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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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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.

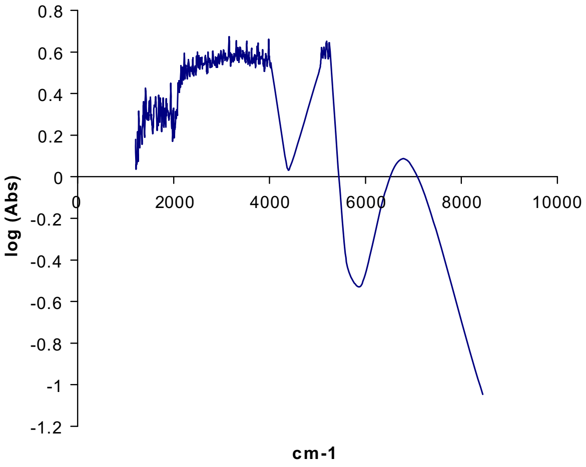

Fig. 1. Near-infrared spectrum of a typical barrel-aged red wine.