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Usefulness of excitation-emission fluorescence *spectralprint* combined with chemometrics for authentication of PDO fortified wines

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ABSTRACT

Fortified wines covered by a Protected Designation of Origin (PDO) are high-quality products appreciated by consumers, whose diversity has increased in recent years, leading to an increased vulnerability to fraud. In this work, for the first time, an excitation-emission fluorescence spectroscopy method combined with two chemometric approaches was developed for the characterization and authentication of PDO fortified wines. A visual assessment of fluorescence landscapes pointed out different trends. The excitation-emission matrix (EEM) was decomposed using Parallel Factor Analysis (PARAFAC) for the extraction of potential fluorophores, or unfolded, and then, the resulting matrices were subjected to Principal Component Analysis (PCA) and Partial Least Squares-Discriminant Analysis (PLS-DA). Both approaches were able to discriminate the wine type within each PDO, the PDO within a wine type, and the production process. The proposed analytical and chemometric tools could be used as an alternative control method for a rapid screening of Spanish PDO fortified wines.

1. Introduction

Fortified wine is a high-quality product appreciated by its organoleptic characteristics, which has increased its diversity in the market in the last years. Among them, the Andalusian fortified wines are of very high quality and due to their uniqueness character have a great worldwide prestige. Some of them are under the protection of the European Union with a 'Protected Designation of Origin' (PDO) being the production associated to the land, the growing area, the grape varieties and the production and aging processes [1]. These include four of the first PDO in Spain: 'Condado de Huelva', 'Jerez Xérès Sherry', 'Montilla-Moriles', and 'Sanlúcar de Barrameda'. The unique characteristics of these fortified wines are determined by the different geographical areas of production, the grape variety used, the climate and the soil [2–4].

These fortified wines are made by two step process: the production phase, in which the base wine is made by fermenting all or part of the grape juice; and a second phase that is the aging in wood barrels to which these wines are subjected after fortification (addition of wine alcohol) to achieve the particular organoleptic and analytical qualities of their respective types of wine. In fact, the 'fortifying' is one of the most characteristic production processes of these wines, giving it its name. In addition to that, within each Andalusian PDO, there are different types of fortified wines, according to their characteristics and the special winemaking conditions for its aging that are described in their corresponding specifications: Fino, Manzanilla, Amontillado, Palo Cortado y Oloroso [2–4]. These wine types could be grouped into three aging types: biological aging, oxidative aging, and a mixture of both.

The Fino fortified wine type, produced by 'Jerez-Xérès-Sherry' (henceforth named 'Jerez'), 'Condado de Huelva' and 'Montilla-Moriles' PDOs, and the Manzanilla fortified wine, produced by 'Sanlucar de Barrameda' PDO, are obtained by biological aging after fortification to an alcohol content of 15° to 15.5°. This alcohol content allows the formation of the so-called 'velo en flor', a film of typical yeasts that is developed spontaneously on the wine surface, under which the wines age, preventing oxidation [2–4]. This phenomenon is undoubtedly one of those that gives these wines their uniqueness since the action of the metabolism of these yeasts causes significant changes in the wine and therefore, in its definitive organoleptic characteristics.

The Oloroso fortified wines, produced in the PDOs 'Jerez', 'Condado de Huelva' and 'Montilla-Moriles', are obtained by the oxidative aging. In this type of aging, the wines are fortified until they reach an alcohol content of 17° to 22°, making biological activity impossible, even for the

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'velo en flor' yeasts, which are particularly resistant to high alcohol levels, and the wine loses the protection that the 'velo en flor' provided against oxygen. Thus, these wines, after the disappearance of the initial 'velo en flor', have an aging process in which they are exposed to the direct action of air, which can be seen visually by the gradual darkening of the wine's color [2–4].

Finally, there are also fortified wines that share both types of aging, such as Amontillado and Palo Cortado fortified wines, produced in the PDOs 'Jerez' and 'Montilla-Moriles'. The production of these wines begins with biological aging under the 'velo en flor', being this period shorter in the case of Palo Cortado wines, and then they continue with oxidative aging. These combination gives them very particular organoleptic characteristics and greater complexity, and consequently reaching higher prices on the market.

The great diversity of fortified wines on the market, together with their high quality and high price, make them susceptible to fraud. For this reason, it is necessary to characterize them, establishing quality and authenticity control parameters that protect them against counterfeit, as well as to demonstrate and defend its identity. However, one of the difficulties is that as they are very complex products, their characterization comprises a wide range of values obtained from physicochemical and sensory parameters [5]. Moreover, their quality and differences are also determined by many factors such as the specific production area, the starting materials used as fermentation substrate, the fermentation process, and the subsequent aging period [6,7]. The common methods used for wine characterization, such as gas or liquid chromatography or mass spectrometry are robust and efficient, but also expensive and laborious [5,6,8,9]. Consequently, there has been a growing need to develop fast, inexpensive, robust, and efficient analytical methods, requiring little sample handling, for the characterization and classification of wine samples [10–13].

Spectroscopic techniques are among these emerging techniques, as they provide a lot of information from a single measurement step with very little or no sample treatment, yielding a unique spectral shape for each sample that can be interpreted as a fingerprint itself, also recently called a *spectralprint* [14]. In this context, excitation-emission fluorescence spectroscopy is an emerging competitive technique for food characterization, since it provides an excitation-emission landscape or matrix (EEM) for each sample in a short time, by acquiring successive excitation and emission spectra at multiple emission or excitation wavelengths, which may be used as a genuine fingerprints of the wine [15,16]. For that reason, this technique can be an excellent candidate to be used for the discrimination of wine samples due to it could reflect the slight differences of total chemical information between them, and it is fast and nondestructive. In fact, some studies have been reported on the applications of three-dimensional fluorescence spectra to the discrimination of different wine samples until now, with the aim of discriminating different production processes [17,18], the grape variety [19,20], or even the geographical origin [11,14,15,21–23].

In addition to these studies, other researchers have also been committed to evaluating the potential of multidimensional fluorescence technique to classify wines according to their origin appellation, e.g., their specific PDO [24]. This aim was also searched by the study of other spectroscopic techniques such as UV–visible (UV-Vis) and near-infrared (NIR) that showed to be able to classify other Spanish PDOs wines of different subzones within a Rías Baixas [25] or the identification of Chinese red wines by UV–vis [26]; as well as it was possible to achieve a good terroir differentiation and different subregions in the Rioja PDO by nuclear magnetic resonance (NMR) [27].

Furthermore, the combination of multidimensional fluorescence with Parallel Factor Analysis (PARAFAC) allows to simultaneously decompose fluorescence Excitation-Emission Matrix (EEM) into different fluorescence components, as well as their relative concentration (scores), extracting the most relevant information from the data useful for building robust models [28]. Hence, in previous studies, this combination proved to be very suitable for studying wines and vinegars [19,21,29–32]. In fact, PDO wine vinegars from the same PDO than Andalusian PDO fortified wines ('Jerez', 'Condado de Huelva' and 'Montilla-Moriles') were also differentiated by multidimensional fluorescence [31]. However, and despite all this, to our knowledge, this is the first time that EEM fluorescence spectroscopy coupled to chemometrics is used in these PDO fortified wines.

Consequently, the aim of this work was to assess, for the first time, excitation-emission fluorescence spectroscopy combined with two chemometric approaches, as a fast, inexpensive, robust, and effective method for the characterization and differentiation of PDO fortified wines that do not require any sample manipulation.

2. Materials and methods

2.1. Fortified wine samples

A total of 104 fortified wines from the four different Andalusian PDOs were analyzed in this study, including samples from different producers, and considering the different types included in each PDO. More information about the samples is shown in Table 1, including the coding and the number of samples per each PDO and type of fortified wine. All these samples were controlled and provided by the Regulatory Councils of each PDO and associated wineries. The number of samples was limited to the production/sale rates of each type produced during the last years (2021–2022), being the reason of the unbalancing of samples within each type and PDO. Among these samples, different cellars and different time of aging were considered.

2.2. Fluorescence analysis

Fluorescence spectra were recorded using a Varian Cary-Eclipse fluorescence spectrophotometer (Varian Iberica, Madrid, Spain), equipped with two Czerny-Turner monochromators, and a Xenon discharge lamp pulsed at 80 Hz with a half peak height of 2 ms (peak power equivalent to 75 kW). A high-performance R298 photomultiplier tube detector was used for collecting the fluorescence spectra. Wine samples were directly analyzed without sample pre-treatment by pipetting them into 3.5 mL quartz cuvettes (Hellma Analytics, Müllheim, Germany) of 1 cm path length, in a Peltier thermostatted cuvette holder (25.00 ± 0.05 °C). The spectrometer was interfaced to a computer with Cary-Eclipse software for spectral acquisition and exportation.

Table 1
Information of the samples analyzed in the study.

Type of aging	Type of wine	Codes	Protected Designation of Origin (PDO)	Codes		Number
Oxidative	Oloroso	OL	Jerez Xérès Sherry	J	JOL	9
			Condado de Huelva	C	COL	8
			Montilla-Moriles	M	MOL	8
Biological	Fino	FI	Jerez Xérès Sherry	J	JFI	9
			Condado de Huelva	C	CFI	5
			Montilla-Moriles	M	MFI	34
	Manzanilla	MA	Sanlúcar de Barrameda	S	SMA	5
Biological and Oxidative	Amontillado	AM	Jerez Xérès Sherry	J	JAM	10
			Montilla-Moriles	M	MAM	9
	Palo cortado	PC	Jerez Xérès Sherry	J	JPC	4
			Montilla-Moriles	M	MPC	3

The fluorescence EEM was obtained by varying the excitation wavelength ranging between 250 and 700 nm (every 5 nm), recording the emission spectra from 300 to 800 (every 2 nm), and the scan rate was fixed to 1200 nm min^{-1}. The system was wavelength-calibrated every day by means of the water Raman peak, serving as a reference for system stability and as a quality control measurement. EEM fluorescence landscapes were registered by duplicate for each sample.

2.3. Data analysis

The global EEM data analysis was performed by using the PLS_Toolbox 7 (Eigenvector Research Inc., Wenatchee, WA) working under Matlab environment (2016, The Mathworks Inc., Natick, MA). First, the EEM matrix was normalized by dividing the spectrum of each sample by the corresponding average calibration Raman spectrum, thus controlling and correcting for possible variations in the stability of the EEM signals throughout the measurement process. Then, EEMs normalized data were pre-processed to correct and remove Rayleigh and Raman scattering by using the FLUCUT function included in the PLS_Toolbox. This function allows to remove the scattering areas in two different options, by removing and replacing them with 0 values, or with interpolated values. After testing both procedures, the interpolation of these values was selected for replacing the scattering since it provided the best results. Finally, the corrected EEM matrix was processed by two different chemometric approaches. The data analysis workflow developed in this study is schematized in Fig. 1.

The first strategy used PARAFAC [28], in order to extract the relevant information useful for characterizing each fortified wine. The proper number of factors was determined using the CORe CONsistency DIAgnostic test (COR-CONDIA) [33], the percentage of explained variance and by the visual inspection of the recovered spectral profiles and residuals of different models performed with an increasing number of factors. Non-negative constraints for all modes were applied. In addition, a PARAFAC model was made for each type of fortified wine to explore in depth the differences.

The second strategy consisted of the unfolding of the EEM in a multiset structure via row-wise augmentation i.e., the EEM data with a dimension of 208 x 101 x 81 was reshaped to a matrix of 208 x 8181 dimension.

In order to perform a screening of samples and to reflect the sample distribution in latent space, principal component analysis (PCA) was applied to the scores of the obtained PARAFAC factors (1st strategy) as well as of the unfolded EEM (2nd strategy). Additionally, significant differences of PARAFAC scores for each factor comparing different groups of samples were obtained by analysis of variance (ANOVA) followed by a post hoc comparison test (Tukey's test) using INFOSTAT software (FCA, Universidad Nacional de Córdoba, Argentina).

Moreover, partial least Squares-discriminant analysis (PLS-DA) was developed with the scores of the extracted fluorophores in the case of the PARAFAC strategy (henceforth named PARAFAC-PLS-DA), and the unfolded matrix in the case of the 2nd strategy (henceforth named Unfolded-PLS-DA), previously preprocessed by autoscaling and mean centering, respectively, to build different classification models for discrimination of the PDO and types of the fortified wines, considering all the possible combinations: 1) the general differentiation of the aging type (biological vs oxidative, and biological vs oxidative vs mixed); 2) Type differentiation within each PDO (CFI/COL, JAM/JFI/JOL/JPC, and MAM/MFI/MOL/MPC)); 3) and the PDO differentiation within each type (FI (C/J/M), PC (J/M), OL (C/J/M), AM (J/M), FI vs MA (J/S)).

The proper number of latent variables for each PLS-DA model were assessed by the minimum classification error rate in cross-validation (venetian blind, five splits). For the validation of the models, the dataset was randomly divided into two groups employing the Kennard–Stone algorithm: a training set comprising the 80 % of the samples according to each classification model, and a test set with the remaining 20 % of the samples. The training set was used for model development and internal validation by means of venetian blind cross-validation, while the test set was used as external independent dataset to evaluate the models. All the models were evaluated comparing the number of latent variables retained and the classification indices derived from confusion matrix: sensitivity, specificity, and correct classification rate (%) of calibration (CAL), cross-validation (CV) and prediction (PRED) parameters.

3. Results and discussion

3.1. Visual assessment of fluorescence landscapes

The fluorescence landscapes (after removing and replacing the scattering) of the EEM of representative samples belonging to the different PDO and types of fortified wines are shown in Fig. 2. These EEMs provide a total emission intensity profile of the sample over the range of excitation and emission wavelengths scanned, that could be

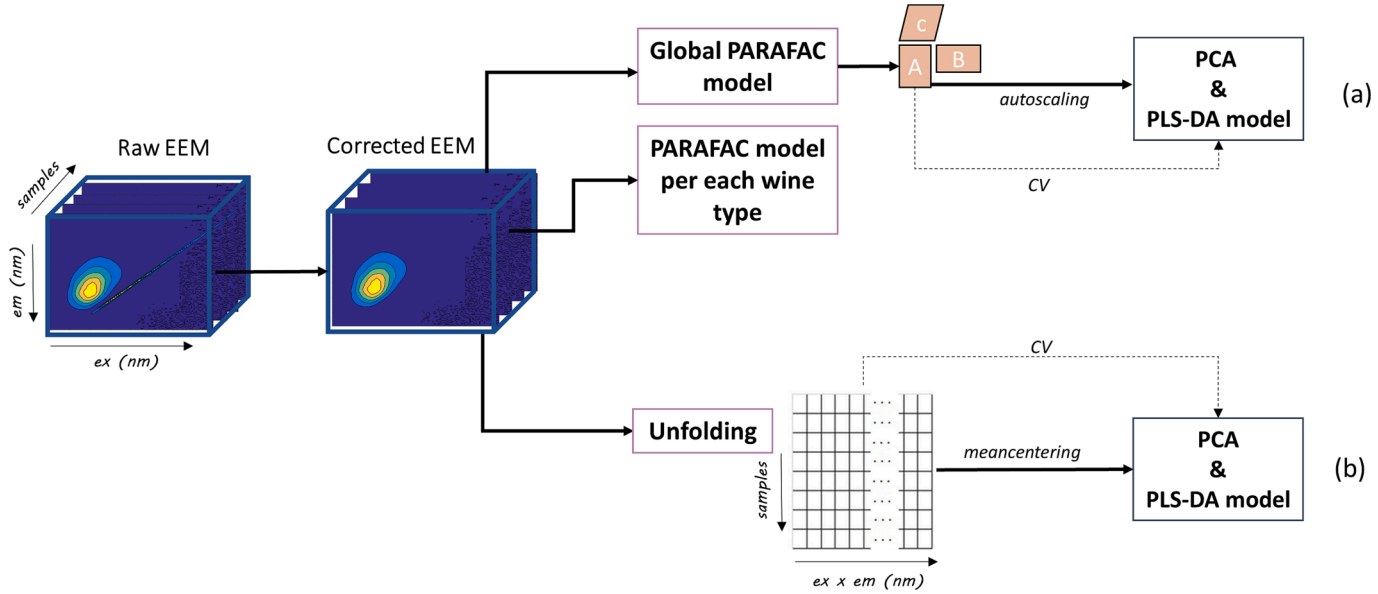

Fig. 1. Data analysis workflow of the study: a) PARAFAC strategy; b) Unfolding strategy.

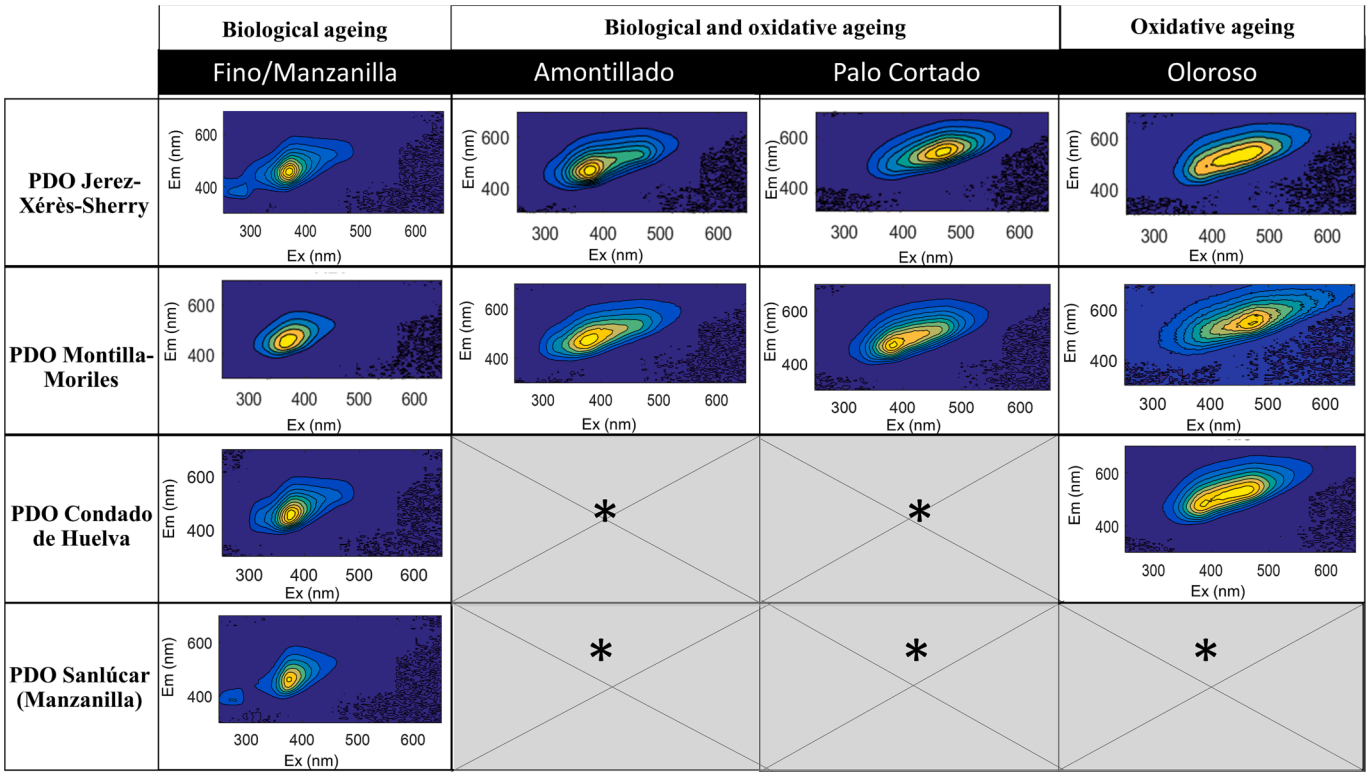

Fig. 2. Emission-Excitation fluorescence landscapes obtained for selected fortified wines belonging to different types according to the production and PDO. Note: * wine types not available for this PDO.

used as *spectralprint* of each wine.

A visual assessment of the fluorescence features showed some similarities between the same type of wine. Thus, in general, it seemed that the spectral features had a general tendency for the spectral maxima to be shifted towards longer excitation and emission wavelengths for wines with oxidative aging. In fact, the fluorescence landscapes of samples with oxidative aging showed a similar shape and maxima than the most aged wine vinegars of the same PDO that were studied in previous works [29,31]. Moreover, Airado-Rodriguez et al. [11] also showed a similar trend of increasing the emission at longer wavelengths with the aging of red wine samples, due an increase in concentration of fluorescence substances [11]. However, apart from this trends, important differences in the whole landscape of the EEM spectra among different types and PDOs could be observed, revealing *a priori* some differences between wines with different aging process or type in each PDO, and even within the same types among PDOs. Thus, for example, fortified wines with biological aging, i.e., Fino and Manzanilla, showed a maximum peak around 370/450 nm for excitation/emission wavelengths (λex/λem), whereas the maximum peaks corresponding to the fortified wines with oxidative aging (i.e., Oloroso) appear at higher wavelengths, around 470–500 nm of λex and 550–600 nm of λem. Finally, the samples with both aging types (i.e., Amontillado and Palo Cortado) showed their maxima around 400/500 nm of λex/λem, being between the aforementioned two types.

3.2. PARAFAC results

After a preliminary visualization of fluorophores in the fluorescence landscape was done, to clarify the potential fluorophores presented in each fortified wine, further decomposition of EEM spectra by PARAFAC will be performed (1st strategy). This procedure helps to identify the fluorophores, which are highly overlapped in the spectra due to wine contains a wide range of naturally fluorescent compounds whose sum contributes to the total EEM of a wine.

The best PARAFAC model with the total amount of samples was obtained with 6 factors, being a robust model as it explained more than 99 % of the variance and had a core consistency over zero. Therefore, the extracted fluorescent components can be considered to be the main ones in the PDO fortified wines. Fig. 3a showed the PARAFAC loadings (excitation and emission spectra) of the 6 extracted factors and the corresponding wavelength of their fluorescence emission and excitation maxima. Moreover, three new PARAFAC models were done, one for each type of wine grouped according to the aging process (i.e., biological, oxidative and the mixture of both) to explore in depth each type of aging, and to better study the differences between them (Fig. 3b).

From Fig. 3a and b it could be concluded that there were three factors that appear in all the models, which were the F1, F2 and F4 in the 6-PARAFAC model (Fig. 3a), with excitation/emission maxima around 335/436 nm, 375/444 nm, and 460/524 nm (λex/λem), respectively. These factors appeared also in the individual PARAFAC models, although with other numbers but the same color: blue, orange, and purple, respectively, being therefore fluorophores in common for all the fortified wines. The profiles of these PARAFAC components agree with the visual inspection of the fluorescence data above discussed (Fig. 2).

The identification of these fluorophores is a difficult task, as was discussed above. However, some assignments of PARAFAC profiles and specific fluorophores could be done thanks to the literature, where the excitation-emission wavelengths of some important wine components have been already described for other wine and wine vinegar samples [11,31]. Thus, among them, it is known that most of these compounds belong to a large family of polyphenols. The maximum λex/λem of F1 (Fig. 3a), a common factor among all the samples colored in blue and with an excitation/emission maxima around 335/435 nm, respectively, matched with the ones reported in the literature for phenolic compounds that have showed an λex/λem maxima around 330/420 nm [11,12,16,19,21,29,34]. These are the best-known fluorescent molecules naturally present in wine, which includes phenolic acids and phenolic aldehydes, as well as oxidation and Maillard reaction products

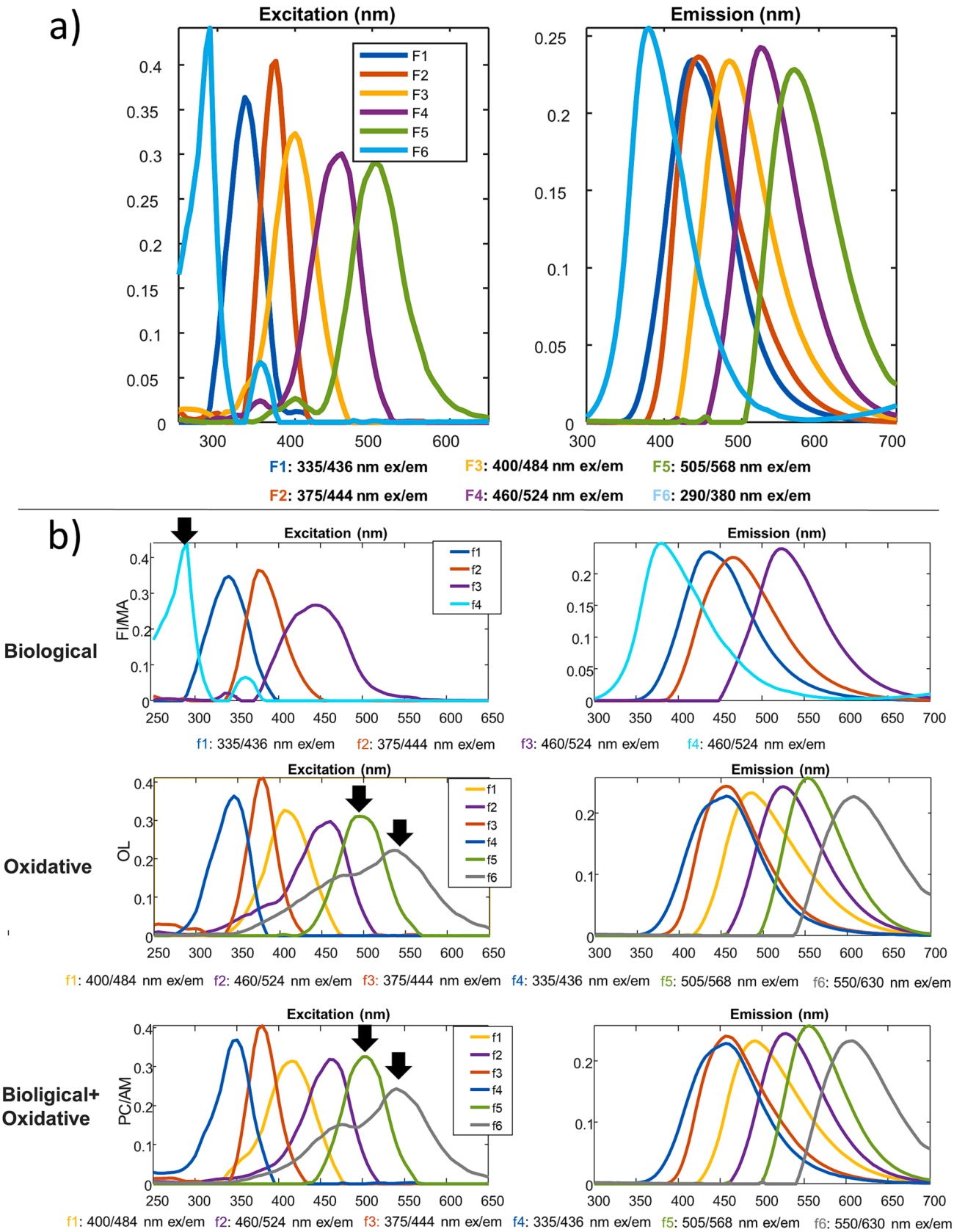

Fig. 3. Excitation and Emission spectra (PARAFAC loadings) of the main fluorophores present in (a) the fortified PDO wines; and (b) on each type of fortified wine according to the aging process.

(present due to browning processes and oxidative mechanisms taking place during aging and storage). According to the excitation/emission maxima of F2 (Fig. 3a), another common factor among all the samples colored in orange and with an λex/λem around 375/444 nm, could be related to the presence of coumarins, tannins and other unknown fluorescent compounds originated from wooden casks [35], as well as phenols and flavonols, naturally presented in wines [11,34]. Finally, the other common factor for all the models was F4 (Fig. 3a), colored in purple in all the models and showing an λex/λem maxima around 460/524 nm ex/em, could be related to the presence of vitamins such as Riboflavin (vitamin B2) and the principal forms of vitamin B2 found in nature such as riboflavin, flavin mononucleotide (FMN), and flavin adenine dinucleotide (FAD) according to the literature [11,29,36].

Other factors seemed to be more related to a specific fortified wine, which were highlighted with a black arrow in Fig. 3b. Thus, F3 (Fig. 3a), colored in yellow in the global model and only appearing in the models of oxidative and mixed aging (Fig. 3b), with an λex/λem maxima around 400/484 nm, could match with the wavelengths of the compound 5-Hydroxymethylfurfural (HMF) that has been related to aging according to Zhu, Ji, Eum, and Zude [37]. This agrees with the fact that biological samples suffer a shorter period of aging since the 'velo en flor' yeast ends up being consumed, while oxidative aging could be as long as desired that could cause the production of new fluorophores as well as the concentration of others.

Moreover, there were two factors that seemed to be only presented in wines that are subjected to oxidative aging, either singly or in combination with biological aging, due to they were not extracted, or they did not appear in the PARAFAC model made with biological samples. These factors were F5 and f5 in Fig. 3a and b respectively, at 505/568 nm λex/λem and colored in green in all the models, and the factor colored in grey and named f6 in the individual PARAFAC models made with oxidative and mixed aging, with λex/λem maxima around 550/630 nm (Fig. 3b). According to the literature, the excitation/emission wavelengths of F5 matched well with the fluorescence of individual molecules such as flavonols such as quercetin, quercitrin, or kaempferol, which are fluorescent molecules previously reported in wine [11,36], whereas the λex/λem profile of the factor f6 did not exactly match with any reported fluorophores to our knowledge. These two factors showed high λex/λem maxima, being consistent with previously observed feature landscapes (Fig. 2), where spectral maxima were found at longer excitation and emission wavelengths in oxidatively aged samples compared to those with biological aging. As was explained before, these two kinds of wines can undergo to a longer aging process, because they do not depend on the life of the 'velo en flor' yeasts. Thus, these factors could be related to the formation of new compounds during oxidative aging, the oxidation of some other compounds, as well as their concentration due to the evaporation of water that occurs during this process. In fact, a similar trend was observed by Airado-Rodriguez et al. [11], whose fluorescence landscapes showed a tendency to increase towards longer emission and excitation wavelengths as aging increased, due to an increase in the concentration of fluorescent substances [11].

On the contrary, F6 in the general PARAFAC model (Fig. 3a), and f4 in the individual PARAFAC model of biological samples (Fig. 3b), both colored in light blue and with a maxima at 290/380 nm λex/λem, seemed to be related to wines with biological production, as it was a factor that was not present in the other models made with wines with oxidative and mixed aging (Fig. 3b). According to its λex/λem maxima, it could be related to compounds such as flavan-3-ols, with a reported excitation and emission wavelengths in the ranges 278–290 and 310–360 nm, respectively, as well as epigallocatechin and some polymeric pro anthocyanidins that have been included in this range [11]. Moreover, this factor could be also associated to *cis*-stilbene-like compounds, with excitation and emission wavelengths reported by other authors around 260 and 400 nm, respectively [38,39].

Although some relations could be made, it should be considered that the fluorescence signals are greatly influenced by the food nature, so a specific fluorophore studied in different foods can present differences in the ex/em wavelengths. For this reason, the wavelengths values above mentioned should be considered as tentatively assignments, and they could not be exactly equal to the values reported in the literature or for pure fluorophores [40]. However, as the aim of this study was not pure characterization, but rather differentiation, the exact assignment of compounds is not so necessary.

In addition, to observe the differences in the presence of these fluorophores in the samples, the mean, standard deviation of scores and Tukey's test results obtained for each factor of the 6-factor PARAFAC model are also showed in Table 2, considering a mean for each type of fortified wine and the mean for each type and PDO. Once again there were clear and significant differences in the fluorescent composition between samples with biological aging (FI and MA), with higher significant scores for F1, F3 and F6, from the samples with oxidative aging or the combination of both which showed higher significant scores for F2, F4 and F5. Furthermore, although some factors showed a high deviation within a sample type possibly due to variability induced by including different PDOs, i.e., different grape varieties, the overall difference in the mean scores of each type was still significant. This difference was also clearly seen within each PDO independently. For example, in 'Condado de Huelva' PDO, there is a clear difference between FI and OL samples, being again the F1, F2 and F3 higher in FI samples and the F4 and F5 predominant in OL samples.

There were also significant differences according to the PDO within the same type of sample (Table 2) in almost all the fluorescent factors. For example, it could be seen that although F1 was a common fluorophore in all the samples, it showed differences between PDOs, mainly observed in the FI samples. Thus, FI samples from 'Montilla-Moriles' PDO (MFI) showed significant higher scores values for this factor in comparison to the other types and PDOs. The differences in all these modelled factors, by means of different ex/em maxima and different mean score values, were probably related to the differences in the chemical composition of these fortified wines, because of the different raw material used (grape variety), geographical area of production and different aging processes for each PDO and type of fortified wines considered in the study.

3.3. *Differentiation of wines according to the aging type and the PDO based on different strategies*

First, to explore the discriminating potential of the PARAFAC model of the first strategy, the score values of the obtained factors from the 6-factor PARAFAC model were represented in a bidimensional plot, being the clearest differentiation found between the two types of aging with the combination of F5 and F6 (Fig. 4).

In addition, to fully visualize the real separation between the different fortified wines, and to assess if multidimensional fluorescence using fluorescent compounds or unfolded matrix could be used to differentiate the different types of fortified wines, a principal component analysis (PCA) was carried out with the 6-factor PARAFAC scores with the total of samples (Fig. 4b and c) and with the unfolded EEM (Fig. 4d and e). Regarding the scores plot on the plane of the first and second principal components (PC1-PC2) in the PCA model performed with the score values of this 6-PARAFAC factors (Fig. 4a), a clear distinction could be observed between the two main types of production (oxidative and biological) along the first principal component (PC1). Looking at the loadings (Fig. 4c), it is possible to notice that F4 and F5 were more related to the biological and oxidative, and F1, F2, F3 and F6 for biological wines, agreeing with the results above discussed. Regarding the unfolded strategy, the differentiation of both types of aging was also observed but with some samples overlapped (Fig. 4d).

As PDO differentiation was not clearly observed by the PCA made with all the samples, different PCA models were developed separately for each type of wine to further explore whether unsupervised analysis of PARAFAC data or unfolded EEM could separate the PDOs (Figs. 5 and

Table 2
Mean, standard deviation of the scores and Tuey's test results obtained by the 6-factor PARAFAC model for each aging type, and for each type of fortified wine.

Fortified wine type		PARAFAC factors (ex/em)																	
		F1 335/436 nm			F2 375/444 nm			F3 400/484 nm			F4 460/524 nm			F5 505/568 nm			F6 290/380 nm		
		Mean	±SD	T*	Mean	±SD	T	Mean	±SD	T	Mean	±SD	T	Mean	±SD	T	Mean	±SD	T
Biological	**FI**	21.6	10.8	b	19.6	6.3	b	15.3	4.6	b	8.4	5.5	b	1.2	0.6	b	3.8	2.5	a
	MA	14.4	9.1	a	13.6	2.0	a	10.5	2.6	a	3.6	1.7	a	0.8	0.3	a	6.2	2.5	b
	T*	***20.9***	***10.9***	***B***	***19.0***	***6.2***	***C***	***14.9***	***4.7***	***B***	***7.9***	***5.5***	***A***	***1.2***	***0.6***	***A***	***4.1***	***2.6***	***B***
Biological+Oxidative	**AM**	4.3	2.5	–	9.0	5.5	–	14.1	5.0	a	14.2	4.4	a	5.8	2.8	a	0.4	0.3	b
	PC	4.1	1.7	–	8.8	3.7	–	17.2	4.6	b	18.4	3.7	b	7.9	3.4	b	0.2	0.1	a
	T	***12.5***	***2.3***	***A***	***13.5***	***5.0***	***B***	***14.3***	***5.1***	***B***	***10.7***	***4.6***	***C***	***3.5***	***3.1***	***C***	***2.2***	***0.3***	***A***
Oxidative	**OL**	3.4	2.7	–	6.4	5.3	–	12.6	5.9	–	11.6	4.3	–	5.2	1.8	–	0.2	0.2	–
	T	***3.4***	***2.7***	***A***	***6.4***	***5.3***	***A***	***12.6***	***5.9***	***A***	***11.6***	***4.3***	***B***	***5.2***	***1.8***	***B***	***0.2***	***0.2***	***A***
FI/MA	**CFI**	18.1	8.3	*bc*	17.0	4.0	*ab*	11.3	3.7	*a*	4.2	1.7	*ab*	0.7	0.3	*a*	2.5	1.9	*a*
	JFI	9.5	9.7	*a*	20.8	6.8	*b*	16.1	4.5	*b*	8.9	6.6	*b*	1.3	0.7	*ab*	4.1	2.4	*ab*
	MFI	26.2	8.0	*c*	20.0	6.0	*b*	15.8	4.5	*b*	8.9	5.4	*b*	1.3	0.6	*b*	4.1	2.5	*ab*
	SMA	14.4	9.1	*ab*	13.6	2.0	*a*	10.5	2.6	*a*	3.6	1.7	*a*	0.8	0.3	*a*	6.2	2.5	*b*
AM	**JAM**	3.6	2.2	–	8.7	5.4	–	13.7	4.9	–	12.8	3.5	**a**	5.4	2.2	–	0.4	0.4	–
	MAM	5.1	2.8	–	9.5	5.7	–	14.5	5.3	–	15.9	4.9	**b**	6.4	3.3	–	0.3	0.3	–
PC	**JPC**	3.3	1.7	**a**	7.5	4.3	–	16.1	5.9	–	18.3	4.6	–	8.9	4.1	–	0.1	0.1	–
	MPC	5.1	0.9	**b**	10.6	1.6	–	18.7	1.5	–	18.5	2.1	–	6.5	1.6	–	0.2	0.2	–
OL	**COL**	2.9	1.6	a	4.7	2.8	a	11.4	5.1	–	11.4	4.4	–	5.5	1.5	ab	0.1	0.1	a
	JOL	1.8	0.6	a	4.9	2.9	a	12.1	4.8	–	11.8	3.9	–	5.8	2.2	b	0.2	0.1	ab
	MOL	5.8	3.3	b	9.7	7.5	b	14.3	7.4	–	11.6	4.8	–	4.2	1.0	a	0.3	0.3	b

T*: Tukey test results obtained for each factor individually. The results of the Tukey test must be read from top to bottom, so different letters in different rows of a specific factor mean a significant difference between the compared samples for this factor: Lowercase letters compared Fi vs MA, or AM vs PC; lowercase and italic letters compare FI/MA PDOs; Bold lowercase letters compare JAM vs MAM and JPC vs MPC; underlined lowercase letters compare OL PDOs. Capital letters in italics compare Biological vs Biological+Oxidative vs Oxidative aging.

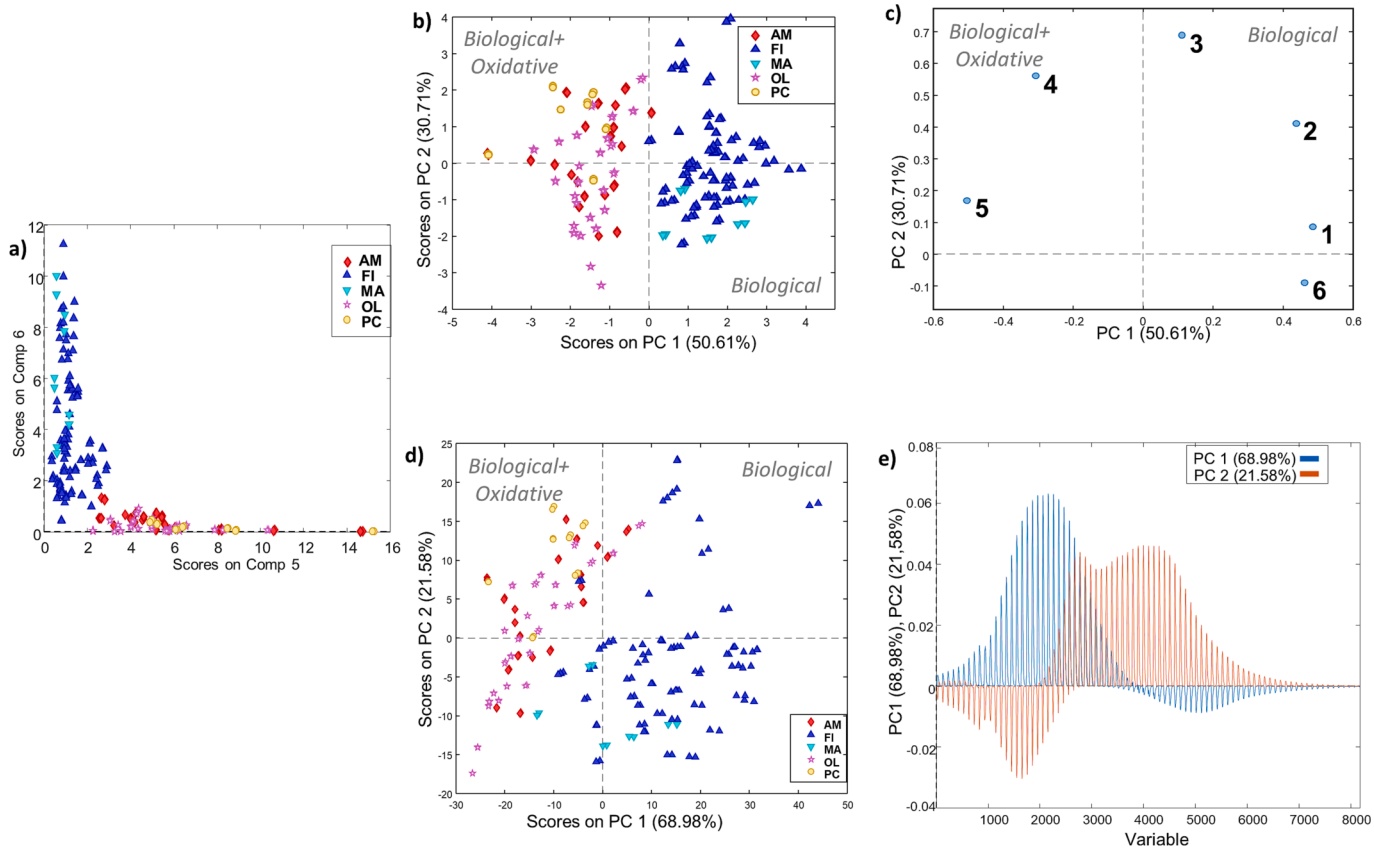

Fig. 4. Bidimensional plot of the scores of the factors 5 and 6 obtained with the 6-factor PARAFAC model (a). Score (b) and loading (c) plots obtained by the PCA carried out with the 6-factor PARAFAC scores with the total of samples. Score (d) and loading (e) plots obtained by the PCA carried out with the unfolded EEM matrix. Sample coding is detailed in Table 1.

6). Thus, five new PCA models were made with the scores of the 6-PARAFAC model and with the unfolded data, considering, in this case, only each type of fortified wine, i.e., biological wines (Figs. 5 and 6, a and b), biological & oxidative wines (Figs. 5 and 6, c and d) and oxidative wines (Figs. 5 and 6, e), with the aim of studying the differentiation between PDOs. The score plots of all the models showed a grouping of the samples according to each PDO considering each type of wine separately, except for FI samples in both strategies (Figs. 5a and 6a).

Looking at the loadings of the first strategy (PARAFAC strategy), in general, it was possible to notice that F1 was more related to 'Montilla-Moriles' PDO in all the models, and therefore, wine types, while F5 seemed to be more related to 'Jerez' PDO. Moreover, although there could not be seen a differentiation of FI samples according to the PDO, this differentiation was observed between FI and MA of the same geographical zone, i.e., between the PDOs 'Jerez' (J) and 'Sanlúcar de Barrameda' (S). In this case, the loadings showed that MA samples had a higher relation to F1 and F6, while FI samples from 'Jerez' were explained by the rest of factors. Regarding the loadings of the unfolded strategy, although they are less informative, the loadings also showed different profiles for each PDO and kind of sample.

These results revealed that for all the wine types under study, the relative values of these factors (scores) vary as a function of the PDO, highlighting the fact that the composition of the fortified wines depends not only on the raw material used (grape variety) but also on the specific geographical location and the different production conditions to which the wines have been subjected in each PDO. Moreover, the results obtained from both strategies could explain that the factors extracted by PARAFAC are as informative than the global EEM and could be able to provide the chance to successfully discriminate the fortified wines according to the type of aging as well as to the PDO of similar wine types, vs from more straightforward models. However, the use of PARAFAC has the disadvantage of being a more complex chemometric approach to be performed than the unfolding of an excitation-emission matrix that is more direct although less informative. As both strategies have its advantages and disadvantages, and the separation of samples seemed to be similar, both strategies were considered to perform classification models.

3.4. Classification of fortified wines according to the aging type and the PDO based on different strategies: PARAFAC-PLS-DA and Unfolded-PLS-DA

To be able to evaluate the classification performance, different models were developed using the scores obtained by PARAFAC (i.e., PARAFAC-PLS-DA strategy) and the unfolded matrix (i.e., Unfolded-PLS-DA strategy). Classification results, in terms global % of correct classification for calibration, cross-validation and prediction, for both approaches are shown in Fig. 7. Moreover, the number of latent variables of the different models, as well as the sensitivity and specificity classification parameters of them, are shown in Table 3.

The two approaches showed similar classification performances (Fig. 7, Table 3); however, in some of the classification purposes the unfolded approach showed slightly better results. This could be explained by the fact that the unfolded matrix keeps the total information while the PARAFAC implies a reduction in information. Nevertheless, although the reduction of the information provided slightly decreases the classification rates, the decrease is not significant, so it can be concluded that the relevant information is almost completely preserved, which is therefore also a satisfactory strategy. Moreover, this happens mostly in the calibration models, but in the prediction stage the

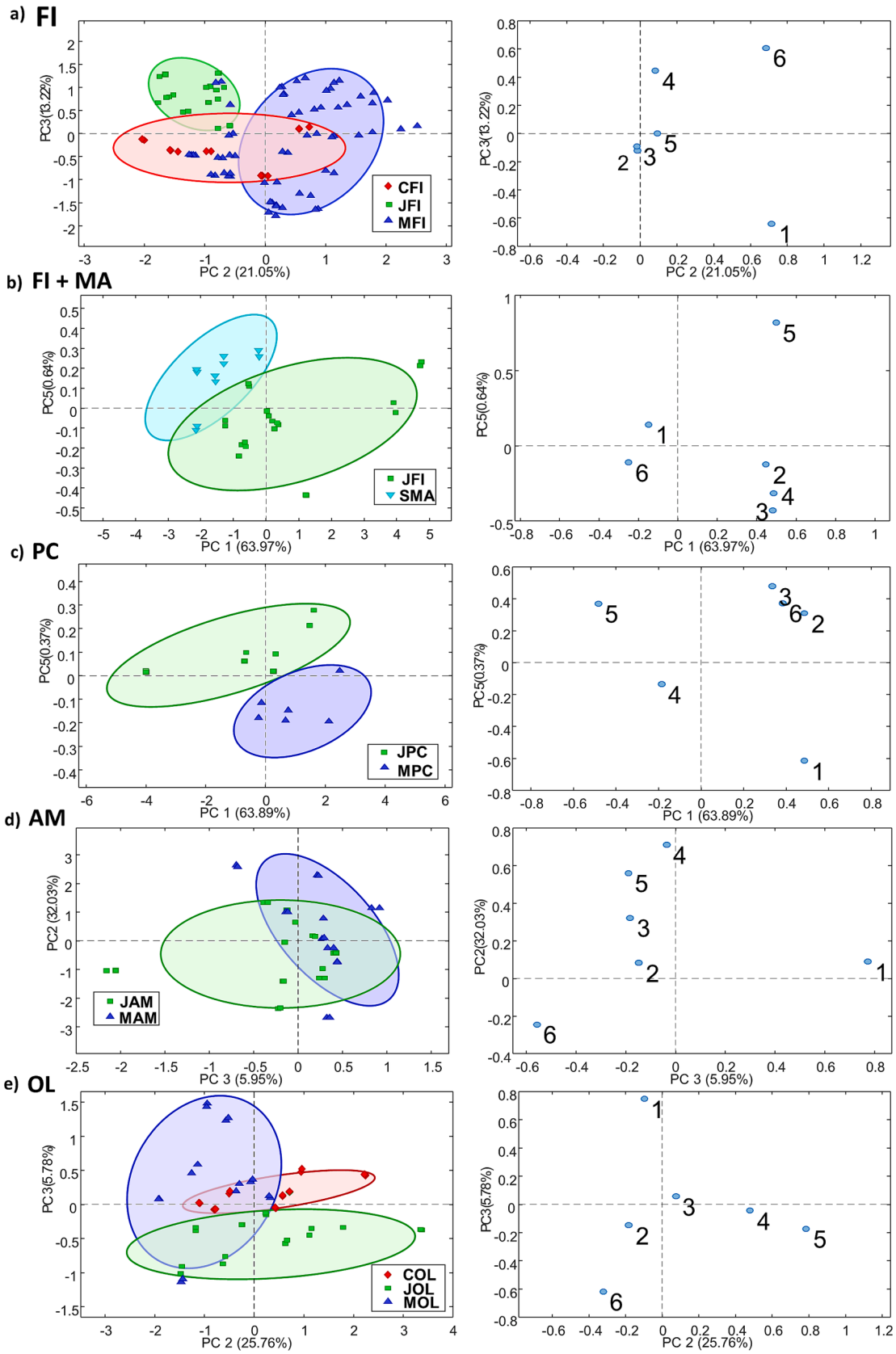

Fig. 5. PCA models developed separately for each type of wine with the scores of the 6-factor PARAFAC model: biological wines (a and b); oxidative + biological wines (c and d); and oxidative wines (e).

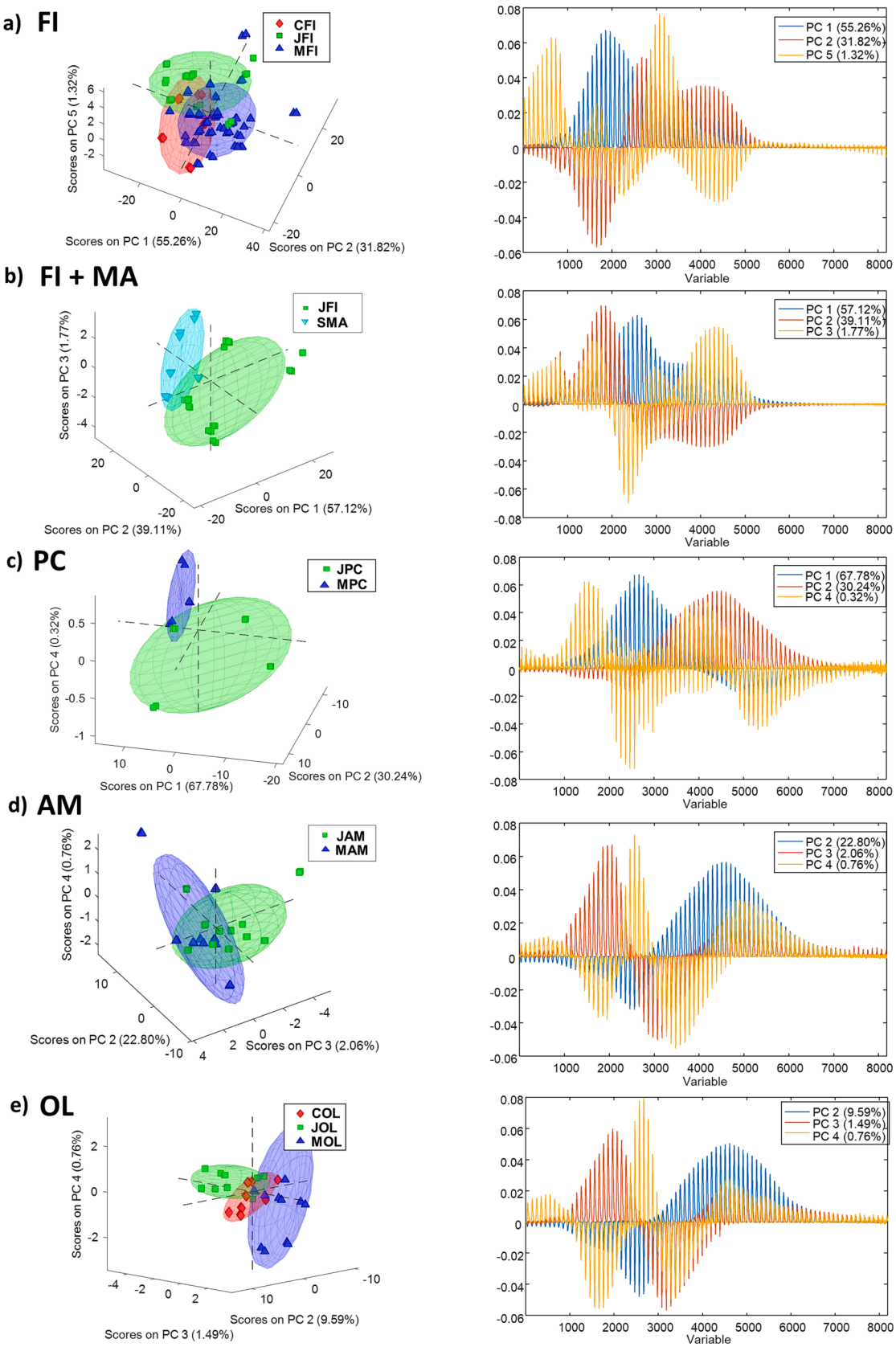

Fig. 6. PCA models developed separately for each type of wine with the unfolded EEM: biological wines (a and b); oxidative + biological wines (c and d); and oxidative wines (e).

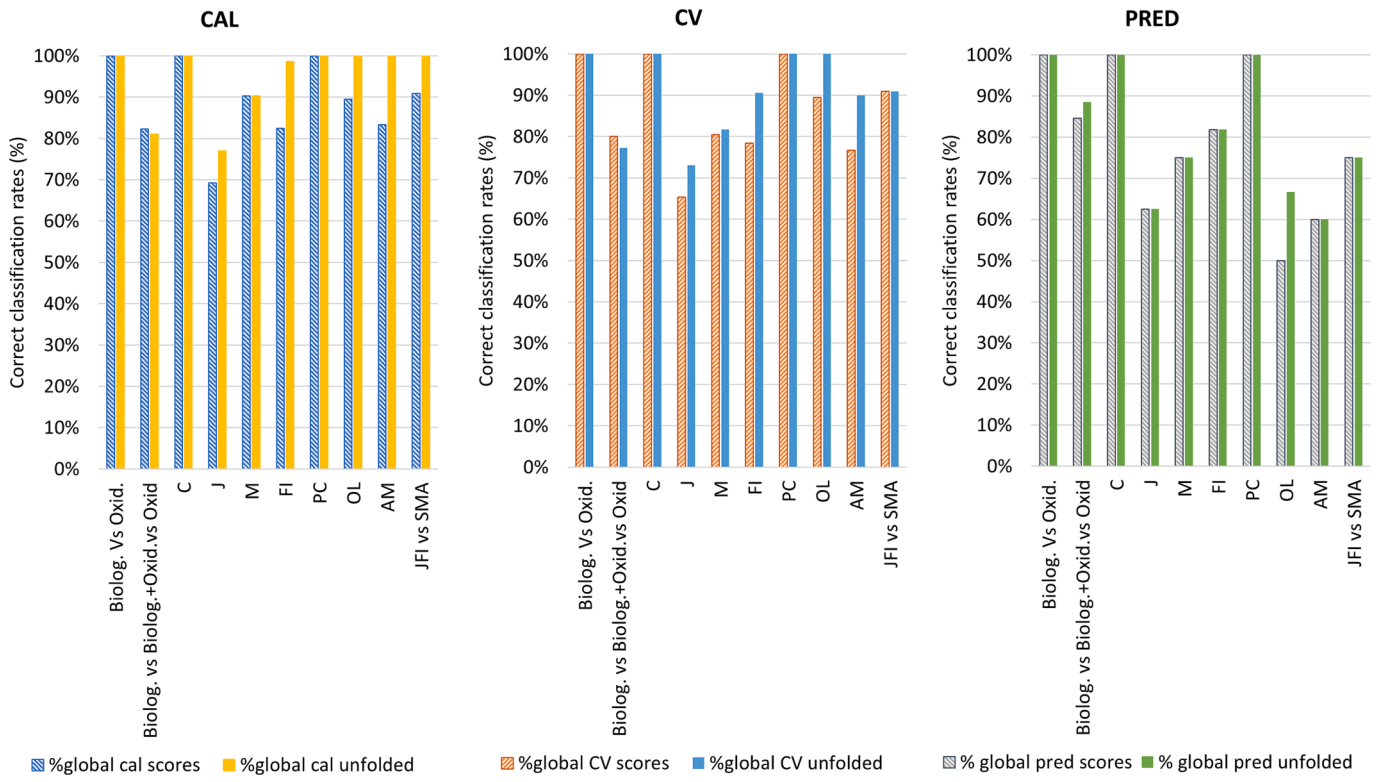

Fig. 7. Global classification rates (%) for calibration (CAL), cross-validation (CV) and prediction (PRED) of the PLS-DA models developed with the PARAFAC scores and the unfolded matrix. Notes: Biolog. = FI & MA; Oxid. = AM, PC & OL; C = CFI vs COL; J = JFI vs JAM vs JOL vs JPC; M = MAM vs MFI vs MOL vs MPC; FI = C vs J vs M; PC = JPC vs MPC; OL = C vs J vs M; AM = JAM vs MAM.

results evened out. Hence, the PARAFAC strategy could be a better option as to its satisfactory classification results, it allows a better understanding of which fluorophores are present in the samples and which are responsible for the classification, while unfolded data provides non-specific information on this. In this regard, other authors who have also recently addressed the evaluation of different EEM data processing strategies using PARAFAC-PLS-DA and Unfolded-PLS-DA for wine classification obtained similar results, with the classification performance of the second strategy being slightly superior [21].

The highest percentages of classification (% of correct classification rate, Fig. 7) were obtained for the differentiation between biological and oxidative in general, or in the case of the PDO 'Condado de Huelva' (Fig. 7), as it was expected according to the previous PCA results in which the samples were clearly grouped. In fact, as it was observed in the PCA results, the type of aging, i.e. biological, oxidative, and mixed, influences the fluorescence profile more than the PDO (geographical origin). For this reason, the classification performance in these models was satisfactory despite considering different geographic locations, varieties, etc. In addition, geographical origin was also seen to affect the fluorescence signals as shown by the satisfactory results obtained when the model was performed for the classification of PDOs within the same type of aging. Thus, the differentiation of PDOs, that is a difficult task, showed also successful classification rates mainly for calibration and cross-validation. The lowest percentages of correct classification were obtained for the predictions sets, that can be explained by the fact that the number of samples in some cases were low, and therefore, a misclassification of one sample represents much more in percentage values than when considering larger number of samples.

According to the exploratory and classification results, both approaches could be satisfactory strategies. The selection of one of them versus the other for the study of PDO fortified wines should be made according to the objective pursued, with PARAFAC being more suitable for characterization while splitting could be more suitable for rapid screening.

4. Conclusions

This study showed, for the first time, that EEM measurement is a fast, clean and no destructive methodology for assessing the type of Andalusian PDO fortified wines. Thus, it was possible to assess a priori differences between the type of production process and type of wine from visual inspection of the EEM matrix of the PDO samples. Two data treatment strategies were tested: the use of the unfolded matrix and PARAFAC model. While unfolded matrix showed slightly better classification results that the PARAFAC approach, this last gave information about the fluorescent molecules that could be considered marker of each wine and their relative importance and differences in their presence in each type of wine according to their production. Therefore, PARAFAC could be a better option for a characterization purpose, while the unfolding strategy provide a simpler classification data analysis, being better for a screening purpose. Although further analyses should be carried out with more samples for some of the wine types, the obtained results serve as a starting point for the task of state and differentiate PDOs regions and types of fortified wines. It is evident from these results that, despite some differences in classification accuracy, an influence of the aging type and the terroir on wine composition can be captured from this spectroscopic technique, allowing their differentiation between aging type and wine geographical origin, even for close regions. Thus, the combination of EEM with chemometrics becomes a powerful tool for the characterization and authentication of these fortified wines. According to these results, this approach could be implemented as an alternative tool for PDO regulatory councils and producers to be implemented in routine analysis or for a rapid screening control.

Table 3
Classification indices in terms of n° of latent variables (LVs) and percentage of sensitivity (Sn), specificity (Sp), and explained variance (e.v.) obtained by the different PLS-DA models made by the two strategies.

Data treatment strategy			PARAFAC-PLS-DA								Unfolded-PLS-DA							
Classification indices			N LVs	%e.v.	Cal		CV		Pred		LVs	%e.v.	Cal		CV		Pred	
					% Sn	% Sp	% Sn	% Sp	% Sn	% Sp			% Sn	% Sp	% Sn	% Sp	% Sn	% Sp
General type differentiation	**Biolog. (B) vs Oxid. (O)**	**B (FI, MA)**	2	72.7	100	100	100	100	100	100	4	97.2	100	100	100	100	100	100
		O (OL, PC, AM)			100	100	100	100	100	100			100	100	100	100	100	100
	Biolog. (B) vs Biolog. + Oxid. (B+O) vs Oxid. (O)	**B (FI, MA)**	3	86.5	100	100	100	100	100	100	5	98.1	100	100	100	100	100	100
		B + O (AM + PC)			90	75	90	75	71	74			90	80	90	80	86	74
		O (OL)			90	73	90	72	100	70			90	77	87	75	100	75
Type differentiation within each PDO	**C**	**CFI**	2	83.2	100	100	100	100	100	100	2	89.6	100	100	100	100	100	100
		COL			100	100	100	100	100	100			100	100	100	100	100	100
	J	**JAM**	2	81.5	88	50	81	53	35	60	5	99.2	100	100	100	100	100	100
		JFI			100	94	100	97	100	100			86	74	86	68	100	83
		JOL			100	66	86	58	100	50			88	78	63	67	100	50
		JPC			67	74	67	72	100	100			67	87	67	83	25	86
	M	**MAM**	4	92.9	100	85	93	82	100	70	5	98.2	100	100	100	100	100	100
		MFI			100	100	100	100	100	100			92	71	83	71	100	80
		MOL			83	71	83	71	100	70			100	85	100	85	100	70
		MPC			100	77	100	80	100	73			100	82	100	82	100	73
PDO differentiation within each type	**FI**	**CFI**	3	85.7	100	82	100	81	50	100	4	95.8	80	94	80	90	50	100
		JFI			88	91	88	90	50	100			100	97	100	97	50	100
		MFI			89	91	83	91	86	50			97	93	94	93	100	50
	PC	**JPC**	2	93.0	100	100	100	100	100	100	3	99.8	100	100	100	100	100	100
		MPC			100	100	100	100	100	100			100	100	100	100	100	100
	OL	**COL**	5	99.7	83	81	83	81	35	67	6	99.7	100	100	100	100	100	65
		JOL			100	96	100	96	100	100			100	100	100	100	50	100
		MOL			83	100	83	96	50	100			100	100	100	100	100	50
	AM	**JAM**	3	91.7	69	100	63	79	67	50	8	99.8	100	100	100	100	100	50
		MAM			100	69	79	63	50	67			100	100	100	100	50	100
	JFI vs SMA	**JFI**	4	96.3	88	100	88	100	50	100	5	99.2	100	100	100	100	50	100
		SMA			100	88	100	88	100	50			100	100	100	100	100	50

Note: Cells marked in gray indicate better classification compared to the other strategy. C: Condado de Huelva PDO; J: Jerez PDO; M: Montilla-Moriles PDO; FI: Fino; PC: Palo Cortado; OL: Oloroso; AM: Amontillado; SMA: Manzanilla Sanlucar de Barrameda PDO; B: Biological aging; O: Oxidative aging; B + O: Biological + Oxidative aging; LVs: Latent variables; e.v.: Explained variance; Sn: Sensitivity; Sp: Specificity; Cal: Calibration; CV: Cross-validation; Pred: Prediction.

CRediT authorship contribution statement

Rocío Ríos-Reina: Funding acquisition, Investigation, Project administration, Writing – original draft. **Juan L. Pérez-Bernal:** Data curation, Methodology, Resources. **Silvana M. Azcarate:** Formal analysis, Investigation, Writing – review & editing. **Raquel M. Callejón:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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