Received: 18 October 2019 | Accepted: 14 June 2020 | Published: 12 August 2020
DOI:10.20870/oeno-one.2020.54.3.2923

Xylovolatile fingerprint of wines aged in barrels or with oak chips

Maurizio Petrozziello[1], Federica Bonello[1], Andriani Asproudi[1], Tiziana Nardi[2*], Christos Tsolakis[1], Antonella Bosso[1], Vincenzo Di Martino[3], Michele Fugaro[4] and Raffaele Antonio Mazzei[4]

[1]CREA - Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria, Centro di Ricerca Viticoltura ed Enologia. Via P. Micca 35, 14100 Asti, Italy
[2]CREA - Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria, Centro di Ricerca Viticoltura ed Enologia. Via XXVIII Aprile, 26, 31015 Conegliano TV, Italy
[3]ICQRF - Dipartimento Ispettorato Centrale della Tutela della Qualita' e della Repressione Frodi dei Prodotti Agroalimentari. Direzione generale della prevenzione e del contrasto alle frodi agroalimentari PREF IV Laboratorio Centrale di Roma. Via del Fornetto, 85 - 00149 Roma, Italy
[4]ICQRF - Dipartimento Ispettorato Centrale della Tutela della Qualita' e della Repressione Frodi dei Prodotti Agroalimentari, Via Casoni 13/B - 31058 Susegana (TV), Italy

[*]corresponding author: tiziana.nardi@crea.gov.it

This article is published in cooperation with the 11th OenoIVAS International Symposium, June 25–28 2019, Bordeaux, France.

ABSTRACT

Aim: In this research xylovolatile aromatic compounds were determined to highlight any compositional differences between wines aged in barrels and those produced using oak chips.
Methods and results: Approximately 200 wines aged using oak chips or wood barrels were analysed, among which about 50 were aged at the experimental winery of the Research Centre of Viticulture and Enology in Asti (Piedmont, Italy). 17 different types of commercial oak chips were used in order to obtain a subset of reference samples. Several factors were considered, including degree of oak wood toasting, wood geographical origin and the type of wine (both red and white). Sample preparation for GC-MS analysis was performed by single-step solid phase extraction, using polymeric SPE cartridges. More than 60 volatile molecules from oak were identified. Analytical results were explained using multivariate statistical analysis. A preliminarily step was carried out using principal component analysis (PCA), which showed interesting compositional differences between barrel and chip-aged wines with regards to methylvanillate, ethylvanillate, as well as furan derivative compounds. Further statistical analysis highlighted the clear impact of the type of wine (red or white) on the extraction of xylovolatile compounds from oak chips. Subsequently, in order to test if and how the selected chemical explanatory variables allow wine treatments to be discriminated, and to predict which group a new observation will belong to, a discriminant analysis (DA) was carried out on an independent dataset. More than 96 % of samples were correctly classified.
Conclusions: Significant differences were highlighted between barrel- and chip-aged wines with regards to xylovolatile compounds. The analysis showed that several factors may influence the amount of aromatic compounds extracted from chips and barrels, especially the matrix composition. It was possible to deduce the aging process that the wines had undergone by selecting key molecules using multivariate methods.
Significance and impact of the study: Via a suitable GC-MS method and a chemometric approach for the identification of discriminant xylovolatiles in wood aged wines, this study offers promising perspectives and useful tools for routine fraud inspection aiming at classifying wines according to their aging process.

KEYWORDS

volatile compounds, chips, PCA, wine, mass spectromery

Supplementary data can be downloaded through: https://oeno-one.eu/article/view/2923

 © 2020 International Viticulture and Enology Society - IVES

INTRODUCTION

The use of wood chips in winemaking is not particularly recent. In Italy, the first evidence of the oenological use of wood fragments dates back to the early 1900s, when small untoasted fragments of poplar wood were employed to assure proteic and microbial stability (Tablino, 2013). Nowadays, their technological use is quite different (Chatonnet, 2008; Tablino, 2013). The modern use of oak chips as a substitute for barrels was first reported in the production of spirits, for ageing and aromatising the raw distillate. In the early 1960s and in 'wine-emerging' countries, the introduction of toasted chips in oenology was quite successful. Due to the spread of the use of containers made of modern materials (concrete, steel, fibreglass), the simultaneous increase of consumer interest for wood-based wines and the rising costs of barrels led many wine producers to opt for the use of alternative products.

However, up until 1993 in the United States and 2005 in the EU, the use of oak chips in wine production was illegal. Nowadays, the use of alternative woods as a substitute for traditional barrels has become common practice almost worldwide. A wide variety of sizes, grain scents, toasting grades and protocols makes their use suitable for the multiple goals that the winemaker may strive to achieve. Oak fragments can be found in a variety of forms, (Hernández-Orte *et al.*, 2014) including: shavings, known as 'oak fragments'; dices, called 'cubes' or 'oak beans'; oak powder; pieces of granulated wood, called 'pencil shavings'; granulates; square pieces referred to as 'blocks' or 'segments'. Bigger pieces can also be found on the market, usually in the form of staves, such as tank staves, wine wood or infusion staves. Finally, old barrels can also be used by adding wooden pieces such as oak chains, sticks or barrel inserts.

Oenological results are influenced by a wide variety of factors, such as size of chips, infusion time, toasting degree, wood type and the wine's extractive capacity. Similarly, traditional refinement in wooden containers can give different results depending on factors, such as contact time of the wine, the use of new or used barrels, the period and frequency of any *batonnage*, and the possibility of using containers of different sizes (*barriques, tonneaux* and larger barrels) (Bosso *et al.*, 2008; Gutiérrez Afonso, 2002; Ortega-Heras *et al.*, 2010).

Therefore, discriminating wines that have been obtained using one refinement technique instead of another is particularly challenging due to the multiplicity of variables involved. However, to ensure sound consumer protection and quality assessment, it is equally clear that the development of either analytical or sensory investigation methods is essential for distinguishing wines aged in barrels from those treated with chips or alternative woods for a faster and cheaper refinement.

It has been shown that it is not possible to obtain wines refined with chips in steel containers with sensory characteristics similar to those that have been preserved in new barrels for a long time (Ortega-Heras *et al.*, 2010). However, young wines treated with chips are almost sensorially indistinguishable from those stored in new barrels for short periods (about three months); both are characterised by light *boisé* olfactory notes. The sensory differences between wines originating in barrels with chips and those produced using new barrels is more nuanced (Cano-Lopez *et al.*, 2008); in general, however, the former have been found to be less preferable than the latter, receiving lower pleasantness scores.

Explaining these sensory differences in chemical terms is tricky. Some differences can be related to the faster release of aromatic compounds to the wine when using chips instead of barrels; this is easily understood considering the large surface area in contact with the wine in the case of chips, which facilitates the phenomena of transfer and diffusion. Wines stored in barrels extract aromatic compounds over a longer period of time, reaching final concentrations generally higher than wines aged with chips (Bautista-Ortín *et al.*, 2008). The long contact time also allows greater integration of the boisée scent to wine and this could justify the preference for these wines. Furthermore, the addition of chips can take place at different points during the winemaking process and can have different technological objectives; therefore, the concentration of wood volatile compounds (xylovolatiles) in the final product can differ widely. In the specific case of white wines, Gutiérrez Afonso (2002) compared wines obtained using chips of different botanical origin - added during fermentation - with wines fermented in barrels. American oak, for instance, confers a higher intensity of boisée and coconut and vanilla notes, and these varietal differences are amplified using chips instead of barrels.

 © 2020 International Viticulture and Enology Society - IVES

Another aspect is related to the possibility of modulating the aromatic intensity of toasted wood scents by adopting different doses of chips, an option that, for obvious reasons, is precluded when using a barrel. Indeed, oak chip quantity is extremely important as it has more impact than other factors on the aromatic profile of the wine (García-Carpintero *et al.*, 2012).

TABLE 1. Oak chips used for the ageing assay.

Code	Producer*	Toasting	Granulometry**	Wood origin
En1	1	Yes	Chips	French
En2	1	Yes	Chips	French
En3	1	Yes	Chips	French
En4	1	Yes	Chips	American
Ga1	2	No	Chips	French
Ga2	2	Yes	Chips	French
Ga3	2	Yes	Chips	American
La1	3	No	Chips	French
La2	3	No	Granulate	French
La3	3	Yes	Chips	French
La4	3	Yes	Granulate	French
La5	3	No	Chips	French
La6	3	Yes	Chips	American
La7	3	Yes	Granulate	American
La8	3	No	Granulate	American
La9	3	Yes	Chips	French
La10	3	Yes	Granulate	French

*Producers: 1, Esseco s.r.l. - Divisione Enartis, Via San Cassiano, 99, 28069 San Martino, Trecate (No); 2, Fabbrica Botti Gamba S.R.L. Sede Operativa e Legale: Via Statale, 108/B 14033 Castell'Alfero (At), Italy. 3, Laffort® Italia S.R.L., S.P. n° 95 per Castelnuovo, 15057 Tortona AL, Italy. Granulometry: chips (7–15mm), granulate (2–7mm). **Granulometry: Chips: between 7 and 15 mm; Granulate: between 2 and 7 mm.

Among other analytic techniques, gas chromatography coupled with mass spectrometry (GC-MS) is nowadays a widespread technique in many laboratories, and has been successfully used as a tool for the identification of volatile wood-released compounds (de Simón *et al.*, 2010; Pérez-Coello and Díaz-Maroto, 2009). Moreover, GC-MS has already been employed to discriminate between Spanish wines produced with chips and those aged in barrels (Hernández-Orte *et al.*, 2014) by detecting certain marker compounds. With this in mind, the present research project was jointly carried out by the CREA Viticulture and Enology Research Centre in Asti with the Central Inspectorate for Quality Protection and Fraud Prevention (ICQRF) aiming to obtain a discriminant method to be routinely used in laboratories. A further aim was to complete and contextualise (in terms of the Italian wine scene) results obtained by other research groups (Del Álamo *et al.*, 2008; Ebeler *et al.*, 2011; Triacca *et al.*, 2013). Therefore, a relevant number of wine samples of known origin were considered, for which information regarding the type of refinement they had undergone was available. Nearly 200 wines were analysed by GC-MS, and about 60 xylovolatiles were detected and quantified to identify the compound markers that would enable discrimination between barrel- and oak chip-aged wines. The aim was to obtain a robust database for the development of a reliable statistical method able to discriminate wines according to the different types of wood used in ageing.

MATERIALS AND METHODS

1. Wines and oak chips employed in the study

Wines aged in barrels or treated with alternative products were analysed by assessing wood-derived volatile compounds. Most wines were obtained from Italian producers mainly in Piedmont. For each wine we attempted to obtain as much information as possible, namely the ageing mode and type of wood used (see supplemental Table 1 and Nardi *et al.*, 2020). Some of the wines were vinified at the Research Centre for Viticulture and Enology in Asti and treated using a defined set of commercial chips; this allowed us to obtain a pool of wines with a completely managed ageing process, and complete and guaranteed information regarding the alternative woods used. These wines are described in the following paragraphs.

2. Chip reference refined wines

Chips reference wines (both red and white) were aged using different types of commercial oak chips. Chips were obtained from 3 different producers (Table 1), encompassing a significant number of alternative products obtained using different oak wood (French oak or American oak), granulometry (7–15 mm pieces or 2–7 mm granules) and toasting levels comprising two different groups: toasted and untoasted. Other degrees of chip toasting have not been considered since the classification of the declared toasting level is not homogeneous among different producers. In detail, 17 samples of chips were used, and their characteristics are listed in Table 1. All the experiments were carried out at the experimental cellar of the Research Centre for Viticulture and Enology in Asti (Italy).

© 2020 International Viticulture and Enology Society - IVES

TABLE 2. Reference wines aged or fermented with chips.

Name*	Type	Grape variety	Total acidity (g/L)	Ethanol (% v/v)	Type of chips used **
OCAW1	Red wine	Barbera and Albarossa	7,11	14,1	En1, En2, En3, En4, Ga1, Ga2, Ga3, La1, La2, La3, La4, La5, La6, La7, La8, La9, La10
OCAW2	Red wine	Corvina, Rondinella, Corvinone, Merlot	5,8	13	La1, La3, La4, La5, La7, La8, La9, La10, En2, En3, En4, Ga2, Ga3
OCAW3	White wine	Cortese	5,25	11,7	En1, En2, En3, En4, Ga1, Ga2, Ga3, La1, La2, La3, La4, La5, La6, La7, La8, La9, La10

*Names: Oak Chips-Aged wines (OCAW); **see Table 1; all wines were produced during the 2015 - 2016 vintages.

TABLE 3. Compounds showing significant differences between chip-treated and barrel wines.

Pyran derivative	Furan derivative	Benzenoid compounds	Vanillin-related compounds	Lactons
Maltol	5-(hydroxymethyl)furfural	4-methylguaiacol	vanillin	t-whiskey-lactone
	5-methylfurfural	4-ethylguaiacol	syringaldehyde	c-whiskey-lactone
	furfural	eugenol	methylvanillate	γ-nonalactone
	solerone	isoeugenol	ethylvanillate	
	methyl-2-furoate	methoxyeugenol	vanillic acid	
	ethyl 2-furoate	4-ethylphenol	acetovanillone	
	2-furyl hydroxymethyl ketone	ethyl 4-ethoxybenzoate	butyrovanillone	
		3-ethylbenzaldehyde	acetophenone	
		4-ethylbenzaldehyde	zingerone	
			syringol	

ANOVA significant differences ($p<0.0001$) between the "barrel" thesis and the "chips" thesis. The compounds are grouped into 5 different homogeneous classes according to structure.

2.1 Oak Chip-aged Wines

Oak chip-aged wines (OCAW) 1, 2 and 3, (Table 2), were aged in 5L capacity tanks and different types of oak fragments were added in 3 g/L doses. The wines and fragments were in contact for 6 weeks at 18 °C, after which the oak fragments were removed by racking and the wine was bottled for analysis.

3. Commercial wines

An additional 130 white and red commercial wines (please see Supplementary Table 1) were included in the database, encompassing different grape varieties. All wines were obtained from producers whose ageing methods (chips or barrel) were ascertained and verified. Thirty-one of them were Barolo DOCG (*Denominazione di Origine Controllata e Garantita, a protected designation of origin*) wines, kindly provided by the Consortium of Protection *Barolo Barbaresco Alba Langhe and Dogliani*. The ageing procedure is guaranteed by the DOCG regulation and was verified by the consortium (Regione Piemonte, 2017).

Moreover, Grignolino wines were kindly provided by "Associazione Monferace". The commercial wines were compared with the previously mentioned wines which were aged *ad hoc* with different types of oak chips.

4. Volatile compound analysis

All standards were purchased from Sigma Aldrich (Milan, Italy); methanol and dichloromethane (HPLC-grade) were purchased from Carlo Erba Reagents (Rodano, Milan, Italy). Ultrapure water was obtained from a Milli-Q gradient A10 instrument (Millipore Corporation, Billerica, USA). The SPE (Solid Phase Extraction) cartridges used for the extraction of samples were Strata X (Phenomenex, Torrence, CA, USA).

The method proposed by Bosso *et al.*, 2008 was used, but with the following changes: 1-heptanol (250 µL of 54.73 mg/L) and 3,4-dimetylphenol (250 µL of 50 mg/L) were added as internal standards to 25 mL of wine, then water was added to reduce the concentration of alcohol to less than 5 %. SPE cartridges were activated with 5 mL of dichloromethane, 5 mL of methanol and 5 mL of ultrapure water in succession without drying the cartridges between each passage.

 © 2020 International Viticulture and Enology Society - IVES

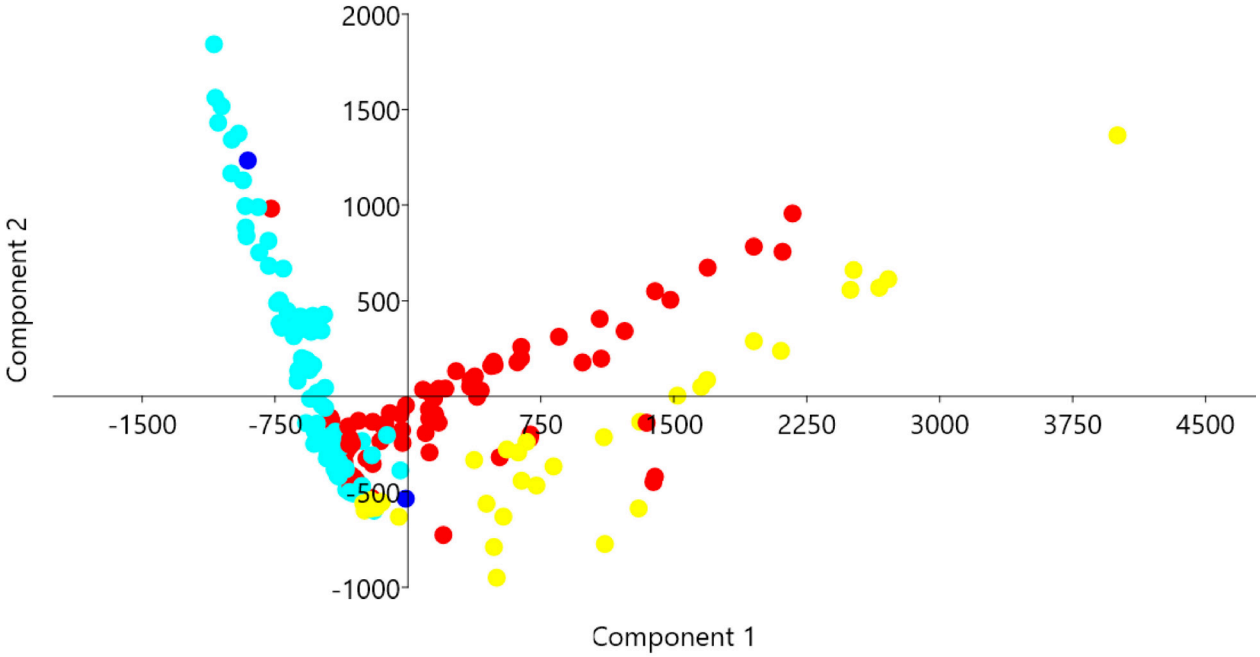


FIGURE 1. Representation of the wines (scores) in the space described by the two first Principal Components (PCA). Elaboration of the whole dataset.

Score plot showing 4 subgroups of samples: 1) aqua: red wines aged in barrels; 2) blue: white wines aged in barrels; 3) yellow: white wines refined with chips; 4) red: red wines refined with chips.

The sample was passed through the cartridge at a maximum flow rate of 2 mL/min on a 24-port SPE manifold, the cartridge was then washed with 5 mL of ultrapure water and dried. The volatile compounds were extracted with 5 mL of dichloromethane, dehydrated with anhydrous sodium sulfate, and then partially concentrated to a volume of 2 mL. Samples were stored at -18 °C until GC analysis. The initial volume was further reduced immediately before analysis to approximately 100 µL using a slight stream of nitrogen. The analysis was performed with a 6890 GC system coupled to a 5973N MSD detector (Agilent Technologies, Santa Clara, CA, USA). 1 µL of extract in dichloromethane was injected in splitless mode. The split/splitless injection port was heated to 250 °C and the split vent was opened after 2 minutes. The column used was a 60 m Stabilwax-MS Column (Restek S.r.l., Via G. Miglioli 2/A, Cernusco sul Naviglio, Italy 20063) fused silica capillary column coated with a 0.25 µm thick polyethylene glycol film. Helium was used as the carrier gas with a linear flux of about 1.1 mL/min. The mass spectra were recorded in TIC (Total Ion Monitoring) mode and integrated in extracted-ion mode (EIC).

All the concentrations are reported as equivalents of the respective internal standard. The selected ion fragments for identification and semi-quantitative analysis are reported in supplemental Table 2.

5. Statistical analysis

Statistical treatments were carried out with the software XLSTAT 19.4 biomed version (Addinsoft NY, USA. 2016). Some analyses and related graphic representations were also carried out using the statistical freeware PAST 3.26 (Hammer, Harper and Ryan, 2001) programme. The variables considered in this work are representative measurements of xylovolatile compounds quantified by the internal standard method. Appropriately selected, they were statistically analysed by univariate (ANOVA) and then multivariate analysis including Principal Component Analysis (PCA) and Discriminant Analysis (DA).

RESULTS AND DISCUSSION

1. Xylovolatile compound differences between chip-aged wines and barrel-aged wines

About 60 compounds were identified during a preliminary test using hydroalcoholic extracts (for a complete list of the compounds, please see supplemental Table 2); 50 were retrieved and

© 2020 International Viticulture and Enology Society - IVES

quantified in wine and then used for statistical analyses. These compounds belong to the following chemical macro-groups: volatile phenols, phenyl ketones, benzoic aldehyde derivatives (grouped in "benzenoid compounds" in Table 3), vanillic and cinnamic aldehyde derivatives, furan derivative compounds, pyran derivative compounds and lactons. A preliminary ANOVA carried out on the whole dataset showed highly significant differences ($p<0.0001$) between oak and barrel wines for the compounds listed in Table 3.

Subsequently, a PCA (Principal Component Analysis) on compounds listed in Table 3, was carried out with the aim of identifying compounds that could better discriminate samples and explain the greater variance depending on the treatment (Figure 1). The wines that underwent barrel ageing cluster are on the left side of the graph, whereas the samples that underwent chip refinement are on the right side of the same scatter plot. Moreover, subgroups exhibit a partial separation between red and white wines (upper and lower sides respectively).

Cumulatively, the two first Principal Components explain about 40 % of the dataset variance.

The variables that best describe the differences between wines aged in barrels and wines aged with chips are related to the first Principal Component (PC) represented in Figure 1. We observed that 4-ethylphenols, vanillic acid esters (namely ethylvanillate) and whiskey lactones are negatively correlated with PC1 and readily illustrate the barrel-aged wines, while the variables positively associated with PC1, such as vanillin, acetophenone and acetovanillone, highlight the samples refined with chips. Among these compounds a close relationship was observed between 4-ethylphenol and barrel-aged samples, which is consistent with previous research that came to similar conclusions, although performed on wines from a different geographic origin (Hernández-Orte *et al.*, 2014). PC2 is negatively correlated with the concentrations of furanic aldehydes, isoeugenol and vanillic acid, while the positive portion is related to vanillin, syringaldehyde and furfural. These data partially confirm the results obtained by Hernandez Horte and co-workers (2014), who stated that wines aged in barrels contain more volatile phenols, lactones and furfural derivatives; conversely, wines aged using alternative products are characterised by high levels of vanilline, syringaldehyde and acetovanillone. Figure 2 represents the loading of the different original variables referred to the first and second Principal Components. Moreover, the results show a small amount of lactonic compounds (namely whiskey lactones) and vanillin in wines treated with toasted chips, whereas quantities of phenolic compounds and isoeugenol are low in wines treated with untoasted ones.

Subsequently, a PCA analysis was only carried out on data referring to the experimental wines treated with chips (Figure 3). The PCA showed that the samples are grouped according to their varietal origin, with a clear discrimination between white and red wines: in the former, furanic compounds and isoeugenol dominate, whereas in the latter phenolic compounds and benzoic aldehyde derivatives are predominant (data not reported). The wine matrix, therefore, affects the extraction of wood-derived compounds significantly. This result was taken into account for the development of the predictive method discussed below.

2. Discriminant Analysis

Discriminant Analysis (DA) was carried out with two main objectives: i) *descriptive*: to find new discriminating functions obtained from the linear combination of original variables, so that the projections of predetermined observation classes are well separated in the new variable space, and ii) *decision-oriented*: to use these new discriminant functions in order to define a rule for assigning new individuals to one of the predetermined classes (Hammer *et al.*, 2001).

The DA performed over the entire dataset did not give satisfactory results (data not shown). Thus, in view of previous considerations, and in light of the clear dissimilarity between white and red wines regarding xylovolatile composition (Figures 1 and 3), we decided to limit the discriminating factor analysis to red wines only.

Three sets of red wine data were then identified: 1) training sets consisting of 97 samples, 2) a validation set of 40 samples, and 3) an independent test set of 36 samples. The training set samples were then divided into three different predetermined groups: barrique-aged wines, wines aged in larger barrels, and wines aged with chips. Explanatory Variables to carry out the DA analysis were initially chosen taking into account the results described above, further choice of the variables to be adopted for the realisation of the model were then automatically improved through an automatic stepwise forward procedure by the statistical software. The following variables were identified as the most discriminating: mellein, furfural, etil-

 © 2020 International Viticulture and Enology Society - IVES

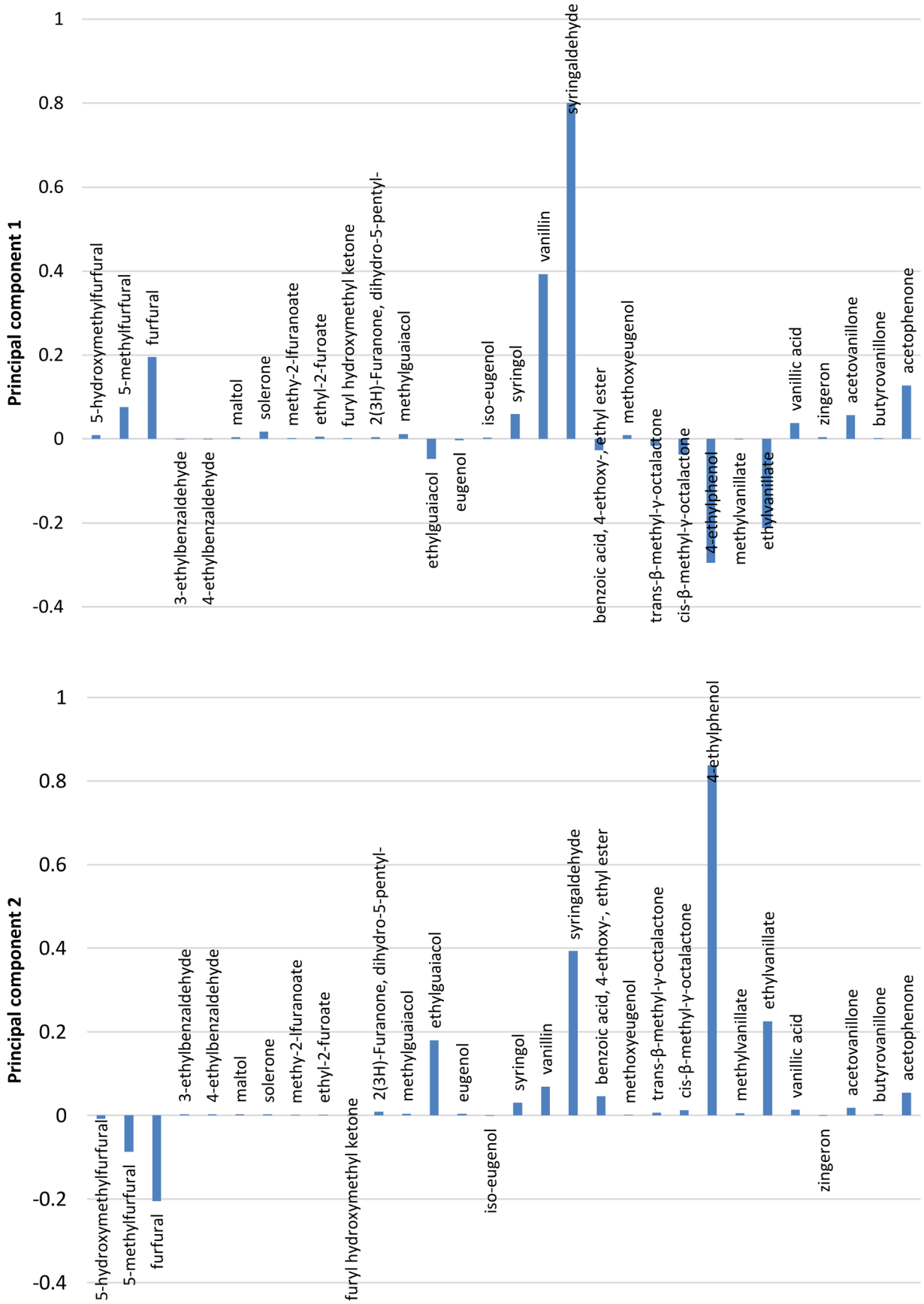


FIGURE 2. Loading plot for PC1 and PC2. Analysed using PAST software.

© 2020 International Viticulture and Enology Society - IVES

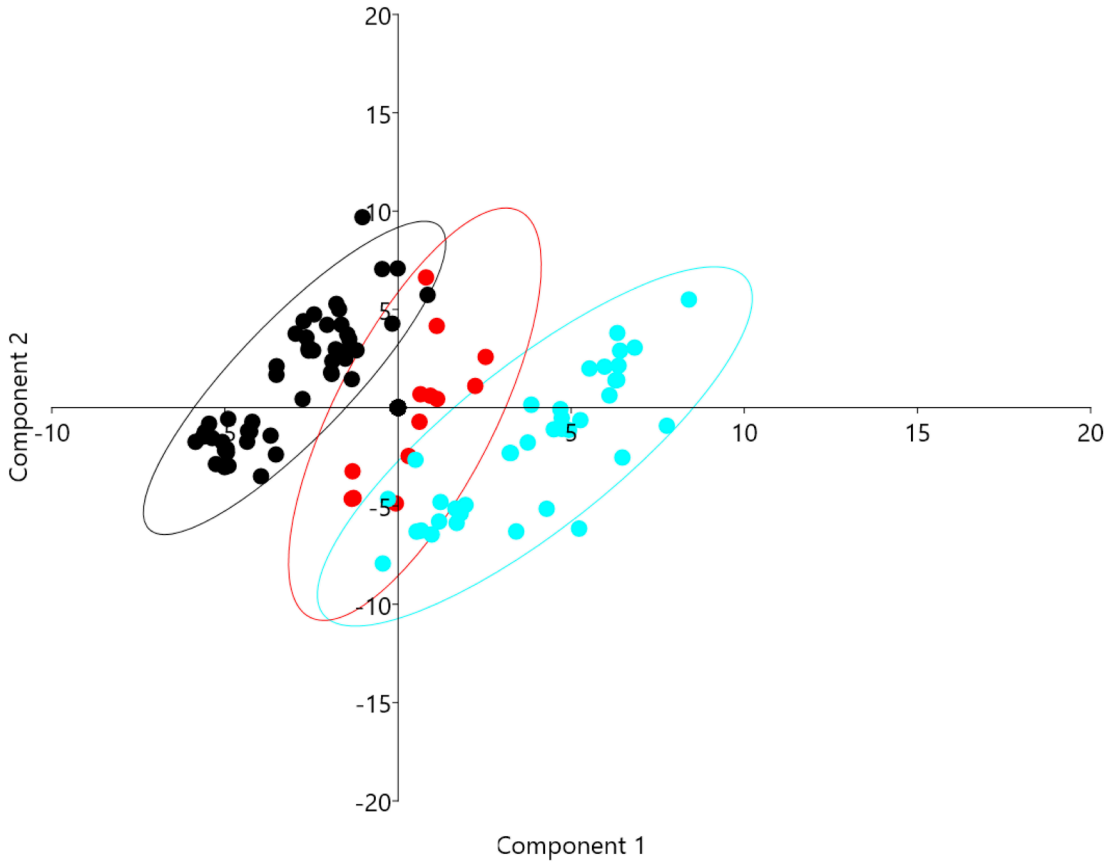


FIGURE 3. PCA analysis on chip-treated wines.
Score plot showing 4 subgroups of samples added with chips: black: OCAW 1 (Albarossa-Barbera); OCAW 2 (Valpolicella); light blue: OCAW 3 (Cortese).

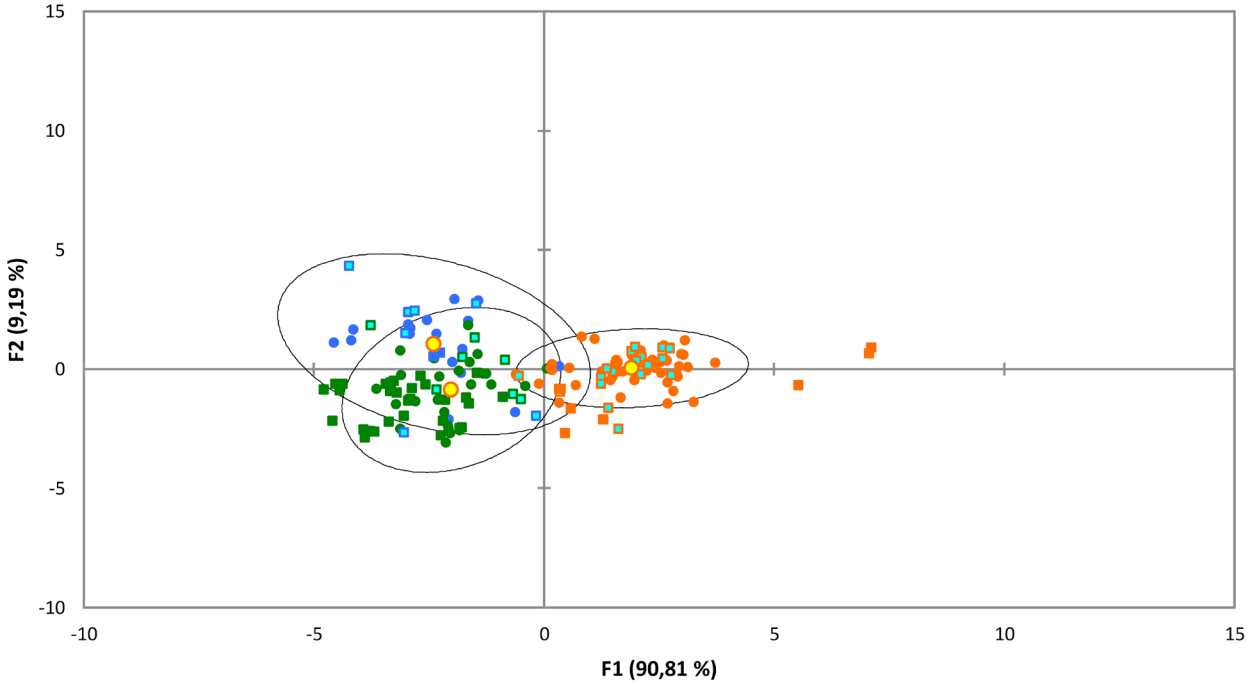


FIGURE 4. DA analysis score plot on the red wine dataset.
Score plot showing 3 subgroups of samples: 1 yellow dot: chips; 2 light blue: barriques; 3 green: other barrels. Points: validation set, squares with a coloured border are included in the validation group, squares without a coloured border belong to the testing set.

 © 2020 International Viticulture and Enology Society - IVES

2-furoate, g-nonalactone, vinylguaiacol, eugenol, ethylbenzoate, methylvanillate, ethylvanillate and acetovanillone. Figure 4 demonstrates how the graphic representation of different types of treatment easily allows traditionally aged wines (barrique/larger wood barrels) and those aged with chips to be distinguished. The overall performance of the DA is appreciable by observing the confusion matrixes. The cross-validation matrix is represented in Table 4, where the diagonal (bold) indicates the correctly identified samples. In accordance with the aim of the study, barrique- and larger barrel-aged wines were grouped together in the same category.

TABLE 4. Matrix of confusion for cross-validation results.

From \ to	Barrique + Barrel	Chips	Total	Correct %
Barrique + barrel	**42**	2	44	97.67
Chips	2	**48**	50	96.00
Total	44	50	**94**	96.80

A matrix of confusion for the results of cross-validation considering wooden containers (barriques and larger barrels together) versus chips.

Cross validation was performed to assess the accuracy of the classification and predictive ability, using 40 random samples of the training set. Cross-validation allows the placement within groups to be verified when individual elements are evaluated one at a time with the classification algorithm, obtained by excluding them from the prediction sample. The confusion matrix summarises the classification of cross-validation samples by the classification algorithm and allows the percentage of well-classified observations (96.8 %) to be easily identified.

The DA was finally tested on an independent dataset to discriminate between samples of barrel-aged red wines and wines aged with chips. The analysis was performed on a sample group comprising 31 red DOCG wines (Barolo and Barbaresco) and 6 wines refined with chips purchased on the market. This analysis gave the following results: 96.7 % of DOCG wine samples (30/31) were assigned to the barrique/barrel category (as provided by the disciplinary) while all 6 wines aged with alternative products were correctly classified in the chips category.

CONCLUSIONS

The present study was carried out in the framework of a project aiming to develop a suitable GC-MS method to identify xylovolatiles in wines, in order to classify wines according to their ageing process. When taking into account the data as a whole, it is possible to infer the relationship between the concentration of volatile substances and the ageing process that some Italian wines had undergone. Wines aged in barrels had a higher concentration of ethylvanillate, 4-ethylphenols, eugenol and whiskey-lactones than wines aged with chips, which were characterised by a generally higher concentration of furanic compounds and hydroxybenzaldehyde derivatives. The presence of 4-ethylphenols at higher concentrations in barrel-aged wines indicates that there is still, in general, a higher risk of contamination from *Brettanomyces bruxellensis* for this type of practice, compared with chip refinement.

Our work confirms that the selection of key molecules using a good chemometric approach is a pivotal step in the development of discriminating methods. Although this approach can be further improved in the future, starting by extending the used database, promising perspectives arise from a preliminary DA application in classifying wines. In this regard, > 96.5 % of correct answers, both in the internal validation check and in an external test check, were obtained. In conclusion, this tool could be a useful preliminary step for orienting institutional inspection activities of fraud control.

Acknowledgements: The described research was carried out in the framework of a project funded by The Italian Ministry of Agricultural, Food and Forestry Policies (MIPAAF) under the grant: «*Strumenti di supporto per la valutazione del rischio di frodi nel sistema agroalimentare*". The authors would like to thank Consorzio di Tutela Barolo Barbaresco Alba Langhe e Dogliani and Piero Ballario (Vino IN snc, Corso Canale, 18/5, 12051 Alba CN), which collaborated in the study by providing wine samples and detailed information about the ageing process.

REFERENCES

Bautista-Ortín A.B., Lencina A.G., Cano-López M., Pardo-Mínguez F., López-Roca J.M. and Gómez-Plaza E., 2008. The use of oak chips during the ageing of a red wine in stainless steel tanks or used barrels: Effect of the contact time and size of the oak chips on aroma compounds. *Australian Journal of Grape and Wine Research*, 14(2), 63–70. doi:10.1111/j.1755-0238.2008.00008.x

Bosso A., Petrozziello M., Santini D., Motta S., Guaita M. and Marulli C., 2008. Effect of grain type and toasting conditions of barrels on the concentration of the volatile substances released by the wood and on the sensory characteristics of Montepulciano

© 2020 International Viticulture and Enology Society - IVES

d'Abruzzo. *Journal of Food Science*, 73(7), S373–S382. doi:10.1111/j.1750-3841.2008.00891.x

Cano-Lopez M., Bautista-Ortin A.B., Pardo-Minguez F., Lopez-Roca J.M. and Gomez-Plaza E., 2008. Sensory descriptive analysis of a red wine aged with oak chips in stainless steel tanks or used barrels: Effect of the contact time and size of the oak chips. *Journal of Food Quality*, 31(5), 645–660. doi:10.1111/j.1745-4557.2008.00226.x

Chatonnet P., 2008. Situation et évolution de l'utilisation des alternatives dans le monde. *La Revue Des Oenologues*, 2(3), 45–48.

de Simón B.F., Cadahía E., Muiño I., Del Álamo M. and Nevares I., 2010. Volatile composition of toasted oak chips and staves and of red wine aged with them. *American Journal of Enology and Viticulture*, 61(2), 157–165.

Del Álamo M., Nevares I., Gallego L., Martin C. and Merino S., 2008. Aging markers from bottled red wine aged with chips, staves and barrels. *Analytica Chimica Acta*, 621(1), 86–99. doi:10.1016/j.aca.2008.05.014

Ebeler S.E., Takeoka G.R. and Winterhalter P., 2011. Progress in authentication of food and wine. Volume 1081. *American Chemical Society*. doi:10.1021/bk-2011-1081

García-Carpintero E.G., Gallego M.G., Sánchez-Palomo E. and Viñas M.G., 2012. Impact of alternative technique to ageing using oak chips in alcoholic or in malolactic fermentation on volatile and sensory composition of red wines. *Food Chemistry*, 134(2), 851–863. doi:10.1016/j.foodchem.2012.02.194

Gutiérrez Afonso V.L., 2002. Sensory descriptive analysis between white wines fermented with oak chips and in barrels. *Journal of Food Science*, 67(6), 2415–2419. doi:10.1111/j.1365-2621.2002.tb09563.x

Hammer Ø., Harper D.A.T. and Ryan P.D., 2001. PAST-palaeontological statistics, ver. 1.89. *Palaeontologia Electronica*, 4(9).

Hernández-Orte P., Franco E., Huerta C.G., García J.M., Cabellos M., Suberviola J., Orriolis I. and Cacho J., 2014. Criteria to discriminate between wines aged in oak barrels and macerated with oak fragments. *Food Research International*, 57, 234–241. doi:10.1016/j.foodres.2014.01.044

Nardi T., Petrozziello M., Girotto R., Fugaro M., Mazzei R.A. and Scuppa S., 2020. Wine aging authentication through Near Infrared Spectroscopy: A feasibility study on chips and barrel aged wines. OENO One, 54(1), 165–173. doi: 10.20870/oeno-one.2020.54.1.2921

Ortega-Heras M., Pérez-Magariño S., Cano-Mozo E. and González-San José M.L., 2010. Differences in the phenolic composition and sensory profile between red wines aged in oak barrels and wines aged with oak chips. *LWT-Food Science and Technology*, 43(10), 1533–1541. doi:10.1016/j.lwt.2010.05.026

Pérez-Coello M.S. and Díaz-Maroto M.C., 2009. Volatile compounds and wine aging. In Wine chemistry and biochemistry (pp. 295–311). Springer. doi:10.1007/978-0-387-74118-5_16

Regione Piemonte, 2017. Regione Piemonte - Disciplinari di Produzione vini DOCG e DOC. Retrieved March 29, 2018, from www.regione.piemonte.it website: http://www.regione.piemonte.it/agri/politiche_agricole/viticoltura/elenco.htm

Tablino L., 2013. Truccioli: Vecchi e nuovi - Lorenzo Tablino - Enologo. Retrieved September 24, 2019, from Lorenzo Tablino - Enologo website: http://tablino.it/592/truccioli-vecchi-e-nuovi/

Triacca M., Boldi M.O. and Rawyler A., 2013. Différenciation des vins de barrique et de copeaux. *Revue Suisse Viticulture*, Arboriculture, Horticulture, 45(4), 240–247.

 © 2020 International Viticulture and Enology Society - IVES