Modeling excitation–emission fluorescence matrices with pattern recognition algorithms for classification of Argentine white wines according grape variety

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ABSTRACT

This paper reports the modeling of excitation–emission matrices for classification of Argentinean white wines according to the grape variety employing chemometric tools for pattern recognition. The discriminative power of the data was first investigated using Principal Component Analysis (PCA) and Parallel Factor Analysis (PARAFAC). The score plots showed strong overlapping between classes. A forty-one samples set was partitioned into training and test sets by the Kennard–Stone algorithm. The algorithms evaluated were SIMCA, N- and U-PLS-DA and SPA–LDA. The fit of the implemented models was assessed by mean of accuracy, sensitivity and specificity. These models were then used to assign the type of grape of the wines corresponding to the twenty samples test set. The best results were obtained for U-PLS-DA and SPA–LDA with 76% and 80% accuracy.

1. Introduction

Wine is a fermented alcoholic beverage containing various compounds of different type, with polyphenols being one of the most important components which influence their quality parameters (Fernández-Pachón, Villaño, García-Parrilla, & Troncoso, 2004). Polyphenols contribute to the organoleptic characteristics, such as color, astringency and bitterness and also exert antimicrobial and antioxidant properties. In addition, other substances such as amino acids, anthocyanin and ethanol, are present in wine (Godoy-Navajas, Aguilar-Caballos, & Gómez-Hens, 2015).

Authenticity and commercial value of wines is often linked to its geographical origin and certain countries or regions are known for producing excellent wines of high commercial value (Šelih, Šala, & Drgan, 2014). Due to its composition and worldwide availability, the controlled denomination of origin (CDO) is usually required to demonstrate the provenance of wines. In the same way, due the cost and/or production volume of several varieties of white wines in comparison to others, the control of grape variety is usually required to avoid the adulteration or fraud in fractioned or selected wines, which can involve the use of high cost analytical methods and well trained analysts (de Villiers, Alberts, Lynen, Crouch, & Sandra, 2003; Wang, Geil, Kolling, & Padua, 2003).

According to data from 2013, Chardonnay, Sauvignon blanc and Torrontés were the main white wines varieties produced in Argentina, while the main producer provinces were Rio Negro Mendoza, San Juan and Salta. Torrontés has been the most exported white wine variety over the last year, followed to Chardonnay and Sauvignon blanc in second and third place, respectively: USA, Canada, Russia and United Kingdom were the main importers of these wines (Instituto Nacional de Vitivinicultura, 2014).

Many efforts have been devoted to the development of new analytical methods for the quality control of wines worldwide (Briz-Cid, Figueiredo-Gonzalez, Rial-Otero, Cancho-Grande, & Simal-Gandara, 2015; González-Álvarez, Noguerol-Pato,

González-Barreiro, Cancho-Grande, & Simal-Gándara, 2013), with molecular absorption spectroscopy and gas or liquid chromatography coupled to mass spectrometry detection (GC–MS and LC–MS) being the most common instrumentation (de Villiers, Alberts, Tredoux, & Nieuwoudt, 2012).

Recently, Markechová and collaborators employed fluorescence excitation–emission matrices (EEM) and Parallel Factor Analysis (PARAFAC) for the determination of brandy adulteration with mixed wine spirit (Markechová, Majek, & Sádecká, 2014). However, the use of fluorescence spectroscopy for quality control of wines regarding the authenticity of the grape type, geographic origin, brand, or fingerprint has been scarcely explored. For example, Dufour et al., employed both excitation and emission spectra for French and German wine classification (Dufour, Letort, Laguet, Lebecque, & Serra, 2006), and Sádecká et al. reported the classification of brandies and wine distillates using total luminescence and synchronous fluorescence spectra (Sádecká, Tóthová, & Májek, 2009), but only first-order data and algorithms were used in an unsupervised manner in both cases. On the other hand, Ariado-Rodrigues and collaborators employed EEM and PARAFAC for fingerprinting of red wines (Airado-Rodríguez, Galeano-Díaz, Durán-Merás, & Wold, 2009) and quality control in the wine industry (Airado-Rodríguez, Durán-Merás, Galeano-Díaz, & Wold, 2011). Interestingly, and different from the present report, an unsupervised approch was used in both reports. Finally, it should be noted that a study of the possibilities of multi-way fluorescence linked to PARAFAC and to classify the different sherry vinegars accordingly to their ageing was presented by Callejón et al. (2012).

In the present work, a methodology is presented for exploring the feasibility of discrimination of Argentinean white wines varieties by using second-order data obtained recording excitation–emission matrices in samples with minimum pre-treatment. Different algorithms for pattern recognition were implemented: PCA, PARAFAC, soft independent modeling of class analogy (SIMCA), discriminant analysis by unfolded partial least squares (U-PLS-DA), discriminant analysis by multi-way partial least squares (N-PLS-DA) and successive projection algorithm (SPA–LDA). All of them were evaluated by using independent sample sets. As will be shown, the best results in terms of accuracy were obtained for U-PLS-DA and SPA–LDA, while the latter algorithm allowed building extremely parsimonious models, i.e. models that accomplish a desired level of explanation or prediction with as few predictor variables as possible.

2. Experimental

2.1. Samples

Forty-one different varieties of commercial white wine samples from four wine-producing provinces of Argentina (Mendoza, San Juan, Salta, and Rio Negro) were included in this study: 12 Torrontés wine (from Mendoza, San Juan, Salta, and Río Negro), 14 Chardonnay wine (from Mendoza and San Juan), and 15 Sauvignon Blanc wine (from Mendoza, San Juan, and Río Negro). Wines samples were selected from the 2011 to 2013 vintages. The alcoholic content ranged from 12.2% to 13.8% vol/vol ethanol. All were purchased from a local supermarket.

2.2. Apparatus

All spectrofluorimetric measures were acquired on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies, Waldbronn, Germany) using a 1x1 cm quartz fluorescence cell, xenon flash lamp and CaryEcplise software package to control the instrument, data acquisition and data analysis. Excitation–

emission matrices were saved in ASCII format, and transferred to a PC for subsequent manipulation.

2.3. Experimental procedure

Prior to the measurements, samples were equilibrated at room temperature. Immediately after opening the bottle, 10 mL of each white wine sample was filtered with 0.45 µm Nylon filter. Each sample was prepared in triplicate and measure using the fluorescence spectrophotometer.

2.4. Data modeling

All calculations carried out in this work were done in Matlab environment (MATLAB, 2010). PARAFAC and N-PLS were applied using the *N-way Toolbox* (Andersson & Bro, 2000) developed BrO and available in http://www.models.life.ku.dk/algorithms. The Kennard–Stone (KS) Algorithm (Harrop Galvao et al., 2005) and SPA–LDA (Carreiro Soares, Gomes, Rodrigues Galvao Filho, Ugulino Araujo, & Harrop Galvao, 2013) were written by the authors. U-SIMCA and U-PLS-DA calculations were conducted in graphical interface *classification-toolbox 3.1* available in http://michem.disat.unimib.it/chm/download/softwares.htm.

2.5. Chemometric tools

The chemometric algorithms applied in the present work, and their corresponding references are listed and briefly at the following:

(a) SIMCA is a method of pattern recognition widespread and used to solve classification problems in chemistry (Wold, 1976). Briefly, the SIMCA method assumes the measurement values for groups of similar samples have a uniform distribution and malleable, and this modeling is based on Principal Component Analysis (PCA) (Bro & Smilde, 2014; Forina, Oliveri, Lanteri, & Casale, 2008).

(b) U- and N-PLS-DA was originally proposed for multivariate calibration, and then used in classification problems. Their mathematical foundations have been described in the literature (Indahl, 2014). In essence both U-PLS and N-PLS for discriminant analysis (Barker & Rayens, 2003; Ouertani, Mazerolles, Boccard, Rudaz, & Hanafi, 2014) are equal for calibration purposes.

(c) The SPA–LDA algorithm is aimed at selecting a subset of variables with small collinearity and suitable discriminating power for use in classification problems involving $Q \geqslant 2$ different classes. For this purpose, it is assumed that a training set of N objects with known class labels is available to guide the variable selection process. In the case of spectroscopic data, for example, each object consists of a spectrum recorded over K wavenumbers (or wavelengths) (Carreiro Soares et al., 2013).

(d) Validation of classifiers: as in calibration, in classification the performance of the model for the training sample set or an independent test set can be accessed using some figures of merit. In that way, for a classification model, the most common figures of merit are accuracy (AC), sensitivity (S) and specificity (SP) (Lavine, 2009, chap. 3). With the purpose of illustration, consider a two-class classification problem (A_1 positive class and A_2 negative class), in which a_1 and a_2 are the quantities of objects A_1 assigned to A_1 and quantities of objects A_2 assigned to A_2, respectively. On the other hand b_1 are objects de A_1 assigned to A_2 and b_2 are objects de A_2

assigned to A_1. In this way, it can be defined the figures of merit for a classifier mathematically as shown below (Lavine, 2009, chap. 3).

$$AC = \frac{a_1 + a_2}{a_1 + b_1 + a_2 + b_2} \qquad (1)$$

$$S = a_1/a_1 + b_1 \qquad (2)$$

$$SP = a_2/a_2 + b_2 \qquad (3)$$

3. Results

3.1. EEM for white wine samples and general considerations

The data set comprises forty-one excitation–emission matrices recorded in the excitation range of 245 at 341 nm with resolution of 2 nm and emission range of 375 at 500 nm with resolution of 5 nm. Then, the data were arranged in a cube structure with dimensions of $41 \times 49 \times 26$. The number of samples per class was fourteen for Chardonnay (C), fifteen for Sauvignon blanc (S) and twelve for Torrontés (T). Fig. 1 shows typical emission and excitation spectra and EEM landscapes for each wine class.

Fig. 1a shows the emission (λex at 340 nm) and excitation spectra (λex at 445 nm) for each wine class. The both excitation and emission spectra are very similar and overlapped. Excitation profiles show a maximum around 340 nm. The excitation spectrum for Sauvignon blanc (S) has a shoulder in 260 nm; and as can be seen in Fig. 1a, the emission profiles are smooth curves with a maximum around 445 nm, in all cases. In addition, the EEM landscapes (Fig. 1b–d), show similar profiles, obtained for all varieties of white wine involved in this work. A preliminary assessment of

the discriminatory power of the EEM matrices was conducted by two approaches. At first the tensor $\underline{\mathbf{X}}$ ($41 \times 49 \times 26$) was unfolded into a two-dimensional array $\mathbf{X}$ (41×1274), followed of a bilinear decomposition by PCA. Then, the three-way array was decomposed using PARAFAC employing non-negativity on the three modes.

In Fig. 2a, the eigenvalues of the $\mathbf{X}$ and the explained variance are plotted as a function of the number of principal components. Inspection of this graph suggests that three factors, with 98% cumulative variance, are suitable to describe the unfolded EEM data. In Fig. 2b, the loadings corresponding to the first three factors are displayed. The blue solid line corresponds to the first factor, and shows a profile that is similar to the emission spectra, with no negative parts. The second factor (green dotted line) presents a high importance in the first wavelengths; fact that can certainly be associated with the shoulder of the wine samples Sauvignon blanc (S) in 260 nm. Finally, the third factor (diamond red line) with only 1% of variance displays negative and positive contributions associated with small information, orthogonal to the main source of radiation captured by the first component. Finally, the bidimensional score plot with 97% of explained variance (Fig. 2c) shows that it is possible to see a reasonable discrimination ability of the wines C and S. On the other side, the T samples exhibit a large scattering and overlapping with C and S samples.

Fig. 3a shows the curves for the CORE consistency test values and the explained variance against the number of PARAFAC factors. As noted for PCA for unfolded data, in PARAFAC three factors also appear to be the best fit, the value of CORE was 71% and the variance explained 99.5%. These values suggest that three factors describe the variance of the data.

As regards the retrieved profiles by PARAFAC in both modes (excitation and emission), which are displayed in Fig. 3b, they
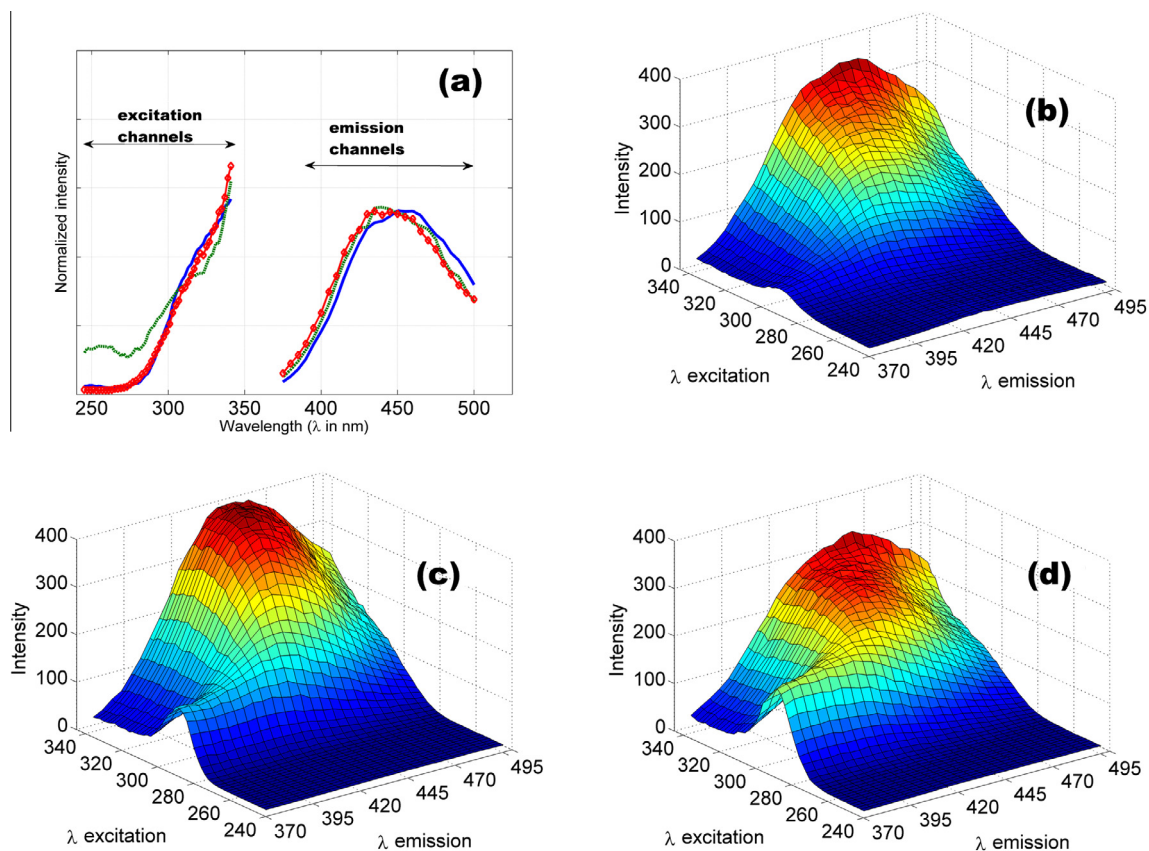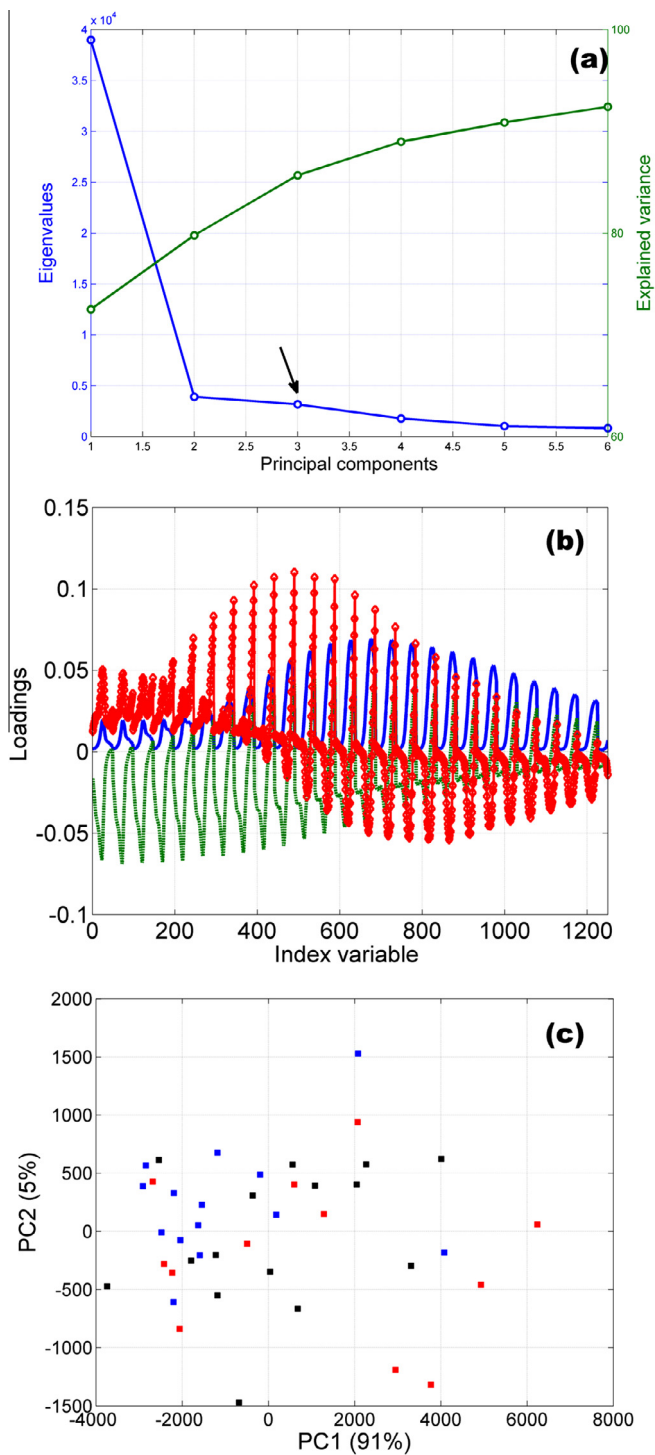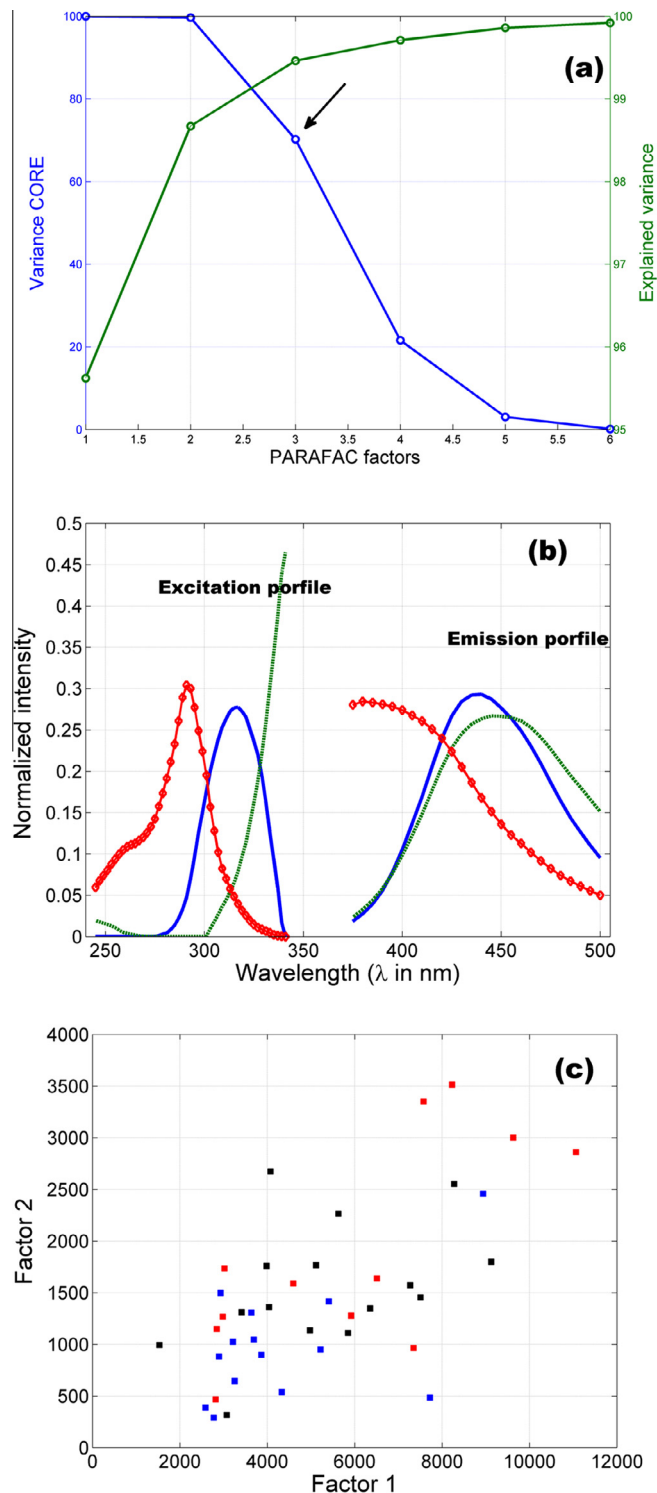

Fig. 1. (a) Emission (λex at 340 nm) and excitation spectra (λex at 445 nm) for each wine class; and typical surface EEM for samples of class (b) Chardonay, (c) Sauvignon blanc, and (d) Torrontés.

Fig. 2. Results of the exploratory analysis with PCA. (a) Eigenvalues of the **X** and the explained variance plotted vs. the number of principal components. (b) Loadings corresponding to the first three PCA factors. (c) Bidimensional score plot.

Fig. 3. Results of the exploratory analysis with PARAFAC. (a) Curves for the CORE consistency test values and the explained variance against the number of PARAFAC factors s. (b) Profiles retrieved by PARAFAC analysis in both modes (excitation and emission). (c) Bidimensional score plot.

are smooth curves with excitation maximum in 291, 317 and 341 nm, respectively. In the emission mode, the maxima are located around 380, 440 and 445 nm. The excitation and emission profiles of factor 1 match with stilbenes compounds such as t-piceid and t-astringin (Vitrac, Monti, Vercauteren, Deffieux, & Mérillon, 2002). Some phenolic acids like gentisic acid, present fluorescent proprieties, that could be related with factor 2. Lastly, the excitation and emission profiles calculated for the factor 3 have not been reported exactly, but some fluorophores as trans-stilbenes are close to this factor. However, it is probable that each

PARAFAC factor correspond to a related fluorescent molecule group, and not necessarily to a single fluorescent molecule (Airado-Rodríguez et al., 2011).

The bidimensional score plot for PARAFAC (Fig. 3c) shows a strong overlapping between all the three classes. The class C proves to be the most cohesive group while the other classes (S and T) show a pattern of scattering.

Table 1
Confusion matrix obtained by full cross-validation.

Models	Predicted											
	SIMCA			N-PLS-DA			U-PLS-DA			SPA-LDA		
Actual	Class C	Class S	Class T	Class C	Class S	Class T	Class C	Class S	Class T	Class C	Class S	Class T
Class C (7)*	3	1	3	6	0	1	7	0	0	6	0	1
Class S (7)*	2	1	4	1	6	0	1	6	0	0	7	0
Class T (7)*	2	1	4	3	0	4	1	0	6	1	0	6

Diagonal green contain the correct assignments.
*Number of samples per class.

Table 2
Confusion matrix obtained for test set.

Models	Predicted											
	SIMCA			N-PLS-DA			U-PLS-DA			SPA-LDA		
Actual	Class C	Class S	Class T	Class C	Class S	Class T	Class C	Class S	Class T	Class C	Class S	Class T
Class C (7)*	7	0	0	6	1	0	7	0	0	7	0	0
Class S (8)*	4	1	3	2	6	0	1	7	3	2	4	2
Class T (5)*	1	2	2	2	2	1	3	2	2	0	0	5

Diagonal green contain the correct assignments.
*Number of samples per class.
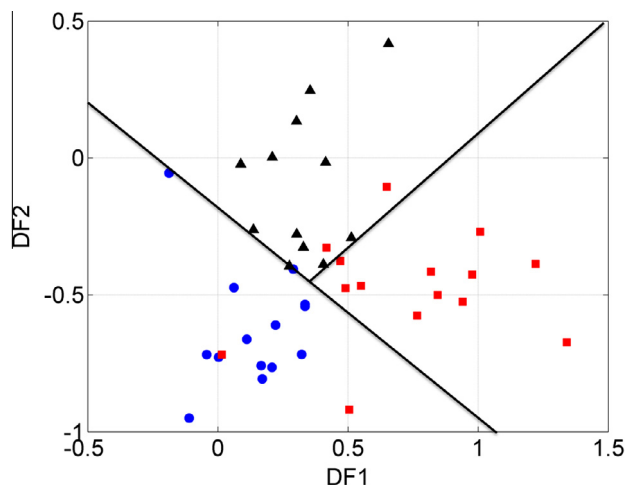
Fig. 4. Discriminant function plot.

In order to build classification models, the data set was partitioned into two groups of samples employing the Kennard–Stone algorithm. The first group or set of training contained twenty-one samples, seven of each class of wine. These samples were used for data modeling and internal validation with the full cross-validation procedure. The second sample group constitutes an independent samples set to evaluate the discriminative power of the models.

3.2. Wine classification

In the development of models for classification samples of white wine according to the grape variety, three approaches, from the point of view of the modeling data, were used: (a) modeling full unfolded data using U-SIMCA and U-PLS-DA; (b) three way data by N-PLS-DA; and (c) hard modeling employing LDA coupled with SPA for selection of a small subset of variables in unfolded data.

3.2.1. Development of classification models and validation

Initially the optimum number of factors/variables using full cross-validation was determined for all models. The optimal number of factors was chosen based on the lower error rate, except for SPA–LDA, which employed the G function as commented above. In all cases the number of PC which minimizes the error rate of cross-validation was one. For N- and U-PLS-DA, an equal number of factors have been selected, i.e. nine in both cases. Applying SPA–LDA, only six variables were selected. In Table 1, the confusion matrix built for cross-validation is shown.

The strong overlapping among the classes observed in the exploratory analysis of data by PCA and PARAFAC, possibly led to SIMCA models that presented a poor outcome in terms of accuracy (AC = 38%). Alternatively, if a larger number of PC is used, the error rate for class 3 increases damaging the final accuracy of the model. The modeling of the data with N- and U-PLS-DA showed a significant improvement, both employing nine factors. When compared to the SIMCA, accuracy of 76% and 90% for full cross-validation were obtained respectively. Comparing the two PLS approaches, U-PLS showed better results that N-PLS. Finally, the LDA model based on only six variables selected by SPA achieved performance equal to that obtained by U-PLS-DA. In addition, the LDA model is very simple from a mathematical view point, where only two linear combinations of the six selected variables were employed, called discriminates functions (DF). Interestingly, most of the variables selected by SPA correspond to the emission intensities recorded at excitation wavelengths higher than 300 nm.

3.2.2. Predicting a set of independent samples

The validated models were then used to predict the class corresponding to twenty wine samples belonging to the test set. The results obtained for the confusion matrix are shown in Table 2.

As in cross-validation, the SIMCA models showed a lower accuracy (50%); although all samples of class C were correctly assigned, the model does not distinguish correctly samples S and T. N-PLS-DA showed higher accuracy (65%) when compared to the SIMCA; however, miss classifications occurred in all classes. The best performances were again obtained for U-PLS-DA and SPA LDA, with accuracies of 76% and 80%, respectively.

For the test set, SPA LDA showed the best approach for samples corresponding to classes C and T, which were correctly classified. A better visualization of the discrimination achieved by LDA, using the subset of variables selected by SPA, can be attained by visual inspection of Fig. 3, which shows the two-dimensional plot of the discriminant functions obtained in the LDA modeling. The black lines represent the borders of the classes and a pattern of separation among classes is observed (see Fig. 4).

4. Conclusions

The modeling of EEM matrices for classification of wines according to grape variety was presented. U-PLS-DA and SPA–LDA have shown to be the most effective tools to achieve the objective of this work, which accuracies of ca. 90% achieved for both models with the cross-validation set, and 76% and 80% for the set of test samples, respectively. In addition, the LDA model based on a small subset of variables selected by SPA generated simple and parsimonious models. On the other hand, it is necessary to take in account that the analyzed wines were not 100% mono-varietals, because a wine is considered mono-varietal when the grape purity is up 85%; this fact could have affected the results obtained by the models (especially N-PLS-DA and SIMCA models).

This methodology, which combined the use of the high sensitivity of fluorescence with the high accuracy of the models U-PLS-DA and SPA–LDA, can be a useful tool to assist the industry of wine producing, as well as in government oversight institutions, to detect the type of grape used in a commercially available wine, or to avoid frauds in the mono-varietal white wines market.

Acknowledgements

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