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Research Article

Minor Volatile Compounds in White Wines from Canary Islands, Madeira, and Pico (Azores) by Headspace Solid-Phase Microextraction-Gas Chromatography-Mass Spectrometry: A Qualitative Study

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Application of headspace solid-phase microextraction (HS-SPME) coupled with high-resolution gas chromatographic (HRGC) analytical system was studied for detection and identification of volatile compounds in wines. Four different SPME fibers were tested, and 138 different compounds were detected and identified. The best fiber for the determination of different groups of compounds was selected. Using these results, a comparative study of Madeira, Tenerife (Canary Islands), and Pico (Azores) was carried out.

1. Introduction

Wine is an alcoholic solution with a high variety of dissolved substances such as sugars, acids, alcohols, phenolic compounds, nitrogen compounds, macromolecular materials, minerals, and a number of volatile organic compounds that have great influence on sensory and variety characteristics of wine.

Techniques of determinants isolation are a critical step for the determination of aroma compounds. Technique selected can influence the flavor profile obtained; therefore, the analyst should keep in mind every time the advantages and disadvantages of different methods of isolation of these determinants. Selection of sampling techniques, sample preparation, determinants separation, detection, and quantification, will be essential and crucial for the proper chemical characterization of aroma-related compounds.

As aroma compounds are intrinsically volatile substances, most of the compounds should be determined by gas chromatography with the exception for thermolabile substances. In this particular case HPLC or SFC is suitable [1].

SPME technique has a great potential for the analysis of aroma-related compounds. The headspace SPME (HS-SPME) avoids the immersion of fiber in complex samples that can reduce fiber life. Besides, gas diffusion coefficients are lower in a gas matrix than in liquid matrix so equilibria are reached earlier for HS-SPME [2]. This is a useful technique for obtaining fingerprints of food flavors, although the most obvious benefit is the ability to isolate and concentrate volatile compounds without interference from matrix components [1]. HS-SPME shows a much higher sensitivity to volatile aromatic compounds and semivolatile than other conventional headspace techniques [3]. In contrast to the extraction techniques based on the total extraction of determinants from the matrix, SPME is based on a balance in the concentrations of the determinants in the sample in the headspace and the fiber stationary phase [4, 5]. SPME is the suitable technique for volatile compounds in wine. A big number of wine aroma compounds have been characterised by this technique [6–16].

The aim of this work was to apply the GC-MS technique combined with automatic headspace (HS) SPME to the identification of minor volatile compounds in wine selecting the best fiber for this purpose.

2. Experimental

2.1. Chemicals and Reagents. A set of expected wine compounds were purchased from Aldrich (Steinheim, Germany, and Milwaukee, USA), Fluka (Buchs, Switzerland) and Firmenich (Switzerland): α-terpineol [7785-53-7], β-Citronellol [106-22-9], 2,5-dimethyl-4-hydroxy-3-(2H)-furanone [3658-77-3], 2,6-dimethoxyphenol [91-10-1], 2-ethyl-1-hexanol [104-76-7], 2-phenylethanol (phenylethyl alcohol) [60-12-8], 2-phenoxyethanol [122-99-6], methyl 4-hydroxybenzoate [99-76-3], 4-hydroxy-4-methyl-2-pentanone [123-42-2], butyl acetate [123-86-4], acetoin [513-86-0], isobutyric acid [79-31-2], isovaleric acid [503-74-2], succinic acid [110-15-6], benzylic alcohol [100-51-6], benzaldehyde [100-52-7], ethyl benzoate [93-89-0], benzophenone [119-61-9], eugenol [97-53-0], guaiacol [90-05-1], ethyl heptanoate [106-30-9], diethyl succinate [123-25-1], E,E-2,4-decadienal [25152-84-5], 4-(4-hydroxyphenyl)-2-butanone [5471-51-2], 2-ethyl furoate [614-99-3], 2-methyl-3-furanthiol [28588-74-1], 2-methoxy-4-vinylphenol [7786-61-0], 3-(methylthio)-1-propanol [505-10-2], 4,5-dimethyl-3-hydroxy-2,5-dihydrofuran-2-one [28664-35-9], 4-ethylphenol [123-07-9], 4-ethylguaiacol [2785-89-9], 4-hydroxybenzaldehyde [123-08-0], octanoic acid [124-07-2], butyric acid [107-92-6], decanoic acid [334-48-5], hexanoic acid [142-62-1], acetic acid [64-19-7], propanoic acid [79-09-4], α-ionone [127-41-3], β-ionone [79-77-6], Z-3-hexen-1-ol [928-96-1], δ-decalactone [705-86-2], ethyl isovalerate [108-64-5], ethyl vanillate [617-05-0], γ-decalactone [706-14-9], γ-hexalactone [695-06-7], γ-nonalactone [104-61-0], geraniol [106-24-1], isoamyl octanoate [2035-99-6], ethyl isobutyrate [97-62-1], methyl vanillate [3943-74-6], vanillin [121-33-5], vanillin acetone [214-096-9], whiskey lactone [39212-23-2], 2.3-pentanedione [600-14-6], E-2-octenal [2548-87-0], E-2-nonenal [18829-56-6], E,2-Z,6-nonadienal [557-48-2], phenylacetaldehyde [122-78-1], 2-aminoacetophenone [613-89-8], 3-aminoacetophenone [99-03-6], 4-aminoacetophenone [99-92-3], hexanal [66-25-1], E-2-hexen-1-al [6728-26-3], octanal [124-13-0], furfural [98-01-1], decanal [112-31-2], 2-nonanone [821-55-6], 5-methylfurfural [620-02-0], acetophenone [98-86-2], ethyl cinnamate [103-36-6], linalool [126-91-0], linalool oxide [60047-17-8], 5-hydroxymethyl-2-furaldehyde [67-47-0], siringaldehyde [134-96-3], 3-methylthio-1-propanol [505-10-2], 2-methylbutyric acid [116-53-0], theaspirane [36431-72-8], farnesol [4602-84-0], and β-damascenone [23726-93-4].

Sodium chloride (Merck p.a., Darmstadt, Germany) [7647-14-5], L(+)-tartaric acid [87-69-4] (Merck p.a., Darmstadt, Germany) and sodium hydroxide (Panreac, Barcelona, Spain) [1310-73-2] were used to control ionic strength and to adjust the pH, respectively.

Individual stock standard solutions in ethanol of each compound were prepared. Synthetic matrix solution containing L(+)-tartaric acid (11 g L^{-1}) and ethanol (13%) was prepared for the identification of them in the different wines and adjusted to pH 3.2 with sodium hydroxide. Synthetic and real samples were prepared in 2 mL vials adding 0.80 mL of sample and 0.24 g of NaCl. The vials were tightly capped with PTFE-lined cap and shaken for 10 min at 200 rpm.

2.2. Equipment. Regularly verified pipettes and class A volumetric flasks were used in solution preparation. A precision balance (Sartorius BP 210-S), a pH meter (WTW, pH 197-S), Milli Q-gradient A10 (Millipore), and a mechanical shaker (Selecta, Rotabit) were used in the study.

2.3. SPME Fibers. Four fibers coated with different stationary phases and various film thicknesses were purchased from Supelco (Bellefonte): Polydimethylsiloxane 100 μm (PDMS/100), Polydimethylsiloxane-Divinylbenzene 65 μm (PDMS/DVB), Polyacrylate 85 μm (PA), Carbowax-Divinylbenzene 65 μm (CW/DVB). All fibers were conditioned according to manufacturer recommendations.

2.4. Chromatography. The analysis was carried out on a 3800 GC gas chromatograph equipped with an 8200 Standalone autosampler, a 1079 split/splitless injector, and a mass spectrometry detector Saturn 2000 (Varian, Walnut Creek, CA, USA). Injections were performed in splitless mode, using a 0.75 mm I.D. liner, which improved GC resolution. Ionization mode used was electronic impact.

Separations were performed using a DB-WAXETR capillary column (60 m × 0.25 mm I.D., 0.5 μm film thickness) (J&W Scientific) with an injector temperature of 250°C (valid for all fibers) and 10 min of desorption time operating in splitless mode, 60 min of extraction time, and an oven temperature program of 40°C (15 min), 2°C · min^{-1}, 240°C, 240°C (35 min). Helium was used as carrier at two mL · min^{-1} flow.

Peak identification was accomplished using the NIST mass spectra database (Standard Reference Data of National Institute of Standards and Technology, USA) above 95% of SIM parameter and the synthetic solution of standards.

2.5. Samples. Samples of four different wine varieties, Gual, Malvasía, Listán blanco, and Marmajuelo were studied.

3. Results and Discussion

Table 1 shows extracted compounds using different fibers and their retention time. Excluding major compounds, a total of 138 different compounds have been detected, 41 alcohols, 42 esters, 22 aldehydes and ketones, 15 organic acids, 7 hydrocarbons, 9 terpenes, and 3 other compounds.

There is a large number of sensorial important compounds. As expected in young wines, there are many fruity flavor esters. Base aroma compounds were detected including fatty acids and fusel alcohols. These compounds contribute to the balance of fruity sensations. Some detected compounds have been reported having high aroma values or have been of special importance. This group comprises 8 esters (ethyl acetate, phenylethyl acetate, isoamyl acetate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl isobutyrate, and ethyl isovalerate), two major higher alcohols (isoamyl alcohol and β-phenylethanol), 8 fatty acids and isoacids

Table 1: Retention time (rt), family classification (F), and detected compounds in the different studied varieties with all fibers. Alcohols (1), esters (2), aldehydes and ketones (3), organic acids (4), hydrocarbons (5), terpenes (6), and other compounds (7).

Compounds	rt (min)	F	CW/DVB				PDMS/100				PDMS/DVB				PA			
			Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj
Isobutyl acetate	18.68	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl butyrate	20.83	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl 2-methylbutyrate	22.23	2	+	+	−	+	+	+	+	+	+	+	+	+	−	+	+	+
Ethyl isovalerate	23.79	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Butyl acetate	24.23	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hexanal	25.06	3	−	−	−	+	−	−	−	−	+	+	−	−	−	+	−	−
1-Penten-3-ol	31.89	1	+	+	+	+	+	+	−	−	+	+	+	+	−	+	−	+
Ethyl hexanoate	38.03	2	+	+	+	+	+	+	−	+	+	+	+	+	+	+	+	+
1-Pentanol	39.13	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Bicyclo (4,2,0)-Octa-1,3,5-trien	39.91	5	+	+	−	+	+	+	+	+	+	+	+	+	+	+	+	+
Hexyl acetate	41.08	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Acetoin	42.28	3	+	+	+	+	−	+	+	−	+	+	+	+	+	+	+	+
3-Hexen-1-ol acetate	43.80	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Methylcyclopentane	43.99	5	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2-Heptanol	44.47	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4-Methyl-1-pentanol	44.95	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl heptanoate	45.55	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl lactate	46.50	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1-Hexanol	46.96	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3-Hexen-1-ol	47.66	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3-Ethoxy-1-propanol	48.49	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Z-3-Hexen-1-ol	49.29	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Methyl heptanoate	49.59	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3-Octanol	49.63	1	−	+	+	+	−	+	+	+	+	+	+	+	+	+	+	+
2-Nonen-1-ol	49.92	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2-Hexen-1-ol	51.28	1	+	+	+	+	+	−	+	+	+	+	+	+	+	+	+	+
Ethyl octanoate	52.64	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
E-Linalool oxide	53.12	6	+	+	+	+	−	+	+	−	+	+	+	+	+	+	+	+
1-Octen-3-ol	53.60	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1-Heptanol	53.88	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Acetic acid	53.94	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2-Furaldehyde	55.02	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3-Hepten-1-ol	56.51	1	−	+	+	−	−	+	−	+	+	+	+	+	+	+	+	−
2-Decen-1-ol	56.98	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Theaspirane I	57.19	5	+	+	+	+	+	−	+	+	+	+	+	+	+	+	+	+
(s)-3-Ethyl-4-methylpentanol	57.45	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2-Nonanol	58.01	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl-3-hydroxybutyrate	58.22	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Benzaldehyde	59.02	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl nonanoate	59.25	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
E-2-Nonenal	59.42	3	+	+	+	+	−	+	+	−	−	+	+	−	−	+	−	+
Propionic acid	59.57	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Table 1: Continued.

Compounds	rt (min)	F	CW/DVB				PDMS/100				PDMS/DVB				PA			
			Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj
Theaspirane II	59.65	5	+	+	−	+	+	+	+	+	+	+	+	+	+	−	+	+
Linalool	59.90	6	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1-Octanol	60.53	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Isobutyric acid	61.42	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Diethyl malonate	62.19	2	+	+	+	+	−	+	+	+	−	+	+	+	+	+	+	+
E-2,Z-6-Nonadienal	62.70	3	+	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
2-Methylundecanoic acid	62.95	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1,5,7-Octatrien-3-ol-3,7-dimethyl	63.87	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Cyclooctyl alcohol	64.11	1	+	+	+	+	−	+	−	−	+	+	+	+	+	+	+	−
Ethoxytriglycol	64.40	1	+	+	+	+	−	+	+	−	+	+	+	+	+	−	+	+
Butyric acid	65.05	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl 2-furoate	65.06	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Methyl benzoate	65.10	2	−	−	−	−	−	−	−	+	+	+	+	+	+	+	+	+
Ethyl decanoate	65.45	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2-Decenal	66.01	3	+	+	+	−	−	+	−	−	+	+	+	+	+	+	−	−
Phenylacetaldehyde	66.44	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Isoamyl octanoate	66.59	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Acetophenone	66.82	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Isovaleric acid	67.62	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl benzoate	67.87	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2-Methylbutyric acid	67.87	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Diethyl succinate	67.97	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4-Decen-1-ol (Z)	68.18	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl 4-decenoate	68.62	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
α-Terpineol	69.13	6	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
γ-Hexalactone	69.72	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
E-2-Decen-1-ol	69.80	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3-(Methylthio)-1-propanol	70.25	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Benzyl acetate	71.27	2	+	+	−	+	+	+	+	+	+	−	+	+	+	+	+	+
1,3-Propanediol diacetate	71.40	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1-Decanol	72.59	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
β-Citronellol	72.87	6	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Methyl salicylate	73.95	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1-Dodecene	74.18	5	−	+	−	+	+	+	−	−	+	−	+	+	+	+	+	+
Phenylacetic acid	74.35	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Z-Geraniol	74.77	6	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
5-Mercapto-1-pentanol	75.02	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
E,E-2,4-Decadienal	75.63	3	+	−	−	−	−	−	−	−	−	−	−	+	+	+	−	+
1-Phenylethanol	75.70	1	−	−	+	−	+	−	+	+	−	−	+	−	+	+	+	+
β-Phenylacetate	76.08	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
β-Damascenone	76.25	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl dodecanoate	76.97	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Table 1: Continued.

Compounds	rt (min)	F	CW/DVB				PDMS/100				PDMS/DVB				PA			
			Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj
Hexanoic acid	77.25	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
α-Ionone	77.76	6	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Dihydropseudoionone	77.85	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
N(3-methylbutyl) acetamide	77.89	7	+	+	+	+	+	+	+	−	+	+	+	−	+	+	+	−
3-Methylbutyl pentadecanoate	77.94	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Guaiacol	78.55	1	−	+	+	+	−	−	+	−	+	+	+	−	+	+	+	−
4,5-Dimethyl-1-hexene	78.79	5	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Benzylic alcohol	79.34	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Octyl acetate	79.38	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl hydrocinnamate	79.73	2	+	+	+	+	+	+	+	−	−	+	+	+	+	+	+	+
Whiskey lactone I	79.93	3	+	+	−	+	−	−	−	−	+	−	+	+	+	+	−	+
2-Phenylethanol	81.15	1	−	−	−	−	+	+	+	+	+	+	+	+	+	+	+	+
γ-Octalactone	81.53	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl palmitate	82.35	2	+	+	−	+	−	−	−	−	+	+	+	+	+	−	+	+
β-Ionone	82.38	6	+	−	−	−	+	−	+	+	+	−	+	+	+	−	+	+
2-Ethylhexanoic acid	82.64	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Heptanoic acid	82.82	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
o-Cresol	85.65	1	+	+	+	+	−	−	−	−	+	+	+	−	+	+	+	+
Phenol	85.84	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Isopropyl myristate	86.81	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
γ-Nonalactone	87.05	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Furaneol	87.11	3	+	+	+	+	+	+	+	+	+	−	+	+	+	+	+	+
4-Ethylguaiacol	87.22	1	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
Ethyl myristate	87.49	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Octanoic acid	88.46	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Isoaromadendrene epoxide	89.04	7	+	+	−	+	+	−	+	+	+	−	−	+	+	−	−	+
m-Cresol	90.19	1	−	+	−	−	−	−	−	−	−	−	−	−	+	+	+	+
Ethyl cinnamate	92.04	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl pentadecanoate	92.37	2	−	+	+	+	+	+	+	−	+	+	−	+	+	+	+	+
2-Phenoxyethanol	92.62	1	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
γ-Decalactone	92.70	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Nonanoic acid	93.18	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
N-Morfolinomethyl-isopropylsulfur	93.47	7	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Eugenol	93.77	1	+	+	+	+	+	+	−	+	+	+	−	+	+	+	−	+
4-Ethylphenol	94.16	1	+	+	−	+	+	−	−	−	+	+	−	−	+	+	+	+
δ-Decalactone	95.02	3	−	+	+	+	+	+	+	+	+	−	−	−	−	−	−	−
2-Methoxy-4-vinylphenol	95.16	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl hexadecanoate	97.06	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1-Hepten-4-ol	97.43	1	+	+	+	+	−	−	−	−	−	+	−	+	+	+	−	−
Decanoic acid	97.99	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
γ-Undecalactone	97.99	3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Dimethyl phthalate	99.62	2	+	+	−	+	+	+	+	+	+	+	+	+	+	+	−	+

Table 1: Continued.

Compounds	rt (min)	F	CW/DVB				PDMS/100				PDMS/DVB				PA			
			Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj	Gu	Mv	Lb	Mj
Farnesol I	99.92	6	−	−	−	+	−	+	−	−	−	−	−	−	−	+	−	−
Farnesol III	101.66	6	+	+	+	+	+	+	+	+	−	+	+	+	+	+	+	+
1-Octadecene	102.54	5	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Furasol	103.08	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4-Vinylphenol	103.89	1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ethyl octadecanoate	105.90	2	−	−	+	−	−	+	−	−	+	+	+	+	−	+	+	−
Benzoic acid	105.95	4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Benzophenone	107.57	3	+	+	+	+	+	+	+	+	−	−	−	−	+	+	+	+
2-Monolinolein	108.81	2	−	−	−	−	−	+	−	−	−	−	−	−	−	+	−	−
Butyl 2-ethylhexyl phthalate	109.63	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Vanillin	110.89	3	+	+	−	+	+	+	+	+	+	+	+	−	+	−	−	+
Octyl butyl phthalate	115.77	2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

(propanoic, butyric, hexanoic, octanoic, decanoic, isobutyric, 2-methylbutyric, and isovaleric), 2 volatile phenols (4-vinylphenol and 4-vinylguaiacol) as well as linalool and β-damascenone [17, 18].

The presence of β-damascenone in all studied wines is remarkable. It is considered a high quality aroma, reminiscent of exotic flowers and fruit. β-Damascenone appears during must fermentation as a by-product of hydrolysis. However, its presence could be related to the particular climate of the Canary Islands that promotes the synthesis of norisoprenoids in grapes [19, 20].

Some fibers show little ability in extracting some compounds. CW/DVB fiber does not extract the following compounds from any of the wines: methyl benzoate, 4-ethylguaiacol, 2-phenoxyethanol, and 2-monolinolein. PDMS/100 fiber does not extract hexanal, E,2-Z,6-nonadienal, whiskey lactone I, o-cresol, m-cresol, ethyl palmitate, 4-ethylguaiacol, 2-phenoxyethanol, or 1-hepten-4-ol. The same happens when using PDMS/DVB fiber and E,2-Z,6-nonadienal, 4-ethylguaiacol, m-cresol, 2-phenoxyethanol, farnesol I, benzophenone, and 2-monolinolein. In relation to the PA fiber does not extract the E,2-Z,6-nonadienal, 4-ethylguaiacol, 2-phenoxyethanol, and δ-decalactone.

Farnesol I and 2-monolinolein were not detected in Gual wine, E,E-2,4-decadienal, farnesol I, and 2-monolinolein were not detected in Listán blanco wine, and E,2-Z,6-nonadienal and 2-monolinolein were not detected in Marmajuelo wine. On the other hand, 2-monolinolein was only detected in Malvasía wine.

Variability in number and compounds was detected when different wines and fibers were used. Table 2 shows the number of compounds extracted for each wine variety and fiber.

Sum of absolute peak area and number of detected compounds along the four wines were used to select the best fiber for each chemical family. When overall compounds were taken in account PA shows the best efficiency followed by PDMS/DVB, CW/DVB, and PDMS/100, respectively, either for number of compound or peak areas. This pattern is similar for alcohols with slight differences.

Esters present the same number of extracted compounds for PA and PDMS/DVB. However, PDMS/DVB shows higher peak areas.

Carbonylic (aldehydes + ketones) compounds were best extracted by CW/DVB followed by PA, PDMS/DVB, and PDMS/100, respectively, either accounting sum of extracted compounds or sum of peak areas.

Hydrocarbon compounds were best extracted with PA fiber. This fiber extracts the higher number of compounds and the higher peak areas too. However, the rest of fibers do not show any pattern.

Acids present the same number of compounds extracted with all fibers but PA presents the higher sum of areas.

Terpene compounds do not show any clear pattern either by sum of areas or by sum of extracted compounds.

Finally, the group catalogued as others was best extracted by CW/DVB fiber.

From all these pieces of information, we can conclude that PA is the more suitable fiber for extracting aroma compounds present in wines. Only carbonylic compounds present better results for CW/DVB than for PA fiber.

Extraction information was analyzed attending to different wines studied. Results are shown in Table 3. PA fiber allows the detection of more compounds in Gual and Malvasía wines, PDMS/DVB fiber in Listán blanco wine, and CW/DVB fiber in Marmajuelo wine. On the other hand, all fibers allow the detection of the highest number of compounds in Malvasía wine. These results indicate that Malvasía wine presents the higher concentrations of compounds among the four wines used for the study. On the other hand, PDMS/100 fiber offers the lowest number of compounds detected in all wines suggesting that it is the worst fiber for this kind of samples.

Once best fibers were selected, PA was used in a comparative study among different wines from Pico (Azores), Madeira, and Tenerife Islands. Three different wine varieties

Table 2: Sumatories of number of detected and identified compounds and total area for studied chemical families.

Fiber	No. of compounds	Total area
	Overall compounds	
PA	482	$4.12E+08$
CW/DVB	469	$3.18E+08$
PDMS/100	444	$2.62E+08$
PDMS/DVB	471	$3.87E+08$
	Alcohols	
PA	133	$1.25E+08$
CW/DVB	125	$1.04E+08$
PDMS/100	111	$6.58E+07$
PDMS/DVB	125	$3.69E+07$
	Esters	
PA	156	$1.70E+08$
CW/DVB	148	$1.47E+08$
PDMS/100	147	$1.64E+08$
PDMS/DVB	156	$1.98E+08$
	Carbonylic	
PA	65	$4.43E+06$
CW/DVB	71	$4.98E+06$
PDMS/100	61	$2.23E+06$
PDMS/DVB	64	$4.28E+06$
	Hydrocarbons	
PA	27	$1.20E+07$
CW/DVB	24	$8.53E+06$
PDMS/100	25	$2.30E+06$
PDMS/DVB	27	$5.75E+06$
	Acids	
PA	60	$9.57E+07$
CW/DVB	60	$8.50E+07$
PDMS/100	60	$5.28E+07$
PDMS/DVB	60	$6.95E+07$
	Terpenes	
PA	32	$2.05E+06$
CW/DVB	30	$3.31E+06$
PDMS/100	30	$4.06E+06$
PDMS/DVB	30	$4.39E+06$
	Others	
PA	9	$2.22E+06$
CW/DVB	11	$2.37E+06$
PDMS100	10	$1.96E+06$
PDMS-DVB	9	$1.25E+06$

were used, Gual, Verdelho, and Malvasía. Verdelho wine is produced in the three islands, but Gual and Malvasía are only present in Tenerife and Madeira.

Figures one to three show the sum of areas of different compounds families for Gual, Malvasía, and Verdelho wines.

Madeira Gual wines showed higher values for all families than Tenerife wines except for alcohols. Higher differences appear in esters and carbonylic compounds (Figure 1).

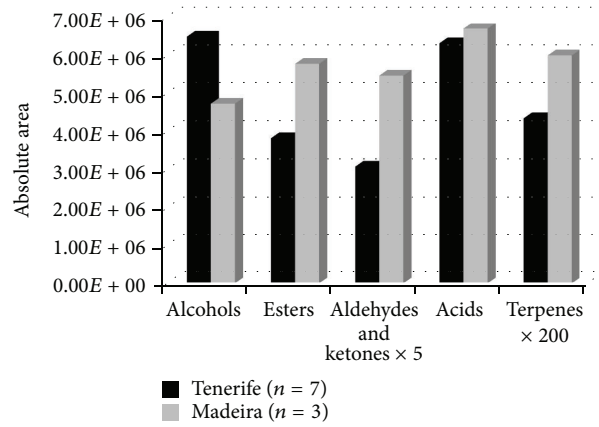

Figure 1: Absolute areas for different compound families in Gual wines.

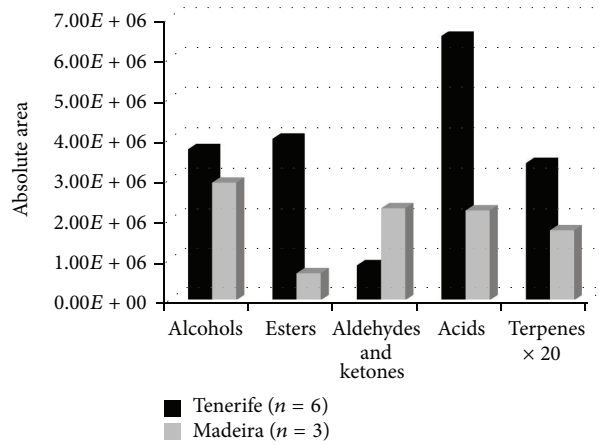

Figure 2: Absolute areas for different compound families in Malvasía wines.

Different patter is shown in Figure 2 for Malvasía wines. Tenerife wines showed higher peak areas for all families except for aldehydes and ketones. This is especially remarkable for acids and esters. Highest areas are presented for alcohols in Madeira wines and acids in Tenerife wines. Minimum area is presented for terpenes in both locations (Figure 2).

Figure 3 presents results for Verdelho wines. Wines from Madeira and Tenerife islands present peak areas much higher than wines from Pico Island for acid compounds.

Esters are higher in Tenerife Verdelho wines than in the rest of Islands. Opposite to the other varieties, alcohols for Madeira and Pico wines present higher peak areas than Tenerife wines. Terpenes continue presenting the lower peak areas.

4. Conclusions

The SPME coupled to gas chromatography-mass spectrometry detector is a useful technique for identification of minor volatile compounds in wine. A total of 138 compounds

Table 3: Number of compounds extracted by fiber and variety of wine.

	PA	PDMS/100	PDMS/DVB	CW/DVB	CAR/PDMS
Gual	124	116	126	129	116
Malvasía	128	122	124	130	121
Listan blanco	118	118	125	123	113
Marmajuelo	127	114	124	126	110

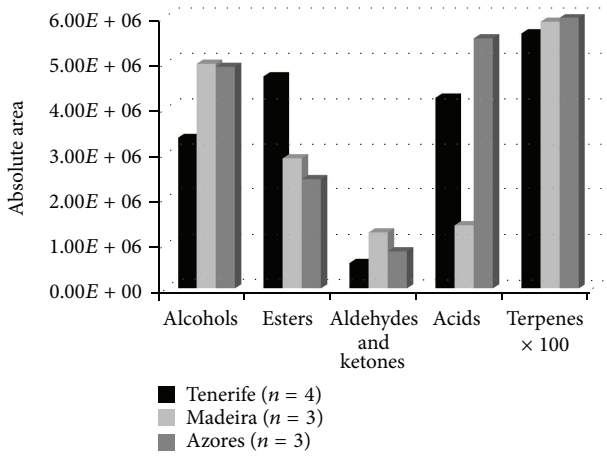

Figure 3: Absolute areas for different compound families in Verdelho wines.

were identified from different chemical families. The largest number of extracted compounds corresponds to alcohols and esters. Among the identified compounds, there are a number of important sensory compounds. All wines studied showed a content of β-damascenone, and whiskey lactone was detected too, unworthy of a young white wine without contact with wood, which could be a peculiarity of the wines from the Canary Islands. Malvasía variety presents the larger number of compounds detected. A comparative study between Tenerife, Madeira, and Pico Islands showed differences in compounds content mainly in alcohols, esters, and acids.

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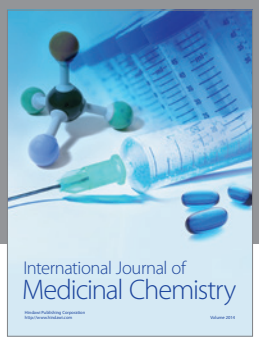

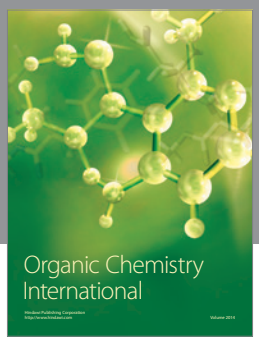

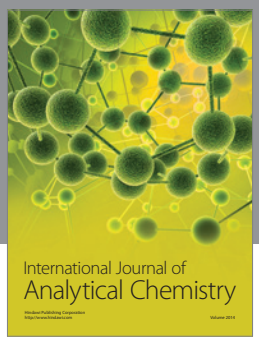

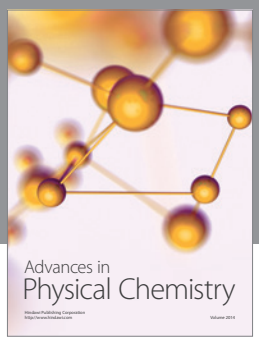

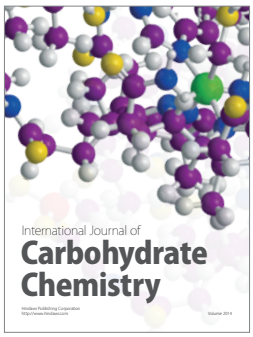

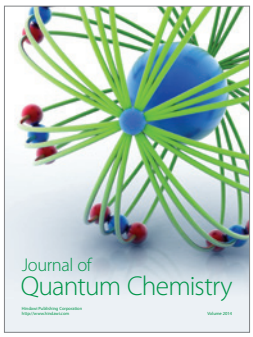

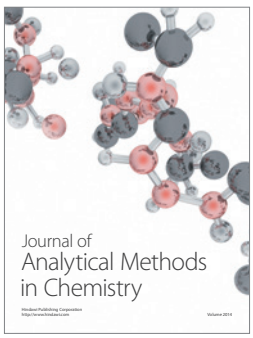

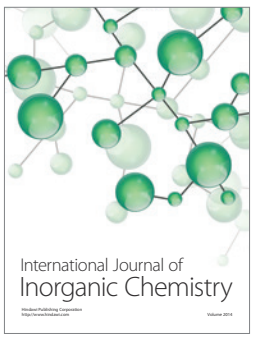

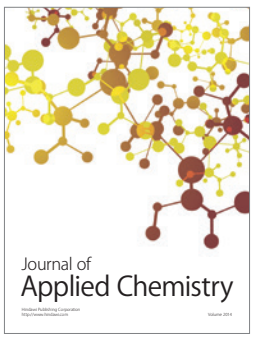

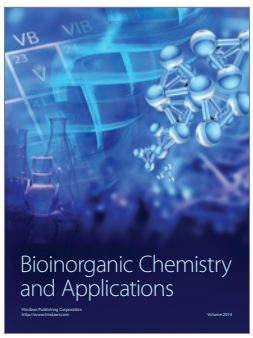

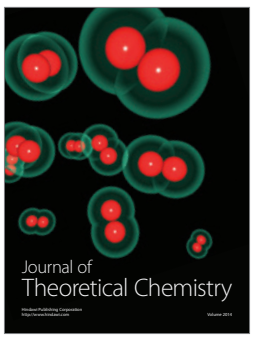

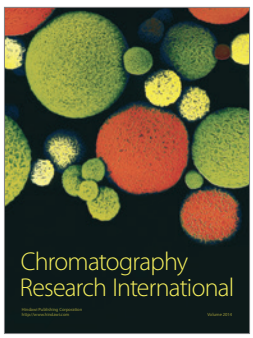

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