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Synchronous fluorescence spectroscopy and multivariate classification for the discrimination of cachaças and rums

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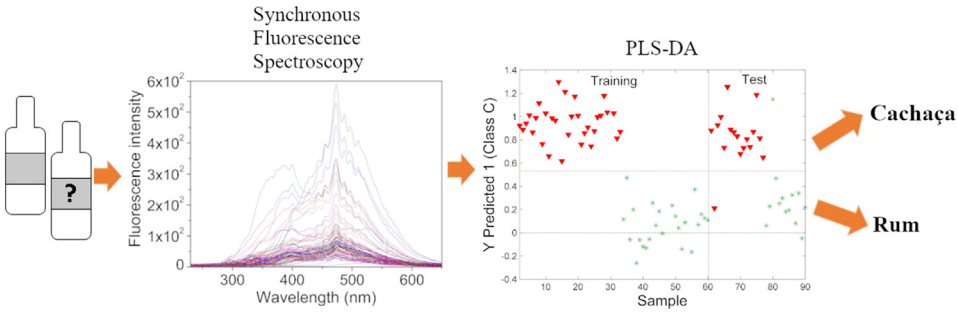
HIGHLIGHTS

- Multivariate classification of commercial cachaça and rum samples was studied.
- Synchronous fluorescence spectra were used for construction of PCA and PLS-DA models.
- Face-centered central composite designs were performed to determine the Savitzky-Golay smoothing parameters.
- PLS-DA model using spectra recorded at $\Delta\lambda$ = 10 nm provided better performance parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

Although cachaça and rum are distilled beverages obtained from the same raw material, they present differences in their chemical compositions. In this study, synchronous fluorescence spectroscopy was used combined with supervised classification models based on the partial least squares discriminant analysis to develop a rapid and low-cost model for discriminating between 50 cachaça and 40 rum samples. Partial least squares discriminant analysis models were constructed using synchronous fluorescence spectra recorded at wavelength differences of 10–100 nm. Initially, spectra were preprocessed by the first derivative with the Savitzky-Golay smoothing, and filter width and polynomial order were selected through face-centered central composite designs. For the construction and validation models, the spectra data were split into two datasets: the training and the test sets containing 60 (C, n = 33; R, n = 27) and 30 (C, n = 17; R, n = 13) samples, respectively. The best discrimination was achieved using fluorescence spectra recorded at wavelength difference 10 nm, allowing the discrimination of cachaça and rum with a classification efficiency of 98%. These results indicate that synchronous fluorescence spectroscopy offers a promising approach for the authentication of cachaças and rums.

1. Introduction

Cachaça and rum are distilled beverages obtained from the same raw material: sugarcane. Cachaça is the distillate of the fermented must from sugarcane juice and produced exclusively in Brazil, whereas rum is the alcoholic distillate of molasses or the mixture of distillates from sugarcane juice and molasses [1]. Rum has a Caribbean origin, and its separation into categories is more difficult because of the different definitions by laws in countries that produce rum. Most rums are made of molasses. An exception is the Rhum Agricole, a type of rum produced in French-speaking islands obtained from the fermentation of fresh sugarcane juice [2]. Both beverages can be total or partially aged in wooden containers [1]. Usually, rum is aged in oak barrels, and cachaça is also aged in Brazilian native wood containers.

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The sugarcane juice is constituted mainly of water. Fermentable carbohydrates such as sucrose, glucose, and fructose represent about 20% of their composition. Nitrogenous compounds, fats, acids, and minerals are present in low concentrations [3]. Molasses - the main byproduct of sugar production - is the residue of the crystallized sugar extraction after boiling sugarcane juice. Molasses is a viscose liquid containing about 55% fermentable sugars, non-sugar compounds, and significant quantities of minerals and other trace elements [2,4,5].

Sugarcane juice and molasses present the same principal carbon source in the fermentation process: sucrose [4]. However, the use of molasses during rum production causes its different chemical composition from cachaça. The distinction between these beverages is necessary once complications may become up during their commercialization [6]. Discriminations between cachaça and rum are reported at the levels of metal contents and organic compounds [7], volatile contents [8–10], and fingerprint characterization [11].

Cardoso et al. analyzed the organic and metal contents in 18 cachaças and 21 rum samples using chromatography (GC–MS, GC-FID, and HPLC-UV–Vis), inductively coupled plasma atomic emission spectrometry (ICP-AES), principal component analysis (PCA), hierarchical cluster analysis (HCA), partial least squares discriminant analysis (PLS-DA), and K-nearest neighbor analysis (KNN), correctly classifying 6 new samples [7]. De Souza et al. separated 8 rums and 29 cachaças aged in Brazilian woods through direct-infusion electrospray ionization mass spectrometry (ESI-MS) using PCA and HCA [11]. De Souza et al. used gas chromatography-olfactometry (GCO) and descriptive sensory analysis (DSA) to separate and characterize the odorants present in cachaça and rum [8]. Cardeal & Marriott presented the application of comprehensive two-dimensional gas chromatography-mass spectrometry (GC × GC–MS) for the aroma analysis of spirit samples, including rum and cachaças [10]. Franitza et al. showed a supervised classification of rums manufactured from sugarcane juice compared to those from molasses using the volatile fractions analyzed by GC × GC–MS. The authors constructed and validated a PLS-DA model using 51 samples, acquiring 88% correct classification [12].

Molecular spectroscopy, chromatography, and mass spectrometry, with multivariate analysis, are techniques commonly used to test the authenticity of beverages [13]. Among these techniques, fluorescence spectroscopy is being widely used due to its simplicity, moderate sensitivity, high selectivity, as well as to propagated use of chemometrics [14]. This technique presents higher sensitivity than electronic spectroscopy due to the low background level in the fluorescent measurements. Unlike fluorescence spectroscopy, in absorbance measurement, the signal is associated with the intensity of the radiation attenuation by an absorbing species, making it more difficult to detect substances in low concentrations [15]. In fluorescence spectroscopy, an emission spectrum is obtained by scanning an emission wavelength (λ_{em}) range when a sample is excited at a fixed excitation wavelength (λ_{exc}). However, the resolution in a multi-component analysis is unsatisfactory, and the emission spectra of beverages are composed of overlapping fluorescent bands containing chemical and structural information of all components present in the sample. A more extensive characterization of multi-fluorophores systems is obtained using synchronous fluorescence spectroscopy (SFS). In the SFS, λ_{em} and λ_{exc} can be varied simultaneously with constant scanning velocity, resulting in a determined wavelength interval ($\Delta\lambda = \lambda_{em} - \lambda_{exc}$) between them [16]. Principal advantages of SFS, compared to conventional spectrofluorimetry, are improved selectivity, higher sensitivity, and decreased light-scattering interference [16]. The SFS has been used in combination with different supervised classification methods to discriminate distilled beverages by type [17–22], geographical origin [23–25], brand [26], and identification of counterfeit [27]. SFS was also used with multivariate calibration for the determination of phenolic acids and scopoletin in brandies [28].

In this study, we used SFS to discriminate among commercial cachaça and rum samples. This analysis is fast, less expensive, and simple since no sample preparation and reagents are required. The PLS-DA models were constructed using synchronous fluorescence spectra recorded at different $\Delta\lambda$ and compared by classification errors in training, cross-validation, and test sets.

2. Material and methods

2.1. Samples

Ninety commercial cachaças and rums purchased in local liquor stores were used in this study. A code was assigned to each distilled beverage: C (cachaça, n = 50), and R (rum, n = 40). All cachaça and rum samples were stored in oak barrels, except two rum samples that were not aged. The rum samples were from seven different countries, including Brazil. The samples were stored at laboratory temperature and were not subjected to any preparation.

2.2. Fluorescence spectroscopy

Synchronous fluorescence spectra were collected using the RF-5301PC Shimadzu spectrofluorophotometer (Duisburg, Germany) equipped with a Xenon lamp, in a 10 mm × 10 mm × 45 mm quartz cell. Excitation and emission slits were set at 10 nm, and the spectral resolution at 1 nm. Synchronous fluorescence spectra were collected by scanning simultaneously the excitation and emission monochromators at the λ_{em} range of 230–650 nm, at constant $\Delta\lambda$ between them. Spectra were recorded for $\Delta\lambda$ from 10 to 100 nm at intervals of 10 nm. Fluorescence measurements were done in triplicate, and the mean values were plotted as a function of the λ_{em} and as contour maps. The spectrofluorophotometer was daily checked using a verification sample.

2.3. Data analysis

Multivariate analysis was conducted using the MATLAB software version 7.10.0 - R2010A (The Math Works, Natick, MA, USA) and the PLS Toolbox, version 5.2.2 (Eigenvector Technologies, Manson, WA, USA).

For each $\Delta\lambda$, synchronous fluorescence spectra were arranged in a two-dimensional matrix (samples × λ_{em} (nm)), and data treatments were realized separately. Fluorescence spectra were preprocessed employing the first derivative with smoothing using the Savitzky-Golay algorithm [29] and mean center. Filter width and polynomial order were evaluated by the face-centered central composite designs. To determine the best combinations, we adopted the response classification errors in training, cross-validation, and test sets in the PLS-DA models.

PCA was used as an unsupervised exploratory analysis to visualize the sample distribution in the multivariate space and to identify natural clustering in the samples that could influence the supervised classification analysis.

For the construction of PLS-DA models, ninety samples were used (C, n = 50; R, n = 40). The spectra data were split into two datasets using the Kennard-Stone algorithm applied to each class separately, in which representative and uniformly distributed samples were selected [30]. Thus, the training and the test sets composed of sixty (C, n = 33; R, n = 27) and thirty (C, n = 17; R, n = 13) samples, were used for constructed and validated models, respectively. The independent variables block (**X** block) contained

fluorescence intensities, and the dependent variable block (**Y** block) consisted of a matrix with values of 1 and 0, depending on whether the sample belonged or not to a specific class, respectively. The threshold values were calculated using Bayesian statistics. If a predicted value was above the threshold, the sample was considered to belong to the class. The **X** and **Y** blocks were decomposed simultaneously in latent variables (LV), which were chosen based on the lowest value of the cross-validation classification error (CVCE) estimated using Venetian Blinds cross-validation.

Samples simultaneously presenting Q residue and Hotelling's T^2 above the critical values at a 95% confidence level, were considered outliers by the model and, consequently, excluded.

Sensitivity (SEN) and specificity (SPE) performance parameters were calculated to evaluate the model quality. SEN is the rate of samples correctly classified as belonging to the modeled class. SPE is the rate of samples correctly classified as not belonging to the modeled class. These performance parameters were calculated separately for training and test sets. Efficiency (EFF) is a single global value to measure the performance of the classification model and was also calculated [31]. The expressions are shown below.

$$SEN = \frac{TP}{TP + FN} \quad (1)$$

$$SPE = \frac{TN}{TN + FP} \quad (2)$$

$$EFF = \frac{TN + TP}{TN + FP + TP + FN} \quad (3)$$

where TP are true positive responses, TN are true negative responses, FP are false positive responses and FN are false negative responses.

3. Results and discussion

3.1. Synchronous fluorescence spectra

Total synchronous fluorescence spectra of cachaça and rum are presented in the contour maps, with the fluorescence intensity as a function of λ_{em} and $\Delta\lambda$; and in fluorescence intensity as a function of λ_{em} for each $\Delta\lambda$ (Fig. 1). As shown in Fig. 1, the synchronous fluorescence spectra of cachaça and rum are very similar. The contour map of the cachaça sample (Fig. 1A) showed fluorescence maxima at λ_{em} about 350 nm for $\Delta\lambda$ = 90 to 100 nm, and contour map spread at the λ_{em} range of 280 to 570 nm. Spectra also presented a band at λ_{em} 280 nm and shoulders at λ_{em} 330 and 470 nm. Regarding the rum sample (Fig. 1B), the contour map spread at the λ_{em} range of 300 to 550 nm and fluorescence maxima at λ_{em} about 360 nm for $\Delta\lambda$ = 70 to 100 nm. Spectra of the rum sample also presented a band at λ_{em} 330 nm and shoulders at λ_{em} 280 and 470 nm. For both cachaça and rum samples, the band at λ_{em} about 470 nm is most clearly seen at $\Delta\lambda$ = 10 nm. The spectra recorded at $\Delta\lambda$ = 10 nm presented other bands and shoulders not observed for the other $\Delta\lambda$s.

3.2. Spectra preprocessing

During the construction of multivariate models, preprocessing is extremely important and should be reported. In this study, synchronous fluorescence spectra of the beverages were preprocessed through the first derivative with smoothing using the Savitzky-Golay algorithm. The arrangement of the derivative with the smoothing is convenient for attenuating baseline deviations and spectral noise and enhancing the variation of spectral bands. There must be a compromise between noise reduction and signal distortion. After smoothing and derivation, spectra were subjected to the mean center.

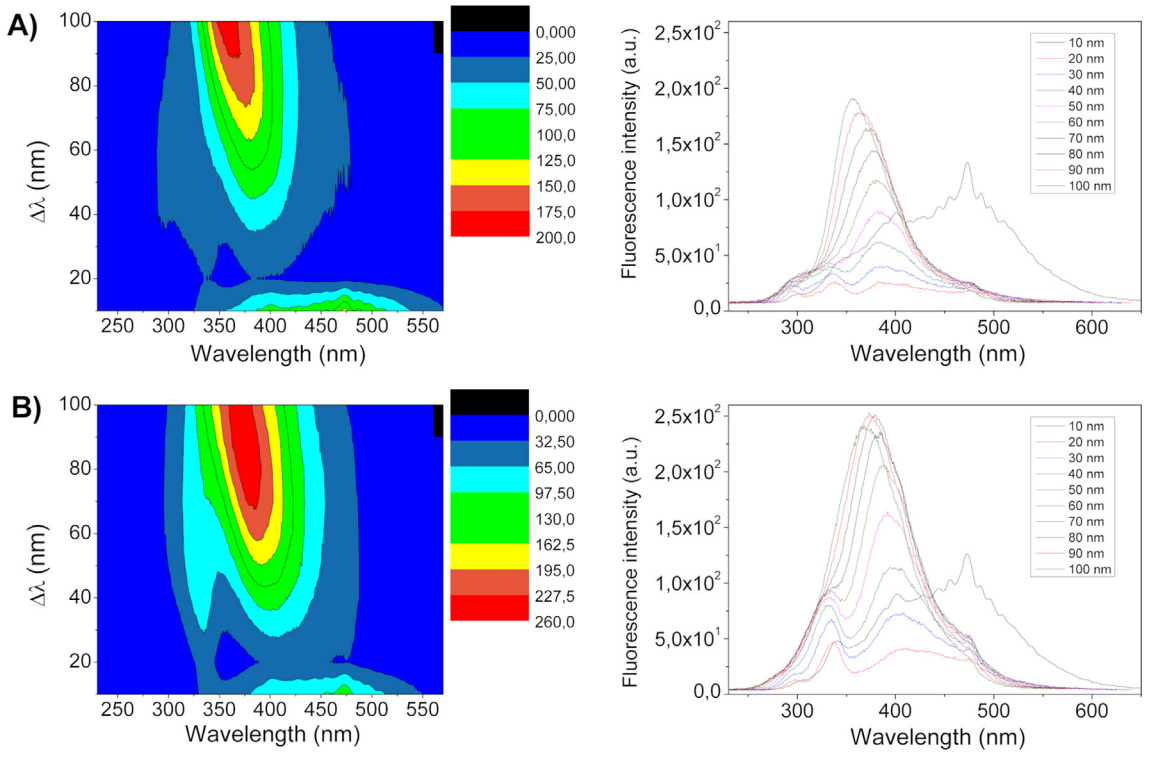

Fig. 1. Contour plots of total synchronous fluorescence spectra and synchronous fluorescence spectra of cachaça (A) and rum (B) samples.

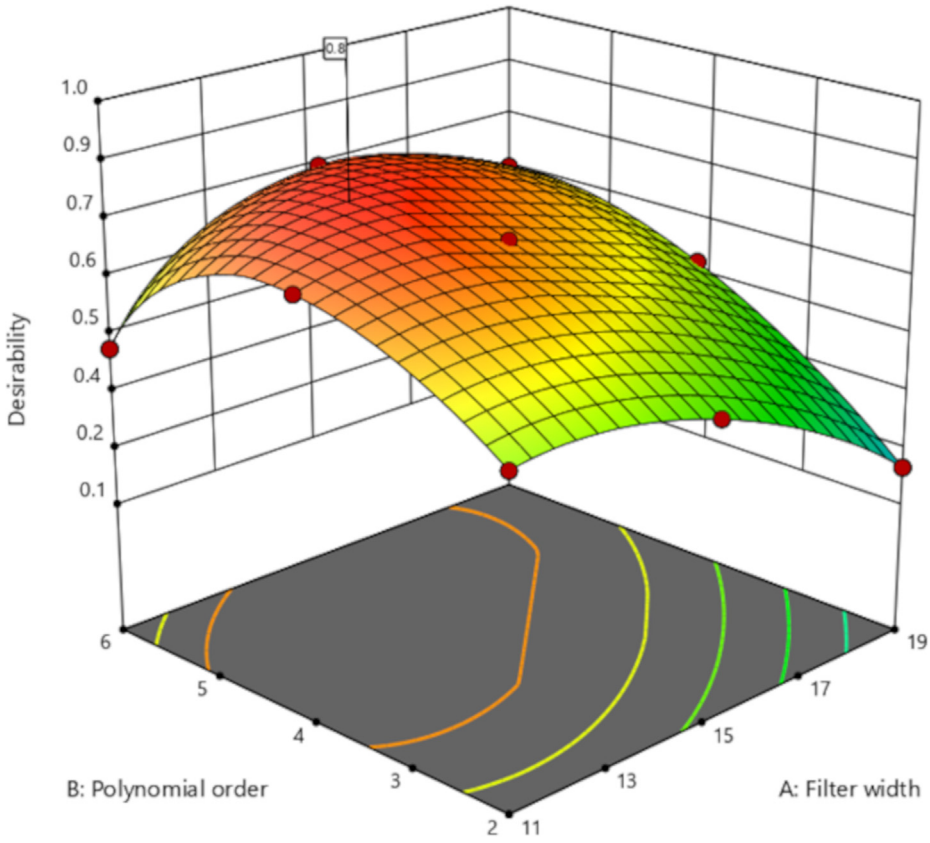

Fig. 2. Desirability surface plot for minimums classification errors in training, cross-validation and test sets for synchronous fluorescence spectra at Δλ = 10 nm.

Table 1
Filter width, polynomial order and classification errors in training, cross-validation and test sets for the each Δλ (nm) model.

Δλ (nm) model	Filter width	Polynomial order	Classification error		
			Training	Cross-validation	Test
10	13	5	0.00	0.26	0.07
20	15	6	0.11	0.23	0.22
30	13	5	0.02	0.31	0.17
40	15	4	0.00	0.25	0.19
50	19	2	0.24	0.24	0.19
60	15	4	0.23	0.30	0.19
70	19	6	0.23	0.26	0.13
80	19	4	0.14	0.24	0.40
90	19	2	0.20	0.20	0.21
100	11	5	0.05	0.23	0.29

To determine the most suitable Savitzky-Golay smoothing parameters (filter width and polynomial order) for each Δλ, face-centered central composite designs were performed, aiming for the minimum classification errors in training, cross-validation, and test sets. Fig. 2 shows the response surface of spectra recorded at Δλ = 10 nm, indicating that the best combination was 13- filter width and polynomial fit five order.

The same procedure was done for the other Δλs, and the best models for each Δλ were constructed using the filter width and polynomial order obtained in the response surface designs. The classification errors in training, cross-validation, and test sets obtained for each model are shown in Table 1. As shown in Table 1, each Δλ showed an optimum combination, which presented the lowest classification error values.

The Δλ = 10 nm model presented the lowest classification errors in the training and test sets (Table 1). Synchronous fluorescence spectra recorded at Δλ = 10 nm, preprocessed employing the Savitzky-Golay algorithm (13- filter width and polynomial fit five order), obtained for all cachaça and rum samples analyzed in this work are shown in Fig. 3. In general, the fluorescence intensities maxima varied between samples, for both cachaças and rums. Moreover, the spectral shape changed, varying in the band and shoulder intensities. Therefore, it was not possible to classify the samples just by visual inspection of the spectra.

Synchronous fluorescence spectra of cachaça and rum samples are the result of the spectral overlap of the various chemical species formed during fermentation, distillation, and aging processes, such tannins, phenolic compounds, and coumarins - formed by reactions involving the beverage and the wood [32]; as well as other compounds which can exhibit different fluorescence characteristics [33–35]. Some fluorescence compounds such as eugenol, β-damascenone, 4-ethylguaiacol, vanillin, diethyl acetal, β-

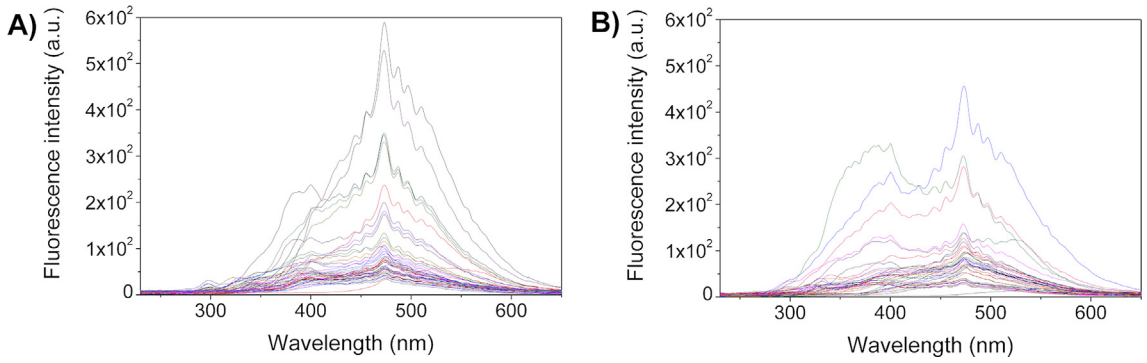

Fig. 3. Synchronous fluorescence spectra recorded at Δλ = 10 nm obtained for all cachaça (A) and rum (B) samples.

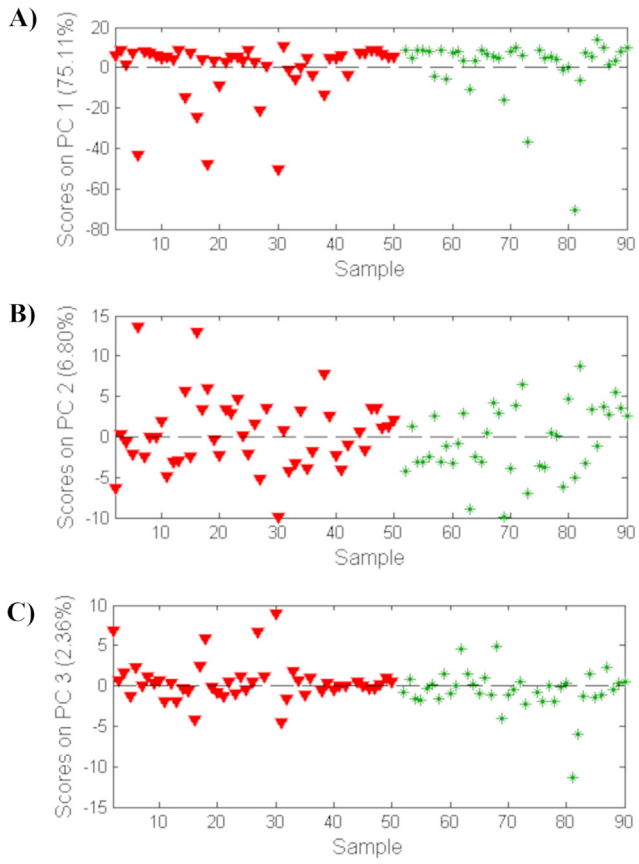

Fig. 4. Scores of PCA model built from Δλ = 10 nm synchronous fluorescence (explained variance): A) scores of PC1 (75.11%); B) scores of PC2 (6.80%); C) scores of PC3 (2.36%). Sample symbols: red down triangles for cachaça, and green asterisks for rum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

methyl-ɣ-octalactone, and phenolic acids, have already been identified in cachaça and rum samples [8,36]. Caramel may also contribute to the observed fluorescence since its use is permitted for color correction [1].

3.3. Multivariate classification

A PCA model applied to the synchronous fluorescence spectra recorded at Δλ = 10 nm presented three principal components (PC) accounted for 84% of total data variance. Scores for each PC are showed in Fig. 4. PC1, PC2, and PC3 did not show any clear separation or trend among beverages samples, probably due to the great variability of beverage production processes. The differences observed between the synchronous fluorescence spectra of the samples can be related not only to the use of molasses or sugarcane juice in their production but also to the aging periods, sugarcane varieties, and procedures involved in the fermentation and distillation processes, but even so, a clear differentiation of cachaça and rum was possible using a supervised classification model.

The best PLS-DA model using the spectra recorded at Δλ = 10 nm was constructed with seven LV, which accounted for 99 and 88% of the **X** and **Y** variances, respectively. The threshold value was 0.53 (Fig. 5). This model presented excellent performance parameters: EFF was 98%, SEN and SPE were 100% in the training set; and SEN and SPE were 94% and 92%, in the test set, respectively.

As shown in Fig. 5, this model provided excellent results of prediction. In the training set, all samples were correctly classified. In the test set, only one cachaça sample was incorrectly classified as rum, and one rum sample was incorrectly classified as cachaça. The only one cachaça incorrectly classified used molasses as raw material, according to the producer's information. However, cachaça is the distillate of the fermented must from sugarcane juice, according to Brazilian legislation. The occurrence of rum samples classified as cachaça may be related to falsification, once they are commercial samples, and we cannot guarantee their authenticity.

The wavelengths that most contributed to the classification between cachaça and rum samples are shown in the variable importance in projection (VIP) scores (Fig. 6). As shown in Fig. 6, the principal wavelengths are 305, 368, 385, 419, 471, 491, and 650 nm. The assignment of these specific wavelengths is difficult since the SFS is not a technique commonly used for fingerprinting.

The developed model exhibited better performance parameters and a greater number of samples than other works reported in the literature [7,11,12]. Additionally, the spectrofluorimetric technique presents some advantages such as simplicity, quickness, low cost, and no need for sample preparation. Therefore, synchronous fluorescence spectroscopy offers a promising approach for the authentication of cachaças and rums. This model can be used for routine analysis as a screening method, assisting in combating frauds, since, in general, rums show higher commercial value compared to cachaças, mainly imported ones. Fluorescence spectroscopy has been also used successfully in the authentication approach for the following distilled beverages: baijiu [37], brandy [18,25,38], fruit spirits [20,22,23,39], juniper-flavored spirits [21], and vodka [27].

CRediT authorship contribution statement

Amanda Lemes Silveira: Methodology, Investigation, Writing – original draft, Writing – review & editing. **Paulo Jorge Sanches**

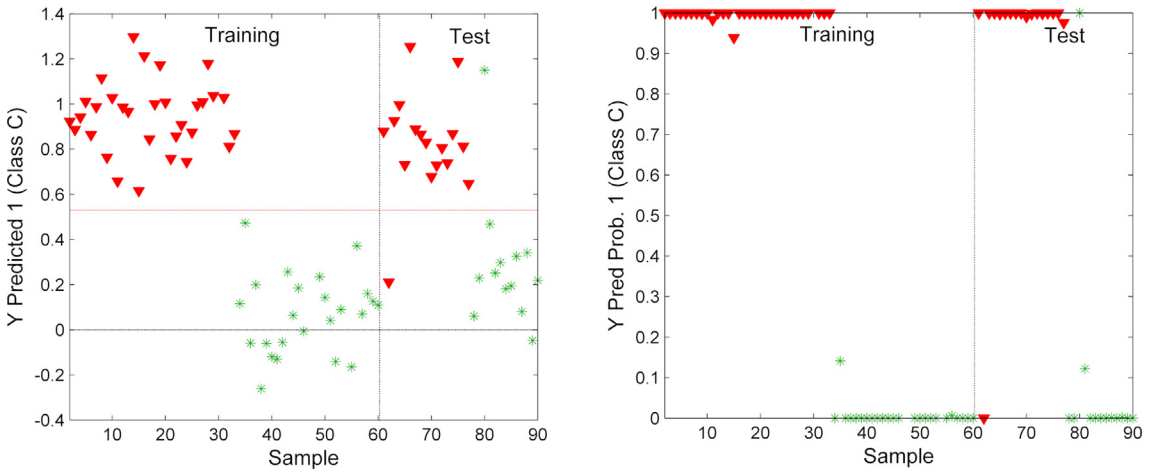

Fig. 5. $\Delta\lambda$ = 10 nm synchronous fluorescence PLS-DA predictions for cachaça class. Vertical dashed lines separate training and test samples, and horizontal dashed lines indicate the threshold class. Sample symbols: red down triangles for cachaça, and green asterisks for rum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

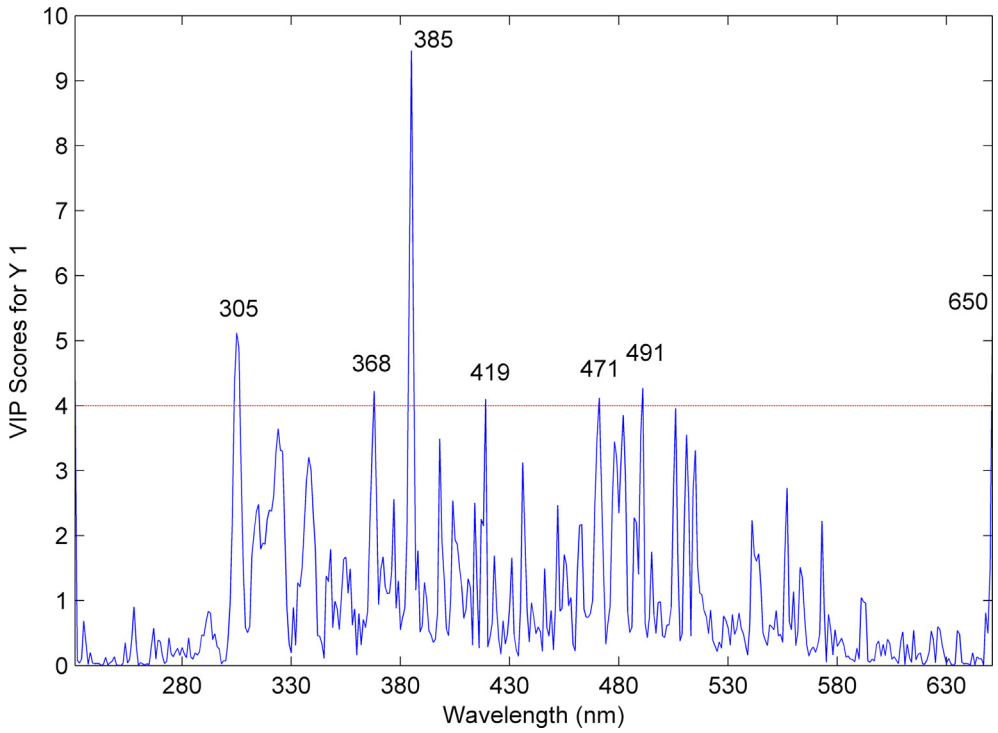

Fig. 6. VIP scores of the $\Delta\lambda$ = 10 nm synchronous fluorescence PLS-DA model for the classification of cachaças and rums.

Barbeira: Conceptualization, Investigation, Writing – review & editing, Supervision.

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.

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