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Determination of fermentative volatile compounds in aged red wines by near infrared spectroscopy

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ABSTRACT

The purpose of this work was to study the possibility of determination of fermentative volatile compounds in aged red wines using NIR spectroscopy. To achieve this, 240 wines belonging to different geographic zones and elaborated with one or two varieties were analyzed. The volatile compounds were quantified by SBSE-GC–MS. Spectra obtained by NIR were co-related with these values using partial least square (PLS) regression. Calibration and validation statistics showed the quality of the model, after all when is done separately for each of the four geographic zones, and in the case of wines elaborated with two varieties. Consequently, near infrared spectroscopy can be used as an easy and rapid tool to determine fermentative volatile compounds in aged red wines.

1. Introduction

Wines aged in oak barrels undergo changes, which modify their aroma remarkably (Garde-Cerdán, Rodríguez-Mozaz, & Ancín-Azpilicueta, 2002; Lorenzo, Pardo, Zalacain, Alonso, & Salinas, 2008). However, there is currently an ever-increasing demand for quality wines aged in oak barrels which also preserve the volatile fermentation products that give freshness, plus floral and fruit flavours. Even though many compounds are formed during alcoholic fermentation, not all of them contribute in the same way to the final flavour of wine. In this sense, ethyl esters of fatty acids, such as ethyl octanoate and ethyl decanoate, and fusel alcohol acetates, such as 2-phenylethyl acetate, are considered very important contributors to wine aroma, exhibiting floral and fruity odours (Díaz-Maroto, Schneider, & Baumes, 2005; Vianna & Ebeler, 2001). Fusel alcohols, mainly 2-phenylethanol, along with short-chain fatty acids, can also contribute to the total wine aroma when they are not at high concentrations (Etiévant, 1991). In addition, ethyl esters of organic acids seem to play only a limited role in the organoleptic qualities of healthy wines (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2001), although it has been observed that they are markers for wines aged in bottles (Francioli, Torrens, Riu-Aumatell, López-Tamames, & Buxaderas, 2003) and in oak barrels (Garde-Cerdán et al., 2009).

The analysis of these compounds is complicated because they are often present in trace amounts, so sophisticated methods and instrumentation have been developed to facilitate the accurate and precise measurement of these compounds in wines. Generally wineries do not have the equipment necessary to determine volatile compounds. During recent years, developments in both chemometrics and instrumentation have resulted in rapid methods relating multivariate spectroscopic and chemical data for predicting the concentration of specific chemical constituents, thus helping to reduce the demand for traditional analysis using chemical reagents. Near infrared spectroscopy (NIR) is both a rapid and non-destructive technique and generally requires minimal sample processing prior to analysis (Deaville & Flinn, 2000; Givens & Deaville, 1999), which is why many wineries purchase this equipment. Quantitative NIR measurements are usually based on the concentration between sample composition, as determined by defined reference methods, and the absorption of light at different wavelengths in the near infrared region measured by either reflectance or transmission spectroscopy.

At present, several studies have been found in relation to the use of NIR spectroscopy to predict different groups of compounds in wines. This technique has been studied to predict phenolic compounds (Cozzolino, Kwiatkowski, Parker, Cynkar, Dambergs, & Gishen, et al., 2004; Tarantilis, Troianou, Pappas, Kotseridis, & Polissiou, 2008), tannins and dry matter (Cozzolino, Cynkar, Dambergs, Mercurio, & Smith, 2008), different elements (Cozzolino, Kwiatkowski, Dambergs, Cynkar, Janik, & Skouroumounis, et al., 2008) and classical enological parameters (Urbano-Cuadrado, Luque de Castro, Pérez-Juan, García-Olmo, & Gómez-Nieto, 2004). However, only one paper was found in the literature in relation to the use of NIR spectroscopy to analyze fermentative volatile compounds in Riesling wine. In that paper, the volatile compounds were grouped according to their chemical nature (Smyth et al., 2008). For the reasons mentioned above, the aim of this work was to study the possibility of determining the presence of volatile

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fermentation products in quality wines aged in oak barrels using NIR spectroscopy. For this purpose, 240 barrel-aged wines from different Spanish Origin Designations (OD) were analyzed. As the sample number was very high, results coming from fermentation products were divided in wines belonging to different geographic zones and wines elaborated with one or two grape varieties.

2. Material and methods

2.1. Samples

In order to obtain a broader and more realistic wine sample distribution from the consumer point of view, samples were selected as follows**:** information was collected from the Spanish Ministry of Agriculture, Fisheries and Food (MAPA, 2004) on domestic trade and wine production volume, which affirmed that 95% of the Spanish Origin Designations produced more than 30,000 hl. Wine selection was then carried out in various local supermarkets of eight Spanish cities according to the data obtained, where four OD (Rioja, Mancha, Ribera del Duero and Valdepeñas) made up approximately 72% of all commercialized red wines. The other Spanish OD selected in this study were chosen for the information given by the MAPA**,** but also trying to extend it in relation to the different geographical wine production zones.

For this study, 240 aged red wines with different brands were analyzed (three bottles of each brand, with each bottle belonging to different lots). Zone 1 included the following origin appellations: Ribera del Duero, Navarra and Rioja (96 samples); zone 2: La Mancha and Valdepeñas (84 samples); zone 3: Jumilla and Valencia (30 samples), and zone 4: Penedés and Somontano (30 samples). Samples were acquired in different shops. Aged red wines were classified into wines elaborated with one grape variety and those elaborated with two varieties. These varieties (and the number of samples) were: *Tempranillo* (111), *Cabernet Sauvignon* (24), *Monastrell* (8), *Graciano* (3), *Tempranillo* + others (87), and others (7).

2.2. NIR analysis

Samples were analyzed by Perkin–Elmer Spectrum One FT-NIR equipment with flow cell quartz 1.0 mm. Data collection was acquired over a wavelength range of 1200–10,000 cm^{-1}. Chemometric analysis was performed using Spectrum Quant + software (Perkin–Elmer). The spectra were pre-processed using the standard normal variate (SNV) transformation followed by first-derivative transformation to reduce baseline variation and enhance the spectral features (Barnes, Dhanoa, & Lister, 1989). Calibrations were developed using partial least square regression (PLS). Global calibration statistics included the standard error of calibration (SEC), the standard error of prediction (SEP) and the coefficient of determination in calibration (R^2 cal). When the calibration was done for each of the four zones and according to the number of varieties, the cumulative *Y*-variance and the regression coefficient (RC) were also included. To evaluate how well the calibration model could predict the volatile composition of wines, we used the full cross validation. Statistics calculated for the full cross validation included the coefficient of determination in validation (R^2) and the standard error of cross validation (SECV).

Table 2
Global calibration statistics for fermentative compounds measured in aged red wines by near infrared spectroscopy (mg/l).

	SEC[a]	SEP[b]	LV[c]
Ethyl octanoate	0.07	0.07	10
Ethyl decanoate	0.04	0.04	10
Ethyl 2-phenylacetate	0.002	0.002	10
Diethyl succinate	0.78	0.80	10
Diethyl glutarate	0.003	0.003	10
2-Phenylethyl acetate	0.02	0.02	10
2-Phenylethanol	3.99	4.08	10
Hexanoic acid	0.15	0.15	10
Octanoic acid	0.28	0.28	10

[a] SEC: standard error of calibration.
[b] SEP: standard error of prediction.
[c] LV: number of latent variables.

2.3. Analysis of fermentative volatile compounds by gas chromatography

In order to focus on the compounds mentioned in the introduction, in addition to prolonging chromatographer life, the detector was opened 10 min after the injection so that the most volatile compounds would not be detected. The volatile compounds ethyl octanoate, ethyl decanoate, ethyl 2-phenylacetate, diethyl succinate, diethyl glutarate, 2-phenylethyl acetate, 2-phenylethanol, hexanoic acid, and octanoic acid (Sigma–Aldrich, Madrid, Spain) were analyzed following the method described by Marín, Zalacain, De Miguel, Alonso, and Salinas (2005). Compounds were extracted by introducing a polymethylsiloxane coated stir bar (0.5 mm film thickness, 10 mm length, Twister, Gerstel, Mülheim and der Ruhr, Germany) into 10 ml of sample, to which 100 µl of internal standard γ-hexalactone solution at 1 µl/ml in absolute ethanol (Merck, Damstard, Germany) was added. Samples were stirred at 700 rpm at room temperature for 60 min. The stir bar was then removed from the sample, rinsed with distilled water and dried with a cellulose tissue, and later transferred into a thermal desorption tube for GC–MS analysis.

In the thermal desorption tube, the volatile compounds were desorbed from the stir bar under the following conditions: oven temperature at 330 °C; desorption time, 4 min; cold trap temperature, −30 °C; helium inlet flow 45 ml/min. The compounds were

Table 1
Descriptive statistics of fermentative compounds in aged red wines (mg/l).

	Mean value	SD[a]	Maximum	Minimum	CV (%)[b]
Ethyl octanoate	2.42	0.83	6.26	0.74	34.35
Ethyl decanoate	0.95	0.39	2.93	0.10	40.73
Ethyl 2-phenylacetate	0.04	0.03	0.16	0.01	70.81
Diethyl succinate	22.36	7.16	63.98	7.75	32.00
Diethyl glutarate	0.11	0.05	0.27	0.03	43.02
2-Phenylethyl acetate	0.27	0.15	0.94	0.07	56.14
2-Phenylethanol	92.90	38.29	248.16	35.48	41.22
Hexanoic acid	3.69	1.62	12.78	0.10	44.02
Octanoic acid	6.92	2.69	22.07	1.79	38.84

[a] SD: standard deviation.
[b] CV = [SD/mean] × 100.