Volatile Compounds of Red and White Wines by Headspace–Solid-Phase Microextraction Using Different Fibers

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Abstract

The behavior of four fibers [polydimethylsiloxane (PDMS), PDMS–divinylbenzene (DVB), carboxen (CAR)–PDMS, PDMS–DVB–CAR), is tested for the analysis of volatile compounds of white and red wine. The PDMS–DVB–CAR fiber is the most appropriate to obtain the most wide volatile profile of wines. The better extraction conditions are 40 min at 35°C. Satisfactory data about the reproducibility and uptake are obtained for more than 40 volatile compounds of red and white wine.

Introduction

Wine aroma is attributable to a large range of molecules coming from different chemical families (e.g., esters, aldehydes, ketones, terpenes, norisoprenoides, acids, alcohols, and sulfur compounds). Some originate from the grape, and others are formed during fermentation or during aging. The aroma of wine is determined traditionally by liquid–liquid (1–9) and solid–liquid extraction (10) and dynamic headspace (11–12). In recent years, solid-phase microextraction (SPME) was applied for different authors on the study of wine flavor composition (5,9,13–22).

For liquid samples, the SPME technique can be applied by immersing the fiber into the sample or sampling the headspace (HS). The HS–SPME is recommended for the analysis of complex samples such as the wine (14–16). The most important advantages of using this technique are the higher sensitivity for the wine volatile compounds and the lower interferences because of the more polar substances. Two equilibria are established: (*i*) between the sample and HS and (*ii*) between the HS and the SPME fiber.

The selectivity and sensitivity of this technique depends on the fiber composition (16,23). A wide range of commercial fibers can be found, however, the polydimethylsiloxane (PDMS) is used more often (16–19,22). Other fibers are used in wine analysis with different behaviors: polyacrilate (PA) is used for the more polar compounds (aldehydes and acids) (13–15), but carbowax (CAR)–divinylbenzene (DVB) is useful to detect esters, acids, and volatile phenols (13,24). The first aim of this work is to try different commercial fibers to determine which of them is more useful to obtain a wide profile of the wine volatile compounds. Four different fibers were chosen (PDMS, PDMS–DVB, CAR–PDMS, and PDMS–DVB–CAR). The first (PDMS) is a nonpolar fiber, but the others are bipolar phase coatings. Using PDMS, the analytes are extracted by partitioning, but using bipolar fibers, the volatile compounds are physically trapped and may compete for the sites. The HS–SPME technique is applied to white and red wines, which differ sensitively in their matrix composition. Red wine is elaborated by skin-contact fermentation. This wine-making technique furnishes a complex volatile profile to wine mainly because of post-fermentative aromas. Red wine, moreover, contains more phenolic compounds that could interact with volatile substances. Thus, it will be possible to estimate how the coating fiber affects to the volatile profile in function of the type of wine. No published studies of the suitability of four fibers (apolar and bipolar coatings) for both red and white wine were found. Then, the optimal conditions of temperature and extraction time, for the most adequate fiber, were assessed and the reproducibility and uptake of the method was determined.

Experimental

Chemicals and reagents

2-Octanol, methyl nonanoate, 2-methylhexanoic acid, ethyl isobutyrate, isobutyl acetate, ethyl butyrate, ethyl isovalerate, isoamyl acetate, ethyl hexanoate, hexyl acetate, isoamyl isovalerate, *cis*-3-hexenyl acetate, ethyl lactate, hexanol, *cis*-3-

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Table IA. Volatile Compounds Detected in Red Wine Using Different Fibers (Area Value*10)

	PDMS area value	PDMS–DVB area value	PDMS–CAR area value	PDMS–DVB–CAR area value
1 Ethyl isobutyrate	451	nd*	423	1171
2 Isobutyl acetate	170	197	282	547
3 Ethyl butyrate	566	661	1689	1951
4 Propanol	309	428	2420	1642
5 Ethyl 2-methylbutyrate	89	125	533	300
6 Ethyl isovalerate	131	140	178	404
7 Isobutanol	7911	10609	10853	30692
8 Isoamyl acetate	5964	7697	13505	19964
9 1-Butanol	55	66	246	295
10 Isoamyl alcohol	72224	112747	144053	306191
11 Ethyl hexanoate	5256	7901	27905	19890
12 Hexyl acetate	nd	103	654	252
13 Isoamyl isovalerate	65	135	860	628
15 Ethyl lactate	1120	2248	4431	6498
16 Hexanol	1085	2085	9667	6200
17 *Cis*-3-hexenol	121	255	1026	841
18 *Trans*-2-hexenol	nd	nd	81	89
19 2-Octanol (IS)	1528	3174	11380	8451
20 Ethyl octanoate	13934	26014	28478	57807
21 1-Octen-3-ol	nd	nd	66	125
22 Furfural	nd	nd	641	138
23 Methyl nonanoate (IS)	1793	4073	3858	5503
24 Benzaldehyde	nd	nd	1319	626
25 Linalool	121	245	268	576
26 Isobutyric acid	68	167	nd	480
27 Ethyl decanoate	5488	6909	1869	8227
28 Butyric acid	nd	82	247	584
29 γ-Butyrolactone	221	586	1031	1048
30 Diethyl succinate	3687	10289	19779	25388
31 Isovaleric acid	nd	nd	524	933
32 α-Terpineol	nd	56	58	168
33 Methionol	nd	166	450	494
34 Citronellol	nd	73	58	144
35 2-Phenylethyl acetate	324	1047	1211	2049
36 Geraniol	55	76	nd	211
37 Hexanoic acid	512	1657	4322	4546
38 2-Methylhexanoic acid (IS)	803	2256	3037	4920
39 Benzyl alcohol	nd	171	494	589
40 *Cis* whiskey lactone	1354	1745	924	3088
41 2-Phenylethanol	5991	28696	71574	71683
42 *Trans* whiskey lactone	610	1374	1398	2440
43 4-Ethyl guayacol	149	561	374	1177
44 Octanoic acid	5977	10173	9249	15293
45 Eugenol	78	179	nd	230
46 4-Ethyl phenol	817	3584	3677	5565
48 Decanoic acid	3428	2936	1178	2937
49 4-Vinyl phenol	nd	nd	439	58
n of compounds determined	32	37	41	44

* nd = not detected.

hexenol, ethyl octanoate, 1-octen-3-ol, furfural, benzaldehyde, linalool, isobutyric acid, ethyl decanoate, butyric acid, γ-butyrolactone, α-terpineol, methionol, citronellol, 2-phenylethyl acetate, geraniol, hexanoic acid, benzyl alcohol, *cis* and *trans* whiskey lactones, 2-phenylethanol, 4-ethyl guayacol, octanoic acid, eugenol, 4-ethyl phenol, 4-vinyl guayacol, decanoic acid, and 4-vinyl phenol were purchased from Sigma-Aldrich and Fluka (St Louis, MO) with a purity higher than 98%.

A model wine was prepared using 11% ethanol, 6 g/L tartaric acid, 5 g/L glycerol, and 1 g/L glucose. This model

Table IB. Volatile Compounds Detected in White Wine Using Different Fibers (Area Value*10)

	PDMS area value	PDMS–DVB area value	PDMS–CAR area value	PDMS–DVB–CAR area value
2 Isobutyl acetate	391	366	422	926
3 Ethyl butyrate	1950	1827	4368	5443
4 Propanol	417	422	1214	2104
6 Ethyl isovalerate	nd	nd	nd	78
7 Isobutanol	1696	1886	1721	5952
8 Isoamyl acetate	43622	42882	56126	110903
9 1-Butanol	52	61	177	370
10 Isoamyl alcohol	31753	40140	44473	116703
11 Ethyl hexanoate	33110	34049	86577	95117
12 Hexyl acetate	10312	11099	37236	33577
14 *Cis*-3-hexenyl acetate	416	538	2063	1809
15 Ethyl lactate	87	138	238	435
16 Hexanol	1188	1768	6599	6259
17 *Cis*-3-hexenol	223	323	1241	1139
19 2-Octanol (IS)	2651	3985	9626	11563
20 Ethyl octanoate	84384	99912	150183	210883
21 1-Octen-3-ol	nd	nd	83	216
23 Methyl nonanoate (IS)	2494	3312	5029	5221
24 Benzaldehyde	nd	nd	1211	1078
25 Linalool	161	217	241	727
26 Isobutyric acid	nd	nd	nd	132
27 Ethyl decanoate	30941	39592	13979	38184
28 Butyric acid	49	100	359	515
30 Diethyl succinate	127	288	690	882
31 Isovaleric acid	nd	nd	nd	296
32 α-Terpineol	nd	49	58	154
34 Citronellol	nd	87	58	127
35 2-Phenylethyl acetate	2844	7120	10240	16357
36 Geraniol	nd	nd	nd	70
37 Hexanoic acid	2747	6599	18302	21276
38 2-Methylhexanoic acid (IS)	1230	2511	3247	6203
41 2-Phenylethanol	2033	8292	22184	25714
44 Octanoic acid	52314	76492	89333	135903
47 4-Vinyl guayacol	103	325	146	281
48 Decanoic acid	39303	37120	21411	45946
49 4-Vinyl phenol	77	222	151	208
n of compounds determined	25	27	29	33

solution was spiked with the standards solutions at usual concentrations in wine. 2-Octanol, methyl nonanoate, and 2-methylhexanoic acid were prepared in hydroalcoholic solution (11%) and used as internal standards in the following concentrations: 0.253, 0.059, and 0.748 mg/L.

Samples

Two wines were analyzed: a base wine elaborated with the traditional white varieties used to elaborate Cava (Spanish Sparkling wine) [Macabeu, Xarel·lo and Parellada, (1:1:1)] and a red wine aged in oak barrels (Tempranillo). Both samples were obtained from the Penedès region (Catalunya, Spain).

Equipment

A mechanical shaker and heater (Selecta, Abrera, Barcelona, Spain) was used for the SPME extraction.

Chromatography

The gas chromatograph used was a 6890 GC (Hewlett Packard, Palo Alto, CA) equipped with a flame ionization detector (FID). The separation was performed with a TRWAX column (60-m × 0.25-mm × 0.25-µm) (Tecknokroma, Sant Cugat del Vallès, Barcelona, Spain).

Helium was used as a carrier gas with a constant flow of 1 mL/min. At the end of the extraction time, the fiber was exposed for 2.5 min in splitless mode at a maximum temperature adequate of each fiber. The temperature program was held at 40°C for 2 min and increased at 2ºC/min to 225°C. The temperature of 225°C was maintained for 15 min. Volatile compounds were identified by comparison of their retention time with those of the pure standards.

SPME fiber coatings

Three of the four coatings used were the commercial Kit 4 of Supelco (Bellefonte, PA), which contained 10 mm PDMS (100 µm), 10 mm PDMS–DVB (65 µm), and 10 mm CAR–PDMS (75 µm), as recommended for flavors and odors. PDMS is the absorbent-type fiber more often used for grape-derived products and specially used for nonpolar compounds, yet PDMS–DVB and CAR–PDMS have adsorbent and bipolar characteristics.

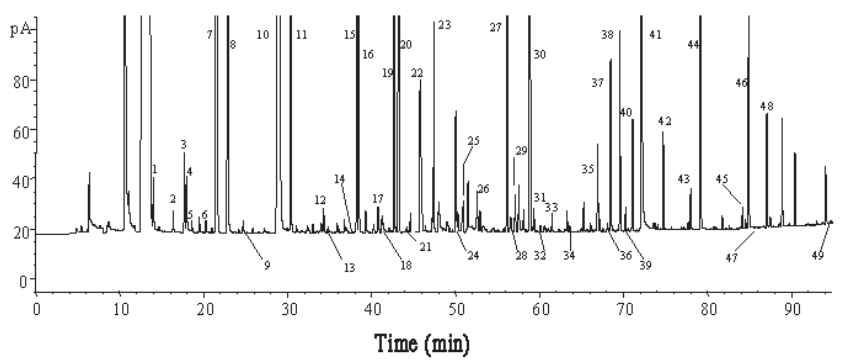

Figure 1. Chromatogram obtained with the PDMS–DVB–CAR fiber of red wine. The extraction conditions were 35°C and 40 min. Peak numbers correspond at numbers in Table IA and IB.

Moreover, according to the catalog recommendations, a triple-phase fiber was chosen. The 20 mm CAR–DVB–PDMS consisted of a layer of DVB suspended in PDMS over a layer of CAR suspended in PDMS. Because the coatings were layered, the larger analytes were retained in the pores of the outer DVB layer, and the smaller analytes migrated through this layer and were retained by the micropores in the inner layer of CAR. This fiber expanded the analyte's molecular weight and enabled the extraction of the analytes at trace level. There was a reduction of the amount of analyte retained compared with the thicker single adsorbent, but this is suitable for many analyses. Thus, this triple phase has bipolar characteristics, due to the absorbent and adsorbent capacity of their components. The most volatile analytes may compete for the sites, and the fiber has limited adsorbent capacity. To enhance the two extraction capacities (adsorbent and absorbent) the largest fiber (20 mm) triple phase is more suitable (25).

Extraction conditions

The extraction was performed in the HS mode with magnetic stirring. Five milliliters of sample was spiked with 50 µL of internal standard solution and was placed in a 10-mL vial (reference 27385) with a Teflon septum. An amount of 1.25 g of NaCl was added in order to increase the concentration of volatile compounds in the HS. Prior to extraction, the sample was shaken in a water bath at the work temperature for 20 min in order to achieve the equilibrium.

Time exposure

Different exposure times of the fibers to the sample HS (10, 25, and 40 min) were evaluated. The analyses were realized in duplicate in red wine with PDMS–DVB–CAR fiber setting and a sample temperature at 35ºC.

Temperature

The temperature effect on the extraction of wine volatiles was studied in the red wine sample at 25°C, 35°C, and 60ºC. The extraction was performed in duplicate with PDMS–DVB–CAR during 40 min.

Identification and quantitation

Compounds were identified (Table IA and IB and Figure 1) by comparison of their retention times with those of pure standard compounds. The area responses of every fiber were evaluated in triplicate in the two types of samples studied (white and red wine) (Table IA and IB). Quantitation was performed using the internal standard (IS) method. For the construction of the calibration curves, four different concentrations of the standards solutions were injected in triplicate at different concentrations as specified in Table II. The slope (a), intercept (b), and linearity were calculated using the following equation:

$$y = ax + b \qquad \text{Eq. 1}$$

where y was the relative area (area com-

pound/area internal standard) and *x* the relative concentration (concentration compound/concentration internal standard).

Reproducibility of the method was calculated in triplicate in both wines (white and red), to show the precision of the method in a wide range of concentrations [expressed as percent relative standard deviation (%RSD)]. The uptake was performed by adding 20 µL of a standard solution to each type of wine (controls). The amounts of volatile compounds in control and spiked wines are shown in Table III. These concentrations were calculated by applying the calibration curves reported in Table II.

Table II. Concentration Range, Slope, and Intercept of the Linear Regression Curves*

		Concentration range (n = 4)		Linear equation	
		(mg/L)	r^2	Slope (a)	Intercept (b)
1	Ethyl isobutyrate†	0.023–1.36	0.9997	0.2366	–0.0144
2	Isobutyl acetate†	0.022–1.33	0.9999	0.2422	–0.0022
3	Ethyl butyrate†	0.052–3.14	0.9998	0.3057	–0.0205
6	Ethyl isovalerate†	0.019–1.15	0.9999	0.7937	0.0185
8	Isoamyl acetate†	0.050–3.01	0.9991	0.7238	–0.0254
11	Ethyl hexanoate†	0.052–3.10	0.9999	2.8468	–0.0163
12	Hexyl acetate†	0.019–1.15	0.9999	2.9664	0.0224
13	Isoamyl isovalerate†	0.020–1.17	0.9999	7.0788	–0.2420
14	*Cis*-3-hexenyl acetate†	0.021–1.28	0.9999	1.5917	0.0047
15	Ethyl lactate†	2.15–129.2	0.9991	0.0011	–0.0133
16	1-Hexanol†	0.048–2.88	0.9996	0.1274	0.0032
17	*Cis*-3-hexenol†	0.021–1.23	0.9999	0.0575	0.0135
20	Ethyl octanoate‡	0.051–3.08	0.9998	0.9328	0.1983
21	1-Octen-3-ol†	0.020–1.22	0.9998	0.6950	0.0063
22	Furfural†	0.027–1.63	0.9996	0.0800	0.0006
24	Benzaldehyde†	0.026–1.56	0.9914	0.8044	0.2364
25	Linalool†	0.003–0.19	0.9998	1.6834	–0.0054
26	Isobutyric acid†	0.022–1.34	0.9994	0.0055	–0.0003
27	Ethyl decanoate‡	0.021–1.26	0.9999	0.7026	–0.0045
28	Butyric acid§	0.023–1.36	0.9999	0.3069	0.0153
29	γ–Butyrolactone§	2.27–136.32	0.9972	0.0034	–0.0092
30	Diethyl succinate§	0.25–14.85	0.9992	0.3087	0.1119
31	Isovaleric acid§	0.022–1.31	0.9993	0.1101	0.0377
32	α-Terpineol§	0.003–0.17	0.9999	4.1701	0.0062
33	Methionol§	0.025–1.52	0.9999	0.0179	0.0028
34	Citronellol§	0.003–0.17	0.9993	8.9011	–0.0121
35	2-Phenylethyl acetate§	0.022–1.31	0.9997	6.2824	0.0855
36	Geraniol§	0.003–0.16	0.9999	3.5061	–0.0038
37	Hexanoic acid§	0.17–10.19	0.9999	0.3227	0.0521
39	Benzyl alcohol§	0.020–1.22	0.9998	0.1625	0.0035
40	*Cis* whiskey lactone§	0.002–1.18	0.9998	0.8476	–0.0038
41	2-Phenylethanol§	1.96–117.32	0.9999	0.2041	0.0698
42	*Trans* whiskey lactone§	0.020–1.18	0.9995	0.8952	–0.0029
43	4-Ethyl guayacol§	0.022–1.31	0.9993	1.2923	–0.0115
44	Octanoic acid§	0.21–12.62	0.9995	1.5718	–0.3419
45	Eugenol§	0.021–1.25	0.9972	0.8225	–0.0124
46	4-Ethyl phenol§	0.020–1.20	0.9978	0.8415	0.0144
47	4-Vinyl guayacol§	0.021–1.26	0.9792	0.0721	0.0040
49	4-Vinyl phenol§	0.018–1.09	0.9993	0.0747	–0.0023

* Equation: $A_C/A_{IS} = a(C_C/C_{IS}) + b$; A_C, area of aroma; A_{IS}, area of internal standard; C_C, concentration of aroma; and C_{IS}, concentration of internal standard
† Internal standard selected: 2-octanol.
‡ Internal standard selected: methyl nonanoate.
§ Internal standard selected: 2-methylhexanoic acid.

Results and Discussion

Selection of the fiber

The Table I shows the area value of the aroma compounds, and the number of aroma compounds determined using the different fiber from red (Table IA) and white wine (Table IB). The time and extraction temperature used were 40 min and 35°C, respectively. In both wines, the number of compounds detected was higher using the triple phase fiber. In fact, some acids and terpenes were detected using only the fiber cited previously.

There were not significant differences in the RSD (%) values between the different fibers tested, except for PDMS, which showed higher values. Decanoic acid is the volatile compound that shows the higher value of RSD (%) using the four fibers tested; ethyl hexanoate, ethyl decanoate, and hexyl acetate are also compounds with a high RSD (data not shown).

The fiber that shows the best response is the triple phase PDMS–DVB–CAR. Using this type of fiber, 76% of the area results were higher than the other fibers tested. Only hexyl acetate, hexanol, *cis*-3-hexenol, and benzaldehyde in both wines were better extracted with PDMS–CAR. The responses of PDMS and PDMS–DVB were sensitively lower than the other two fibers (Table IA and IB).

Extraction conditions

Figure 2 shows the normalized percentage of the area values for some volatile compounds in the sample of red wine at different extraction times of 10, 25, and 40 min using a temperature of 35°C. The extraction of more volatile analytes (with lower retention time) was similar among the three times tested, while the extraction of less volatile compounds was higher, increasing the time of exposure. This different behavior could be attributable to the different time necessary to achieve the equilibrium. For the more volatile substances, 10 min extraction was sufficient, but for the less volatile compounds longer extraction time was required.

Figure 3 shows the normalized percentage of the area values of some volatile compounds using different extraction temperatures (25°C, 35°C, and 60ºC) for 40 min. It could be observed according to Whiton (24) that the less volatile compounds are better extracted at 60°C. On the other hand, the extraction of the more volatile compounds decreases increasing temperature, except the diethyl succinate and 2-phenylethyl acetate (with higher retention time). This trend could be attributable to a decrease of the fiber/HS partition coefficient at higher temperatures (26). In conclusion, for the extraction of volatile compounds of wine, the conditions of 35°C for 40 min were evaluated as better.

In Table II it could be observed that the linear regressions (r^2) were satisfactory for all compounds, in fact several of them were higher than 0.999. The method was useful for the determination of volatile compounds of wine according to the wide range of concentrations used to calculate the linear regression. These equations (Table II) were used to quantitate the amount of the each compound in red and white wines (Table III).

In order to estimate the suitability of the proposed method to determine the volatile compounds of white and red wine, reproducibility and uptake were carried out (Table III). The reproducibility values, expressed as RSD (%), are mainly lower or similar at 5%, and this result is satisfactory following the Horwitz criteria (27). The spiked amounts found are also satisfactory in both types of wines. Concentrations of the volatile compounds found in the spiked wines were statistically more significant than those found in nonspiked wines. Furthermore, the obtained amounts calculated using the internal standard method were reasonable according to the added amounts (Table III).

Conclusion

An HS–SPME method for the determination of aroma compounds in wines has been proposed. The utilization of

Table III. Reproducibility and Uptake Carried Out by the Internal Standard Method

		White wine		Red wine		Amount	Amount spiked	
		Amount*	%RSD	Amount*	%RSD	Added*	White wine	Red wine
1	Ethyl isobutyrate	0.051	<1	0.182	2	0.181	0.221	0.396
2	Isobutyl acetate	0.110	<1	0.095	1	0.177	0.299	0.293
3	Ethyl butyrate	0.428	1	0.223	1	0.419	0.886	0.737
6	Ethyl isovalerate	0.011	1	0.027	1	0.152	0.160	0.205
8	Isoamyl acetate	3.376	2	0.837	3	0.401	3.925	1.419
11	Ethyl hexanoate	1.132	3	0.314	7	0.412	1.356	0.963
12	Hexyl acetate	0.346	1	nd	–	0.154	0.393	0.222
13	Isoamyl isovalerate	nd	–	0.022	1	0.156	0.141	0.225
14	*Cis*-3-hexenyl acetate	0.013	4	nd	–	0.171	0.190	0.210
16	1-Hexanol	1.074	3	1.459	4	0.384	1.522	2.056
17	*Cis*-3-hexenol	0.406	2	0.411	6	0.164	0.558	0.632
20	Ethyl octanoate	2.716	8	0.602	2	0.410	3.293	1.250
21	1-Octen-3-ol	0.003	26	0.002	18	0.163	0.177	0.184
22	Furfural	nd	–	0.011	52	0.218	0.234	0.252
24	Benzaldehyde	nd	–	nd	–	0.208	0.191	0.259
25	Linalool	0.005	5	0.006	3	0.025	0.037	0.042
26	Isobutyric acid	0.594	2	2.292	9	1.979	1.915	4.237
27	Ethyl decanoate	1.044	6	0.235	4	0.168	1.162	0.517
28	Butyric acid	1.652	5	2.520	3	1.981	3.672	4.701
32	α-Terpineol	0.002	11	0.004	1	0.023	0.027	0.028
34	Citronellol	0.002	3	0.003	5	0.023	0.022	0.023
35	2-Phenylethyl acetate	0.340	5	0.060	1	0.176	0.450	0.244
36	Geraniol	0.003	2	0.010	7	0.022	0.020	0.027
37	Hexanoic acid	8.021	2	2.067	5	1.358	8.750	3.772
39	Benzyl alcohol	0.027	20	0.605	4	0.163	0.190	0.898
40	*Cis* whiskey lactone	nd	–	0.529	3	0.106	0.115	0.672
41	2-Phenylethanol	15.106	3	55.810	4	15.642	31.014	83.004
42	*Trans* whiskey lactone	nd	–	0.406	4	0.052	0.053	0.503
43	4-Ethyl guayacol	nd	–	0.161	3	0.174	0.192	0.312
45	Eugenol	nd	–	0.093	2	0.168	0.195	0.226
46	4-Ethyl phenol	nd	–	1.046	5	0.160	0.185	1.350
47	4-Vinyl guayacol	0.207	5	nd	–	0.168	0.370	0.161
49	4-Vinyl phenol	0.335	5	0.175	9	0.144	0.418	0.285

* Amounts in mg/L.

PDMS–DVB–CAR fiber for 40 min at 35°C were the best extraction conditions for both white and red wines. The suitability of the method (reproducibility and uptake) for both types of wine has been established. The method is easy, economic, and environmentally safe, and it was demonstrated that it was useful for the determination of the wine aroma.

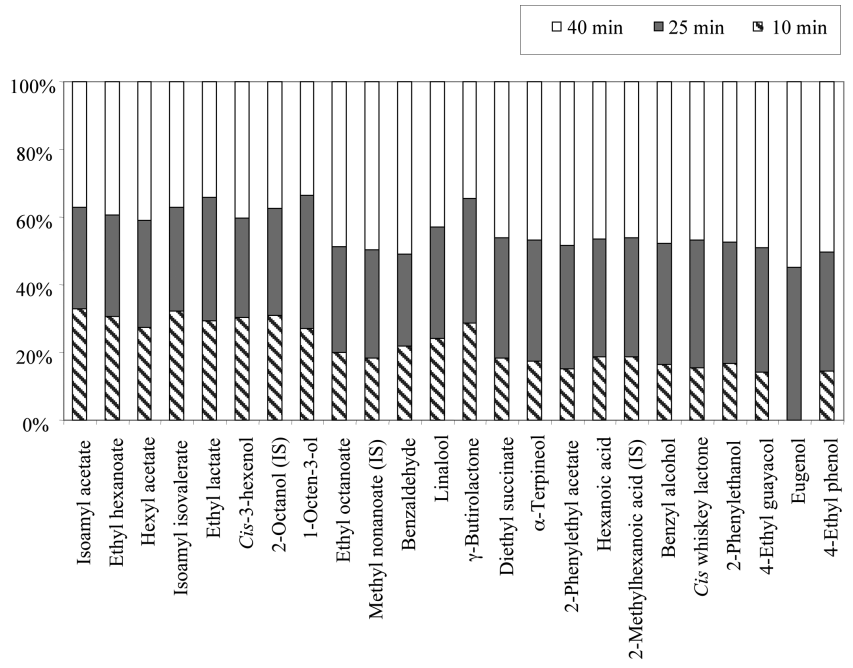

Figure 2. Comparison of the percentage of the extraction of some volatile compounds normalized at 35°C during 10, 25, and 40 min of extraction time.

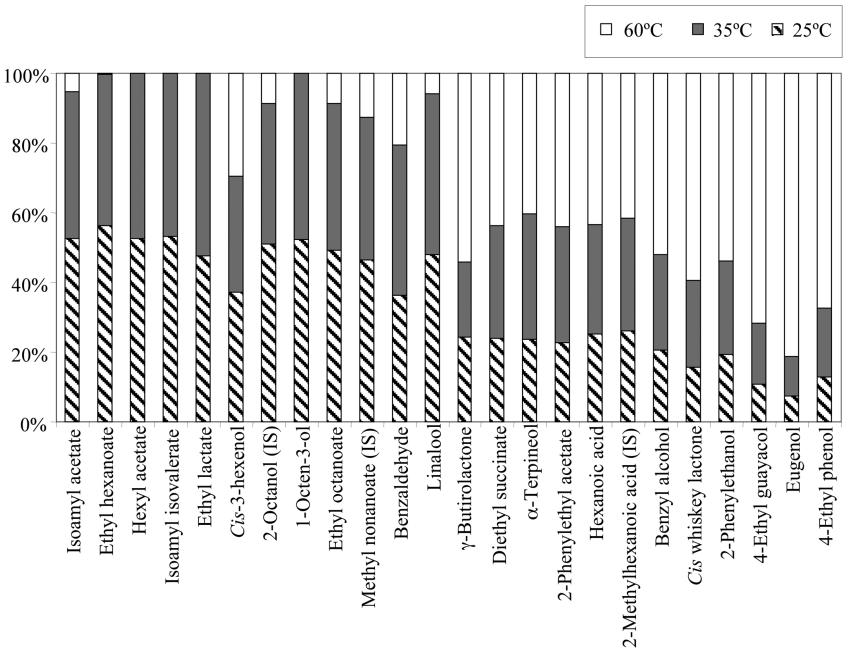

Figure 3. Comparison of the percentage of the extraction of some volatile compounds normalized at 25°C, 35°C, and 60°C for 40 min.

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