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Fast Screening Method for Volatile Compounds of Oak Wood Used for Aging Wines by Headspace SPME-GC-MS (SIM)

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A headspace solid-phase microextraction (HS-SPME) method is proposed for analyzing the main volatile components from a sensory standpoint (furfural, oak lactones, eugenol, vanillin, and syringaldehyde) present in nontoasted and toasted oak wood of different origins. To maximize the yield of compounds extracted from wood chips and to obtain a good precision of the method, the most important variables affecting HS-SPME have been studied. The best results were obtained when the sample was heated at 70 °C and the headspace extracted for 40 min with a DVB/CAR/PDMS fiber, which gave the overall best recovery. The values for the repeatability ranged from 6.4 to 7.8%, and those for the reproducibility from 5.4 to 8.7%. The precision of the results obtained makes the proposed technique appropriate for its use in characterizing oak wood samples of different origins and in the selection of the most suitable oak wood to age wines and spirits, on the basis of the chemical composition of the wood samples.

INTRODUCTION

Wines aged or fermented in oak barrels contain substances extracted from the wood. Many volatile compounds have been described in natural oak wood, but only a few of them are significant for their impact in the sensory characteristic of wines. *cis-* and *trans-β*-methyl-*γ*-octalactones (oak lactones) have been described as responsible for the oak flavor, having a low perception threshold (*1, 2*). Vanillin is the only aldehyde from lignin that exerts an effect on the aroma of wines aged in oak. Small free phenols such as eugenol and guaiacol provide spice and smoke attributes (*3*).

Oak species frequently used for barrel production are *Quercus alba* from North America, and *Quercus petraea* and *Quercus robur* from Europe, mainly from France and to a lesser extent from central Europe (Hungary, Bulgaria) and Russia.

The amount of components released by the wood during aging will depend on the species of wood, individual cask history (including manufacture, seasoning, toasting, and number of times it was previously used), and warehouse conditions (*3–6*). There is a high variability in the physical and chemical composition of oak wood among species, regions, and individual trees (*7–9*).

The extractive compounds of oak wood may influence the flavor of aged wines (*7, 10*). For this reason, rapid analytical methods that provide information about the volatile composition of oak barrels or chips before their use in wine aging could be of interest to the wine industry.

A variety of methods have been used for the determination of oak wood volatile components, most of them based on the extraction with organic solvents directly or from wood previously macerated in aqueous alcoholic solutions, followed by analysis of the extracts by gas chromatography (*9, 11–15*). These methods are time-consuming and in general require large amounts of sample. For a rapid screening of volatile compounds in oak wood, automated thermal desorption can be used; however, high temperature must be applied to the sample (*16*).

Solid-phase microextraction (SPME) is a fast, simple, and solvent-free technique that, with the availability of different types of single or mixed fiber adsorbents with a wide range of polarities, makes it possible to isolate trace compounds from different substrates (*17, 18*). The choice of the fiber depends on the target compounds of the sample of interest.

SPME has been used to analyze volatile compounds of cork (*19*) and toasted oak wood samples using a polydimethylsiloxane (PDMS) fiber (*20*). Although operating conditions were not optimized, HS-SPME was found to be a promising method to analyze oak wood volatile compounds. Recently, the introduction of mixed coating fibers has enabled the detection of a wider range of compounds, especially polar compounds, with a higher recovery than PDMS and polyacrylate (PA) fibers (*21*). The more polar compounds are best extracted by polar fibers such as Carbowax/divinylbenzene (CW/DVD) and PA (*22–24*). A PDMS/DVD fiber showed the highest recovery for polar compounds of low volatility (*25, 26*), whereas a Carboxen (CAR)/PDMS fiber provides the highest recovery of small molecules and acids (*27, 28*). A new method to quantify

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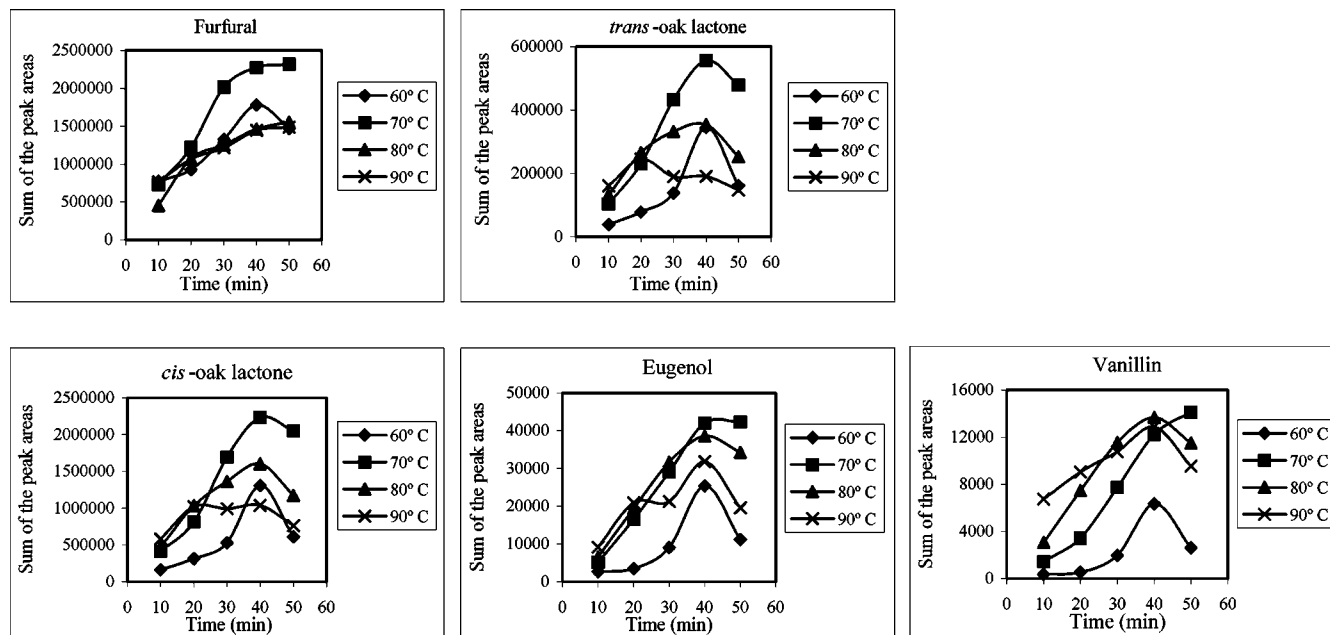**6858** *J. Agric. Food Chem.,* Vol. 52, No. 23, 2004

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Figure 1. Effect of sampling conditions (adsorption temperature and time) on the amounts of nontoasted American oak wood volatile compounds extracted by SPME.

some volatile oak compounds by SPME has just been presented (*29*). However, this method requires a preliminary extraction of wood samples, because it can be applied only to oak extracts.

In this study, we report a simple method based on HS-SPME for the rapid screening of the main volatile compounds of oak wood used for aging wines, without any preliminary sample preparation.

MATERIALS AND METHODS

Samples. Oak wood chips (sized 1 cm × 0.5 cm × 0.1 cm) of different origins, *Q. alba* (American) and *Q. sensiliflora* (French, Hungarian, and Russian), and with different treatments (nontoasted and toasted) were obtained at a Spanish cooperage (Magreñan, La Rioja, Spain) (average annual temperature, 13.9 °C; total precipitation, 370 mm^3/year; sun hours, 2800/year). Natural seasoning in the open air was carried out for 36 months in the case of *Q. alba* and for 18 months for *Q. sensiliflora*. Toasted samples were obtained over the same type of oak wood fire at a medium intensity level (45−50 min; temperature on the wood surface, 160−170 °C).

SPME Extraction. A nontoasted American oak sample (1.5 g) was placed in a 30-mL glass vial, which was sealed with a screw-capped top containing a Teflon-lined septum. A conditioned SPME fiber coated with 50/30 μm of DVB/CAR/PDMS was exposed to the headspace of the sample at 70 °C for 40 min. The fiber was then retracted and inserted into the gas chromatograph injector. Volatile compounds absorbed in the SPME fiber were thermally desorbed at 250 °C for 5 min (splitless mode for 0.5 min). Each extraction was performed in triplicate.

Analysis of Volatile Compounds. A Hewlett-Packard G 1800 B GCD system equipped with a gas chromatograph and a quadrupole mass detector (Hewlett-Packard, Palo Alto, CA) and fitted with an SPB-1 methyl silicone column (50 m × 0.25 mm; 0.25 μm of film thickness) was used. Oven temperature was set at 80 °C for 3 min, then temperature programmed at 3 °C/min to 250 °C, and then held for 20 min. Transfer line temperature was 280 °C.

Compounds were detected by mass spectrometry in the electron impact (EI) ionization mode at 70 eV, and spectra were recorded in the selective ion monitoring (SIM) mode. Mass spectral data and retention times were determined for standard compounds. The ions monitored in SIM mode were as follows: furfural, *m/z* 96; *cis-* and *trans-β*-methyl-*γ*-octalactone (oak lactones), *m/z* 99; eugenol, *m/z* 164; vanillin, *m/z* 152; syringaldehyde, *m/z* 182. These ions were chosen because of their relative ion abundances, high *m/z* values, and lack of

interference from other oak wood components. Perez-Coello et al. (*16*) used the same ions to quantify these oak wood components.

RESULTS AND DISCUSSION

Optimization of the Sampling Conditions. To maximize the yield of compounds extracted from wood chips and to obtain a good precision of the method, the most important variables affecting HS-SPME were studied. Initially, a sample of non-toasted American oak chips was used to determine the optimum time and temperature conditions, using a 50/30 μm DVB/CAR/PDMS fiber. This fiber is well suited for analyzing volatile and semivolatile compounds of medium polarity (*30−32*). Extraction was carried out at 60, 70, 80, and 90 °C and with adsorption times of 10, 20, 30, 40, and 50 min at each temperature. **Figure 1** shows the recoveries obtained for each volatile compound, expressed as the area of peak for each compound (SIM peak areas) and set of conditions. All of the extractions were made in triplicate. The best results for all compounds were obtained at 70 °C for 40 min.

The precision of the headspace sampling technique was estimated by measuring the relative standard deviation from four replicates using the optimal experimental conditions (70 °C for 40 min). The values ranged for the repeatability from 6.4 to 7.8%, and those for the reproducibility from 5.4 to 8.7%.

Heating of the sample helped to release analytes into the headspace and facilitated the extraction process during SPME sampling, because, as has already been reported (*18*), when one is working with solid samples, increasing the temperature improves the recovery of volatile compounds. However, as the temperature increases, the fiber coating begins to lose its ability to adsorb analytes (*18*). This phenomenon was observed in all compounds analyzed (**Figure 1**).

As the time increased, the adsorption of volatile compounds also increased, until the equilibrium was reached. Then the analyte concentration in the fiber decreased. Compounds with low volatility and high fiber affinity are absorbed by the fiber from the headspace more rapidly than they are released from the matrix to the headspace (*33*). For this reason, once equilibrium between the fiber and headspace is reached, this

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Table 1. HS-SPME-GC-MS[a] Abundance of the Volatile Components of Nontoasted American Oak Wood Obtained with the Different Fibers Tested

compound	50/30 μm DVB/CAR/PDMS	65 μm DVB/PDMS	100 μm PDMS
furfural	14576277[b]	1110570	167126
trans-oak lactone	5245675	3252474	359116
cis-oak lactone	17314473	11658356	1410067
eugenol	405343	343848	18653
vanillin	2392	4663	Tr[c]
syringaldehyde	15110	9176	7885

[a] Adsorption temperature and time: 70 °C for 40 min. [b] SIM peak area. [c] Traces.

could shift back toward the headspace. This effect is more pronounced at low temperatures, because as the temperature increases, the release of volatile compounds to the headspace from the matrix also increases. A similar behavior has been observed in other solid samples such as spices (*34*).

To evaluate the trapping ability of the triple-coated fiber used, another two commercially available SPME fibers (100 μm PDMS and 65 μm DVB/PDMS) were used in the same optimal conditions of time and temperature, previously selected. The results obtained are shown in **Table 1**. PDMS is a liquid phase widely used for analyzing flavor compounds from different matrices, such as fruits, oak wood, wine, or spices (*20, 34–37*). However, the PDMS fiber had the lowest recovery for the compounds analyzed. The best results were obtained with the fibers containing two phases, one liquid phase (PDMS) and one or two porous solid (DVB or DVB/CAR). Adsorbent phases are very suitable for more polar components, so the combination of these with PDMS allows the extraction of both nonpolar and polar volatile compounds (*21, 22, 38*). Although DVB/PDMS was very effective, DVB/CAR/PDMS gave the overall highest recovery. This fiber has been chosen as the best for the aroma analysis of aromatic plants (*39*) or truffles (*32*).

Main Volatile Compounds of Oak Wood Chips from Different Origins. Table 2 shows the most important volatile compounds from a sensory standpoint extracted from nontoasted oak wood chips of different origins by HS-SPME. The data are

shown in SIM peak areas, obtained by the integration of each compound positively identified by GC-MS.

The *cis*- and *trans*-β-methyl-γ-octalactones (oak lactones) were found in American and French oaks in high amounts; however, Hungarian and Russian oaks presented both compounds in lower quantities. There is little information about the chemical composition of Russian and Hungarian oaks, but similar concentrations of oak lactones in wines aged in French and Hungarian oak barrels were found (*5*). For most oak species, *cis*-β-methyl-γ-octalactone was found to appear in higher concentrations than *trans*-β-methyl-γ-octalactone (*4, 41, 42*).

American oak was also higher in eugenol than European oak. This compound has a characteristic clove odor (*3*). In general, American oak is lower in tannic compounds and higher in volatile extractable compounds such as lactones and volatile phenols than European oak (*3, 43*), although differences between production zones and variation among barrels and individual trees have been established (*5, 8, 9*).

Vanillin and syringaldehyde, volatile compounds related to lignin, were found in similar amounts in American and French oaks. In all cases, syringaldehyde was present in higher quantity than vanillin. Similar results have been obtained by other authors (*15, 16*).

Furfural appeared in all of the nontoasted samples, mainly in American oak, followed by Russian, Hungarian, and French oaks, the furfural contents of which were quite similar. The level of furfural can increase after drying or seasoning, mainly when high temperatures are used (*6*).

Toasting of the wood causes significant changes in its chemical composition, which can greatly influence the quality of the wines aged with oak wood (*20, 44, 45*). **Table 3** shows oak volatile compounds extracted from toasted oak wood chips of different origins by HS-SPME. After toasting, the oak lactones significantly decreased in all of the samples. Both isomers tend to decrease as toasting increases, probably by volatilization or pyrolysis during toasting (*46*). On the other hand, compounds arising from polymer (cellulose, hemicellulose, and lignin) degradation, such as furfural, eugenol, vanillin, and syringaldehyde, increased considerably with toasting. These

Table 2. Main Volatile Compounds of Nontoasted Oak Wood Chips from Different Origins Isolated by HS-SPME[a]

compound	flavor note[b]	American oak mean ($n = 3$)	RSD (%)	French oak mean ($n = 3$)	RSD (%)	Hungarian oak mean ($n = 3$)	RSD (%)	Russian oak mean ($n = 3$)	RSD (%)
furfural	sweet, baked bread, caramel	14576277[c]	2.8	5746745	5.1	6339976	6.8	7891343	7.9
trans-oak lactone	oak woody, coconut	5245675	11.5	1679733	11.7	22833	0.9	1940	8.4
cis-oak lactone		17314473	11.6	11074463	11.2	187297	1.7	14890	9.2
eugenol	cinnamon, clove, spice, strong	405343	5.7	102971	8.2	20807	8.6	5832	4.6
vanillin	sweet, vanilla, fragrant	2392	8.7	3144	6.6	689	6.6	894	8.5
syringaldehyde	not described	15110	8.8	12967	9.5	2631	8.6	39523	7.1

[a] Fiber coating: DVB/CAR/PDMS. Adsorption temperature and time: 70 °C for 40 min. [b] Sensory properties of the most characteristic oak wood volatile compounds from refs *1–3* and *40*. [c] SIM peak area.

Table 3. Main Volatile Compounds of Toasted Oak Wood Chips from Different Origins Isolated by HS-SPME[a]

compound	American oak mean ($n = 3$)	RSD (%)	French oak mean ($n = 3$)	RSD (%)	Hungarian oak mean ($n = 3$)	RSD (%)	Russian oak mean ($n = 3$)	RSD (%)
furfural	23510980[b]	4.4	25491937	9.7	28377960	2.0	22437402	2.8
trans-oak lactone	502282	3.5	270367	7.4	Tr[c]		Tr	
cis-oak lactone	3746346	3.7	2113334	5.9	43982	6.5	Tr	
eugenol	353583	7.3	262962	5.3	834357	8.2	111961	9.1
vanillin	2346053	4.8	1655215	8.7	8406797	7.7	946548	9.8
syringaldehyde	748036	4.7	619956	9.3	1665231	7.9	250075	8.0

[a] Fiber coating: DVB/CAR/PDMS. Adsorption temperature and time: 70 °C for 40 min. [b] SIM peak area. [c] Traces.

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compounds tend to be formed at light and medium toast levels (*20*, *46*), and this increase has an important sensory impact.

In summary, HS-SPME-GC-MS is a rapid and facile method that enables extraction and identification of volatile compounds from different oak woods. The proposed method reduces the time of analysis and the quantity of sample required and avoids the use of solvent. Furthermore, it permits the study of wood volatile compounds without heating the sample at high temperatures and, thus, avoids the formation, increase, or decrease of some compounds. Among the several SPME fibers commercially available, DVB/CAR/PDMS gives the overall best recovery.

The precision of this method makes the proposed technique appropriate for its use in characterizing oak wood samples of different origins and in the selection of the most suitable oak wood to age wines and spirits, on the basis of the chemical composition of the wood samples. The characterization must be used only for comparison purposes, because the results obtained by the proposed method are relative values.

ABBREVIATIONS USED

HS-SPME, headspace solid-phase microextraction; GC-MS, gas chromatography−mass spectrometry; EI, electron impact; SIM, selective ion monitoring; PDMS, polydimethylsiloxane; PA, polyacrylate; CW/DVD, carbowax/divinylbenzene; CAR/PDMS, carboxen/polydimethylsiloxane; DVB/CAR/PDMS, divinylbenze/carboxen/polydimethylsiloxane; DVB/PDMS, divinylbenze/polydimethylsiloxane; Tr, traces.

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