of analysis was 14% for compounds with a relative area lower than 1000 and 7% for those with a relative area higher than 1000.

2.7. Statistical procedures

Discriminant analysis was carried out with the aroma compounds that had median value and also, it was performed to discriminate samples of organic agriculture from those of conventional production. The Statgraphics Plus 4.1 (1999) program was used.

3. Results and discussion

Figs. 1–3 showed the GC-FID volatile profile of apricot, peach and pear juice, respectively obtained by CW column. The peak numbers in the chromatograms corresponded to the compounds listed in Tables 3–5, respectively. The aroma compounds were numbered according to their retention time by CW column. These tables showed the Kovats Indexes obtained with CW column and using the SPB-1 column to confirm the identity of the aroma, the identification method (retention time and/or mass spectrum) and the compounds, which were previously reported in the literature using other methods. Some of the compounds were not iden-

Table 2
Absolute response factors of standards, concentration intervals, lineality (r), and limits of detection and quantification

	Concentration interval μg/L ($n = 9$)	Absolute response factor slope (a)	$r(p < 0.001)$	LD μg/L	LQ μg/L
Limonene	0.12–0.5	957,146	0.999	0.2	0.8
Ethyl hexanoate	20–80	1947	0.998	0.2	0.4
Hexyl acetate	1–5	189,323	0.996	0.2	0.4
1-Hexanol	60–240	2915	0.998	0.2	0.6
Ethyl octanoate	20–80	32,518	0.995	0.2	0.6
Ethyl nonanoate (IS)	2–8	651,984	0.995	0.2	0.5
Benzaldehyde	2–6	77,844	0.954	0.2	0.8
Linalool	14–55	61,432	0.998	0.8	2.2
2-Octanol	4–14	35,413	0.999	0.2	0.6
Ethyl decanoate	20–80	13,206	0.997	0.4	1.2
α-Terpineol	10–40	27,306	0.998	0.4	1.2
Geraniol	3–12	41,880	0.999	1.8	4.6
Ethyl dodecanoate	20–80	47,439	0.998	0.6	1.4
Ethyl tetradecanoate	20–80	22,973	0.993	1.6	4.2
2-Phenylethanal	10–40	9486	0.931	0.8	2.2
γ-Butyrolactone	10–40	979	0.992	0.4	0.8

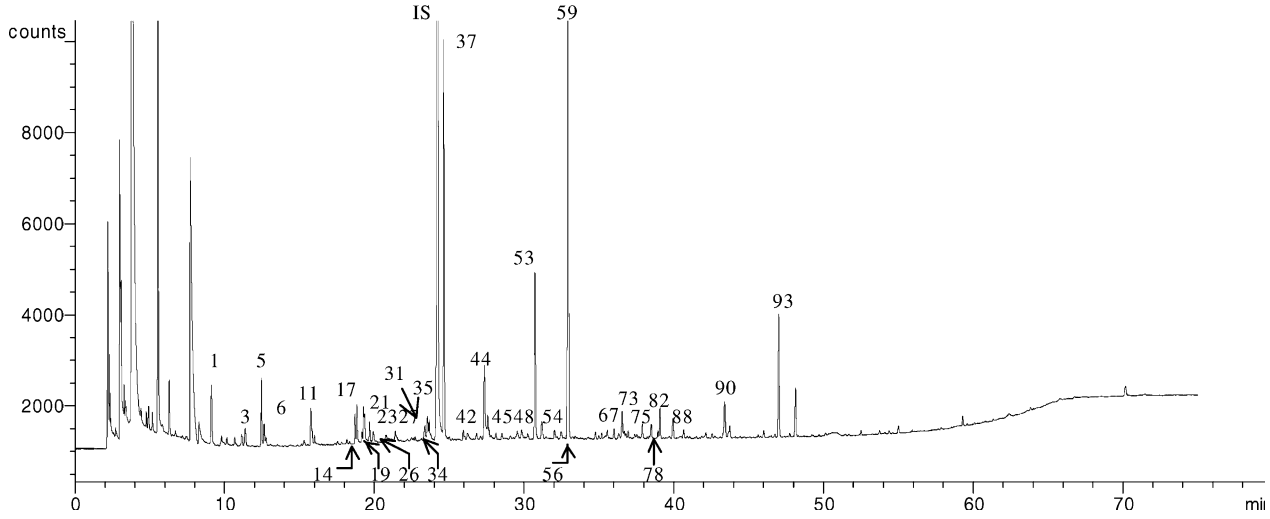

Fig. 1. Chromatogram of apricot sample obtained by CW column and FID detector. Peak numbers correspond to the compounds listed in Table 3.

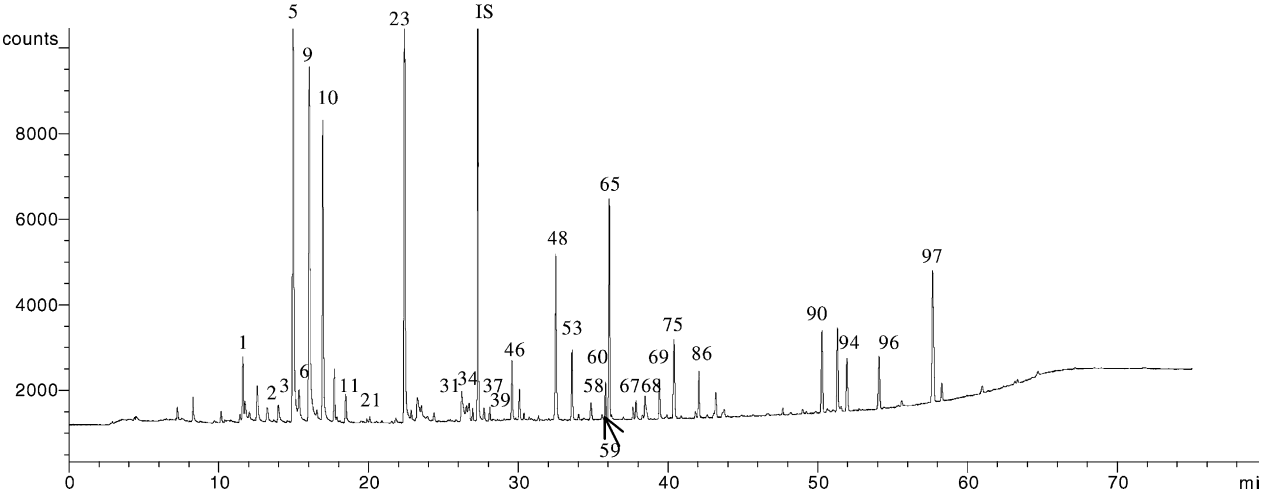

Fig. 2. Chromatogram of peach sample obtained by CW column and FID detector. Peak numbers correspond to the compounds listed in Table 4.

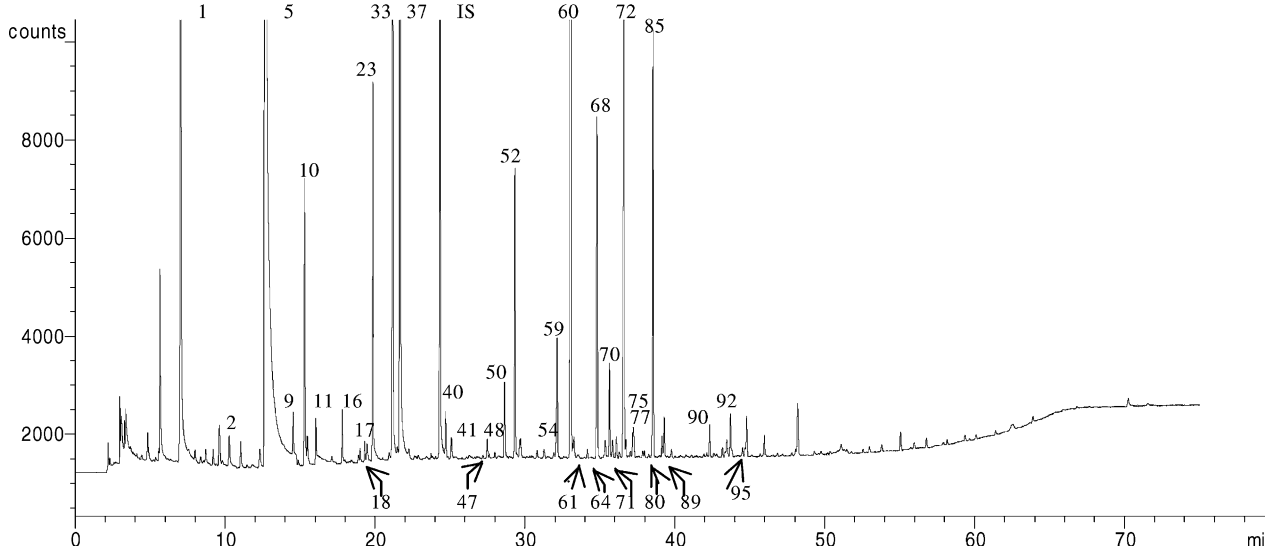

Fig. 3. Chromatogram of pear sample obtained by CW column and FID detector. Peak numbers correspond to the compounds listed in Table 5.

Table 3
Volatile compounds of apricot juice

		KI[a] Cw[b] phase	KI SPB-1[c] phase	Id.[d]	Ref.[e]	Mean[f]	Standard deviation[f]	No. samples[g]
1	Limonene	1206	1017	A,B	[4,6,7]	54	92	4
3	β-Ocimene	1250	1038	B	[4]	13	14	4
4	Isoamylbutyrate[h]	1259	1042	B		13	27	1
5	Hexyl acetate	1262	997	A,B	[1,3]	7	14	1
6	α-Terpinolene	1287	1074	B	[4]	35	55	5
7	Isoamylvalerate[h]	1287	1091	B		22	45	1
11	1-Hexanol	1339	858	A,B	[2,4,6,7]	22	13	5
14	Butyl hexanoate[h]	1350	1174	B		3	6	1
17	Hexyl butyrate[h]	1398	1175	B		5	8	3
19	Hexyl isovalerate[h]	1424	1068	B		21	6	5
21	3,8,8-Trimethyltetrahydro naphthalene[h]	1424	1000	B		5	4	3
22	1,2,3,4-Tetrahydro-1,1, 6-trimethylnaphthalene	1425	1117	B	[6]	3	7	1
23	Ethyl octanoate	1428	1180	A,B	[2]	6	5	3
26	Acetic acid	1465	1137	A,B	[4,6]	14	9	5
27	Unknown peak 1	1465	1137			4	4	3
28	2-Furancarboxyaldehyde	1467	815	B	[6]	14	27	2
31	Vitispirane[h]	1505	1260	B		8	10	3
32	Unknown peak 2	1505	1075			39	64	3
34	Benzaldehyde	1508	926	A,B	[1–4,6,7]	6	8	2
35	Unknown peak 3	1511	1122			35	45	5
37	Linalool	1537	1083	A,B	[1–7]	75	73	5
42	Unknown peak 4	1568	1275			25	38	3
44	Hexyl hexanoate[h]	1599	1268	B		10	20	1
45	Megastigma-4,6,8-triene[h]	1604	1147	B		45	61	4
48	Ethyl decanoate	1656	1375	A,B		17	20	5
53	α-Terpineol	1661	1166	A,B	[2,4,6,7]	95	71	5
54	α(*Z*, *E*)-Farnesene[h]	1692	941	B		12	7	5
56	1,2-Dihydro,1,1, 6-trimethyl- naphthalene	1717	1474	B	[6]	6	8	4
59	α(*E*, *E*)-Farnesene	1740	1492	B	[4]	146	291	4
67	Geraniol	1797	1234	A,B	[2,4–7]	5	7	2
73	Unknown peak 5	1836	1424			15	21	4
75	Ethyl dodecanoate	1844	1582	A,B		10	12	5
78	Unknown peak 6	1869	1558			15	15	4
82	β-Ionone	1924	1454	A,B	[4,6,7]	22	24	4
88	Cinnamaldehyde[h]	1996	1506	B		35	17	5
90	Ethyl tetradecanoate	2027	1780	A,B		1	3	1
93	γ-Decalactone	2101	1418	B	[1,3,6,7]	29	31	4

[1] Guichard (1988); [2] Polesello et al. (1989); [3] Guichard et al. (1990); [4] Chung, Eiserich, and Shibamoto (1993); [5] Nishimura (1995); [6] Di Cesare et al. (1996); [7] Gomez and Ledbetter (1997).

[a] Kovats Index.

[b] Carbowax phase.

[c] Silicone phase.

[d] Identification (A, retention time, B, mass spectrometry).

[e] References.

[f] (Peak area/IS area) × 1000.

[g] Number of samples where the compound was found.

[h] Tentatively identified.

tified by retention time or MS and were included in the tables as unknown peaks with Kovats Indexes. These compounds were analysed in the study because they were found in most of the samples and were not impurities of the fibre (100 m/z). We detected 37 compounds in apricot juice, 60 in peach juice and 49 in pear juice. More compounds were found in our juice samples (Tables 3–5) than in other studies for fresh fruits (Derail et al., 1999; Di Cesare et al., 1996; Gomez & Ledbetter, 1997; Guichard, 1988; Guichard et al., 1990; Horvat & Chapman, 1990; Narain et al., 1990; Polesello et al., 1989; Suwanagul & Richardson, 1998a, 1998b; Visai & Vanoli, 1997). This may be due to the different fruit characteristics (e.g., varieties, ripening, origin) and to the distinct treatments used for juice extraction (e.g., enzymes, heat, filtration). The heterogeneity of the

Table 4
Volatile compounds of peach juice

		KI[a] Cw[b] phase	KI SPB-1[c] phase	Id.[d]	Ref.[e]	Mean[f]	Standard deviation[f]	No. samples[g]
1	Limonene	1206	1017	A,B	[3,4]	4601	9714	12
2	Ethyl hexanoate	1223	982	A,B		2	10	1
3	β-Ocimene	1250	1038	B	[4]	15	47	4
5	Hexyl acetate	1262	997	A,B	[1,3,6]	385	891	7
6	α-Terpinolene	1287	1074	B	[4,6]	1	4	1
8	γ-Terpinene	1291	1057	B	[4,6]	128	509	3
9	3-Hexenyl acetate	1300	988	B	[2,3]	102	240	4
10	2-Hexenyl acetate	1315	997	B	[3,6]	8	27	3
11	1-Hexanol	1316	858	A,B	[3,4,6]	11	22	6
12	Acetoin	1336	1007	B	[6]	56	231	1
13	Unknown peak 1	1339	1000			22	55	7
14	Butyl hexanoate[h]	1388	1174	B		24	82	2
17	Hexyl butyrate[h]	1410	1175	B		3	11	1
20	Octyl acetate	1424	1193	A,B		26	56	6
21	3,8,8,Trimethyltetrahydro-naphthalene[h]	1424	1000	B		69	223	3
23	Ethyl octanoate	1428	1180	A,B	[3]	196	417	11
24	3-Hexenol	1434	847	A,B	[2–4,6,7]	3	7	3
25	1,2,3,4-Tetrahydro-1,6-dimeth-yl-4-(1-methylethyl) naphtha-lene[h]	1435	1518	B		21	83	3
26	Acetic acid	1465	1137	A,B	[4,5]	237	769	5
28	2-Furancarboxyaldehyde	1467	815	B	[3]	2	3	5
29	2-Methylethyl octanoate[h]	1471	1178	B		46	86	7
30	3-Hexenyl isobutyrate	1504	1275	B	[2]	14	33	4
31	Vitispirane[h]	1505	1260	B		9	31	2
34	Benzaldehyde	1508	926	A,B	[1–4,6]	17	41	5
36	Trimethyltetrahydronaphtha-lene[h]	1520	1068	B		71	202	4
37	Linalool	1537	1083	A,B	[4–7]	156	301	12
38	Caryophyllene	1537	1246	B	[4]	4	15	1
39	1,2,3,4-Tetrahydro-1,1,6-tri-methyl naphthalene[h]	1545	1255	B		13	38	4
44	Hexyl hexanoate[h]	1599	1268	B		4	11	3
46	1,2,3,4-Tetrahydro-1,6,8-tri-methyl naphthalene[h]	1610	1239	B		102	292	3
48	Ethyl decanoate	1624	1378	A,B		31	69	7
49	Citronellyl acetate	1645	1335	B	[5]	8	22	3
51	Unknown peak 2	1656	1375			51	164	5
53	α-Terpineol	1661	1166	A,B	[4]	112	171	13
54	α(*Z*, *E*)-Farnesene[h]	1692	941	B		12	24	6
57	Ethyl benzoate	1728	1154	B	[2,3]	5	19	1
58	Estragole[h]	1728	1170	B		84	267	2
59	α(*E*, *E*)-Farnesene	1740	1492	B	[4]	170	250	11
60	Geranyl acetate[h]	1745	1360	B		81	226	4
62	1,2,4a,5,8,8a-Hexahydro-4,7-dimethyl-1-(1-methylethyl) naphthalene[h]	1761	1524	B		1	5	1
65	Benzyl acetate[h]	1788	1131	B		88	236	5
66	Neryl acetate[h]	1789	1345	B		98	349	3
67	Geraniol	1797	1234	A,B	[4]	51	91	8
68	β-Damascenone	1806	1354	B	[7]	13	38	3
69	1,2-Dihydro-1,4,6-trimethyl-naphthalene[h]	1809	1233	B		7	18	4
70	Anethole	1809	1254	B		5	17	2
72	Ethyl 2,4 (*E*, *Z*)-decadienoate[h]	1832	1443	B		13	42	3
75	Ethyl dodecanoate	1844	1558	A,B		10	32	4
76	α-Ionone	1857	1416	A,B		0	1	1
81	Damascenone A[h]	1891	1476	B		46	93	4
82	β-Ionone	1924	1454	A,B	[4]	44	138	3
83	2-Ethyl hexanoate[h]	1932	1717	B		0	0	1
86	Methyl tetradecanoate	1990	1707	A,B		1	4	2

Table 4 (*continued*)

		KI[a] Cw[b] phase	KI SPB-1[c] phase	Id.[d]	Ref.[e]	Mean[f]	Standard deviation[f]	No. samples[g]
88	Cinnamaldehyde[h]	1996	1506	B		76	134	16
90	Ethyl tetradecanoate	2027	1780	A,B		4	15	2
91	Ethyl octadecanoate	2047	1506	A,B		1	3	1
93	γ-Decalactone	2101	1418	B	[1,3,6,7]	596	1123	17
94	δ-Decalactone	2144	1442	B	[1,3,6,7]	40	96	4
96	γ-Undecalactone	2210	1523	B	[1,3,6]	91	193	6
97	γ-Dodecalactone	2317	1630	B	[3,6,7]	7	27	1

[1] Polesello et al. (1989); [2] Guichard et al. (1990); [3] Narain et al. (1990); [4] Chung et al. (1993); [5] Nishimura (1995); [6] Visai and Vanoli (1997); [7] Derail et al. (1999).

[a] Kovats Index.

[b] Carbowax phase.

[c] Silicone phase.

[d] Identification (A, retention time, B, mass spectrometry).

[e] References.

[f] (Peak area/IS area) × 1000.

[g] Number of samples where the compound was found.

[h] Tentatively identified.

Table 5
Volatile compounds of pear juice

		KI[a] Cw[b] phase	KI SPB-1[c] phase	Id.[d]	Ref.[e]	Mean[f]	Standard deviation[f]	No. samples[g]
1	Limonene	1206	1017	A,B	[2]	330	684	6
2	Ethyl hexanoate	1223	982	A,B	[3,4]	3	11	1
5	Hexyl acetate	1268	997	A,B	[1,3,4]	2965	5747	11
9	3-Hexenyl acetate	1300	988	A,B	[3]	4	14	1
10	2-Hexenyl acetate[h]	1315	997	B		43	99	2
11	1-Hexanol	1316	858	A,B	[1–4]	67	88	9
13	Unknown peak 1	1339	1000			137	477	3
15	Heptyl acetate	1361	1095	B	[3,4]	131	425	2
16	Methyl octanoate	1378	1107	B	[3,4]	5	15	2
17	Hexyl butyrate	1398	1174	B	[3,4]	18	47	4
18	Hexyl isobutyrate[h]	1418	1175	B		663	2066	5
20	Octyl acetate	1424	1193	A,B	[3,4]	176	587	4
23	Ethyl octanoate	1428	1180	A,B	[3,4]	286	594	9
26	Acetic acid	1465	1137	A,B	[2,4]	38	70	6
28	2-Furancarboxyaldehyde	1467	815	B		5	10	3
33	Ethyl 4-octenoate[h]	1505	1075	B		67	193	3
37	Linalool	1537	1083	A,B	[2]	9	16	4
40	*n*-Octanol	1546	1061	A,B	[1,3,4]	3	9	3
41	Ethyl 2-octenoate	1557	1275	B	[3]	2	9	1
43	Methyl decanoate	1581	1307	A,B	[3,4]	1	3	1
44	Hexyl hexanoate	1599	1268	B	[3,4]	137	402	6
47	Methyl 4-decenoate	1611	1171	B	[3,4]	27	55	5
48	Ethyl decanoate	1624	1378	A,B	[3,4]	52	66	9
50	3-Hexenyl hexanoate[h]	1646	1361	B		27	91	3
52	Ethyl 4-decenoate	1657	1375	B	[1,3]	113	194	7
54	α (*Z*, *E*)-Farnesene	1692	1478	B	[3,4]	282	529	7
55	Methyl 2-decenoate	1694	1411	B	[3,4]	8	8	6
59	α(*E*, *E*)-Farnesene	1740	1492	B	[2–4]	2254	3248	10
60	Geranyl acetate[h]	1745	1254	B		8	19	2
61	Ethyl 2-decenoate	1750	1166	B	[3]	27	62	2
63	Methyl 2,4 (*Z*, *E*)-decadienoate	1768	1332	B	[1,3]	555	808	6
64	Methyl 2,4 (*E*, *Z*)-decadienoate	1785	1369	B	[1,3,4]	333	637	8
68	β-Damascenone[h]	1806	1354	B		29	43	6
70	Anethole	1819	1254	B	[1]	33	50	6
71	Unknown peak 2	1820	1222			136	364	6
72	Ethyl 2,4 (*E*, *Z*)-decadienoate	1832	1443	B	[1,3,4]	2827	2668	11
74	Unknown peak 3	1836	1424			26	38	5
75	Ethyl dodecanoate	1844	1582	A,B		34	60	6
77	Geranyl isobutyrate[h]	1860	1325	B		30	53	3

Table 5 (*continued*)

		KI[a] Cw[b] phase	KI SPB-1[c] phase	Id.[d]	Ref.[e]	Mean[f]	Standard deviation[f]	No. samples[g]
79	Unknown peak 4	1869	1398			26	54	5
80	Ethyl 3-hydroxy dodecanoate[h]	1886	1574	B		95	210	4
84	Geranyl butirate[h]	1964	1535	B		240	600	3
85	Ethyl 2,4 (*E*,*E*)-decadienoate	1986	1414	B	[3]	107	158	8
87	Nerolidol	1991	1553	B	[2]	17	28	4
88	Cinnamaldehyde[h]	1996	1506	B		26	22	9
89	Ethyl 2,6 (*Z*,*E*)-dodecadienoate[h]	2000	1717	B		1	3	1
90	Ethyl tetradecanoate	2027	1780	A,B	[3]	16	52	1
92	Amyl benzoate[h]	2055	1506	B		10	15	5
95	Methyl tetradecadienoate	2174	1707	A,B	[3]	10	14	6

[1] Polesello et al. (1989); [2] Chung et al. (1993); [3] Suwanagul and Richardson (1998a); [6] Chervin, Speirs, Loveys, and Patterson (2000).
[a] Kovats Index.
[b] Carbowax phase.
[c] Silicone phase.
[d] Identification (A, retention time, B, mass spectrometry).
[e] References.
[f] (Peak area/IS area) × 1000.
[g] Number of samples where the compound was found.
[h] Tentatively identified.

sample formulation (Table 1) may also explain the variability of the volatile compounds determined in the fruit juice samples of the same kind (apricot, peach and pear).

Apricot aroma was composed of esters (ethyl, acetate and hexyl esters), some terpenoids, and naphthalene-like compounds (Fig. 1 and Table 3). Alcohol and aldehydes of six carbon atoms, responsible for the herbaceous odour of several fruits (Gomez & Ledbetter, 1997; López-Tamames et al., 1997), were poorly detected in the current study. This finding could be due to their low factor responses (see 1-hexanol in Table 2), although these compounds were highly volatile and plentiful. However, eleven substances were detected in all the apricot samples and some of them, were tentatively identified for the first time in apricot juices (α-terpinolene, hexyl isovalerate, α-farnesene, and cinnamaldehyde).

Commercial peach juices contained compounds such as esters and lactones (Fig. 2 and Table 4), although only γ-decalactone was present in all the peach juices. In other studies, which used distinct analytical methods (Dynamic Headspace, Vacuum Distillation, Solid Phase Extraction and Steam Distillation), lactones were the main compounds responsible for peach fruit flavour aroma (Derail et al., 1999; Horvat & Chapman, 1990; Narain et al., 1990; Polesello et al., 1989; Visai & Vanoli, 1997). We also detected several terpenoids and norisoprenoids (Table 4), which could be explained by the high affinity of the PDMS fibre for these compounds (Steffen & Pawliszyn, 1996). Although we analysed commercial juices and taking into account that aroma were more diluted than those of the raw material, we measured more compounds than most of other studies. Only Narain et al. (1990), determined 104 substances, but many of them are herbaceous aldehydes and alcohols that were poor detected on the current study. Several compounds as naphthalene derivatives were tentatively identified for the first time in peach products.

In commercial pear juices (Fig. 3 and Table 5), only hexyl acetate and ethyl 2,4 (*E*,*Z*)-decadienoate were present in all the pear samples. Some authors (Polesello et al., 1989; Suwanagul & Richardson, 1998a, 1998b) reported that methyl, ethyl and acetate esters are the main pear aroma compounds. Comparing our results with those of Chervin et al. (2000), which applies SPME to pear fruits, they detected some alcohols (phenylethanol and dodecanol) and aldehydes (2-hexenal, nonanal, and 2-octenal).

3.1. Discriminant characteristics of the aroma compounds by HS/SPME

The volatile contents of apricot, peach and pear juices are shown in Tables 3–5, respectively, by mean and standard deviation for the various samples of a given fruit juice. Fig. 4 showed the Discriminant Analysis with the most representative aroma compounds, pH and °Brix of apricot, peach, and pear juices. The separation between juices obtained from apricot, peach and pear was the 100% according to the classification made by cross validation. The discriminant Function 1 was defined for hexyl isovalerate (tentatively identified) and unknown peak KI 1505 while Function 2 was defined by pH, unknown peak KI 1836, β-ocimene, hexanol, hexyl hexanoate (tentatively identified), methyl 2-decenoate, methyl 2,4 (*E*,*Z*)-decadienoate, anethole and ethyl 2,4 (*E*,*Z*)-decadienoate.

Moreover, the discriminant analysis was then applied in order to discriminate the nectars according to its

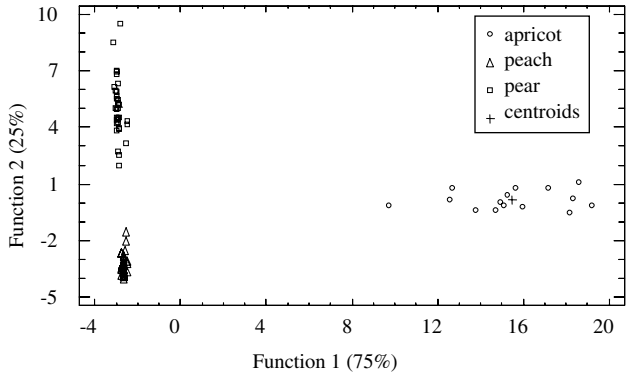

Fig. 4. Discriminant analysis of characteristic aroma of peach, apricot, and pear juices and nectars.

production, organic or conventional and also, taking into account the flavoured samples (Table 1) (data not shown). The 100% of the flavoured samples were correctly classified according to the classification made by cross validation. The 94% of the organic nectars were correctly classified and the 92% of the conventional ones. Only two samples of peach were wrong identified, one of them of organic production and the other, conventional. These preliminary results indicate that various groups of volatiles are potential markers of organic fruit juices, even if specific studies and more HS-SPME data were required to verify and confirm this possibility.

In conclusion, the HS-SPME method was applied satisfactorily to analyse the aroma profile of approximately 30 commercial fruit juices. Although this method has low response factors for herbaceous aldehydes and alcohols, it detects a wide profile of aroma compounds in commercial peach, apricot, and pear juice. This HS-SPME method offers to the fruit juice industry an alternative technique for routine analysis to rapidly control the quality of aroma. This method could provide data on fruit markers and the type of agriculture used (conventional or organic).

Acknowledgements

This study was supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) (Spain) with project VIN01-051, the Ministerio de Educación y Cultura (MEC) (Spain) with HI1999-0121 project, the Generalitat de Catalunya (*Autonomous Government*), with the project 2001SGR00131. M. Riu-Aumatell, a PhD student, received a grant from the Universitat de Barcelona.

References

Arthur, C. L., & Pawliszyn, J. (1990). Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry, 62*, 2145–2148.

Botondi, R., DeSantis, D., Bellicontro, A., Vizovitis, K., & Mencarelli, F. (2003). Influence of ethylene inhibition by 1-methylcyclopropene on apricot quality, volatile production, and glycosidase activity of low- and high-aroma varieties of apricots. *Journal of Agricultural and Food Chemistry, 51*, 1189–1200.

Chervin, C., Speirs, J., Loveys, B., & Patterson, B. D. (2000). Influence of low oxygen storage on aroma cmpounds of whole pears and crushed pear flesh. Short communication. *Postharvest biology and technology, 19*, 279–285.

Chung, T. Y., Eiserich, J. P., & Shibamoto, T. (1993). Volatile compounds isolated from edible korean chamchwi (*Aster scaber* thunb). *Journal of Agricultural and Food Chemistry, 41*, 1693–1697.

Comission Regulation (EC) No. 223/2003 of 5 February 2003 on labelling requirements related to the organic production method for feedingstuffs, compound feedingstuffs and feed materials and amending Council Regulation (EEC) No. 2092/91.

Council Regulation (EEC) No. 2092/91 of 24 June 1991 on organic production of agricultural products and indications referring there to on agricultural products and foodstuffs.

Council Directive No. 2001/112/EC of 20 December 2001 relating to fruit juices and certain similar products intended for human consumption.

Derail, C., Hofmann, T., & Schieberle, P. (1999). Differences in key odorants of handmade juice of yellow-flesh peaches (*Prunus persica* L.) induced by the the workup procedure. *Journal of Agricultural and Food Chemistry, 47*, 4742–4745.

Di Cesare, L. F., Nani, R., Mariani, N., & D'Angelo, V. (1996). Influenza delle maltodestrine, ciclodestrine e dell'olio di palma sulla ritenzione degli aromi nei disidratati di albicocca. *Industrie delle Bevande, 25*, 101–107.

Douillard, C., & Guichard, E. (1990). The aroma of strawberry (*Fragaria ananassa*): Characterization of some cultivars and influence of freezing. *Journal of the Science of Food and Agriculture, 50*, 517–531.

Gomez, E., & Ledbetter, C. A. (1997). Development of volatile compounds during fruit maturation: Characterization of apricot and plum × apricot hybrids. *Journal of the Science of Food and Agriculture, 74*, 541–546.

Guichard, E. (1988). Quantification of some volatile aromatic compounds of apricot by adding standards. A research note. *Journal of Food. Science, 53*(6), 1902–1904.

Guichard, E., Schlich, P., & Issanchou, S. (1990). Composition of apricot aroma: Correlations between sensory and instrumental data. *Journal of Food Science, 55*(3), 735–738.

Horvat, R. J., & Chapman, G. W. (1990). Comparison of volatile compounds from peach fruit and leaves (cv. Monroe) during maturation. *Journal of Agricultural and Food Chemistry, 38*, 1442–1444.

Ibañez, E., López-Sebastián, S., Ramos, E., Tabera, J., & Reglero, G. (1998). Analysis of volatile fruit components by headspace solid-phase microextraction. *Food Chemistry, 63*(2), 281–286.

Jia, M., Zhang, Q. H., & Min, D. B. (1998). Optimization of solid-phase microextraction analysis for headspace flavor compounds of orange juice. *Journal of Agricultural and Food Chemistry, 46*, 2744–2747.

Lambert, Y., Demazeau, G., Largeteau, A., & Bouvier, J. M. (1999). Changes in aromatic volatile composition of strawberry after high pressure treatment. *Food Chemistry, 67*, 7–16.

Lin, J., Rouseff, R. L., Barros, S., & Naim, M. (2002). Aroma composition changes in early season grapefruit juice produced from thermal concentration. *Journal of Agricultural and Food Chemistry, 50*, 813–819.

López-Tamames, E., Carro-Mariño, N., Ziya Gunata, Y., Sapis, C., Baumes, R., & Bayonove, C. (1997). Potential aroma in several varieties of Spanish grapes. *Journal of Agricultural and Food Chemistry, 45*(5), 1729–1735.

Matich, A. J., Rowan, D. D., & Banks, N. H. (1996). Solid phase microextraction for quantitative headspace sampling of apple volatiles. *Analytical Chemistry, 68*, 4114–4118.

Mawele Shamaila, M., Powrie, W. D., & Skura, B. J. (1992). Analysis of volatile compounds from strawberry fruit stored under modified atmosphere packaging (MAP). *Journal of Food Science, 57*(5), 1173–1176.

Narain, N., Hsieh, T. C.-Y., & Johnson, C. E. (1990). Dynamic headspace concentration and gas chromatography of volatile flavor components in peach. *Journal of Food Science, 55*(5), 1303–1307.

Nishimura, O. (1995). Identification of the characteristic odorants in fresh rhizomes of ginger (*Zingiber officinale* Roscoe) using aroma extract dilution analysis and modified multidimensional gas chromatography–mass spectroscopy. *Journal of Agricultural and Food Chemistry, 43*, 2941–2945.

Pawliszyn, J. (2000). Theory of solid-phase microextraction. *Journal of Chromatographic Science, 38*, 270–278.

Polesello, A., Di Cesare, L. F., & Nani, R. (1989). Recupero degli aromi dagli ortofrutticoli mediante estrazione in fase solida. *Industrie delle Bevande, 18*, 93–101.

Rizzolo, A., Polesello, A., & Polesello, S. (1992). Use of headspace capillary GC to study the development of volatile compounds in fresh fruits. *Journal of High Resolution Chromatography, 15*, 472–477.

Servili, M., Selvaggini, R., Taticchi, A., Begliomini, A. L., & Montedoro, G. (2000). Relationships between the volatile compounds evaluated by solid phase microextraction and the thermal treatment of tomato juice: Optimization of the blanching parameters. *Food Chemistry, 71*, 407–415.

Song, J., Gardner, B. D., Holland, J. F., & Beaudry, R. M. (1997). Rapid analysis of volatile flavor compounds in apple fruit using SPME and GC/time-of-flight mass spectrometry. *Journal of Agricultural and Food Chemistry, 45*, 1801–1807.

Song, J., Fan, L., & Beaudry, R. M. (1998). Application of solid phase microextraction and gas chromatography/time-of-flight mass spectrometry for rapid analysis of flavor volatiles in tomato and strawberry fruits. *Journal of Agricultural and Food Chemistry, 46*, 3721–3726.

Steffen, A., & Pawliszyn, J. (1996). Analysis of flavor volatiles using headspace solid-phase microextraction. *Journal of Agricultural and Food Chemistry, 44*, 2187–2193.

Suwanagul, A., & Richardson, D. G. (1998a). Pear fruit volatiles characterized by SPME and capillary GLC/mass spectroscopy. *Acta Horticulturae, 475*, 599–603.

Suwanagul, A., & Richardson, D. G. (1998b). Identification of headspace volatile compounds from different pear (*Pyrus communis* L.) varieties. *Acta Horticulturae, 475*, 605–623.

Validation of compendial methods (1225) (1989). *The United States Pharmacopeia* (U.S.P. XII ed, pp.1710–1712). Easton: Mack Printing.

Vendramini, A. L., & Trugo, L. C. (2000). Chemical composition of acerola fruit (*Malpighia punicifolia* L.) at three stages of maturity. *Food Chemistry, 71*, 195–198.

Visai, C., & Vanoli, M. (1997). Volatile compound production during growth and ripening of peaches and nectarines. *Scientia Horticulturae, 70*, 15–24.

Zhang, Z., & Pawliszyn, J. (1993). Headspace solid-phase microextraction. *Analytical Chemistry, 65*, 1843–1852.