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Analytical Methods

Employment of near infrared spectroscopy to determine oak volatile compounds and ethylphenols in aged red wines

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ABSTRACT

The aim of this work was to study the ability of NIR spectroscopy to determine oak volatile compounds and ethylphenols levels in aged red wines. For this purpose 510 wines aged with different storage time and in different oak barrel types were analyzed. Calibration models were developed from SBSE-GC–MS and NIR data using partial least squares (PLS) regression. In order to validate the calibration, full cross validation was employed. Results showed that the calibration statistics were very good ($R^2 > 0.86$) for all the compounds studied. In wines aged in French and in American and French oak barrels, and in "*reserva*" and "*gran reserva*" wines, the residual predictive deviation (RPD) obtained was higher than 1.5 in all the compounds and it was higher than 2 in some of the cases. In conclusion, near infrared spectroscopy can be used as a rapid tool to determine oak volatile compounds and ethylphenols in aged red wines.

1. Introduction

Oak wood compounds extracted to the wine during barrel aging are of great importance since they modify their aroma remarkably (Díaz-Plaza, Reyero, Pardo, and Salinas, 2002; Garde-Cerdán & Ancín-Azpilicueta, 2006; Lorenzo, Pardo, Zalacain, Alonso, & Salinas, 2008), contributing to the woody, smoky and spicy hints of wines. It is known that the quantity of compounds potentially extractable from oak barrels by wine depends mainly on the geographical origin and on the species of oak (Miller, Howell, Michaelis, & Dickmann, 1992; Mosedale, Puech, & Feuillat, 1999), on the seasoning of the staves (Cadahía, Muñoz, Fernández de Simón, & García-Vallejo, 2001), on the toasting of the barrel (Hale, McCafferty, Larmie, Newton, & Swan, 1999) and on the age of the barrel (Garde-Cerdán, Rodríguez-Mozaz, & Ancín-Azpilicueta, 2002a; Pérez-Prieto, López-Roca, Martínez-Cutillas, Pardo-Mínguez, & Gómez-Plaza, 2002). Once extracted, the compounds from oak wood can undergo chemical or biochemical transformations in the wine (Boidron, Chatonnet, & Pons, 1988) and, in consequence, their concentration can be modified (Garde-Cerdán, Torrea-Goñi, & Ancín-Azpilicueta, 2002b). Moreover, wine composition can also affect the accumulation of volatile compounds coming from oak wood (Garde-Cerdán, Torrea-Goñi, & Ancín-Azpilicueta, 2004; Garde-Cerdán et al., 2008; Ortega-Heras, González-Sanjosé, & González-Huerta, 2007).

The analysis of these compounds is complicated because they have different chemical natures and are often only present in trace amounts. Therefore, sophisticated methods and instrumentation, like gas chromatography, have been developed in order to facilitate the accurate and precise measurement of these compounds in wines. Generally the wineries don't have this kind of equipment, which is necessary to determination of volatile compounds. During recent years, developments in both chemometrics and instrumentation have resulted in rapid methods which relate multivariate spectroscopic and chemical data in order to predict the concentration of specific chemical constituents and also to reduce the demand for traditional analysis using chemical reagents. Near infrared spectroscopy is a rapid and non-destructive technique, generally requiring minimal sample processing prior to analysis (Deaville & Flinn, 2000; Givens & Deaville, 1999). Quantitative near infrared spectroscopy measurements are usually based on the relation between the concentration of sample components, 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 carried out in relation to the use of near infrared spectroscopy to predict different groups of compounds in wines. This technique has been studied to predict phenolic compounds (Cozzolino et al., 2004; Tarantilis, Troianou, Pappas, Kotseridis, & Polissiou, 2008), tannins and dry matter (Cozzolino, Cynkar, Dambergs, Mercurio, and Smith, 2008), fermentative compounds in Riesling wine (Smyth et al., 2008) and in barrel-aged red wines (Lorenzo, Garde-Cerdán, Pedroza, Alonso, & Salinas, 2009), different elements (Cozzolino et al., 2008) and classical enological parameters (Urbano-Cuadrado, Luque de Castro, Pérez-Juan, García-Olmo, & Gómez-Nieto, 2004). In these

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papers, the compounds analyzed were found in the wines at levels of µg/l and mg/l, except in the last work, in which enological parameters were determined, in general, at concentrations of g/l. However, no reports were found in the literature in relation to the use of near infrared spectroscopy to analyze oak volatile compounds and ethylphenols in wines. Therefore, the purpose of this work was to study the possibility of determining these volatile compounds in wines using near infrared spectroscopy.

2. Material and methods

2.1. Samples

In order to have the broadest and most realistic wine sample distribution from the consumer point of view, the selection of samples was done as follows. The starting point was the information afforded by the Spanish Ministry of Agriculture, Fisheries and Food (MAPA, 2004) about domestic trade and wine production volume, which affirmed that 95% of the Spanish Origin Designations (O.D.) produced more than 30,000 hl. Wine selection was carried out in local supermarkets in 8 Spanish cities according to the data obtained, where four O.D. (Rioja, Mancha, Ribera del Duero and Valdepeñas) commercialized around 72% of all red wines. The selection of the other Spanish O.D. was based on the information given by the MAPA but also trying to extend it in relation to the different geographical wine production areas.

For this study, 510 aged red wines were analyzed, from a total of 170 brands (3 bottles of each brand, with each bottle belonging to different lots). Aged red wines are classified, according to their ageing process, into three different administrative categories: "*crianza*" wines (red wines with an ageing of at least 6 months in oak barrels), "*reserva*" (red wines with an ageing time of at least 12 months in barrels), and "*gran reserva*" (exceptional quality red wines aged for at least 18 months in oak barrels). The total amount of samples analyzed in this study was: 267 "*crianza*" wines, 189 "*reserva*" wines, and 54 "*gran reserva*" wines. 390 wines were aged in American oak barrels, 54 were aged in American and French oak barrels, and 66 were aged in French oak barrels.

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 1200–10000 cm^{-1} but the water absorption regions (4500–5500 and 7000–7800 cm^{-1}) were not employed. 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). Calibration statistics included the standard error of calibration (SEC), the standard error of prediction (SEP) and the coefficient of determination in calibration (R^2cal). To evaluate how well the calibration model could predict 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).

2.3. Analysis of volatile oak compounds and ethylphenols by gas chromatography

The volatile compounds cis-oak lactone, trans-oak lactone, guaiacol, eugenol, furfural, 5-methylfurfural, 4-ethylphenol, and 4-ethylguaiacol (Sigma–Aldrich, Madrid, Spain) were analyzed following the method described by Marín, Zalacain, De Miguel, Alonso, and Salinas (2005). Compounds were extracted by introducing the 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 at 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 transferred into the Hewlett–Packard LC 3D mass detector (Palo Alto, USA) with a fused silica capillary column (BP21 stationary phase 50 m length, 0.22 mm i.d., and 0.25 µm film thickness) (SGE, Ringwood, Australia). The chromatographic program was set at 50 °C (held for 5 min), raised to 180 °C at 2.5 °C/min (held for 2 min) and to 230 °C (5 °C/min) and held for 20 min. For mass spectrometry analysis, electron impact mode (EI) at 70 eV was used. The mass range varied from 35 to 500 *m/z* and the detector temperature was 150 °C. Identification was carried out using the NIST library and by comparison with the mass spectrum and retention index of chromatographic standards designed by us and data found in the bibliography. Quantification was based on 5-point calibration curves of respective standards ($R^2 > 0.94$) in a 12% ethanol (v/v) solution at pH 3.6.

3. Results and discussion

The NIR spectroscopic technique is based on measurement of the frequencies of vibrations of chemical bonds in functional group such as C-C, C-H, O-H, C = O and N-H upon absorption of radiation in the NIR region. For the functional groups present in the volatile compounds studied, the vibration bands corresponding to C-H are at 1340–1470, 2850–2970 and 3010–3100 cm-1; the band corresponding to O-H is at 3590–3650 cm-1; to C = C is at 1500–1680 cm-1; the vibration band corresponding to C-O is at 1050–1300 cm-1 and to C = O is at 1690–1760 cm-1. In Fig. 1 is shown a NIR spectrum of a wine.

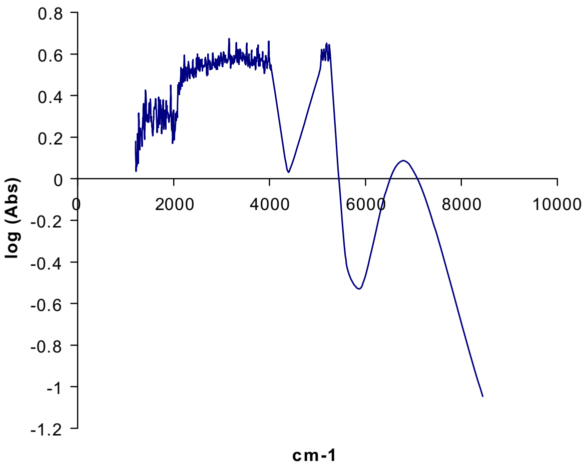

Fig. 1. Near-infrared spectrum of a typical barrel-aged red wine.

3.1. Content of volatile oak compounds and ethylphenols in the wines

In a previous paper of our research group about the analysis of these compounds, we observed that the detection limit (LOD) was between 0.10 ng/l for 5-methylfurfural and 38.93 µg/l for guaiacol and the quantification limit (LOQ) was between 0.11 ng/l for 5-methylfurfural and 39.23 µg/l for guaiacol (Marín et al., 2005). The maximum value of furfural in the wines studied (Table 1) was above its perception threshold (20 mg/l) (Boidron et al., 1988). Nevertheless, 5-methylfurfural was not over its perception threshold (45 mg/l) (Boidron et al., 1988) in any of the samples studied. These two compounds, which possess a grilled almond aroma and enhance the perception of oak lactones (Reazin, 1981), are present in some of the wines (Table 1). In the case of guaiacol, its mean value was slightly above its perception threshold (0.075 mg/l) (Boidron et al., 1988), and there was no presence of this compound in some samples (Table 1). Eugenol was below its perception threshold (0.5 mg/l) (Boidron et al., 1988). These two volatile phenols, guaiacol and eugenol, add smoky and spicy aromas to the wine.

Table 1
Descriptive statistics of oak volatile compounds and ethylphenols (mg/l) in aged red wines (crianza, reserva and gran reserva) from the different geographic areas.

	Mean value	SD[a]	Maximum	Minimum	CV (%)[b]
Total wines					
Furfural	4.94	4.47	23.65	0.00	90.60
5-Methylfurfural	0.21	0.25	1.06	0.00	116.35
Guaiacol	0.09	0.11	0.59	0.00	116.94
Eugenol	0.10	0.06	0.34	0.00	63.06
cis-Oak lactone	1.37	0.93	5.61	0.08	67.55
trans-Oak lactone	0.21	0.14	0.83	0.01	67.57
4-Ethylphenol	1.72	1.58	9.73	0.00	91.52
4-Ethylguaiacol	0.54	0.51	3.23	0.00	94.20
Ratio cis/trans	7.18	2.80	19.48	1.51	38.95
Ratio 4-EP/4-EG	3.07	1.71	8.05	0.00	55.71
Crianza wines					
Furfural	4.56	4.10	22.72	0.00	89.89
5-Methylfurfural	0.19	0.24	1.06	0.00	125.82
Guaiacol	0.07	0.11	0.59	0.00	150.40
Eugenol	0.10	0.06	0.33	0.00	62.60
cis-Oak lactone	1.29	0.85	5.03	0.17	66.48
trans-Oak lactone	0.19	0.12	0.61	0.03	64.54
4-Ethylphenol	1.45	1.30	5.78	0.00	89.44
4-Ethylguaiacol	0.60	0.57	3.23	0.00	95.22
Ratio cis/trans	7.23	2.68	19.48	1.63	36.13
Ratio 4-EP/4-EG	2.19	1.05	5.33	0.00	48.14
Reserva wines					
Furfural	5.33	4.59	19.65	0.00	86.07
5-Methylfurfural	0.25	0.26	0.90	0.00	102.80
Guaiacol	0.12	0.10	0.48	0.00	85.91
Eugenol	0.10	0.06	0.34	0.00	63.61
cis-Oak lactone	1.37	0.94	5.61	0.08	68.28
trans-Oak lactone	0.21	0.13	0.65	0.01	64.78
4-Ethylphenol	1.96	1.91	9.73	0.00	97.36
4-Ethylguaiacol	0.45	0.44	2.27	0.00	97.52
Ratio cis/trans	7.27	2.76	14.49	1.51	37.94
Ratio 4-EP/4-EG	3.97	1.91	8.05	0.00	48.16
Gran reserva wines					
Furfural	5.42	5.63	23.65	0.00	103.94
5-Methylfurfural	0.19	0.23	0.85	0.00	125.26
Guaiacol	0.10	0.11	0.37	0.00	108.40
Eugenol	0.13	0.07	0.29	0.00	59.79
cis-Oak lactone	1.81	1.12	5.45	0.32	61.82
trans-Oak lactone	0.36	0.19	0.83	0.04	52.26
4-Ethylphenol	2.23	1.27	5.31	0.00	57.05
4-Ethylguaiacol	0.52	0.28	1.32	0.00	53.30
Ratio cis/trans	5.68	3.08	14.21	2.01	54.22
Ratio 4-EP/4-EG	4.23	1.12	5.93	0.00	26.54

[a] SD: Standard deviation.
[b] CV=[S. D./mean]x100.

The only compounds coming from oak wood that were present in all the wines studied were the two isomers, *cis* and *trans*, of the β-methyl-γ-octalactone (Table 1). Therefore, these compounds could be used as indicators to show that a wine has been aged in the presence of oak wood. *cis*-Oak lactone was above its perception threshold (0.046 mg/l) (Wilkinson, Elsey, Prager, Tanaka, & Sefton, 2004) in all the wines (Table 1); in the case of the *trans* isomer, its mean value for all the samples (0.21 mg/l) was inferior to its perception threshold (0.46 mg/l) (Chatonnet, Boidron, & Pons, 1990). These two lactones produce woody and coconut-like aromas in the wine, which add quality. The mean value of 4-ethylphenol (4-EP) and 4-ethylguaicol (4-EG) in wines was, in all cases, above the values from which these compounds can contribute negatively to wine quality (0.62 mg/l and 0.14 mg/l, respectively) (Chatonnet, Dubourdieu, Boidron, & Pons, 1992), since these are responsible for the medicinal and horsey off-odours found in some red wines.

The mean value of the ratio *cis*/*trans* (7.18) confirmed that most of the wines studied were aged in American oak barrels, since American oak species give a greater quantity of *cis*-oak lactone to the wine as compared to European oaks. Several studies confirm this affirmation (Díaz-Plaza, Reyero, Pardo, Alonso, & Salinas, 2002; Garde-Cerdán et al., 2002a; Pérez-Prieto et al., 2002; Towey & Waterhouse, 1996). The mean value of the ratio 4-EP/4-EG was 3.07, a value inferior to the 8.0 value found by Pollnitz, Pardon, and Sefton (2000). These authors observed that this ratio is a function of the grape variety, observing values from 3.5 for the *Pinot Noir* variety to 10.1 for the *Cabernet Sauvignon* variety. Within the wines, a wide range of concentrations of 4-ethylphenol and 4-ethylguaiacol was observed, consistent with the results of Pollnitz et al. (2000) and Chatonnet et al. (1992), who have demonstrated the importance of winemaking practices in the formation of these compounds.

As can be observed in Table 1, the coefficient of variation for these compounds was high, which is reasonable when taking into account the great variability in ageing time, geographic area and barrel type for wines studied, factors greatly affecting the concentration of these compounds.

3.2. Calibration and validation for the volatile compounds using NIR spectroscopy

Table 2 and Fig. 2 show the PLS calibration for the volatile compounds studied. The value for the coefficient of determination in calibration (R^2) was similar in all the compounds (0.87, except in 5-metylfurfural and 4-ethylguaiacol, in which it was 0.86) (Fig. 2). As can be observed, the correlation between the values determined by GC-MS and the values estimated by the NIR calibra-

Table 2
Calibration statistics for oak volatile compounds and ethylphenols measured in aged red wines by near infrared spectroscopy (mg/l).

	SEC[a]	SEP[b]	LV[c]
Furfural	1.60	1.62	10
5-Methylfurfural	0.09	0.10	10
Guaiacol	0.04	0.04	10
Eugenol	0.02	0.02	10
cis-Oak lactone	0.33	0.34	10
trans-Oak lactone	0.05	0.05	10
4-Ethylphenol	0.57	0.58	10
4-Ethylguaiacol	0.19	0.19	10
Ratio *cis*/*trans*	0.98	0.99	10
Ratio 4-EP/4-EG	0.63	0.64	10

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

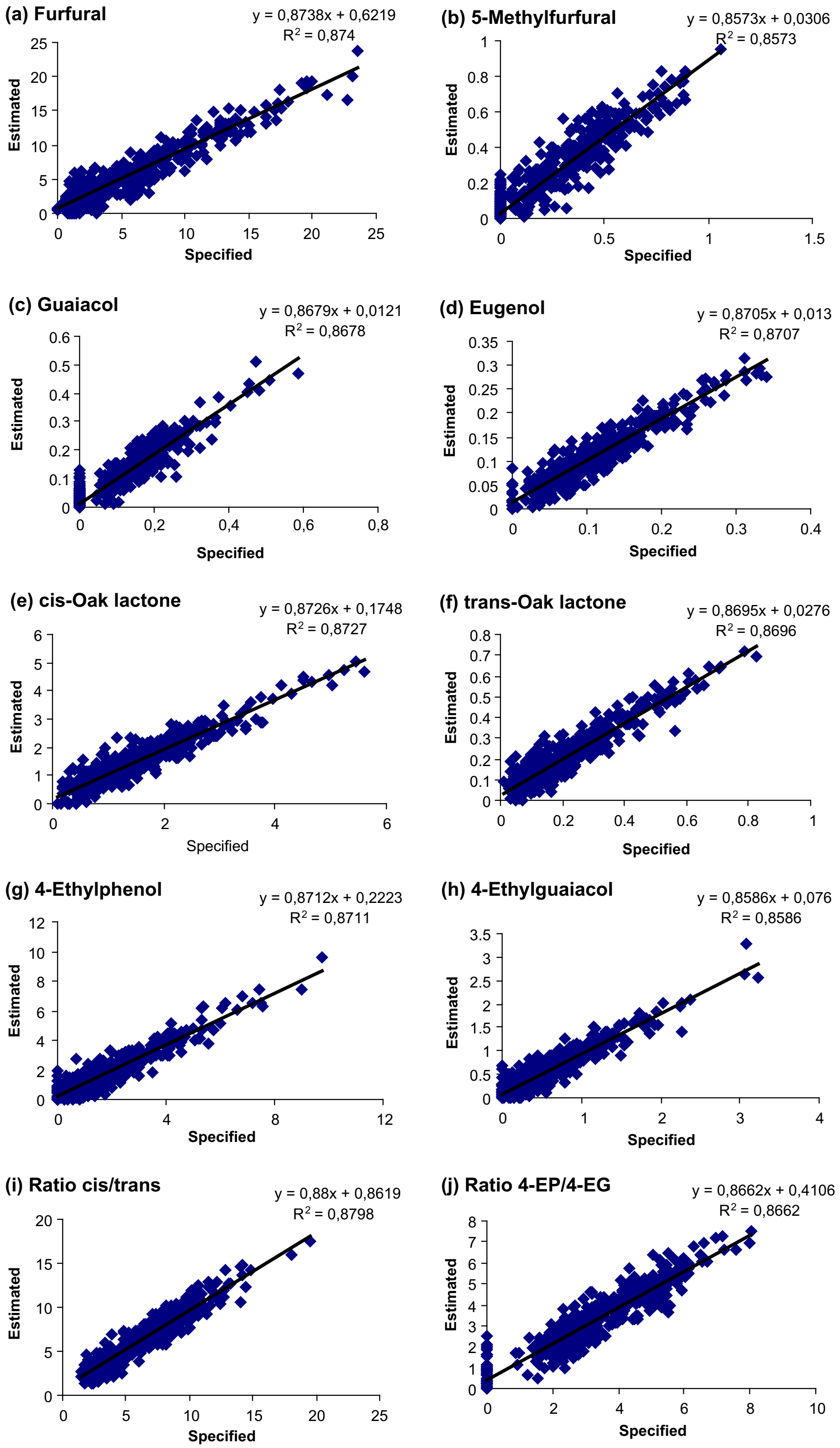

Fig. 2. Correlation between the concentration of oak volatile compound and ethylphenols (mg/l) determined by GC-MS, and the values estimated by the NIR using PLS in aged red wines.

tion for the volatile compounds was very good. The model did not remove any samples since there was no dispersion of values and therefore no outliers. The SEC was between 1.60 in furfural and 0.02 in eugenol, and SEP ranged from 1.62 in furfural to 0.02 in eugenol (Table 2). These results showed that NIR spectroscopy provides a suitable prediction of volatile compounds, indicating that the PLS models based on NIR spectra explain the 86–87% of the variation in the data.

Table 3
Full cross validation statistics for oak volatile compounds and ethylphenols measured in aged red wines by near infrared spectroscopy (mg/l).

		Furfural	5-Methyl furfural	Guaiacol	Eugenol	*cis*-Oak lactone	*trans*-Oak lactone	4-Ethylphenol	4-Ethylguaiacol	Ratio *cis*/*trans*	Ratio 4-EP/4-EG
Total (N = 510)	R^2	0.34	0.32	0.32	0.32	0.33	0.34	0.32	0.27	0.24	0.29
	SECV	3.60	0.21	0.09	0.05	0.76	0.12	1.30	0.43	2.44	1.45
	RPD	1.24	1.19	1.22	1.20	1.22	1.17	1.22	1.19	1.15	1.18
American (N = 390)	R^2	0.39	0.34	0.35	0.40	0.41	0.40	0.40	0.35	0.32	0.33
	SECV	3.60	0.20	0.09	0.05	0.74	0.09	1.18	0.43	1.88	1.32
	RPD	1.29	1.25	1.22	1.40	1.30	1.33	1.30	1.23	1.21	1.23
French (N = 66)	R^2	0.79	0.71	0.71	0.71	0.75	0.69	0.79	0.71	0.78	0.83
	SECV	1.80	0.14	0.05	0.03	0.31	0.11	0.68	0.25	0.86	0.77
	RPD	2.16	1.86	1.80	1.67	2.00	1.73	2.16	1.84	2.13	2.44
American and French (N = 54)	R^2	0.79	0.74	0.79	0.74	0.73	0.77	0.81	0.80	0.71	0.75
	SECV	1.80	0.13	0.05	0.03	0.43	0.07	0.84	0.17	1.53	0.97
	RPD	2.15	1.92	2.20	1.67	1.91	2.00	2.27	2.29	1.85	2.00
Crianza (N = 267)	R^2	0.37	0.41	0.48	0.40	0.43	0.33	0.34	0.33	0.43	0.40
	SECV	3.27	0.19	0.08	0.05	0.65	0.10	1.06	0.47	2.04	0.82
	RPD	1.25	1.26	1.38	1.20	1.31	1.20	1.23	1.21	1.31	1.28
Reserva (N = 189)	R^2	0.55	0.58	0.50	0.53	0.59	0.62	0.58	0.57	0.56	0.56
	SECV	3.07	0.17	0.07	0.04	0.60	0.08	1.24	0.29	1.83	1.28
	RPD	1.50	1.53	1.49	1.50	1.57	1.63	1.54	1.52	1.51	1.49
Gran Reserva (N = 54)	R^2	0.79	0.84	0.79	0.82	0.80	0.73	0.81	0.81	0.82	0.75
	SECV	2.51	0.09	0.05	0.03	0.50	0.10	0.56	0.12	1.31	0.57
	RPD	2.24	2.56	2.20	2.33	2.24	1.90	2.27	2.33	2.35	1.96

N: number of samples in validation.
R^2: coefficient of determination in full cross validation.
SECV: standard error in full cross validation.
RPD: residual predictive deviation (SD/SECV).

In order to validate the calibration we chose the full cross validation. This technique is based on the calibration data only. First, sample one in the calibration set is deleted. Then, the calibration is performed on the rest of the samples before it is tested on the first sample by comparing the specified value (determined by GC-MS) with the estimated. The first sample is then put back into the calibration set, and the procedure is repeated by deleting sample two. The procedure continues until all samples have been deleted once (Naes, Isaksson, Fearn, & Davies, 2002).

Due to the high number of samples (510), the full cross validation was not adequate (Table 3), as also found by other authors (Geladi & Kowalski, 1986). Therefore we grouped the samples according to oak type used for ageing (American, French, American and French), and also according to wine storage time in the barrels (“*crianza*”, “*reserva*”, “*gran reserva*”). As can be observed in Table 3, the lower the number of samples, the better the validation was, as show by some of the most important statistics. For example, the coefficient of determination in cross validation (R^2) for one of the most important oak volatile compounds, i.e. *cis*-oak lactone, was 0.43 for “*crianza*” wines (N = 267), 0.59 for “*reserva*” wines (N = 189) and 0.80 for “*gran reserva*” wines (N = 54); and SECV was 0.65 mg/l for “*crianza*” wines, 0.60 mg/l for “*reserva*” wines and 0.50 mg/l for “*gran reserva*” wines.

The residual predictive deviation (RPD), defined as the ratio between the standard deviation of the population (SD) and the SECV for the NIR predictions, is a useful statistic that is often applied to evaluate how well a calibration model can predict the volatile compounds (Fearn, 2002). If the SECV is large compared with the range of compositions (as SD), a relatively small RPD value results, and the NIR calibration model is not considered robust. A RPD value greater than 3 is considered fair and recommended for screening purposes (Smyth et al., 2008). However, a more qualitative interpretation of the RPD is given by other authors where a RPD value lower than 1.5 was considered insufficient for most applications, while NIR calibration models with values greater than 2 were considered excellent (Williams, 2001). The RPD obtained was higher than 1.5 in all the compounds in wines aged in French and in American and French oak, and in “*reserva*” and “*gran reserva*” wines, and it was higher than 2 in some of the cases (Table 3).

4. Conclusions

Oak volatile compounds and ethylphenols in aged red wines can be determined easily and rapidly by near infrared spectroscopy. The first group of compounds is very important for their positive contribution to total aroma of the wines. In addition, the presence of ethylphenols may cause rejection of wines by consumers with the resulting economic loss to the wineries. Therefore, the wineries could have a reasonable tool to the determination of these compounds in wines, which does not require for its management qualify personal, although it is necessary to calibrate the NIR in parallel with GC/MS.

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