Determination of Volatile Aroma Compounds of Bläufrankisch Wines Extracted by Solid-Phase Microextraction

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Abstract

A solid-phase microextraction (SPME) technique is used to study volatile wine aroma compounds. SPME coupled with gas chromatography and gas chromatography–mass spectrometry is found to be very sensitive and is suitable for characterization of wine aroma compounds without complicated sample preparation procedures.

Introduction

Aromas are very important compounds of wines. Over 1000 of them have been identified. These compounds originate from grapes, and some are formed at pre- and post-fermentation. Aroma production can be influenced by various factors: environment (soil, climate), grape variety, ripeness, fermentation conditions (pH, temperature, yeast flora) (1–3), the wine production process (enological methods, treatment substances), ageing (bottle maturation), etc. Wine aromas contain various classes of compounds (hydrocarbons, alcohols, terpene alcohols, esters, aldehydes, ketones, acids, ethers, lactones, bases, sulphur-containing compounds, halogenated compounds, nitriles, etc.) (4) that present a large range of volatility and polarity.

Direct headspace analysis is of limited use because of the low concentration of most volatile components in wine (5). Extraction and concentration are usually necessary before analysis by high-resolution gas chromatography (HRGC) or by HRGC coupled with mass spectrometry (HRGC–MS) is performed. Several extraction–concentration methods are used. Among them are liquid–liquid extraction (6–9), liquid–liquid extraction with ultrasound (10), simultaneous distillation–extraction (11), solid-phase extraction (12), and other techniques (13–15). The main reason for isolation and concentration is to obtain more concentrated samples, but eliminating interfering substances and thereby improving detection limits for specific compounds is also very important. However, there is no generally useful procedure which is suitable for all samples under all conditions.

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The specific advantages and disadvantages of these methods should always be emphasized in order to select the most adequate technique for a given problem. Solid-phase microextraction (SPME) is a new technique, developed a few years ago (16) for the concentration of samples prior to analysis. It has been used in various fields (in the context of the present paper, most importantly in the analysis of flavors in food [17] and also in wine headspace analysis [18]). Its main advantages are that it is simple, provides quick analysis times, and requires very little sample manipulation. SPME can be performed either for headspace analysis or direct analysis of liquids. SPME is a solvent-free technique, which is very important for the analysis of volatiles because there is no solvent overloading the column or co-eluting with the volatiles. There are several different phase-coating SPME extraction fibers which concentrate compounds of different polarity and volatility. The purpose of this work is to apply SPME–gas chromatography (SPME–GC) and SPME–GC–MS techniques to the qualitative or semi-quantitative study of wine aromas and to compare various types of SPME extraction methods.

Experimental

Samples

A standard solution (in water) was prepared containing 22 different compounds often found in wine aromas (Table I). The components of standard solution were purchased from Sigma (St. Louis, MO). This solution was used to optimize GC and SPME conditions. All studied wine samples were Bläufrankisch, grown in the "Felsötornyos" vineyard of the Eger wine region in Hungary. The wines were fermented using three different yeasts (type ALB, 2-2056, and 228, Uvaferm, Darmstadt, Germany) at two different temperatures (12°C and 20°C). After fermentation, wines were clarified once and stored in 25-L glass barrels at cellar temperature (14°C).

Sample preparation

Wines and the standard solution were studied using an SPME

technique according to the following protocol. Wine (125 mL) was put into a 130-mL sampling bottle. The extraction fiber was inserted into the headspace and held in place for 10 min or, alternatively, immersed in the liquid for 1 h at ambient temperature (22°C). During sampling, the liquid phase was stirred with a magnetic stirrer at 200 rpm. During this time, aroma compounds were adsorbed and concentrated in the extraction fiber. After sampling, the fiber was manually inserted into the hot (250°C) GC injector for 5 min, where the compounds were desorbed and entered into the capillary GC column for analysis.

Two different SPME extraction fibers were used with an apolar polydimethylsiloxane (PDMS) and a polar polyacrylate (PA) phase coating (Supelco, Bellefonte, PA). Film thicknesses were 100 µm and 85 µm, respectively. PDMS coating is primarily suitable for extracting apolar compounds, and PA coating is primarily suitable for extracting polar compounds.

For comparison, a "classical" and often-utilized solvent–solvent extraction method was also used. A wine sample (200 mL) was extracted three times with 60 mL organic solvent (*n*-pentane–dichloro-methane, 1:2). The organic phase was dried with anhydrous Na_2SO_4. The extract was concentrated to 500 µL with a Vigreux-column apparatus at 40°C. To obtain a more concentrated sample, the aroma extract was concentrated to 100 µL under continuous N_2 at –15 to –20°C. From this extract, a 1-µL aliquot was directly injected manually into the GC injector. To avoid overloading the column with these samples, a 1:50 split ratio had to be used.

GC and MS

Semi-quantitation (peak area measurement) was performed using GC with a flame ionization detector (FID). A Hewlett-Packard (Palo Alto, CA) 5890 series II GC equipped with a two-channel electronic pressure control and an FID detector was used with a J&W Scientific (Folsom, CA) 40-m × 0.182-mm fused-silica capillary column coated with a poly-ethylene-glycol (PEG) stationary phase (0.30-µm film thickness). The injector and the FID detector temperatures were 250°C. The splitless purge valve was closed for 5 min. The carrier gas was hydrogen (UCAR, Cleveland, OH, purity 5.5). The gas flow was 1.42 mL/min. The temperature program of the GC was as follows: initial temperature, 35°C, held 5 min; first ramp, 5°C/min to 100°C, held 0 min; second ramp, 3°C/min to 200°C held 1 min; third ramp, 20°C/min to 240°C, held 2 min.

The compounds were identified by GC–MS and by Kováts retention indices. In these analyses, the same GC with a Hewlett-Packard 5972 mass-selective detector in electron impact ionization mode (70 eV) was used. The temperature of the GC–MS transfer line was 200°C, and the source temperature was 140°C. GC run parameters were the same as previously described, except that the carrier gas was He. Retention indices were calculated twice a day from retention times using external calibration, utilizing software written by János Harangi (Hewlett-Packard, Budapest, Hungary). The calibration mixture contained 20 aliphatic hydrocarbons (C_8–C_{27}). Day-to-day reproducibility of retention index determination was ± 1 unit.

Table I. List of Standard Compounds Relative Sensitivities Using Different Sampling Techniques

Compound name	Retention index	Abbreviation	Standard concentration (ppb)	SPME headspace sampling using 100-µm PDMS fiber		Solvent–solvent extraction	
				RSD%	Relative sensitivity	RSD%	Relative sensitivity
Acetaldehyde	538	A	50	15.4	1.7	25.6	280.8
Ethylacetate	715	B	50	10.8	0.8	143.9	88.8
Ethanol	868	C	1000000	9.7	0.003	29.6	0.001
Ethyl butanoate	1044	D	10	9.1	9.2	29	98.0
Butylacetate	1075	E	50	8.7	3.8	29.6	5.4
2-Methyl-propanol	1114	E	50	ND		28.8	3.7
Isoamyl acetate	1126	G	50	3.8	9.5	32	4.6
Butanol	1163	H	50	2.8	10.5	27.8	2.4
Hexyl acetate	1282	I	10	1.6	58.6	31.4	9.0
Ethyl lactate	1356	J	50	9.5	1.7	47.1	2.2
Hexanol	1363	K	50	4.3	1.7	28	6.4
3-Hexen-1-ol (Z)	1375	L	25	4.5	2.7	28.1	6.6
3-Hexen-1-ol (E)	1392	M	25	6.8	4.5	42.7	15.6
Ethyl octanoate	1436	N	10	4.7	100.0	76.2	45.0
Acetic acid	1463	O	100	8.1	6.1	32.3	0.8
Linalool	1535	P	10	5.2	21.6	139	36.2
Linalyl acetate	1563	R	10	9	284.2	27.1	19.0
Ethyl decanoate	1646	S	10	5.7	105.0	30	8.4
Diethyl succinate	1698	T	50	8.4	4.9	19	9.6
Terpineol	1715	U	10	7.6	4.9	50.6	9.6
Citronellol	1779	X	10	7.7	3.7	28.6	4.9
Phenethylacetate	1833	Y	10	4.8	12.1	28.8	20.7
Gearniol	1873	V	10	6	6.6	30.4	15.2
Benzyl alcohol	1893	Z	50	11	1.2	28.9	10.6
Phenethyl alcohol	1929	W	10	3	4.8	24.8	30.0

Statistical calculations and calibration

Data presented in this paper represent the average of three parallel measurements except when mentioned otherwise. Reproducibility is defined as the relative standard deviation of data expressed in percentages. Semi-quantitation was performed by comparing relative peak areas observed using FID detection. The results (Tables I–III) are expressed in percentages relative to the peak area of ethyl octanoate observed using headspace analysis with PDMS fibers. This implies that the numbers given in Tables II and III are proportional to the amount of compounds injected onto the column, but the relative sensitivity of FID and extraction efficiency for individual components are not taken into account. The combined effects of FID sensitivity and extraction efficiency for individual compounds are characterized in Table I in a semi-quantitative manner: peak areas divided by the concentration in solution and compared again to that of ethyl octanoate using headspace analysis with PDMS fiber. Estimation of the quantity of individual components in the wine samples (in ppm or mg/L) has not been attempted.

Results and Discussion

Wines produced under different fermentation conditions were analyzed by headspace and immersion analysis using SPME–GC–FID and SPME–GC–MS. SPME exhibits selectivity, concentrating different wine components to various degrees. Relative sensitivity and reproducibility (as described in the Experimental section) of the SPME technique (headspace analysis with PDMS

Table II. Semi-Quantitative Comparison of Different Extraction Methods in the Case of a Bläufrankisch Wine Fermented at 20°C Using ALB Yeast*

Compound name	Retention index	Abbreviation	Headspace PDMS	Immersed PDMS	Immersed PA	Solvent extracted
Acetaldehyde	538	1	0.3	0.4	0.8	1.4
Ethyl acetate	715	2	9.4	6.8	4.4	1.1
Methanol	746	3	0.5	0.4	1.1	12.4
Ethanol	868	4	408.8	360.3	989.4	808.7
Propanol	905	5	15.5	4.2	0.0	0.1
Butyl acetate	1075	6	0.4	0.1	0.0	0.0
2-Methyl-propanol	1114	7	3.0	2.1	4.7	26.8
Isoamyl acetate	1126	8	7.7	6.4	1.7	0.6
Butanol	1163	9	0.1	0.0	0.0	0.0
2-Methyl-1-butanol	1220	10	8.8	0.2	13.4	0.0
3-Methyl-1-butanol	1223	11	42.1	7.1	59.3	316.7
Ethyl hexanoate	1238	12	12.5	40.8	3.1	0.4
3-Hydroxy-2-butanone	1336	13	0.3	0.2	0.1	0.2
Ethyl lactate	1356	14	0.7	0.7	1.4	24.4
Hexanol	1363	15	1.4	1.1	2.2	2.7
3-Hexen-1-ol (E)	1392	16	0.5	0.3	0.2	0.1
Ethyl octanoate	1436	17	100.0	40.3	9.0	0.3
Isoamyl hexanoate	1440	18	2.6	0.5	0.4	12.3
Acetic acid	1452	19	1.6	5.8	5.6	0.2
Benzaldehyde	1518	21	0.5	0.6	0.8	0.1
Linalool	1548	22	0.3	0.1	0.1	0.0
5-Methyl-furfural	1590	23	1.1	0.5	0.7	0.0
Ethyl decanoate	1646	24	61.1	12.9	4.6	4.0
Isoamyl octanoate	1663	25	1.3	0.3	19.8	0.0
Diethyl succinate	1698	26	2.3	0.7	0.7	1.6
Terpineol	1715	27	0.1	0.2	0.2	0.1
Citronellol	1779	28	0.1	0.2	0.1	0.3
Ethyl dodecanoate	1850	29	3.7	0.9	0.3	0.0
Hexanoic acid	1857	30	0.3	0.4	2.7	1.8
Geraniol	1868	31	0.4	0.1	0.2	0.0
Benzyl-alcohol	1893	32	0.1	0.5	0.6	0.5
Phenethyl-alcohol	1929	33	5.8	6.7	44.2	68.2
Ethyl tetradecanoate	2072	34	2.0	3.0	14.9	2.2
Glycerin	2358	35	28.6	102.3	47.9	1.3
Unknown	1448	20	0.2	2.8	0.4	0.0
Unknown	1554	36	0.5	8.2	3.1	12.6
Unknown	1598	37	0.7	3.1	1.4	2.8
Unknown	2201	38	2.2	10.6	9.0	0.0

* Peak areas are scaled to that of ethyl octanoate (= 100) observed using headspace analysis with a PDMS fiber.

fiber) and solvent–solvent extraction were compared using the standard. The results are listed in Table I. The chromatogram of the standard solution using SPME headspace analysis with a 100-µm PDMS fiber is shown in Figure 1. The sensitivity is based on the peak areas divided by sample concentration in standard solution; relative sensitivity is compared to that of ethyl octanoate sampled by SPME. Under the experimental conditions employed, the approximate detection limit for some components is in the low-ppt level (ethyl-octanoate, ethyl-decanoate, terpene-alcohols, β-phenethyl-alcohol); for some other components, it is in the low-ppb level (ethyl-acetate, alcohols). The reproducibility of the technique was also checked. Depending on the aroma components, these were found to be between 1 and 15% relative standard deviation (RSD). The values are listed in Table I. Reproducibility of solvent–solvent extraction is poorer than that of SPME. Immersion analysis with a PDMS fiber shows surprisingly lower sensitivity than headspace analysis for most aroma components. However, polar compounds of low volatility (glycerine, for example) are detected with better sensitivity using immersion rather than headspace analysis. Immersion analysis of Bläufrankisch wine (Table II) with a PA fiber shows a similar overall sensitivity to that of the PDMS fiber. The selectivity for various components of the aroma mixture is significantly different using the two different fibers (19), which may be an advantage in the detection of individual aroma components. Headspace analysis with a PA fiber has a lower sensitivity over two orders of magnitude and therefore is not suitable for wine aroma characterization. For this reason, these data are not

Table III. Semi-Quantitative Comparison of Aroma Components of Bläufrankisch Wines Produced by Different Fermentation Conditions Using PDMS Headspace Analysis*

Compound name	Retention index	Abbreviation	Fermentation type					
			ALB (20°C)	2-2056 (20°C)	228 (20°C)	ALB (12°C)	2-2056 (12°C)	228 (12°C)
Acetaldehyde	538	1	0.3	0.5	0.3	0.6	0.6	0.6
Ethyl acetate	715	2	9.4	7.2	10.1	9.2	10.6	9.6
Methanol	746	3	0.5	0.3	0.5	0.4	0.4	0.4
Ethanol	868	4	408.8	361.8	381.4	353.0	351.3	384.1
Propanol	905	5	15.5	0.0	0.0	0.0	0.0	0.0
Butyl acetate	1075	6	0.4	0.2	0.6	0.2	0.4	0.4
2-Methyl-propanol	1114	7	3.0	3.0	3.7	3.0	3.1	3.4
Isoamyl acetate	1126	8	7.7	6.6	6.3	8.3	7.6	7.0
Butanol	1163	9	0.1	0.1	0.1	0.0	0.0	0.0
2-Methyl-1-butanol	1220	10	8.8	8.3	9.7	7.2	7.1	7.4
3-Methyl-1-butanol	1223	11	42.1	37.6	40.4	37.4	38.1	40.8
Ethyl hexanoate	1238	12	12.5	12.0	11.9	13.4	14.7	13.6
3-Hydroxy-2-butanone	1336	13	0.3	0.2	0.3	0.4	0.4	0.3
Ethyl lactate	1356	14	0.8	0.5	0.6	0.3	0.3	0.2
Hexanol	1363	15	1.4	1.3	1.4	1.6	1.5	1.5
3-Hexen-1-ol (E)	1392	16	0.5	0.3	0.4	0.3	0.3	0.3
Ethyl octanoate	1436	17	100.0	91.5	95.7	112.2	116.0	100.4
Isoamyl hexanoate	1440	18	2.6	0.2	2.4	0.4	2.2	2.5
Acetic acid	1452	19	1.6	3.5	1.4	2.6	2.7	2.6
Benzaldehyde	1518	21	0.5	0.6	0.5	0.4	0.4	0.3
Linalool	1548	22	0.3	0.3	0.3	0.3	0.3	0.3
5-Methyl-furfural	1590	23	1.1	0.8	0.6	0.7	0.7	0.7
Ethyl decanoate	1646	24	61.1	57.0	65.3	79.7	83.1	61.6
Isoamyl octanoate	1663	25	1.4	1.3	1.7	1.9	2.1	1.7
Diethyl succinate	1698	26	2.3	2.3	2.9	3.3	4.4	2.9
Terpineol	1715	27	0.1	0.2	0.1	0.1	0.1	0.1
Citronellol	1779	28	0.1	0.1	0.1	0.1	0.1	0.1
Ethyl dodecanoate	1850	29	3.7	3.2	5.0	4.4	6.0	3.0
Hexanoic acid	1857	30	0.3	0.3	0.3	0.5	0.5	0.5
Geraniol	1868	31	0.4	0.5	0.7	0.5	0.7	0.4
Benzyl-alcohol	1893	32	0.1	0.2	0.1	0.0	0.1	0.0
Phenethyl-alcohol	1929	33	5.8	6.3	4.7	5.1	4.8	4.6
Ethyl tetradecanoate	2072	34	2.0	2.1	2.2	2.4	2.5	2.2
Glycerin	2358	35	28.6	14.6	14.2	1.0	1.7	1.0
Unknown	1448	20	0.2	12.1	11.1	9.2	10.1	8.1
Unknown	1554	36	0.5	3.1	0.3	0.2	0.3	0.2
Unknown	1598	37	0.7	1.8	0.7	0.6	0.6	0.5
Unknown	2201	38	2.2	14.4	1.0	0.0	0.0	0.0

* Peak areas are scaled to that of ethyl octanoate (= 100) observed using headspace analysis with a PDMS fiber and ALB yeast at 20°C.

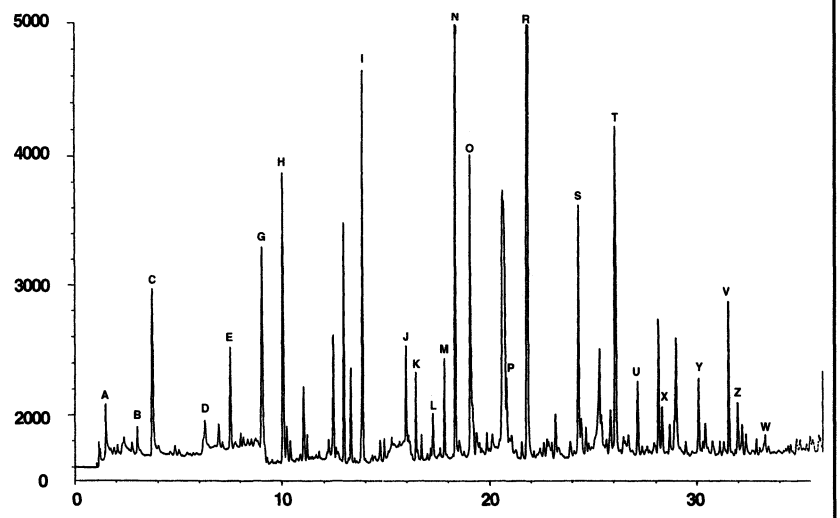

Figure 1. Headspace chromatogram of the standard solution using a 100-µm PDMS extraction fiber.

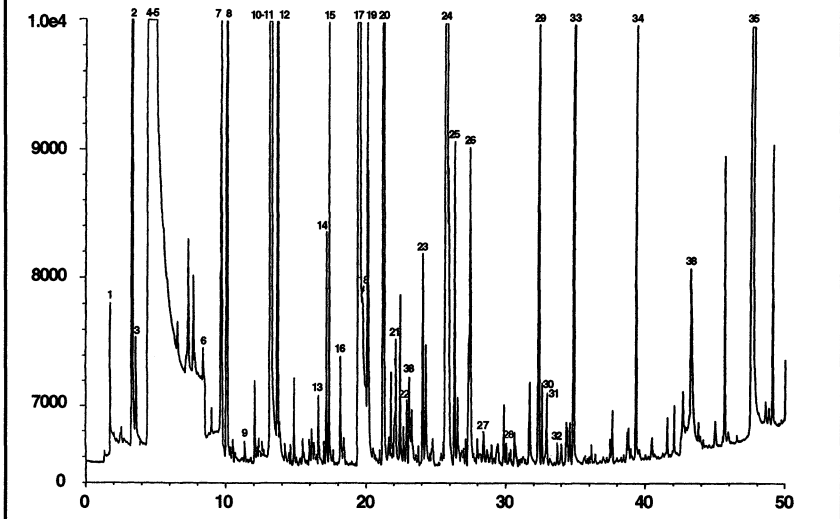

Figure 2. Headspace chromatogram of Bläufrankisch wine using a 100-µm PDMS extraction fiber. This wine was produced by ALB (Uvaferm) yeast at 20°C fermentation temperature.

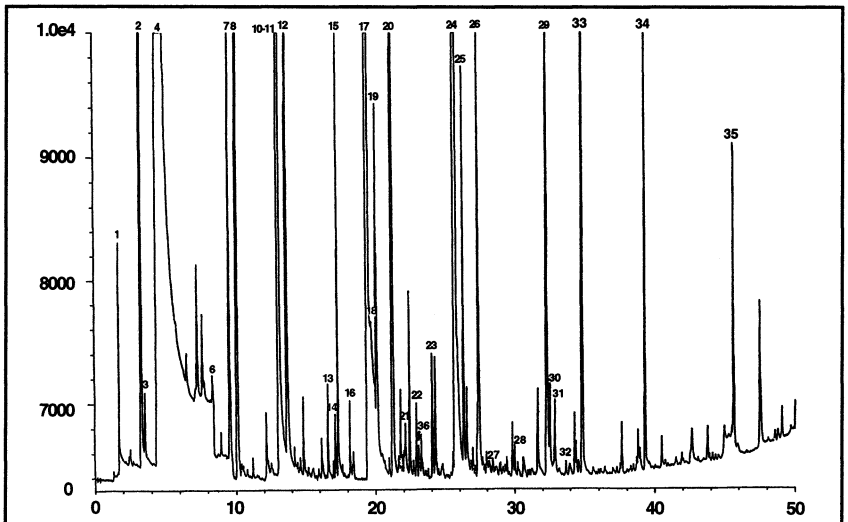

Figure 3. Headspace chromatogram of Bläufrankisch wine using a 100-µm PDMS extraction fiber. This wine was produced by ALB (Uvaferm) yeast at 12°C fermentation temperature.

shown in Table I. Among the techniques described, headspace analysis using a PDMS fiber seems most suitable for a rapid and general characterization of wine aromas.

A typical gas chromatogram of the headspace of Bläufrankisch wine using SPME–GC–MS is shown in Figure 2. This wine was produced by the ALB yeast at 20°C. The chromatogram shows more than 100 peaks of significant intensity. More than 30 of the most abundant peaks were identified by their mass spectra and retention indices. A list of these is shown in Table II. This data, along with data shown in Table I, indicate that headspace analysis using SPME with a PDMS fiber is a very sensitive technique for the detection of ethyl-esters and terpene alcohols, which are important fragrance compounds. The technique provides good results for other aroma components as well. Immersion sampling with a 100-µm PDMS fiber can extract a larger amount of polar compounds from wines. Its main disadvantage is that it is slower than headspace analysis (it requires more time to reach equilibrium conditions in the solvent phase than in the gas phase). Headspace analysis using a PA fiber has low sensitivity and is not recommended for wine analysis. Immersion sampling with PA fiber also has low sensitivity (except with alcohols). A further disadvantage is that the fiber is damaged after only approximately 20 analyses (in typical cases, fibers can be used for hundreds of analyses). This is probably caused by a very strong binding of polyphenols to this fiber.

For comparison, a commonly used solvent–solvent extraction was also performed (as detailed in the Experimental section); the results are shown in Table II. The presence of a solvent peak in the chromatogram is disadvantageous in this case because it limits the amount of sample which can be injected onto the column. This is, in fact, the reason for the 1:50 split ratio that had to be used following solvent–solvent extraction, whereas it is possible to use splitless injection with the SPME technique. Extraction is also more expensive and more time-consuming than that of the SPME technique.

The results of the wine sample confirm the findings using the standard solution; SPME headspace analysis using a PDMS fiber is an advantageous analytical technique for fast, sensitive, and general qualitative and semi-quantitative characterization of wine aroma components. The following studies were performed using this technique.

The influence of different fermentation conditions on the production of wine aromas was studied using three different yeasts in fermentation at two different temperatures. A semi-quantitative comparison of the data (peak areas of

main aroma compounds) is shown in Table III. Fermenting wine at 20°C using the three different yeast cultures resulted in wine aroma patterns which were very similar to each other. This correlates well with the sensory evaluation: the wines were tested by a 52-member panel using a 20-point (positive) score sheet. The mean score for these wines were 17.7, 17.4, and 17.5 (for ALB, 2-2056, and 228, respectively), which indicates that these wines are of similar quality. At low-temperature fermentation, the concentration of some aroma compounds (e.g., isoamyl-acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, isoamyl octanoate) is higher than that at high-temperature fermentation. However, at low temperature, a smaller number of aroma compounds are produced; there are over 110 peaks in the headspace chromatogram of wines fermented at 20°C,whereas there are only 80–90 in those obtained at 12°C. This is illustrated by a comparison of Figure 2 (ALB yeast at 20°C) with Figure 3 (ALB yeast at 12°C). In the case of low-temperature fermentation, the three yeast cultures produced characteristic differences in the wine aroma pattern. The score for sensory evaluation of wines fermented at low temperature is much worse (by 0.9 points, on average; 17.1, 16.7, and 16.1 in the sequence previously mentioned). Panel discussion after tasting suggests that the main result of worse quality is a less "full-bodied" taste of these wines.

Conclusion

This study demonstrates that the SPME sample preparation technique coupled with GC analysis is well suited for a qualitative and semi-quantitative analysis of aroma compounds in wines. The results are suitable to compare and optimize fermentation conditions and can be correlated to sensory evaluation. SPME provides a simple, fast, sensitive, and reproducible alternative to solvent–solvent extraction and is especially well-suited to GC analysis using either FID or MS detection. Quantitation using standard solutions and a dilution series seems feasible, although it has not been the object of the present paper.

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