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Classification of Sherry vinegars by combining multidimensional fluorescence, parafac and different classification approaches

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ABSTRACT

Sherry vinegar is a much appreciated product from *Jerez-Xérès-Sherry*, *Manzanilla de Sanlúcar* and *Vinagre de Jerez* Protected Designation in southwestern Spain. Its complexity and the extraordinary organoleptic properties are acquired thanks to the method of production followed, the so-called "criaderas y solera" ageing system. Three qualities for Sherry vinegar are considered according to ageing time in oak barrels: "Vinagre de Jerez" (minimum of 6 months), "Reserva" (at least 2 years) and "Gran Reserva" (at least 10 years).

In the last few years, there has been an increasing need to develop rapid, inexpensive and effective analytical methods, as well as requiring low sample manipulation for the analysis and characterization of Sherry vinegar. Fluorescence spectroscopy is emerging as a competitive technique for this purpose, since provides in a few seconds an excitation-emission landscape that may be used as a fingerprint of the vinegar.

Multi-way analysis, specifically Parallel Factor Analysis (PARAFAC), is a powerful tool for simultaneous determination of fluorescent components, because they extract the most relevant information from the data and allow building robust models. Moreover, the information obtained by PARAFAC can be used to build robust and reliable classification and discrimination models (e.g. by using Support Vector Machines and Partial Least Squares-Discriminant Analysis models).

In this context, the aim of this work was to study the possibilities of multi-way fluorescence linked to PARAFAC and to classify the different Sherry vinegars accordingly to their ageing. The results demonstrated that the use of the proposed analytical and chemometric tools are a perfect combination to extract relevant chemical information about the vinegars as well as to classify and discriminate them considering the different ageing.

1. Introduction

Wine vinegar is the result of two fermentation processes (the conversion of sugars of the must into ethanol by yeasts and the oxidation of the ethanol to acetic acid by acetic acid bacteria). From a technological point of view, there are two well defined methods for its production: fermentation with surface and submerged culture. In the first one, the acetic acid bacteria are placed on the air–liquid interface in direct contact with atmospheric air. Thus, oxygen availability to the acetic acid bacteria is not boundless, and a long period of time is required to obtain a high acetic degree [1]. This process usually takes place in wood barrels. As a consequence, chemical modifications related with ageing and with the microbiological activity occur at the same time. All these factors provide characteristic organoleptic properties to these products, being highly appreciated by consumers. Hence, vinegar produced by slow traditional surface methods, such as Sherry vinegar, generally fetches higher prices due to its great sensory quality [2].

Sherry vinegar is commodity produced in *Jerez-Xérès-Sherry*, *Manzanilla de Sanlúcar* and *Vinagre de Jerez* Protected Designation of origin in south-western Spain [1]. Its main features are a high acetic degree (legally at least 7°) and a special flavour, which resembles that of Sherry wine. Its complexity is the consequence of chemical composition of the product, and the extraordinary organoleptic properties are acquired thanks to the methods of production followed, the so-called *criaderas y solera* system or *añada* [3]. The first

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one consists of a dynamic ageing system in contrast with the not so usual static method *añada*, in which vinegar is produced and aged in a single butt.

The Regulations establish three categories for Sherry vinegar according to their ageing time in oak wood barrels: *Vinagre de Jerez* (minimum of 6 months), *Reserva* (at least 2 years) and *Gran Reserva* (at least 10 years) [4]. These three qualities of vinegars have different price in the market due to the fact that the longer ageing time the better quality of vinegars and higher cost of its production. This fact makes that these products are subject to frequent frauds. By this reason, it is necessary more objective analytical methodologies to guarantee the authenticity.

Vinegar characterization comprises a wide range of values obtained from physicochemical and sensory parameters [5]. The composition and sensory characteristics of Sherry vinegar have been studied by different authors. The changes of several components (volatile compounds, polyphenols, etc.) during ageing have also been studied [6–8]. However, up to now, there are scarce researches to distinguish vinegars belonging to the three different categories. Recently, Callejón et al. [9] studied aroma composition, key odorants and sensory profile of the different categories of Sherry vinegar.

The most commonly reported methods for the analysis and characterization of Sherry vinegar, such as gas chromatography–mass spectrometry (GC–MS) [9], high-performance liquid chromatography (HPLC) [2] or capillary electrophoresis (CE) [10], are often time-consuming, expensive, requires highly trained staffs [11]. The range of compounds, which must be quantified to ensure authenticity, is continuously increasing. This demand is due to the high costs connected to routine use of sensory evaluation and the lack of satisfactory instrumental methods [12]. Consequently, there has been a growing need to develop rapid, inexpensive and effective analytical methods in the last years, as well as requiring low sample manipulation [13,14].

Fluorescence spectroscopy is emerging as a competitive technique in the field of characterization and classification of intact food [15]. Fluorescence spectroscopy is a non-destructive method, characterized by its high sensitivity and specificity and also by its speed and relatively cost. It is reported to be up to 1000 times more sensitive than other spectrophotometric techniques [11,16]. For instance, it has been demonstrated to be suitable for the analysis and authentification of different food systems [15], differentiating the botanical origin of honey [17], identifying the geographic origin of cheeses [18] or wines according to variety, typicality and ageing [19–21], monitoring the texture of meat emulsions [22], classifying brandies and wine distillates [23] or characterizing ice cream formulations [23] and ripening of *Cabernet Franc* grapes [11]. Grapes and wines contain a wide range of fluorescent compounds most of which are polyphenols [20]. The types and amounts of these molecules vary as a function of the variety and of the maturity of grapes. Besides, wine processing and ageing also have effects on the phenolic compounds [21]. Apart of polyphenols, other fluorescent molecules present in wine are amino acids, such as tryptophan, and vitamins, such as vitamin A (retinol) and vitamins of the B-complex, which are most abundant in wines [20]. Fluorescence spectroscopy has been rarely applied in vinegar; hence, there is little information about its fluorescence profile. However, this product is derived from wine, and it should have similar fluorescent compounds.

Intact food, and specifically speaking, vinegar is a complex chemical system. Therefore, the fluorescence signals arising from those systems are a combination of individual signals from different intrinsic fluorescent molecules, at the same time influenced by the physical–chemical environment of the food matrix (temperature, color, pH, etc.). To handle this complexity, multivariate and multi-way data analysis can be applied [15].

The analysis of multi-component mixtures can be hindered when the conventional excitation or emission spectra are measured at a single emission or excitation wavelength, respectively. However, instead of measuring a single emission spectrum at a selected excitation wavelength λ_{ex}, a set of fluorescence spectra at different λ_{ex} can be recorded. As a result, a bi-dimensional landscape is obtained for each sample, the so-called fluorescence excitation–emission matrix (EEM) [24] (Fig. 1). The main advantage of EEMs is that they contain more information about the fluorescent species than conventional excitation and emission spectra, because they include emission bands excited at varying excitation wavelengths that potentially correspond to different emissive species.

The potential of EEM technique can be improved by applying multi-way methods in the analysis of the fluorescence results such as Parallel Factors Analysis (PARAFAC) [25–27]. Multi-way data analysis is a powerful tool for simultaneous determination of various fluorescent components, because it extracts the most relevant information from the data and allows building further robust calibration and/or classification models. Multi-way techniques are able to extract selective information (pure excitation and emission spectra for each fluorescent molecule as well as the relative concentration of them in each sample) without the use of separation or extraction methods [25–27].

With this selective information it becomes easier the task of developing robust and reliable classification methods by using techniques as Partial Least Squares-Discriminant Analysis (PLS-DA) [28] or Support Vectors Machine for classification (SVM) [29]. Thus, the development of classification models, by using the selective results obtained by multi-way techniques, will enable the generation of very accurate and robust classification tools for detecting any fraudulent sample or counterfeits in vinegars.In this context, the aim of this work is the development of a combined methodology that uses:

(1) Multi-dimensional fluorescence for the intact and fast measurement of different Sherry vinegars and for obtaining the excitation–emission matrices (EEMs) which were described and interpreted according to the literature.
(2) PARAFAC as the multi-way technique to extract the selective information of fluorescence EEM.
(3) Classification techniques for developing robust classification models: PLS-DA and SVM-classification.

2. Brief description of PARAFAC, PLS-DA and SVM

The multi-way (PARAFAC) and multivariate (PLS-DA, SVM) techniques used in this work have been widely described in the literature [25,28,29]. Therefore, we will briefly describe them below. The readers are encouraged to read the suggested references in each section for further information.

2.1. PARAFAC as a standard method to analyse EEM datasets

PARAFAC model [25–27] is becoming one of the standard tools for analysing EEM landscapes [15]. This is due to the intrinsic linear relationship between the excitation and emission intensities with the concentration of each component. The principle of PARAFAC decomposition is to minimize the sum of the square of the residual, e_{ijk}, as indicated in Eq. (1), based on a least-squares algorithm:

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk} \quad (1)$$

The element x_{ijk} represents the data for sample i in the corresponding excitation j and emission k wavelength. The three way

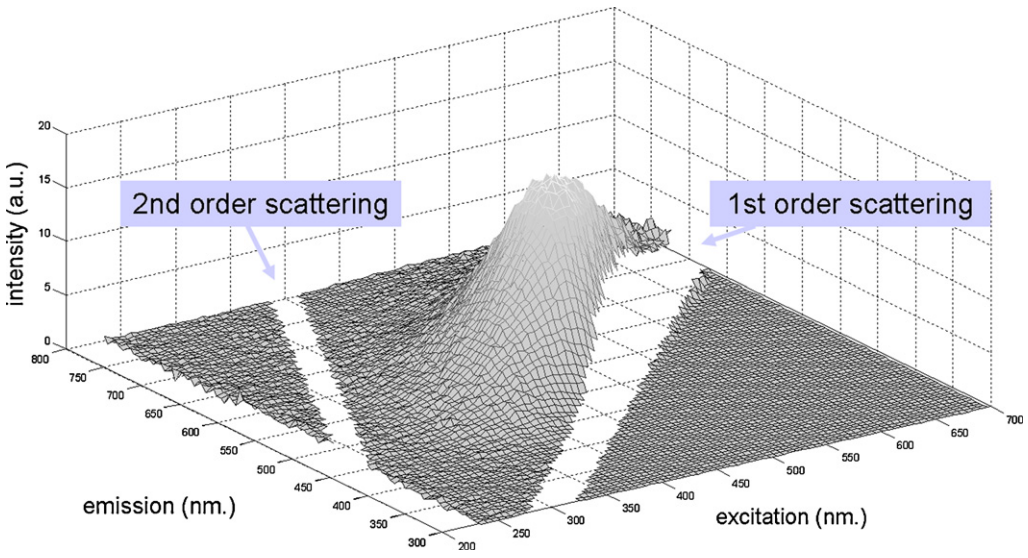

Fig. 1. Excitation–emission landscape obtained for a vinegar sample by using EEM. The Rayleigh scattering (first and second order scattering) has been removed from the sample.

array, $\boldsymbol{X}$, is decomposed into a set of sample scores (a_{if}), loadings for the excitation mode (b_{if}) and loadings for the emission mode (c_{if}). The number of factors, F (i.e. the number of components) describes the systematic variation in the data array, lefting in the residuals the noise associated to the measurements. As an example, a graphical representation of the decomposition of $\boldsymbol{X}$ by PARAFAC model into two factors is given in Fig. 2.

One of the main advantages of PARAFAC with respect to other resolution techniques is the uniqueness of the solution. That is, there are no mathematical ambiguities in the final model. Therefore, PARAFAC model can be seen as a complete chemical description of the fluorescent molecules involved in the analysed samples.

2.2. PLS-DA

Partial Least Squares-Discriminant Analysis (PLS-DA) is a PLS2-based classification method [28,30]. Thus, the response matrix **Y** (I,C), also called dummy matrix in PLS-DA context, contains as many columns C as classes. In our case, since there are three classes (six months, 2 years and 10 years ageing) **Y** will contain three columns. The values on Y are 0 for each sample not belonging to a determined class and 1 if the sample belongs to the assigned class. Then, the PLS model is calculated in the usual way [31] and the classification is then based on a Bayesian approach using the scores obtained from PLS. The classification ability of the model is assessed by using the classical parameters of sensitivity, specificity and the classification error.

2.3. SVM for classification

Support Vector Machines (SVM) is a classification technique developed by Vapnik group [29] based on kernel learning. SVM is gaining in interest respect to other classification techniques due to its ability to perform linear and nonlinear classifications, being successfully applied to a number of classification problems [32,33].

Briefly, the classification problem may be restricted to a two-class problem (Fig. 3). The quest is to find the optimal separating hyperplane (OSH) between the different classes involved that will work well on unknown samples. This is done by maximizing the distance between the hyperplane and the closest samples of the training set (the support vectors).

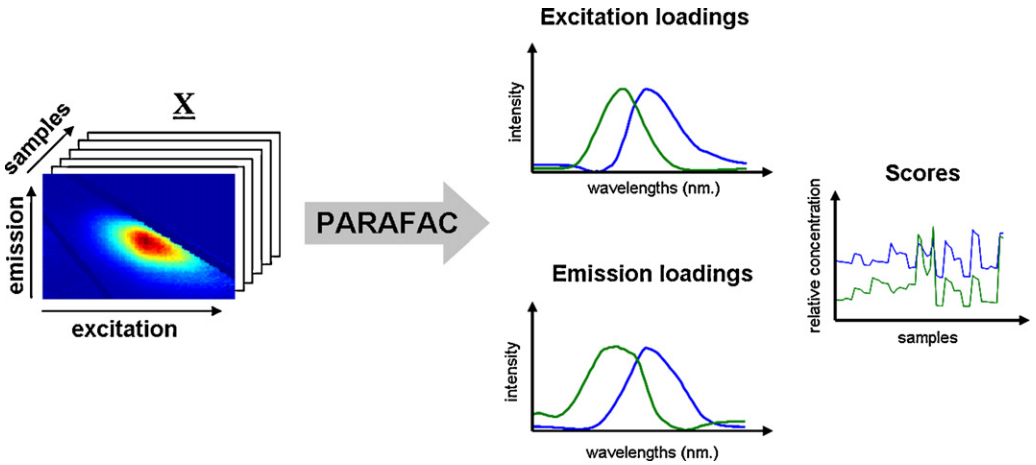

Fig. 2. Principles of a PARAFAC decomposition of a three way data array, X into two factors (denoted as blue and green profiles). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

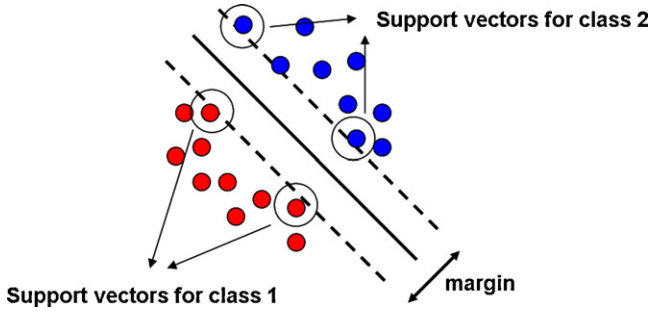

Fig. 3. Representation of the classification of two classes (red and blue dots). The solid line represents the optimal separating hyperplane (OSH); whereas the dashed lines identify the margin. The dots on the margin are called support vectors. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

To determine the optimal hyperplane it is necessary to solve the following problem shown in Eq. (2):

$$\min\ \Phi(\omega, \xi) = \frac{1}{2}\|\omega\|^2 + C\sum_{i=1}^{I}\xi_i \qquad (2)$$

where ω is a weight vector, C a parameter that control the error of misclassification, and ξ a lack variable that will allow the violation of the margin constraints of the hyperplane.

3. Materials and methods

3.1. Samples

A total of 19 Sherry vinegars from 14 different producers were analysed in this study (Table 1): 6 "*Vinagres de Jerez*" (VJ), 9 "*Vinagres de Jerez Reserva*" (VR) and 4 "*Vinagres de Jerez Gran Reserva*" (VGR). All of them were acquired from local supermarkets and were stored at room temperature. Samples were filtered before analysis.

3.2. Fluorescence measurements

Multi-dimensional fluorescence spectra were obtained with a Varian Cary-Eclipse Fluorescence Spectrometer (Varian Iberica, Madrid, Spain) equipped with a thermostatted (25 °C) cuvette holder, a xenon discharge lamp pulsed at 80 Hz with a half peak height of ~2 μs (peak power equivalent to 75 kW), two Czerny-Turner monochromators and a R-298 photomultiplier tube detector. Measurements were carried out in a standard quartz cell (10 mm × 10 mm). The spectrometer was interfaced to a computer with Cary-Eclipse software for Windows 98/NT for spectral acquisition and exportation.

The EEM fluorescence spectra were obtained by recording the emission spectra (from 300 to 800 nm, at 1 nm intervals) corresponding to excitation wavelengths ranging between 250 and 700 nm, set at 5 nm steps between successive excitation spectra. For these measurements, excitation and emission slits were both set at 5 nm, and scan rate was fixed to 600 nm min-1. EEM fluorescence spectra were registered by triplicate for each sample.

Table 1
Sherry vinegars analysed.

Categories	Samples	Producers
Jerez	VJ1	1
	VJ2	2
	VJ 3	3
	VJ4	4
	VJ5	6
	VJ6	7
Jerez Reserva	VR1	8
	VR2	9
	VR3	10
	VR4	11
	VR5	12
	VR6	4
	VR7	13
	VR8	3
	VR9	14
Jerez Gran Reserva	VGR1	1
	VGR2	12
	VGR3	1
	VGR4	4

3.3. Software

The obtained EEM landscapes were exported, and the Rayleigh scattering (first and second order scattering) was removed for each sample by using in-house routines working under MATLAB environment [34] and freely available on the web (http://www.models.life.ku.dk/. Last access September 2011).

PARAFAC model was calculated by using EEMizer [36]. EEMizer is a new automatic PARAFAC model builder for fluorescence EEM data recently developed by Bro and Vidal [36]. The algorithm can be freely downloaded from the web (http://www.models.life.ku.dk/. Last access September 2011). It works under MATLAB environment [34] and requires PLS-Toolbox [35]. PLS-DA and SVM models were calculated by using PLS-Toolbox [35] also working under MATLAB environment [34].

4. Results and conclusions

Fig. 4 depicts three landscapes belonging to different types of vinegars, after removing Rayleigh scattering. The areas in which the compounds appear vary between samples, allowing us to confirm an *a priori* difference between vinegars with different ageing. For instance, most of the vinegars named VGR (*Gran reserva*) showed a well defined and highly intense fluorescent area between 480–510 nm in the excitation and 540–610 nm in the emission wavelength range (central black spot in Fig. 4). On the contrary, the shape and the position of this area for VR and VJ vinegars are not as stable as for VGR vinegars. Further conclusions on the fluorescence signal can be extracted after PARAFAC application.

4.1. PARAFAC results

After the application of EEMizer, the best PARAFAC model was found to be the one with non-negativity constraint in the three modes. Five fluorescent compounds were found to be the main ones in the vinegars (Fig. 5), giving a final model that explains more than 99% of the variance and with a core consistency over zero (Fig. 6). Both parameters indicated that the model was enough robust and that it corresponded to the inherent chemical behaviour of the vinegars.

As shown in Fig. 5, the first-component excitation profile (blue) has a maximum centered around 520 nm and an emission maximum at 570 nm, approximately. The pair of excitation/emission wavelengths corresponding to the maximum fluorescent intensity for the second component (green) is 460/520. The third component (red) is a peak centered around 570 and 630 nm, respectively. The fourth component (cyan) has an excitation maximum around 370, with a shoulder at 230 nm, and the emission one centered at 470 nm. Finally, the fifth component (purple) is situated close to the third one, with an excitation maximum around 630 nm, and an emission broad peak centered between 670 and 740 nm.

According to Airado-Rodriguez et al. [19], fluorescent properties of compounds are highly dependent on the working medium,

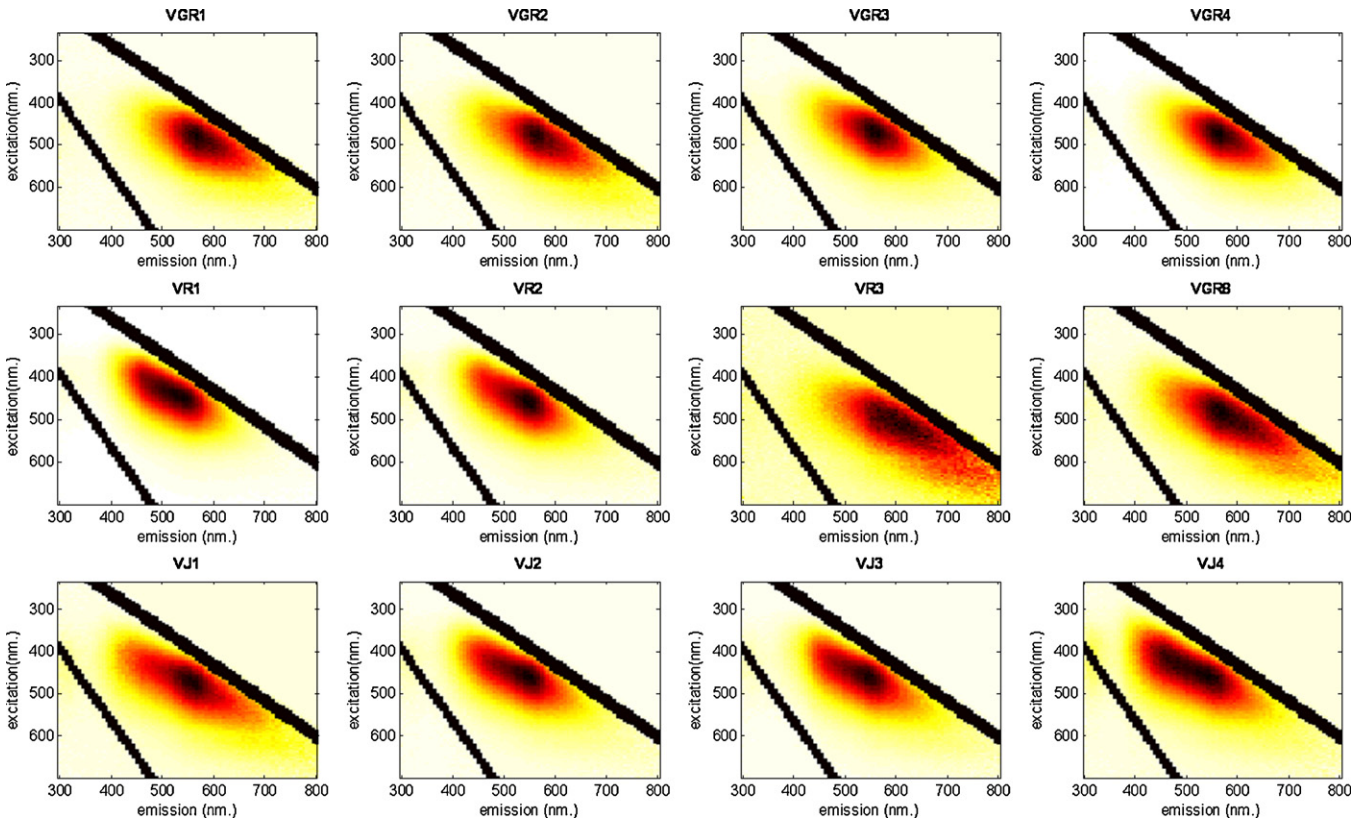

Fig. 4. Excitation–emission landscape obtained for vinegars with different ageing. The color scale varies between zero (white) and 26 (dark red). The two black stripes appearing on each picture denotes the removed Rayleigh scattering (first and second order scattering) from the samples. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

being influenced by variables such as the acidity or the composition of the medium. It is known that fluorescent behaviour is highly affected by the pH and sometimes by the content of organic solvents such as ethanol or acetic acid. Vinegars fluorescent compounds have not been reported yet, but, as all vinegars analysed in this work are wine vinegars, at least some of them should be the same. Hence, according to literature, the best known fluorescent molecules in wines such as phenolic acids, cinnamic acids, coumarins, Maillard reaction products, tannins and other unknown fluorescent compounds match well with those of PARAFAC component 4 [20,21,37]. Zhu et al. [38] found that the maximum excitation and emission wavelengths measured at 400 and 493 nm had high correlation with 5-hydroxymethylfurfural (HMF) concentration in apple juice. This compound appeared during the Maillard reaction and it is has been determined in Sherry vinegars [6]. Sádecká et al. [13] reported that the emission spectra of caramel recorded after excitation at 390 nm showed a maximum located around 482 nm, hence could be also associated with PARAFAC component 4. Other compound present in Sherry vinegar is 5-(hydroxymethyl)furan-2-carbaldehyde in vinegar has traditionally been attributed to the employment of cooked must or to the addition of caramel [1]. Vitamin B_2 and the principal forms of vitamin B_2 found in nature such as riboflavin, flavin mononucleotide (FMN), and flavin adenine dinucleotide (FAD) have an emission/excitation maximum around 450 and 550 nm, respectively [37] and hence, these compounds could be related to PARAFAC component 2.

On the other hand, some acetic bacteria strains present in vinegar form pig colonies and are able to produce brown pigments which are soluble in water due to porphyrins [39]. These compounds could be associated to the PARAFAC component 1, according to the fluorescent properties described by Christensen et al. [15].

The scores plot depicted in Fig. 5 denoted two important aspects:

- The good repeatability of the EEM measurements, since all replicates for each sample appeared together.
- A good separation between ten years and six months ageing samples. The two years ageing class had a peculiar shape. It was also quite well separated from the other classes, but totally divided into two sub-clusters. Vinegars of this class have been at least two years in wood barrels. Hence, all Sherry vinegars with an ageing between two and ten years belong in this category. This wide range among time of ageing of these vinegars can explain the differences observed among them. Thus, vinegars with more years of ageing will be more similar to vinegars from *Gran Reserva* category, and, on the contrary, vinegars with only two years of ageing will be near vinegars from 6 month class.

This lecture of the data was done by using the first and the second factor in PARAFAC (the blue and green profiles in the excitation emission loadings plots of Fig. 5, respectively). To fully visualize the real separation between the classes, all possible combination between factors should be checked. PARAFAC gave us a really good qualitative visualization of the chemical model as well as a first impression of the separation between different classes. Nevertheless, to be able to quantify this separation (in terms of classification), advanced classification tools were applied by using the scores obtained by PARAFAC.

4.2. Classification results

For developing robust classification models, the samples were divided into two groups. Around the 75% of the samples were

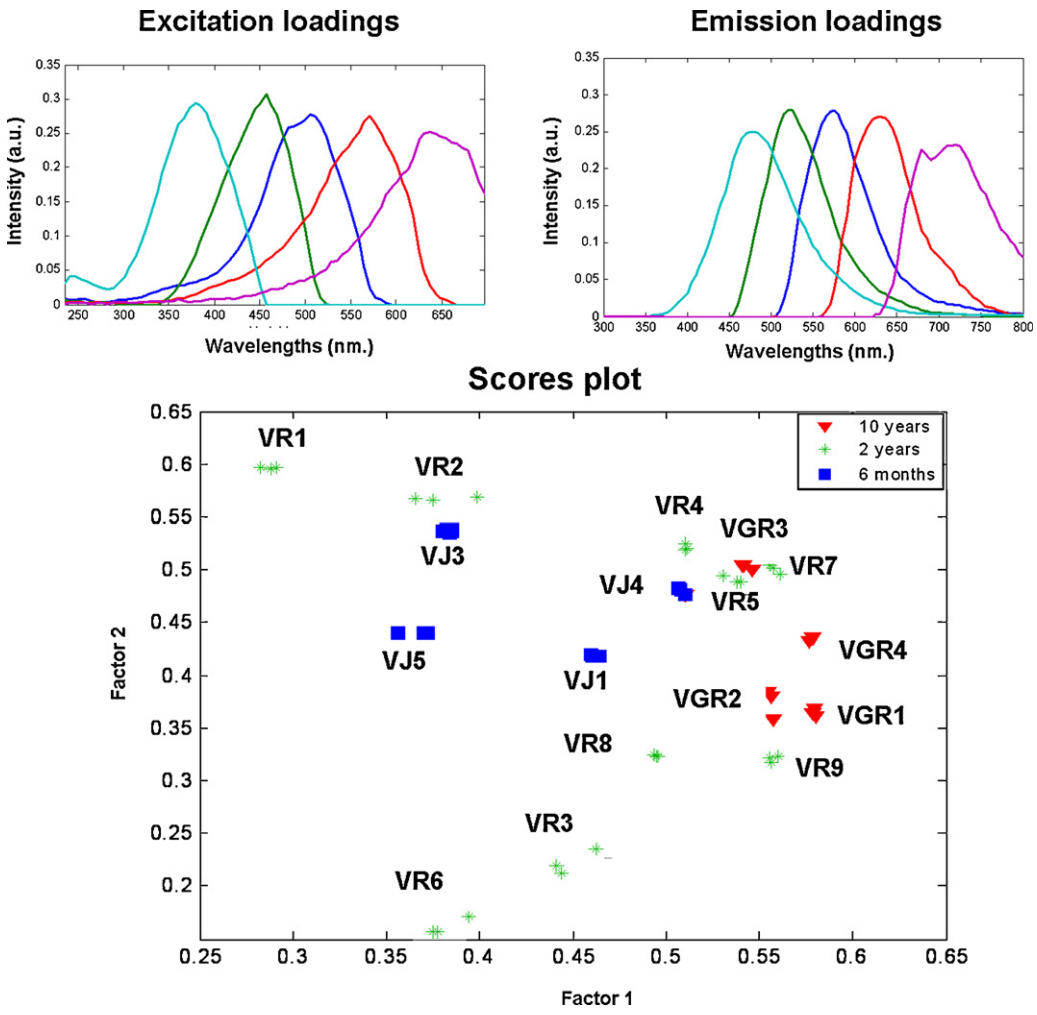

Fig. 5. PARAFAC results obtained by using EEMizer. The best model was found with five factors. The scores plot depict the relationship between Factors 1 and 2 (blue and green, respectively, in the excitation–emission loadings). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

randomly selected for the calibration and cross-validation models; whereas the other 25% of the samples was used as external test. The cross validation procedure was performed in a segmented manner by excluding all the replicates for the same sample in each segment (leave-replicates-out). The ability of PLS-DA and SVM for classifying the different samples with their corresponding class was assessed by calculating statistical parameters as sensitivity, specificity and classification error of calibration (CAL), cross-validation (CV) and prediction (PRED) were calculated and compared.

The results obtained for both models are shown in Table 2. In general, both methods performed quite satisfactorily. The results obtained between CAL, CV and PRED were pretty similar, denoting the robustness of the model.

The best PLS-DA model was obtained by using 4 latent variables (LVs). This number was selected accordingly to the PRESS curve. In the optimization of SVM, $\log_{10}(C)$ and $\log_{10}(\xi)$ were found to be 1.5 and 0.5, respectively.

For PLS-DA model, sensitivity, specificity and classification error obtained for the three classes was among the expectations. The two years class was the worse classified, with classification errors close to 25% and with sensitivity and specificity close to 80%. Instead, the results obtained for SVM model were significantly good in terms of the ability of predicting external samples (PRED values). For all the classes the results for sensitivity and

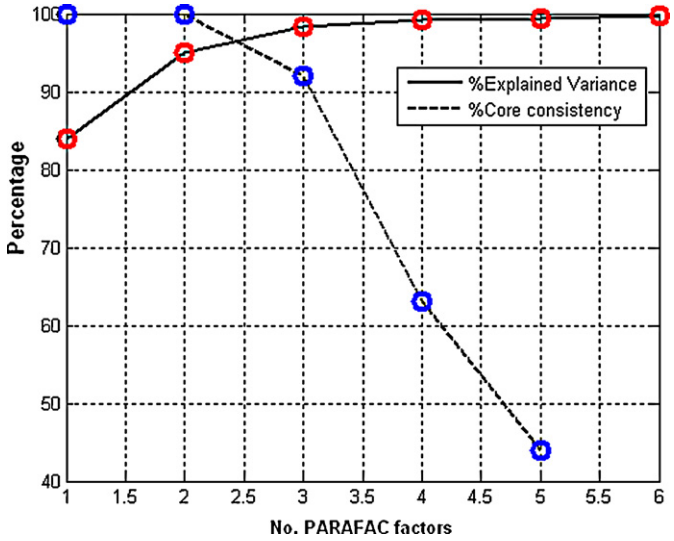

Fig. 6. Percentages of explained variance (solid line with red circles) and core consistency (dashed line with blue circles) with the number of components. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

Table 2
Sensitivity, specificity and classification error obtained for PLS-DA and SVM.

	PLS-DA			SVM		
	10 years	2 years	6 months	10 years	2 years	6 months
Sensitivity CAL[a]	0.875	0.778	0.800	1.000	1.000	1.000
Sensitivity CV	0.875	0.722	0.800	0.714	0.889	1.000
Sensitivity PRED	1.000	0.778	0.800	1.000	1.000	1.000
Specificity CAL	0.786	0.889	0.885	1.000	1.000	1.000
Specificity CV	0.679	0.778	0.846	1.000	0.882	0.920
Specificity PRED	0.857	0.778	0.846	1.000	1.000	1.000
Class. Error CAL	0.170	0.167	0.158	0.000	0.000	0.000
Class. Error CV	0.223	0.250	0.177	0.143	0.114	0.040
Class. Error PRED	0.071	0.222	0.177	0.000	0.000	0.000

[a] cal refers to calibration sub-set. CV refers to the cross-validation results of the calibration sub-set. PRED refers to the external prediction sub-set ("blind" samples).

specificity were 100%; whereas the classification error obtained was 0%.

5. Conclusions

The complete methodology proposed in this paper (EEM measurements, a multi-way resolution model (PARAFAC) and different classification approaches) has resulted in a perfect understanding of the fluorescent molecules involved in different categories of Sherry vinegar and their adequate classification accordingly to the time of ageing in wood barrels:

- EEM measurements were robust and shown high repeatability.
- PARAFAC gave information about the fluorescent molecules and their relative amount for each sample.
- SVM demonstrated to be the most adequate classification technique for such a problem.

That is, this paper reports a fast, clean and no destructive (without any sample preparation) methodology for assessing the category of Sherry vinegars. This may promote the usage of the proposed methodology as a fast technique to detect fraudulent samples and to assess the quality of the final product in comparison with other similar products found in supermarkets. The critical aspect of the classification results might be the few number of samples used for the study (a total of 57 samples, three replicates for 19 different varieties of Sherry vinegars). Nevertheless, since the methodology has been satisfactorily demonstrated its usefulness, the database will be increased with more vinegars of different producers.

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