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CLASSIFICATION OF RED WINES FROM CONTROLLED DESIGNATION OF ORIGIN BY ULTRAVIOLET-VISIBLE AND NEAR-INFRARED SPECTRAL ANALYSIS

CLASSIFICAÇÃO DE VINHOS TINTOS DE DENOMINAÇÕES DE ORIGEM ATRAVÉS DA ANÁLISE ESPECTRAL ULTRAVIOLETA-VISÍVEL E INFRAVERMELHO PRÓXIMO

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SUMMARY

Spectroscopy has become one of the most attractive and commonly used methods of analysis in many agricultural products. Chemometrics combined with ultraviolet (UV), visible (VIS) and near-infrared (NIR) spectral analysis were evaluated to classify wines between two controlled designation of origin (DO) of Spain (Rías Baixas and Riberia Sacra). The aim of this work was to determine the feasibility of using the UV-VIS-NIR spectroscopy combined with chemometrics tools to discriminate between red wines of different DO. Support Vector Machine (SVM) and Linear Discriminant Analysis (LDA) were applied to classify the red wines by their UV-VIS-NIR spectra. Several pre-treatments were applied to improve the classification. The best classification of red wines was obtained in UV-VIS-NIR raw data for LDA models (100% of classification). Results of classification with SVM classification models were slightly lower than LDA results (97.3% for the pretreatment Centred and scaled). This shows the importance of a good selection of the chemometric method of classification. UV, VIS and NIR spectral data with chemometrics tools showed the feasibility of classifying red wines.

RESUMO

A espectroscopia tornou-se um dos métodos de análise mais atrativos e de uso comum em muitos produtos agrícolas. A análise quimiométrica combinada com as análises espectrais no ultravioleta (UV), no visível (VIS) e no infravermelho próximo (NIR) foram avaliadas para classificar vinhos de duas denominações de origem (DO) espanholas (Rías Baixas e Ribeira Sacra). O objetivo deste trabalho consistiu na determinação da viabilidade do uso da espectroscopia UV-VIS-NIR combinada com ferramentas quimiométricas para discriminar vinhos tintos de diferentes DO. Máquina de Vectores de Suporte (SVM) e Análise Linear Discriminante (LDA) foram aplicadas para classificar os vinhos tintos com base nos seus espectros UV-VIS-NIR. Vários pré-tratamentos foram aplicados para melhorar a classificação. A melhor classificação dos vinhos tintos foi obtida com dados brutos UV-VIS-NIR em modelos LDA (100% da classificação). Os resultados da classificação com modelos de classificação SVM foram ligeiramente mais baixos do que os resultados da LDA (97,3% para o pré-tratamento Centrado e escalado). Estes aspetos evidenciam a importância de uma boa seleção do método quimiométrico de classificação. É ainda demonstrada a viabilidade da utilização de dados espectrais UV, VIS e NIR combinados com ferramentas quimiométricas para a classificação de vinhos tintos.

Key words: NIR, LDA, SVM, red wine, Chemometrics, PCA.
Palavras-chave: NIR, LDA, SVM, vinho tinto, quimiometria, PCA.

INTRODUCTION

The wine production sector is one of the most important industry in Spain, having 69 designation of origin (DO). Galicia is a region of Norwest of Spain with high tradition of wine industry. This region has climatic and topographic conditions different to other regions of production in Spain, allowing wines with different component profile from others. Galicia has five DO (Rías Baixas, Ribeira Sacra, Monterrei, Valdeorras and Ribeiro) (Figueiredo-González *et al.*, 2012).

There is a public interest in wine quality, methods of production and safety of production and consumption (Cozzolino *et al.*, 2011). The wineries demand techniques and highly controlled processes to obtain the highest quality for their products. Furthermore, the methods must be rapid, wide-ranging and easy (Garde-Cerdán *et al.*, 2012a,b).

Grape and grape products, as wine, are a natural source of compounds with important health benefits such as antioxidant, anti-inflammatory, antibacterial and anticarcinogenic activities (Atanacković *et al.*, 2012; Chouchouli *et al.*, 2013; Toaldo *et al.*, 2013).

Wine is a complex mixture of different compounds at several concentrations (Tarantilis *et al.*, 2008; Astray *et al.*, 2010; Ferrer-Gallego *et al.*, 2011; Shen *et al.*, 2012a). Water and ethanol are the main compounds. However, other compounds as glycerol, sugars, organic acids, metals and polyphenols provide different characteristics to wines (Caruso *et al.*, 2012). Generally different methods used to analyse

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concentrations, compositions and differentiation of wines, such as gas chromatography, mass spectrometry and liquid chromatography waste time and require time and are labour intensive due to sample preparation, time of analysis, preparation of reagents which can be expensive (Cozzolino *et al.*, 2012; Fudge *et al.*, 2013).

Different methods and analytical techniques together inexpensive and powerful computers have developed and optimized to analyse wine composition in several fields as medical, pharmaceutical, petrochemical or food production. These techniques and methods combined with chemometric analyses allow to determine origin of foods, adulterated foods and composition (Cozzolino *et al.*, 2011; Perez *et al.*, 2011; Villagra *et al.*, 2012; Alamprese *et al.*, 2013). Recently, techniques of spectroscopy become in promising techniques that increase the speed of analysis and the same time they decrease the cost. Additionally, they have minimal requirements and preparation of samples are not needed (Canaza-Cayo *et al.*, 2012)

Techniques based on spectral data have been applied to determine composition, characterization and detection of adulterations of agricultural products (Fudge *et al.*, 2011) as oil (Rohman and Man, 2011; Luna *et al.*, 2013; Pizarro *et al.*, 2013), honey (Rios-Corripio *et al.*, 2012), meat (Villagra *et al.*, 2012; Alamprese *et al.*, 2013), diverse vegetables (Serranti *et al.*, 2013) and fruit and juices (Ferrer-Gallego *et al.*, 2012).

Near infrared spectroscopy (NIR) is a non-destructive method for measuring of chemical compounds in heterogeneous products as wine (Chauchard *et al.*, 2004; Martelo-Vidal *et al.*, 2013). This technique is used to determine properties of foods for obtaining the characteristics (Cozzolino *et al.*, 2012) and chemical composition. Sometimes, Visible (VIS) and Ultraviolet (UV) spectral data are included due to the presence of pigments in foods like red wines (Alamprese *et al.*, 2013; Martelo-Vidal and Vázquez, 2014a). Characterisation of wines using multivariate data analysis according the geographical origin can be very useful when there is a large quantity of experimental data. The analysis of spectral data usually is performed using statistical procedures called chemometrics tools.

Principal component analysis (PCA) is a multivariate technique that uses a mathematical procedure to transform a set of correlated response variables into principal components (PCs), generating a new set of non-correlated variables. This principal component represent de pattern of observations in maps (Abdi and Williams, 2010; Martelo-Vidal *et al.*, 2013) and provide information about structure of data (Martelo-Vidal *et al.*, 2013).

Supervised and unsupervised methods are the two principal methods to classify and interpret data matrix (Cozzolino *et al.*, 2011). In unsupervised methods, the samples give the algorithm without information on belong to any class, however in supervised methods, data training are composed by a set of training samples and to perform the models and output of cases, are used training samples (Cetó *et al.*, 2013).

For the supervised method Linear Discriminant Analysis (LDA), the categories are defined previously and samples are belonging each category (Cozzolino *et al.*, 2011; Cetó *et al.*, 2013; Martelo-Vidal *et al.*, 2013). LDA method search discriminate functions achieving maximum separation between categories maximize variance between classes and minimising the variance in the class (Pizarro *et al.*, 2013). LDA technique can use three methods (linear, quadratic and mahalanobis methods).

Support Vector Machine (SVM) is another supervised method of classification. SVM can classify linear and no linear multivariate samples. It is a method of classification that successfully applied to high number of classifications. Advantages of SVM over other classification methods are that produce a solution unique and are less susceptible to overfitting (Callejón *et al.*, 2012; Martelo-Vidal *et al.*, 2013). SVM can use four methods (linear, polynomial, Radial Basic Function and Sigmoid methods).

The aim of this work was to determine the feasibility of using the UV, VIS and NIR spectroscopy combined with chemometrics tools to discriminate between red wines of different DO. All the chemometrics tools cited above were used to classify different red wines of DO Rías Baixas and Ribeira Sacra (Spain) in this study.

MATERIAL AND METHODS

Samples

The samples were obtained from Regulatory Council of Rías Baixas (19 samples, Table I) and Regulatory Council of Ribeira Sacra (20 samples, Table II). All samples were stored in refrigeration at 5ºC until the time of analysis.

Spectral measurements

Samples were analysed in spectrophotometer V-670 (Jasco Inc, Japan) using transmittance mode in UV/VIS/NIR regions from 190 nm to 2500 nm at 2 nm intervals. Quartz cell with 1 mm path length was used to scan samples (Martelo-Vidal *et al.*, 2013). Samples were equilibrated at 33 ºC (Cozzolino *et al.*, 2007) for 10 min before scanning (Martelo-Vidal *et al.*, 2013). Samples were scanned in duplicate obtaining 78 spectra.

Multivariate data analysis

Data were exported from Spectra Manager^{TM} II software (Jasco Inc, Japan) and imported into Unscrambler software (version X 10.2; CAMO ASA, Oslo, Norway) for pre-treatment and classification analysis. Two replicates of each sample (78 spectra) were analysed in Unscrambler software.

TABLE I

Red wines of DO Rías Baixas analysed in this study

Vinhos Tintos da DO Rías Baixas analisados neste estudo

Sample	DO	Variety	Vintage
RB-1	Rías Baixas	Sousón	2011
RB-2	Rías Baixas	Sousón (n.e.), Bancellao (n.e.), Caiño (n.e)	2011
RB-3	Rías Baixas	Loureira	2010
RB-4	Rías Baixas	Sousón(85%), Mencía (10%), Espadeiro (5%)	2011
RB-5	Rías Baixas	Mencía	2011
RB-6	Rías Baixas	Caíño	2010
RB-7	Rías Baixas	Mencía	2011
RB-8	Rías Baixas	Caíño (n.e.), Mencía (n.e.)	2010
RB-9	Rías Baixas	Mencía	2011
RB-10	Rías Baixas	Caíño	2011
RB-11	Rías Baixas	Brancellao (60%), Caíño (40%)	2011
RB-12	Rías Baixas	Espadeiro	2010
RB-13	Rías Baixas	Pedral	2011
RB-14	Rías Baixas	Mencía	2010
RB-15	Rías Baixas	Sousón	2011
RB-16	Rías Baixas	Mencía	2011
RB-17	Rías Baixas	Mencía	2011
RB-18	Rías Baixas	Caíño	2011
RB-19	Rías Baixas	Caíño (n.e.), Mencía (n.e.), Sousón (+70%)	2011

DO: Designation of Origin

PCA was applied to explore data and to obtain relevant information such as to detect outliers and the possible grouping of samples (Cozzolino *et al.*, 2012; Ferrer-Gallego *et al.*, 2012; Cetó *et al.*, 2013; Kečkeš *et al.*, 2013; Martelo-Vidal *et al.*, 2013; Shen *et al.*, 2012b).

The spectra were pre-treated with different techniques and combinations of then (application of a sequence of several pretreatments on the same spectra) to reduce noise and remove or minimise different phenomenon as scatter effects or baseline variations (Luna *et al.*, 2013). Multiplicative Scatter Correction (MSC), Savizky-Golay smoothing, Centred and Scaled, Savizky-Golay second derived, Standar Normal Variate (SNV), De-trending, Baseline correction and their combinations were applied in this study (Martelo-Vidal and Vázquez, 2014b).

TABLE II

Red wines of DO Ribeira Sacra analysed in this study

Vinhos Tintos da DO Ribeira Sacra analisados neste estudo

Sample	DO	Variety	Vintage
RS-1	Ribeira Sacra	Mencía	2010
RS-2	Ribeira Sacra	Mencía	2010
RS-3	Ribeira Sacra	Mencía	2010
RS-4	Ribeira Sacra	n.e.	2010
RS-5	Ribeira Sacra	Mencía	2011
RS-6	Ribeira Sacra	Mencía	2011
RS-7	Ribeira Sacra	Mencía	2010
RS-8	Ribeira Sacra	Mencía	2010
RS-9	Ribeira Sacra	Mencía	2011
RS-10	Ribeira Sacra	n.e.	2010
RS-11	Ribeira Sacra	Mencía	2011
RS-12	Ribeira Sacra	Mencía	2011
RS-13	Ribeira Sacra	Mencía	2011
RS-14	Ribeira Sacra	Mencía	2011
RS-15	Ribeira Sacra	Mencía	2011
RS-16	Ribeira Sacra	Mencía	2010
RS-17	Ribeira Sacra	Mencía	2010
RS-18	Ribeira Sacra	Mencía	2011
RS-19	Ribeira Sacra	Mencía	2011
RS-20	Ribeira Sacra	Mencía	2011

DO: Designation of Origin; (n.e.) not especified

LDA and SVM calibration models were developed to raw and pre-treated data using cross validation to validate models of classification.

RESULTS AND DISCUSSION

Red wines UV-VIS-NIR spectra are shown in Figure 1. Visual differences can be found. UV and VIS zones (290 to 850 nm) showed clear differences between the wines of study. NIR zone also showed differences although they were not so clear as UV and VIS zones.

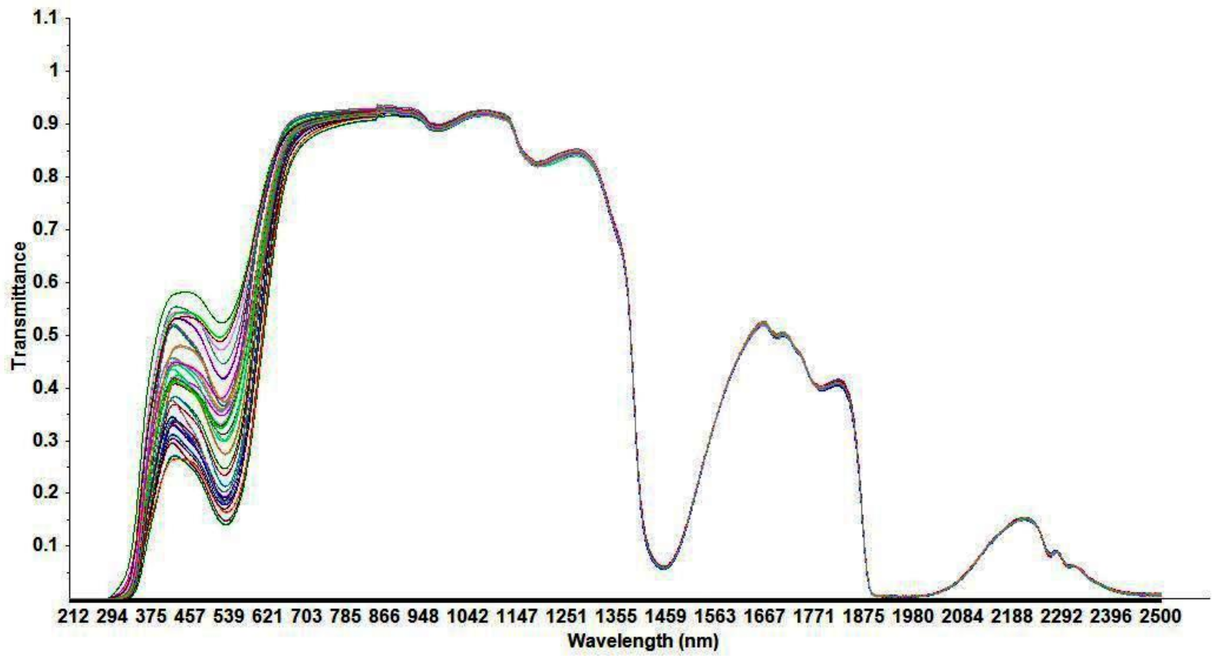

Figure 1 - Spectral data of red wines.

Dados espectrais dos vinhos tintos

First and second derived of Savitzky-Golay derivation transformations showed the zones of absorption of wines are showed with peaks more pronounced as can be seen in Figure 2 (Cozzolino *et al.*, 2003, 2004). Ethanol absorptions at 1600 and 1900 nm are related to O-H combinations and C-H stretch first overtones, water absorption bands at 950 and 1460 nm are related with third overtone of O-H. Around 540 nm and 2200-2300 nm are related to combinations vibration and overtones of ethanol, sugars, phenolic compounds, condensed tannins and nitrogen compounds (Cozzolino *et al.*, 2004). Aromatic acids and sugars present variations in 990 nm by O-H stretch second overtones and sugars. Absorptions were observed at 1690 nm and 1750 nm related to C-H_3 stretch first overtone and C-H_2, C-H stretch first overtone respectively in glucose, ethanol and water (Martelo-Vidal *et al.*, 2013).

Score plot of PCA (Figure 3) of raw data for two first principal components explain 97 % of total variance of the spectra in wines analyzed. Separation of DO Rías Baixas and Ribeira Sacra is not clear because the samples are overlapped. However, there are a tendency of samples of wines from DO Ribeira Sacra are spread along of PC1 and samples from DO Rías Baixas are spread along of PC2.

The eigenvectors of PCA were analysed to investigate the basis of the separation obtained between DO Rías Baixas and DO Ribeira Sacra. In Figure 4 shows the first two PCs explain 97 % of variation observed. First PC explains 96 % of variation present highest loading around 350 to 600 nm. This spectral region is characteristic of pigments from red wines. For example, oenin has at maximum absorption at 530 nm and malvin at 529 nm (Martelo-Vidal and Vázquez, 2014a,c). Second PC explain 1% of the variation and the loading showed inverse correlation with visible and ultraviolet region, around 1500 nm, 1800 nm and around 2300 nm (Cozzolino *et al.*, 2012).

LDA and SVM were performed for classification analysis of the red wines. The classification methods were applied to raw and pre-processed data.

Table III show the proportion of DO Rías Baixas and Ribeira Sacra wines correctly classified when SVM was applied. Pre-processed data with centred and scaled data were showed a proportion of right classification of 97.37 % with 100 % of right

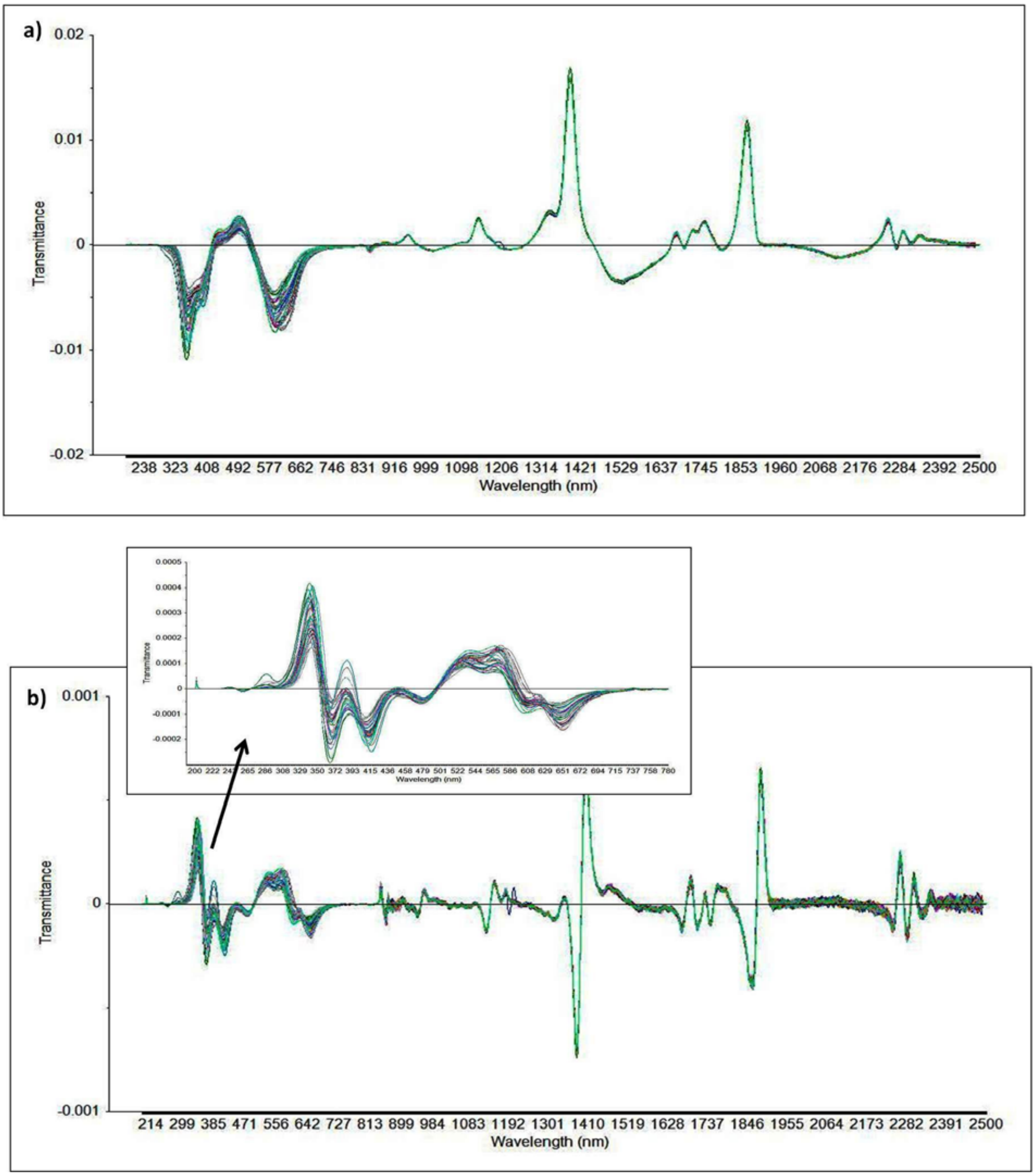

Figure 2 - Spectral data of red wines in first (a) and second (b) Savicky-Golay derived.

Dados espectrais dos vinhos tintos na primeira (a) e segunda (b) derivada Savicky-Golay.

classification of wines for Ribeira Sacra DO and 94.74 % right classification for Rías Baixas DO wines. Raw data and Smoothing, MSC, SNV + Smoothing and MSC + Baseline showed a 94.74 % of total corrected classification of wines being 89.47 % corrected classification proportion for Rías Baixas DO wines and 100 % corrected classification proportion for Ribeira Sacra DO wines. Worse classification were obtained with SNV + Smoothing + 2nd derived and MSC + Baseline + 2nd derived pre-treatments being the poorest classification for Rías Baixas DO wines with 5.26 % of corrected classification. The SVM models obtained did not allowed a total classification of 100%.

Classification rates with LDA of Rías Baixas and Ribeira Sacra red wines according their DO are showed in Table IV. In this case, a total classification

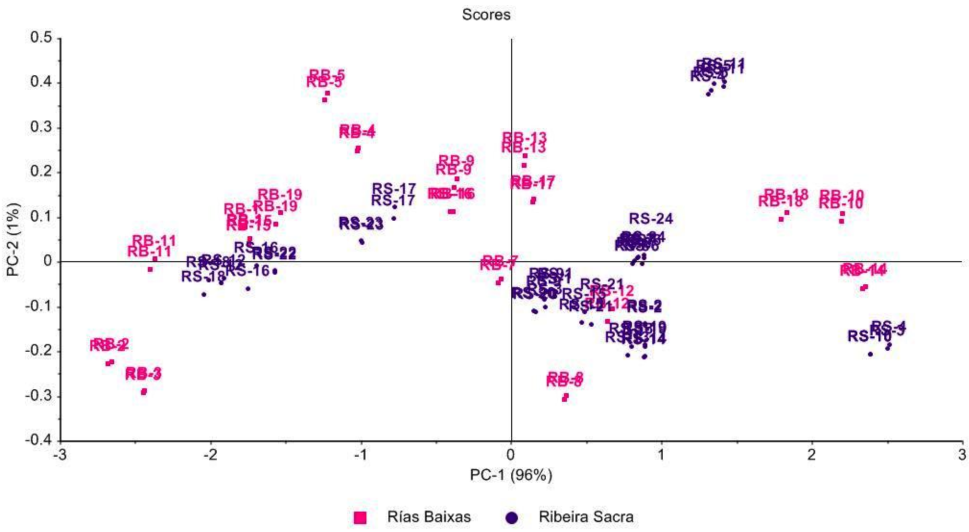

Figure 3 - Score plot of two first principal components (PC) of Rías Baixas and Ribeira Sacra red wines.

Projeção das classificações dos vinhos tintos de Rías Baixas e de Ribeira Sacra nas duas primeiras componentes principais (PC).

of 100 % was obtained with raw data and pre-treatments smoothing, MSC, SNV + De-trending, SNV + Smoothing, MSC + Smoothing and Centred and Scaled. With pre-treatment SNV + Smoothing + 2nd derived and with MSC + Smoothing + 2nd derived the proportion of classification was 98.68 % (100 % corrected classification for DO Ribeira Sacra and 97.37 % corrected classification for DO Rías Baixas), followed by pre-treatments Normalize + SNV + 2nd derived, SNV + De-trending + 2nd derived, MSC + Baseline + 2nd derived and with MSC + Baseline proportion of right classification were 97.43 % (97.37 % correct classification for DO Rías Baixas and 97.50 % for DO Ribeira Sacra). The results showed models for a total classification of 100%. Note that wines from DO Ribeira Sacra was almost all done with mencia grape variety. This variety exists also in some wines from DO Rias

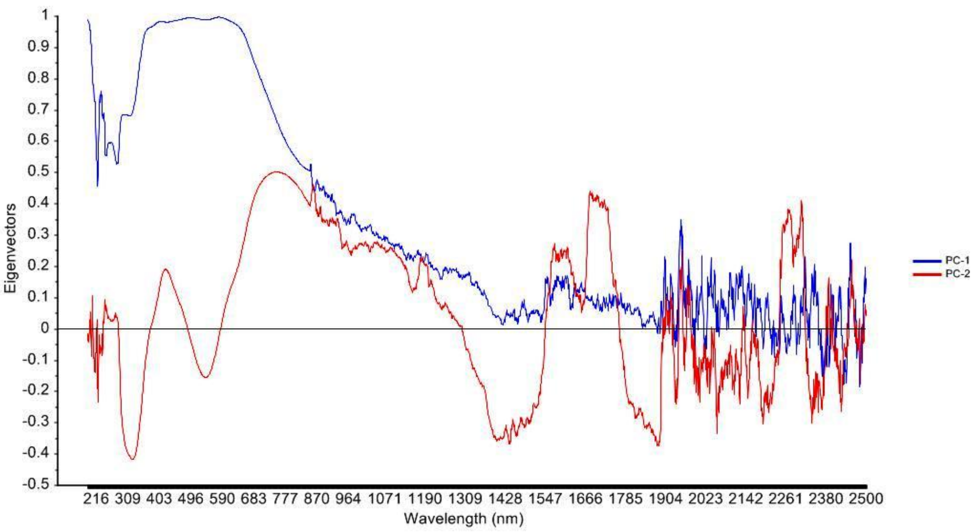

Figure 4 - Eigenvectors for the PCA of two principal components (PC) of red wines analysed from Rías Baixas and Ribeira Sacra Designation of Origin.

Eigenvectors das duas componentes principais (PC) da análise PCA dos vinhos tintos das Denominações de Origem Rías Baixas e Ribeira Sacra.

Baixas. The 100% classification means that the variety is not the origin of the differences in the wine spectra. The regions have different climatic and topographic conditions allowing wines with different component profile from others. This allows the application of this technique to authentication purposes of red wines although they were made with the same grape variety.

TABLE III

Proportion (%) of support vector machine (SVM) classification of red wines according to Designation of Origin

Proporção (%) de classificação da máquina de vectores de suporte (SVM) de vinhos tintos em função da Denominação de Origem

Pre-treatment	RíasBaixas (%)	RibeiraSacra (%)	Total Classification (%)
Raw	89.47	100.00	94.74
Smoothing	89.47	100.00	94.74
Normalize + SNV + 2nd derived	63.16	90.00	76.58
MSC	89.47	100.00	94.74
SNV + De-trending + 2nd derived	60.53	80.00	70.26
SNV + De-trending	89.47	92.50	90.99
SNV + Smoothing + 2nd derived	5.26	97.50	51.38
SNV + Smoothing	89.47	100.00	94.74
MSC + Smoothing + 2nd derived	5.26	100.00	52.63
MSC + Smoothing	94.74	70.00	82.37
MSC + Baseline + 2nd derived	5.26	97.50	51.38
MSC + Baseline	89.47	100.00	94.74
Centred and scaled	94.74	100.00	97.37

TABLE IV

Proportion (%) of linear discriminant analysis (LDA) classification of red wines according to Designation of Origin

Proporção (%) de classificação da análise linear discriminante (LDA) de vinhos tintos em função da Denominação de Origem

Pre-treatment	RíasBaixas (%)	RibeiraSacra (%)	Total Classification (%)
Raw	100.00	100.00	100.00
Smoothing	100.00	100.00	100.00
Normalize + SNV + 2nd derived	97.37	97.50	97.43
MSC	100.00	100.00	100.00
SNV + De-trending + 2nd derived	97.37	97.50	97.43
SNV + De-trending	100.00	100.00	100.00
SNV + Smoothing + 2nd derived	97.37	100.00	98.68
SNV + Smoothing	100.00	100.00	100.00
MSC + Smoothing + 2nd derived	97.37	100.00	98.68
MSC + Smoothing	100.00	100.00	100.00
MSC + Baseline + 2nd derived	97.37	97.50	97.43
MSC + Baseline	97.37	97.50	97.43
Centred and scaled	100.00	100.00	100.00

CONCLUSIONS

UV, VIS and NIR spectral data with chemometrics tools showed the feasibility of classifying red wines from DO Rías Baixas and Ribeira Sacra. The best classification of red wines was obtained in raw UV-VIS-NIR raw data for LDA models. Results of classification with SVM classification models were slightly lower than LDA results. This shows the importance of a good selection of the chemometric method of classification.

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REFERENCES

Abdi H., Williams L.J., 2010. Principal component analysis. *Wiley Interdiscip. Rev. Comput. Stat.,* **2**, 433-459.

Alamprese C., Casale M., Sinelli N., Lanteri S., Casiraghi E., 2013. Detection of minced beef adulteration with turkey meat by UV-vis, NIR and MIR spectroscopy. *Lwt-Food Sci. Technol.,* **53**, 225-232.

Astray G., Castillo J.X., Ferreiro-Lage J.A., Galvez J.F., Mejuto J.C., 2010. Artificial neural networks: A promising tool to evaluate the authenticity of wine redes neuronales: Una herramienta prometedora para evaluar la autenticidad del vino. *Cyta-J. Food,* **8**, 79-86.

Atanacković M., Petrović A., Jović S., Bukarica L.G., Bursać M., Cvejić J., 2012. Influence of winemaking techniques on the resveratrol content, total phenolic content and antioxidant potential of red wines. *Food Chem.,* **131**, 513-518.

Callejón R.M., Amigo J.M., Pairo E., Garmón S., Ocaña J.A., Morales M.L., 2012. Classification of sherry vinegars by combining multidimensional fluorescence, parafac and different classification approaches. *Talanta,* **88**, 456-462.

Canaza-Cayo A., Cozzolino D., Alomar D., Quispe E., 2012. A feasibility study of the classification of alpaca (< i> lama pacos) wool samples from different ages, sex and color by means of visible and near infrared reflectance spectroscopy. *Comput. Electron. Agr.,* **88**, 141-147.

Caruso M., Galgano F., Morelli M.A.C., Viggiani L., Lencioni L., Giussani B., Favati F., 2012. Chemical profile of white wines produced from 'greco bianco' grape variety in different italian areas by nuclear magnetic resonance (NMR) and conventional physicochemical analyses. *J. Agric. Food Chem.*, **60**, 7-15.

Cetó X., Gutiérrez-Capitán M., Calvo D., Del Valle M., 2013. Beer classification by means of a potentiometric electronic tongue. *Food Chem.,* **141**, 2533-2540.

Chauchard F., Cogdill R., Roussel S., Roger J., Bellon-Maurel V., 2004. Application of LS-SVM to non-linear phenomena in NIR spectroscopy: Development of a robust and portable sensor for acidity prediction in grapes. *Chemometr. Intell. Lab.,* **71**, 141-150.

Chouchouli V., Kalogeropoulos N., Konteles S.J., Karvela E., Makris D.P., Karathanos V.T., 2013. Fortification of yoghurts with grape (*Vitis vinifera*) seed extracts. *Lwt-Food Sci. Technol.,* **53**, 522-529.

Cozzolino D., Cynkar W.U., Shah N., Smith P., 2011. Multivariate data analysis applied to spectroscopy: Potential application to juice and fruit quality. *Food Res. Int.,* **44**, 1888-1896.

Cozzolino D., Kwiatkowski M.J., Parker M., Cynkar W.U., Dambergs R.G., Gishen M., Herderich M.J., 2004. Prediction of phenolic compounds in red wine fermentations by visible and near infrared spectroscopy. *Anal. Chim. Acta,* **513**, 73-80.

Cozzolino D., McCarthy J., Bartowsky E., 2012. Comparison of near infrared and mid infrared spectroscopy to discriminate between wines produced by different *Oenococcus oeni* strains after malolactic fermentation: A feasibility study. *Food Control,* **26**, 81-87.

Cozzolino D., Smyth H., Gishen M., 2003. Feasibility study on the use of visible and near-infrared spectroscopy together with chemometrics to discriminate between commercial white wines of different varietal origins. *J. Agric. Food Chem.,* **51**, 7703-7708.

Ferrer-Gallego R., Hernández-Hierro J.M., Rivas-Gonzalo J.C., Escribano-Bailón M.T., 2012. A comparative study to distinguish the vineyard of origin by NIRS using entire grapes, skins and seeds. *J. Sci. Food Agr.,* **93**, 967-972.

Ferrer-Gallego R., Hernandez-Hierro J.M., Rivas-Gonzalo J.C., Escribano-Bailon M.T., 2011. Multivariate analysis of sensory data of *Vitis vinifera* L. cv. graciano during ripening. correlation with the phenolic composition of the grape skins. *Cyta-J. Food,* **9**, 290-294.

Figueiredo-González M., Simal-Gándara J., Boso S., Martínez M.C., Santiago J.L., Cancho-Grande B., 2012. Anthocyanins and flavonols berries from *Vitis vinifera* L. cv. brancellao separately collected from two different positions within the cluster. *Food Chem.,* **135**, 47-56.

Fudge A.L., Wilkinson K.L., Ristic R., Cozzolino D., 2011. Classification of smoke tainted wines using mid-infrared spectroscopy and chemometrics. *J. Agric. Food Chem.,* **60**, 52-59.

Fudge A.L., Wilkinson K.L., Ristic R., Cozzolino D., 2013. Synchronous two-dimensional MIR correlation spectroscopy (2D-COS) as a novel method for screening smoke tainted wine. *Food Chem.,* **139**, 115-119.

Garde-Cerdán T., Lorenzo C., Alonso G.L., Salinas M.R., 2012a. Review of the use of near infrared spectroscopy to determine different wine parameters: Discrimination between wines. *Curr Bioact Compd.,* **8**, 353-369.

Garde-Cerdán T., Lorenzo C., Zalacain A., Alonso G.L., Salinas M.R., 2012b. Using near infrared spectroscopy to determine haloanisoles and halophenols in barrel aged red wines. *Lwt-Food Sci. Technol.,* **46**, 401-405.

Kečkeš S., Gašić U., Veličković T.Ć, Milojković-Opsenica D., Natić M., Tešić Ž., 2013. The determination of phenolic profiles of serbian unifloral honeys using ultra-high-performance liquid chromatography/high resolution accurate mass spectrometry. *Food Chem.,* **138**, 32-40.

Luna A.S., da Silva A.P., Ferre J., Boque R., 2013. Classification of edible oils and modeling of their physico-chemical properties by chemometric methods using mid-IR spectroscopy. *Spectrochim. Acta A,* **100**, 109-114.

Martelo-Vidal M., Domínguez-Agis F., Vázquez M., 2013. Ultraviolet/visible/near-infrared spectral analysis and chemometric tools for the discrimination of wines between subzones inside a controlled designation of origin: A case study of rías baixas. *Aust. J. Grape Wine Res.,* **19**, 62-67.

Martelo-Vidal M., Vázquez M., 2014a. Determination of polyphenolic compounds of red wines by UV–VIS–NIR spectroscopy and chemometrics tools. *Food Chem.*, **158**, 28-34.

Martelo-Vidal M., Vázquez M. 2014b. Application of artificial neural networks coupled to UV–VIS–NIR spectroscopy for the rapid quantification of wine compounds in aqueous mixtures. *Cyta-J. Food* (In press. http://dx.doi.org/10.1080/19476337.2014.908955).

Martelo-Vidal M., Vázquez M., 2014c. Evaluation of ultraviolet, visible and near infrared spectroscopy for the analysis of wine compounds. *Czech J. Food Sci*., **32,** 37-47.

Perez Trujillo J.P., Perez Pont M.L., Conde Gonzalez J.E., 2011. Content of mineral ions in wines from canary islands (spain). *Cyta-J. Food*, **9**, 135-140.

Pizarro C., Rodríguez-Tecedor S., Pérez-del-Notario N., Esteban-Díez I., González-Sáiz J.M., 2013. Classification of spanish extra virgin olive oils by data fusion of visible spectroscopic fingerprints and chemical descriptors. *Food Chem.,* **138**, 915-922.

Rios-Corripio M.A., Rojas Lopez M., Delgado Macuil R., 2012. Analysis of adulteration in honey with standard sugar solutions and syrups using attenuated total reflectance-Fourier Transform Infrared spectroscopy and multivariate methods. *Cyta-J. Food,* **10**, 119-122.

Rohman A., Man Y.B.C., 2011. Analysis of chicken fat as adulterant in cod liver oil using Fourier Transform Infrared (FTIR) spectroscopy and chemometrics. *Cyta-J. Food,* **9**, 187-191.

Serranti S., Cesare D., Marini F., Bonifazi G., 2013. Classification of oat and groat kernels using NIR hyperspectral imaging. *Talanta*, **103**, 276-284.

Shen F., Li F., Liu D., Xu H., Ying Y., Li B., 2012a. Ageing status characterization of chinese rice wines using chemical descriptors combined with multivariate data analysis. *Food Control,* **25**, 458-463.

Shen F., Yang D., Ying Y., Li B., Zheng Y., Jiang T., 2012b. Discrimination between shaoxing wines and other Chinese rice wines by near-infrared spectroscopy and chemometrics. *Food and Bioprocess Tech.,* **5**, 786-795.

Tarantilis P.A., Troianou V.E., Pappas C.S., Kotseridis Y.S., Polissiou M.G., 2008. Differentiation of Greek red wines on the basis of grape variety using attenuated total reflectance Fourier Transform Infrared Spectroscopy. *Food Chem.,* **111**, 192-196.

Toaldo I.M., Fogolari O., Pimentel G.C., de Gois J.S., Borges D. L.G., Caliari V., Bordignon-Luiz M., 2013. Effect of grape seeds on the polyphenol bioactive content and elemental composition by ICP-MS of grape juices from *Vitis labrusca* L. *Lwt-Food Sci. Technol.,* **53**, 1-8.