Geographical origin authentication of southern Brazilian red wines by means of EEM-pH four-way data modelling coupled with one class classification approach

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ABSTRACT

EEM data recorded at different pH values was exploited by MCR-ALS in order to determine qualitative information about Brazilian red wines. In addition, the geographical traceability of wines produced in the Serra Gaúcha (Rio Grande do Sul) was carried out by DD-SIMCA considering 53 samples from the target class and 20 from other producing regions. The fluorescence signal corresponds to 9 EEMs recorded at different pH (3–11), generating four-way data. By MCR-ALS decomposition, eight factors were retrieved and related to typical chemical compounds found in red wine. In addition, the EEM pH data was used to build a one-class classification model, considering that MCR scores and all samples of the target class were properly recognised as belonging to the target class, with maximal sensitivity equal to 1. Samples of the non-target class were also adequately rejected by the model, and the specificity was found to be 0.97.

1. Introduction

Red wine is one of the oldest beverages in the world, being appreciated and cultivated today (Johson, 1989), and it has stood out more and more in the consumer market due to its different aromas, textures, and flavours from the grape varieties and the winemaking process. For this reason, it is also one of the most famous drinks in the world, with its price ranging from very cheap to thousands of dollars per bottle (Álvarez, Moreno, Jos, Cameán, & Gustavo González, 2007; Marisa, Almeida, & Vasconcelos, 2003). All wine characteristics depend on the environment in which the grapes are grown (Duley et al., 2021).

Geographical origin usually adds to the commercial value of a wine; some regions are famous for producing excellent wines with high commercial value. The origin of a product is an important issue for the food industry, not only for consumers but also for producers and distributors

(Luykx & Van Ruth, 2008). In Brazil, the state of Rio Grande do Sul stands out as a wine-producing region, and the Serra Gaúcha (SG) is the most important grape-producing area, including fine red wine (*Vitis vinifera*) (Almeida, Almeida, Godoy, Pierre, & Godoy, 2016; Giuliani, 2007). The Serra Gaúcha is a mountainous region, and it is cut by the 29th parallel with altitudes from 500 to 800 m. It has a precipitation index of about 1.800 mm/year and a humid climate with acidic and sandy soils that are rich in organic matter, with little efficient drainage. Despite the problems of excess rain during the months of the grape harvest season, the climate and methods of planting used in Serra Gaúcha make it possible to produce grapes with high acidity (Farias, 2014; Flores & Medeiros, 2013; Guerra, Mandelli, Tonietto, Zanus, & Camargo, 2005; Souza, Meneghin, Coelho, Maia, & Silva, 2006).

Due to its popularity, wine has become the target of investigation because of fraud including adulteration, false age declaration, and false
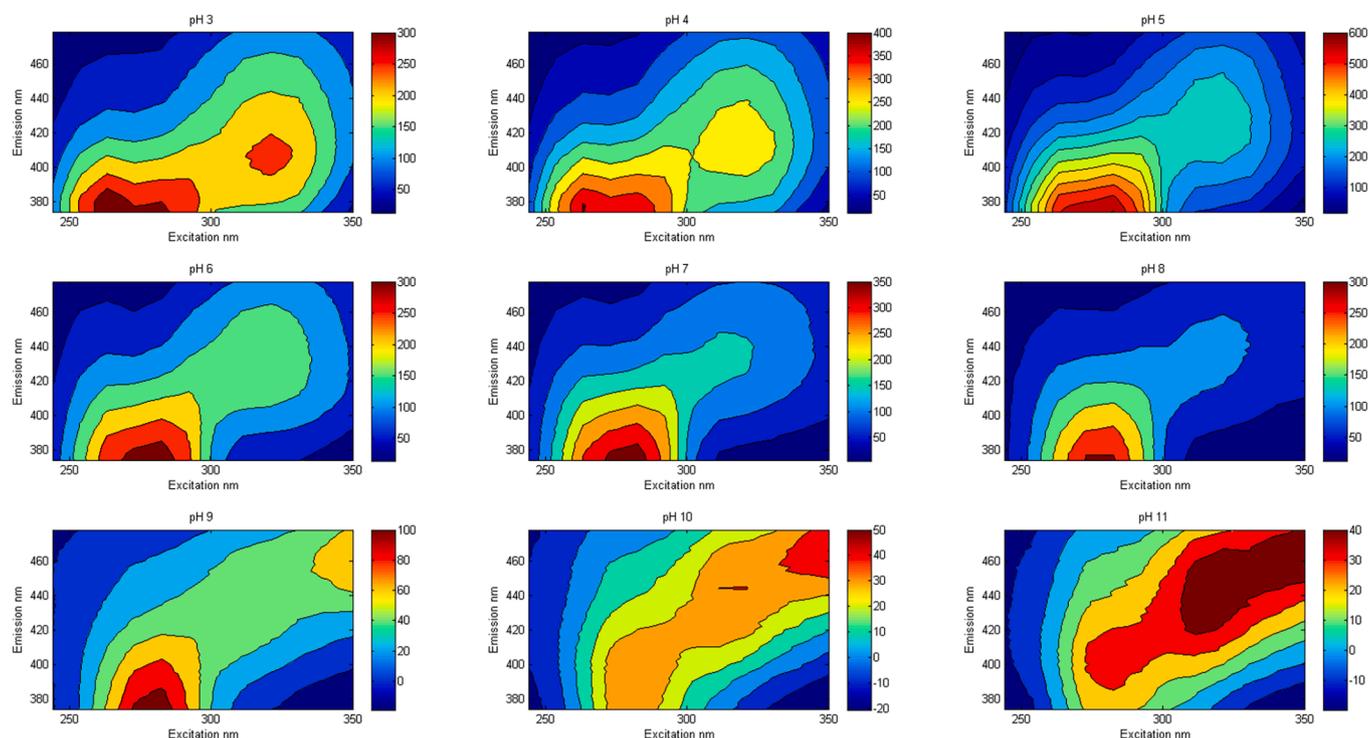
Fig. 1. Typical fluorescence landscape at different pH values.

indication of geographical origin. Much effort has been invested in the development of methods for assessing wine quality to avoid fraud and to indicate its true geographical origin (Álvarez et al., 2007). The literature has a number of reports of analytical approaches to establish the composition and authenticity of wine according to its geographical origin and grape variety. For instance, among more conventional approaches, there are liquid and gas chromatography coupled to several detectors (mass (MS), diode array (DAD), MS-MS, and fluorescence) (Ballabio, Skov, Leardi, & Bro, 2008; Dimitrovska, Tomovska, & Bocevska, 2013; Rodríguez, Aguilar-Caballos, & Gómez-Henz, 2006; VILLIERS, VANHOENACKER, MAJEK, & SANDRA, 2004) and atomic spectrometry, such as inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) (Šelih, Sala, & Drgan, 2014; Shen, Wu, Ying, Li, & Jiang, 2013). These analytical techniques are effective at elucidating the organic and elemental composition of wines but require steps involving sample preparation, costly equipment, and high maintenance, which may represent a limiting factor for small industries, producers, and consumers.

In addition, alternative methods have been carried out using spectroscopic techniques coupled to chemometric tools. These include proton nuclear magnetic resonance (^{1}H NMR) (Anastasiadi et al., 2009; Lee, Hwang, Van Den Berg, Lee, & Hong, 2009), near infrared spectroscopy (NIR) (Cozzolino, Smyth, & Gishen, 2003; Liu et al., 2008), Fourier transform infrared with attenuated total reflectance spectroscopy (FTIR-ATR) (Schmidtke, Smith, Müller, & Holzapfel, 2012), capillary electrophoresis (CE-DAD) (Rodríguez, Durán-Merás, Galeano-Díaz, & Wold, 2011), UV–Vis spectroscopy (Azcarate et al., 2015), and fluorescence spectroscopy (Rodríguez et al., 2011; Azcarate et al., 2015; Saad, Bouveresse, Locquet, & Rutledge, 2016). Mainly due to the resulting lack of the need for a sample preparation step, the combination of spectroscopic techniques and chemometrics has advantages such as relative higher speed and lower cost of execution, and they are non-destructive and/or non-invasive, have low reagent consumption, and, last but not least, can be used on site (Gredilla, de Vallejuelo, Elejoste, de Diego, & Madariaga, 2016).

In the specific case of fluorescence spectroscopy for wine analysis,

some advantages of this method, such as high sensitivity and selectivity, deserve attention when compared with other spectroscopic approaches (Lakowicz, 2006). The fluorescent properties of a specific chemical compound may change as a function of the pH. For example, anthocyanins and polyphenols present in wine affect the recording of the fluorescence signal at different pH values, allowing for better characterisation of the fluorescent compounds present in the wines (Gredilla et al., 2016; Lakowicz, 2006; Saad et al., 2016).

Moreover, the versatility of the instruments lies in the different forms of signal recording: a simple fluorescence value obtained for a specific excitation and emission wavelength; emission spectra with a sample excited at a fixed excitation wavelength; and a fluorescence map corresponding to several emission spectra obtained by distancing excitation wavelengths (Kumar & Mishra, 2012; Lakowicz, 2006). These types of data are arranged in an excitation-emission matrix (EEM).

The present work was devoted to the development of a fluorescent pH-dependent fingerprint of Brazilian red wines based on 3D front face fluorescence and extended multivariate curve resolution with alternating least squares (e-MCR-ALS) (Azcarate, Gomes, de la Peña, & Goicoechea, 2018) for classification proposes with respect to geographical origin, considering the most famous region as the target class, the Serra Gaúcha, by means of one class method: data driven soft independent modelling of class analogy (DD-SIMCA).

2. Experimental

2.1. Reagents and materials

Buffer solutions were prepared from pH values of 3 to 11 using the following reagents: potassium dihydrogen phosphate (KH_2PO_4) from Êxodo Científica, Hortolândia, SP, Brazil; phosphoric acid (H_3PO_4) from Nuclear, Diadema, SP, Brazil; acetic acid (CH_3COOH) from Química Moderna, Barueri, SP, Brazil; and sodium acetate ($CH_3COONa·3H_2O$), anhydrous bibasic potassium phosphate (K_2HPO_4), sodium bicarbonate ($NaHCO_3$), and sodium carbonate (Na_2CO_3) from Dinâmica, Indaiatuba, SP, Brazil. Ultrapure water (Resistivity > 18 MΩ Milli-Q, Millipore) was used for the solution preparations.

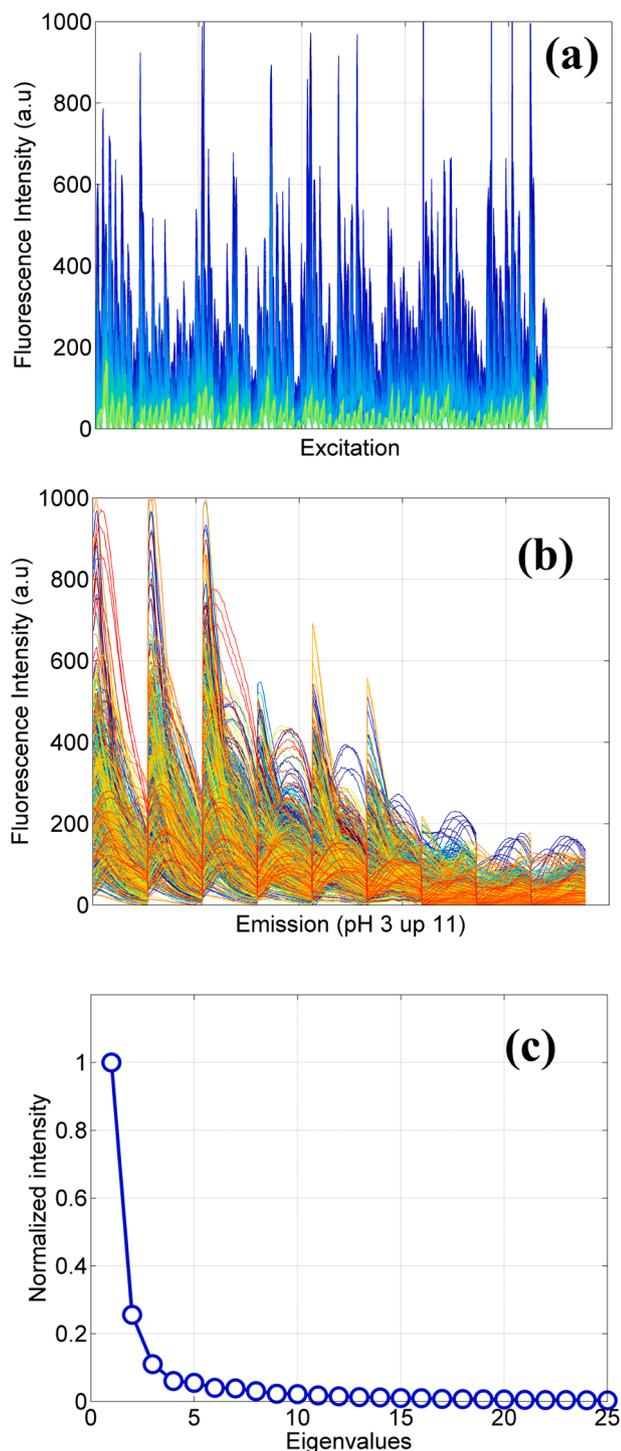**Fig. 2.** Augmented data plot: (a) augmented mode (excitation) and (b) unfolded mode pH × emission and in (c) eigenvalue of **Daug** data.

Fig. 3. Retrieve profiles by MCR-ALS in (a) unfolded mode and (b) augmented mode.

2.2. Wine samples

Seventy-three samples were used, of which 53 came from Serra Gaúcha and 20 from the other regions (Campanha and Serra do Sudeste) in the same state. The samples included 10 red grape varieties harvested in 2017 and 2018: Cabernet Sauvignon (CS), Pinot Noir (PN), Merlot (MT), Marselan (MN), Teroldego (TO), Tannat (TT), Malbec (MC), Cabernet Franc (CF), Ancellotta (AA), and Petit Syrah (PS). For each pH (3–11), buffer solutions were adjusted using a bench pH meter (Ultra Denver Instrument©). Four hundred fifty microlitres of sample were
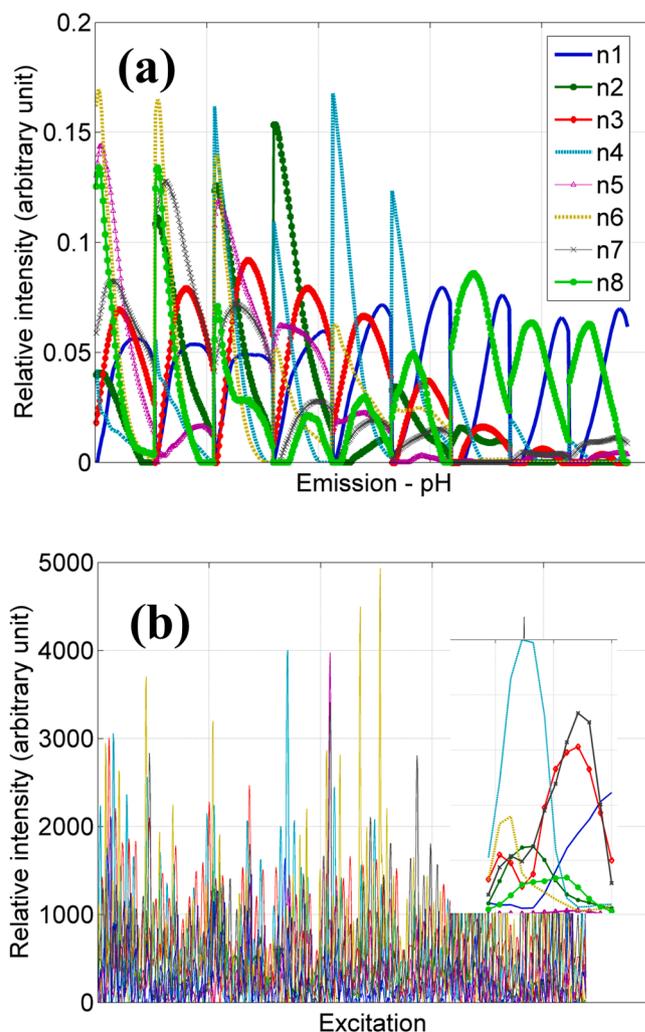
added to 15 mL of buffer for each pH. All samples were donated by *EMBRAPA Uva e Vinho/Bento de Gonçalves (Rio Grande do Sul)* and kept at room temperature.

2.3. EEM measurements

Fluorescence spectral measurements were performed using a Varian Cary Eclipse Spectrophotometer with two Czerny-Turner monochromators and a xenon flash lamp connected to a PC microcomputer via a serial RS232 (GPIB) interface. The excitation and emission monochromator slit widths were both set to 10 nm. A 600 V PMT Detector with Cary Eclipse software was used to acquire the data. The EEM measurements were recorded as a set of excitation spectra from 244 to 340 nm and emission wavelengths of 368–468 nm.

2.4. Chemometric procedures

The fluorescent EEM records at different pH values were arranged in an augmented matrix (**Daug**) in the column wise direction. For each sample, 9 EMMs were obtained (pH values of 3 to 11). These EEM for the same sample were arranged in an unfolded matrix (Excitation × Emission-pH) sized 12 × 447. All 73 arrays were stacked, forming **Daug** (876 × 447). Fig. S1 shows a schematic illustration of how the input matrix for the MCR was generated. All chemometric calculations were carried out in the MATLAB® version 7.1.0 (The MathWorks Inc., MA, USA)
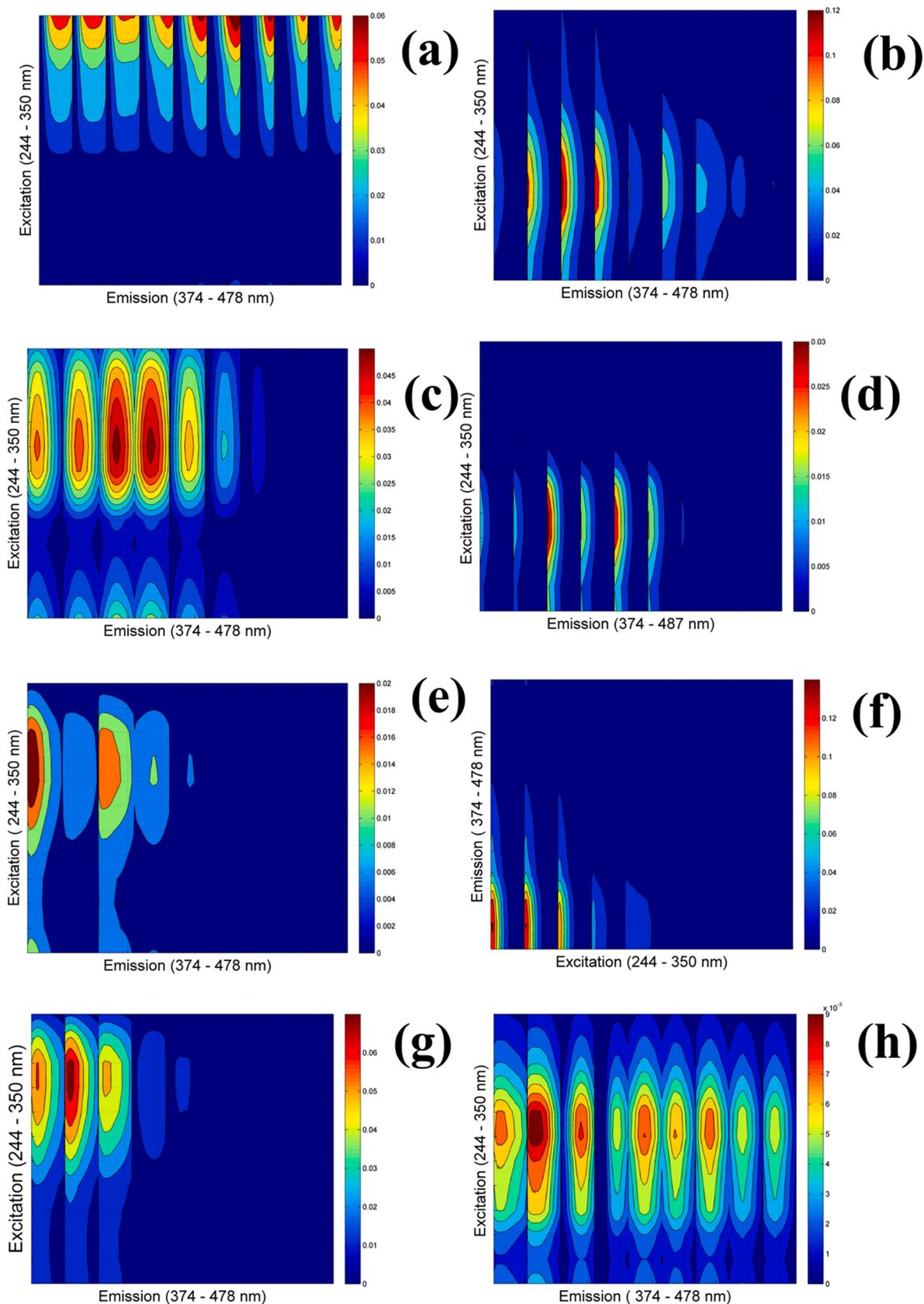
Fig. 4. Fluorescence surfaces recovered for each factor by MCR-ALS (letters a, b, c, d, e, f, g and h correspond to factors 1, 2, 3, 4, 5, 6, 7 and 8 respectively).

Table 1
Attempt to assign profiles retrieved via MCR-ALS based on previous literature data.

MCR retrived profile	Ex (nm)	Em (nm)	Assignment	Fluorescent properties	References
1	350	432	Fluorescente Back ground	–	–
2	280	<368	Flavonoids like Catechin and Epicatechin	278–360	Rodríguez-Delgado, Malovaná, Pérez, Borges, and García Montelongo (2001); Airado-Rodríguez, Galeano-Díaz, Durán-Merás, and Wold (2009); Rodríguez et al., 2011
3	253/321	403	phenolic acids like vanillic acids	241, 282, 305 354	Rodríguez-Delgado et al. (2001); Airado-Rodríguez et al. (2009); Rodríguez et al., 2011
4	272	<368	phenolic acids like gallic	318–385 300/330–370/392	Rodríguez-Delgado et al. (2001); Airado-Rodríguez et al. (2009); Rodríguez et al., 2011
5	321	384	phenolic acids liek caffeic acid, ferulic acid and p-coumaric acid	262–426 260–400 260–422	Rodríguez-Delgado et al. (2001); Airado-Rodríguez et al. (2009); Cabrera-Bañegil et al. (2017); Rodríguez et al., 2011
6	263	380	Anthocyanins like Cyanidin and Malvidin Glycosides	280–355	Rodríguez-Delgado et al. (2001); Airado-Rodríguez et al. (2009); Rodríguez et al., 2011; Forino, Gambuti, Luciano, and Moio (2019)
7	263/321	394	stilbenoid glucoside like *t*-Resveratrol and *t*-Piceid	290–300/390–395 318–385 300/330–370/392	Rodríguez-Delgado et al. (2001); Höfener, et al. (2013); Airado-Rodríguez et al. (2009); Rodríguez et al., 2011
8	301	388	unknown	278–360	–

environment. MCR-ALS and pattern recognition models were obtained by means of the MCR ALS toolbox (Jaumot & Tauler, 2010) (http://www.mcrals.info/) and DD-SIMCA, which is freely available at GitHub (https://github.com/yzontov/dd-simca.git) (Zontov, Rodionova, Kucheryavskiy, & Pomerantsev, 2017). For the classification models, the pool of samples was partitioned through the Kennard-Stone method using a homemade MATLAB routine. The set of samples of the target class was partitioned into training (33 samples), validation (10

Table 2
Statistical summary of fit and prediction.

	PC	Regular	Extreme	Outlier	[a]Sensitivity
Training set (33)[b]	2	32	1	0	0.97
	3	33	0	0	1
	4	32	1	0	0.97
	5	32	1	0	0.97
	PC	Regular	Extreme	Outlier	[a]Sensitivity
Validation set (10)[c]	2	10	0	0	1
	3	10	0	0	1
	4	10	0	0	1
	5	10	0	0	1

[a] Sensitivity = 100%(Samples – Extremes)/Samples. [b] Traniging Samples and [c]Validation Samples.

samples), and test (10 samples) sets. The 10 samples of the set were aggregated, with 20 samples not belonging to the target class.

3. Results and discussion

3.1. General comments

Red wine, in addition to water and ethanol, contains a complex mixture of organic compounds, resulting in an average pH of about 3.5. Under this chemical condition, several compounds are present in the protonated form. However, increasing the pH to near neutral values or even strongly basic values promotes deprotonation, thus modifying the fluorescence profile of the wine constituents. The anthocyanins, responsible for the main wine colour, are in equilibrium, for example the flavinic cation (AH^+)/quinoidal base (A), carbinol (B)/chalcone (C) (Saad et al., 2016; Tòrres et al., 2011). Changes in pH favour some of the species by increasing or decreasing the fluorescence signal (see Fig. 1).

As can be seen, by comparing the fluorescence maps obtained at different pH values, but still in an acidic medium, there is a predominance of protonated species such as cation (AH^+) and carbinol (B). These compounds exhibit the maximum emission observed for smaller wavelengths (see Fig. 1). The pH detachments for higher values increase the chalcone and quinone contents, characterised by the blue–violet colour that the wine starts to exhibit (see Fig. S2). In addition, the maximum values of fluorescence intensity occur at longer wavelengths, denoting less energetic transitions.

In a strongly basic medium, a brown colour is predominant due to the binding of anthocyanins to other phenolic compounds, a process called co-pigmentation (Boulton, 2001; Guerrero, Puertas, Jiménez, Cacho, & Cantos-Villar, 2010; Murias et al., 2005; Saad et al., 2016; Tòrres et al., 2011). These compounds show very different fluorescence when compared with substances that predominate in acidic medium. The sensitivity to pH of the chemical constituents of the wine, with respect to its fluorescent properties, can then be exploited with the purpose of providing distinction based on geographical origin and grape variety.

3.2. MCR decomposition and feasibility solution

In Fig. 2a and b, the **Daug** matrix is depicted in column and row space, respectively. Recorded excitation profiles for the 73 samples are displayed. Fig. 2a and in b show the emission profiles for each investigated pH value. Here, it is also possible to visualise the changes in the formation and intensity of the spectra due to the increase in pH.

Estimation of the MCR factors was carried out by means of **Daug** matrix singular value decomposition (SVD), and this approach indicated eight factors, as can be seen in Fig. 2C. The initial estimate was obtained for the mode emission pH (non-augmented mode) by means of pure variable detection. Alternating least squares optimisation was carried out under non-negativity constrain in both directions. It reached convergence after 51 iterations. The final solution corresponds to 98.9%
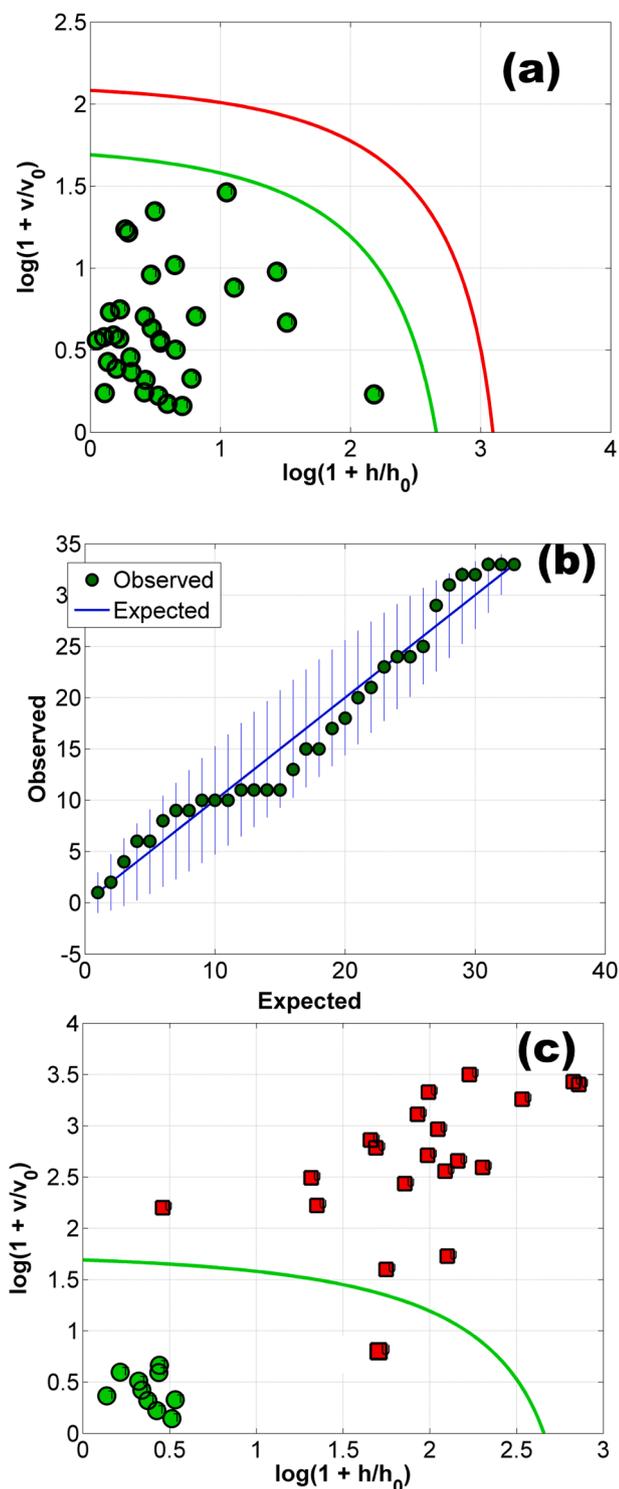
Fig. 5. DD-SIMCA results: (a) acceptance area established for training set (green line is the border of regular samples and red line is the border of outlier samples. Sample between both lines is called extreme samples. In (b) Extreme plot and (c) results of applying the model to the test set (green circles are samples of the target class and red squares are samples not belonging to the target class). Specificity = 100% *(External objects)/Samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the explained variance, and the lack of fit (LOF) was equal to 10.4%. This value is very small considering PCA LOF (9.3%). Fig. 3 depicts the optimised MCR profiles.

As can be seen in Fig. 3a, both the shape and intensity of the retrieved emission profiles change when pH increases. Some profiles are more intense in an acidic pH, in other hand other ones in basic pH. This behaviour allows for the determination of more information about wine samples. Fig. 3b shows the excitation retrieve profiles that also change inter samples and zoom to the excitation profiles of sample 1 are shown highlighted. The intensity (or area) related to this profiles is proportional to the concentration.

In order to investigate the feasibility of the MCR solution, the magnitude of the rotational ambiguity that affects the received profiles was examined by calculation of the relative maximum (f_{max}) and minimum (f_{min}) contribution of every component in the total signal (Guerrero et al., 2010). The f_{max} and f_{min} values are displayed in Table S1.

Note that the differences between f_{max} and f_{min} are very close to zero. This suggests that the solution found is practically free of rotational ambiguity. This is due to the use of fluorescence matrices for the same sample having been recorded at different pH values, drastically reducing the possibility of rotating the MCR solution without losing fit.

In addition, the profiles retrieved by the MCR provide valuable information about the samples. Fig. 4 shows how each of the eight profciles changes in shape and intensity with increasing pH.

In general, samples show lower fluorescence intensities at high pH values (neutral or basic medium, for example). In an attempt to find a correspondence between profiles recovered by MCR-ALS and the chemical compounds present in wine, the results presented in Table 1 were obtained.

The first one was attributed to the fluorescence background; note that it is practically constant for all pH values (see Fig. 4a). The second (Fig. 4b) was attributed to the fluorescence of flavonoids such as catechin and epicatechin; both compounds exhibit very similar excitation and emission profiles. In recent work, Cabrera-Bañegil, Hurtado-Sánchez, Galeano-Díaz, and Durán-Merás (2017) reported the joint quantification of these two polyphenols by fluorescence and PARAFAC. This corroborates the idea of a single MCR factor associated with these two compounds. Phenolic acids such as vanillic, gallic, and caffeic/ferulic/p-coumaric were related to profiles three (Fig. 4c), four (Fig. 4d), and five (Fig. 4e), respectively. Factor six (Fig. 4f), in turn, corresponds to the typical fluorescence signal from anthocyanins such as cyanidin and malvidin glycosides, which are both abundant in red wines. The seventh (Fig. 4h) profile recovered by the MCR is related to stilbenoid glucosides such as *trans*-resveratrol and *trans*-piceid. Nothing related to profile eight (Fig. 4h) was found in the literature.

3.3. Geographical traceability

In order to build a method for recognising the authenticity of samples that belong to Serra Gaúcha, a one-class approach based on DD-SIMCA was fitted on the MCR score. Different models were fitted considering different numbers of principal components and applied to predict samples from the validation set, and the results are shown in Table 2.

As can be seen in Table 2, for all numbers of PCs evaluated, maximum sensitivity was achieved in the validation set. However, there was no extreme sample in the training set for 3 PCs. Therefore, 3 PCs were selected for the final model. Fig. 5a and b show the acceptance area for the training set and the extreme plot, respectively.

As can be seen in Fig. 5a, all training samples showed status of rules being positioned within the boundary delimited by the established green line considering α of 0.01. In addition, the absence of an outlier was confirmed by the extreme plot (see Fig. 5b). Note that all samples are contained in the elliptical region.

When this model was applied to the test set containing both samples of the target class and those not belonging to the target class, their position with respect to the decision boundary can be seen in Fig. 5c. All

samples of the target class were properly recognised as belonging to the target class, with maximal sensitivity equal to 1. Samples of the non-target class were also adequately rejected by the model, and the specificity was found to be 0.97.

4. Conclusions

This work demonstrated the modelling of four-way data generated by the recording of EEM at different pH values by MCR-ALS in order to recover the contributions of the main fluorescent compounds present in red wine. Good agreement between the results and the literature data was found. The scores of the MCR model were used to build a model for authenticating samples from the main wine-producing region of Brazil, Serra Gaúcha, based on a one-class approach called DD-SIMCA. The model exhibits a high capacity to recognise samples of the target class as well as to reject samples not belonging to Serra Gaúcha. Therefore, this methodology, in addition to extracting valuable quantitative information, was useful in the task of geographic authentication. This approach is an important contribution to the characterisation and quality control of red wines. Furthermore, the work addresses an important yet little exploited chemometric field, for-way data modelling in classification problems.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2021.130087.

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