RIGHT-ANGLE FLUORESCENCE SPECTROSCOPY FOR DIFFERENTIATION OF DISTILLED ALCOHOLIC BEVERAGES

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Abstract: Total luminescence and synchronous scanning fluorescence spectroscopic techniques were investigated for differentiating brandies from mixed wine spirits. The studies were performed on 16 brandies from 3 different producers and 30 mixed wine spirits from 5 different producers. Differentiation between samples was accomplished by multivariate data analysis methods (principal component analysis, hierarchical cluster analysis, and linear discriminant analysis). Correct classification was obtained using emission spectra (400–650 nm) recorded at excitation wavelength 390 nm, excitation spectra (225–460 nm) obtained at emission wavelength 470 nm and synchronous fluorescence spectra (200–700 nm) collected at wavelength interval 80 nm. These results indicate that right-angle fluorescence spectroscopy offers a promising approach for the authentication of brandies as neither sample preparation nor special qualification of the personnel are required, and data acquisition and analysis are relatively simple when compared to front-face technique.

Keywords: Brandy, Mixed wine spirit, Fluorescence, Chemometric, Authentication

1. Introduction

Brandy is a general term for distilled wine, usually 40–60% ethanol by volume. Types of brandies, originally at least, tended to be location-specific. Brandy has to be aged for a certain period in oak casks. Toasting wood to be used in oak casks for aging brandy produces a great number of volatile and odoriferous substances. In addition, aging involves various processes producing significant changes in the composition of ageing spirit and being very important for the quality of the final products (taste, flavor and color) (MOSEDALE and PUECH, 1998). Mixed wine spirits are legally produced using wine distillates diluted with ethanol from other sources. They are frequently blended with sugar, brandy aroma and caramel. Some mixed wine spirits contain honey or colorants. Owing to the low price of this mixed wine spirit, it is sometimes used for a counterfeiting brandy. This usually occurs in restaurants and therefore affects the consumer and places honest traders at a financial disadvantage. For this reason, there is a need for a rapid method for drink authentication to reassure consumers, protect regional designations and ensure fair competition.

Several analytical methods have been published for classification of brandies. Gas chromatography-mass spectrometry is a powerful tool in the analysis of volatile components of brandies (CALDEIRA *et al*., 2004; WATTS *et al*., 2003). High-performance liquid chromatography has been widely used for the analysis of phenolic compounds and furanic derivatives of brandies. The direct injection allows classification of the brandies according to the botanical species of the wood barrel (CANAS *et al.*, 2003). Capillary zone electrophoresis has been applied successfully in the analysis of phenolic compounds. Counterfeit brandy is easy to recognize by the

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absence of sinapaldehyde, syringaldehyde, and coniferaldehyde (PANOSSIAN *et al*., 2001).

Analytical method used to verify the quality and authenticity of alcoholic beverages should to perform an analysis without sample pre-treatment. In addition, it should to accomplish a fast data acquisition and carry out the data treatment accurately with relatively low costs. The combination of chemometric and spectroscopic methods is a good way to reach these premises.

The aim of this paper is to show that right-angle fluorescence spectroscopy and multivariate statistical methods (PCA, HCA, linear discriminant analysis (LDA)) can be used for distinguishing between commercial samples of brandies and mixed wine spirits as an alternative method to front-face fluorescence technique (SÁDECKÁ *et al.*, 2009), exigent of special front surface accessory.

2. Materials and methods

2.1. Samples and chemicals

The studies were performed on 16 brandies (B) from 3 different producers (B_1, n=8; B_2, n=4; B_3, n=4) and 30 mixed wine spirits (D) from 5 different producers (D_1, n=12; D_2, n=10; D_4, n=4; D_5, n=2; D_6, n=2). Samples were purchased from the local supermarkets besides four brandies which were obtained directly from the manufacturers. Brandy B_1, a traditional Slovak product from the Small Carpathian viticulture region, is made of the grape using a classic method of aging wine spirit in small 300 L oak barrels for a minimum five years. The wine spirit then goes to 20,000 L barrels for next 3 years. Brandy B_2 is made of the pure high quality foreign wine spirit matured by natural way in oak barrels. B_3 is made of the wine spirit from the East Slovak viticulture region matured by natural way in oak barrels.

Mixed wine spirits are produced using wine spirits diluted with ethanol from other sources. They are frequently blended with sugar, brandy aroma and caramel (E 150a). Mixed wine spirits D_1 contain honey and colorants (E 102, E 110, E 120, E 122, E 132 and E 151). Samples were stored in the dark at room temperature until the day of analysis.

The plain caramel (E 150a, Color No. 525) was a commercial caramel produced by D.D.Williamson (UK). The physicochemical characteristics of this product are: color intensity (absorbance of 0.1% w/v solution at 610 nm through a 1 cm square cell) 0.030–0.035, specific gravity (15.56°C) 1.340–1.360 kg L^{-1}, baume (15.56°C) 36.8–38.4, pH, as is 3.0–4.0. A stock solution, 1.000 g L^{-1}, of caramel product was prepared in ethanol:water (40:60, v/v). The stock solution of caramel was diluted with ethanol:water (40:60, v/v) in order to have system with absorbance values similar to those of mixed wine spirit. Ethanol, ACS spectrophotometric grade, 95.0%, from Sigma-Aldrich and water (Milli-Q system) were used.

2.2. Fluorescence spectroscopy

Fluorescence spectra were recorded using a Perkin-Elmer LS 50 Luminescence spectrometer equipped with a Xenon lamp. Excitation and emission slits were both set at 5 nm. Scan speed was 200 nm/min.

Fluorescence excitation spectra were recorded between 200 and 500 nm (increment 0.5 nm), repeatedly, at emission wavelengths from 300 to 600 nm, spaced by 10 nm interval in the emission domain.

Fluorescence emission spectra were recorded from 250 to 700 nm (increment 0.5 nm), repeatedly, at excitation wavelengths from 200 to 500 nm, spaced by 10 nm interval in the excitation domain.

Synchronous fluorescence spectra were collected by simultaneously scanning the excitation and emission monochromator in the excitation wavelength range 200–700 nm, with constant wavelength differences $\Delta\lambda$ between them. Spectra were recorded for $\Delta\lambda$ interval from 10 to 100 nm, in steps of 5 nm. Fluorescence intensities were plotted as a function of the excitation wavelength.

The right-angle geometry was used for samples in 10 mm × 10 mm × 45 mm quartz cell. Fluorescence measurements were done in triplicate for each sample.
The spectrometer was connected to a computer supplied with FL Data Manager Software (Perkin-Elmer) for spectral acquisition and data processing.

Contour maps of total luminescence and synchronous scan fluorescence spectra were plotted using Windows-based software OriginPro 7.5 (OriginLab, USA, 2002).

2.3. UV-visible absorption spectroscopy

Absorption spectra were obtained with a Spectronic 20 Genesys spectrophotometer (Thermo Fisher Scientific) using 10 mm square cuvette and 8 nm slit width. The measurements were made between 325 nm and 700 nm.

2.4. Mathematical analysis of data

To investigate the differences between fluorescence spectra of the samples PCA and HCA were applied. PCA is an unsupervised (we have no prior knowledge of the groups to be expected) pattern recognition method that reduces the dimensionality of the original data matrix while retaining the maximum amount of variability as well as recognizing the data structure (GELADI, 2003).

HCA is an unsupervised pattern recognition method detecting natural grouping in data. Objects are grouped in clusters in terms of their similarity. We used hierarchical (agglomerative) cluster analysis, where similarity extent was measured by Manhattan (city-block) distances and cluster aggregation was based on Ward's method. Finally, a supervised pattern recognition method, LDA, was used to classify samples according to their origin. LDA method is an excellent tool to obtain vectors showing the maximal resolution among categories, maximal separation and compactness of the categories.

Microsoft Excel 2000 and Statistica software version 6.0 (StatSoft, USA, 2001) were used for statistical analysis.

3. Results and discussion

3.1. Total luminescence spectra

Figure 1 shows total luminescence spectra of the brandy and mixed wine spirit as contour maps, constructed in such a way that x-axis represents the emission and y-axis

the excitation wavelengths, while the contours are plotted by linking the points of equal fluorescence intensity. Brandy total luminescence contour map spreads in the excitation wavelength range 380–500 nm, in contrast to mixed wine spirit that spreads in the excitation wavelength range 200–240 nm and 300–500 nm, respectively. The contours for brandy are concentrated in the emission wavelength region 510–570 nm and excitation wavelength region 430–480 nm, while the contours for mixed wine spirit are concentrated in the emission wavelength region 460–530 nm and the excitation wavelength region 380–420 nm.

In general, spectral features and fluorescence intensity values of all brandies are typical of brandies of similar origin and nature. The fluorescence spectra of brandies B_1 are characterized by the main fluorophores centered at an excitation/emission wavelength pair of 460/540 nm. The other brandies have the following excitation/emission maxima: B_2 - 450/523 nm, B_3 - 450/524 nm. However, the excitation/emission wavelength values of the major peaks of the brandies are generally longer than those usually measured for mixed wine spirits, e.g., D_1 - 396/494 nm, D_2 - 390/476 nm.

As mentioned, the mixed wine spirits are frequently colored with caramel (E 150a) to imitate the effect of long aging in wooden casks. Therefore we assumed that the major peak originates from this colorant. To support this assumption, the stock solution of caramel was diluted with ethanol:water (40:60, v/v) in order to have system with ethanol volume and absorbance values similar to those of mixed wine spirit, and total luminescence spectra of caramel were recorded. Emission spectra recorded after excitation at 395 nm showed a maximum located around 494 nm (Fig. 1c). The light observed at 450–550 nm under excitation at 200–240 nm is probably scatter originating from caramel colloidal aggregates. A comparison of fluorescence spectra, particularly of those recorded at excitation/emission maxima of caramel supports an earlier assumption. We should note, however, that exact position of maxima of caramel fluorescence vary from one mixed wine spirit to another, which may results from difference in the respective caramel composition and/or from the technological process used.

As it is clearly shown in Fig. 1 the shape and the fluorescence intensities are different between the two classes of beverages. It appears that total luminescence spectroscopy can be used to characterize brandy and mixed wine spirit samples using suitable wavelength regions.

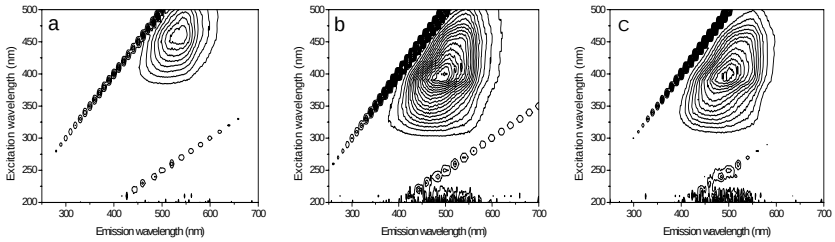

Fig. 1. Contour plots of total luminescence spectra of brandy (a), mixed wine spirit (b), and caramel (0.750 g L^{-1} in ethanol:water, 40:60, v/v) (c). Contours join the points of equal fluorescence intensity.

Besides the fluorescence band, Fig. 1 shows the presence of the first and the second order Rayleigh scatter bands. The first order Rayleigh scatter line is centered at the emission wavelength equals excitation wavelength, the second order Rayleigh scatter at the emission equals twice the excitation. Scattering is much more intense and/or heterogenous for mixed wine spirits than for brandies. This phenomenon may result from the higher heterogeneity of mixed wine spirit, e.g., presence of colloids, with respect to brandy. The light observed at 450–550 nm under excitation at 200–240 nm is probably scatter, partially originated from caramel colloids in mixed wine spirit. Hence, the differences between brandy and mixed wine spirit are also due to scatter bands. Because these bands have no information about the fluorophores in the samples the wavelength range where they are located will be discarded from the subsequent data analysis.

3.2. Total synchronous fluorescence spectra

The contour plots of total synchronous fluorescence (TSF) spectra were obtained by plotting the fluorescence intensity (z-axis) as a function of excitation wavelength (x-axis) and wavelength interval $\Delta\lambda$ (y-axis). The TSF spectra of a brandy sample are given in Fig. 2a. It shows that the TSF contour map spreads in the excitation wavelength 380–550 nm and $\Delta\lambda$ 10–100 nm. The contours are concentrated in the excitation wavelength region 440–480 nm and $\Delta\lambda$ 60–100 nm. The plot shows only one fluorescence maximum blue-shifted from 500 to 450 nm with increasing $\Delta\lambda$. The maximum fluorescence intensity was recorded at excitation wavelength 460 nm ($\Delta\lambda$ = 80 nm), 450 nm ($\Delta\lambda$ = 75 nm) and 450 nm ($\Delta\lambda$ = 75 nm) for brandy B_1, B_2 and B_3, respectively.

The TSF spectra of a mixed wine spirit sample are given in Fig. 2b. The contour map spreads in the excitation wavelength 320–550 nm and $\Delta\lambda$ 10–100 nm. Two overlapping bands with maxima at 420 and 479 nm are apparent for $\Delta\lambda$ = 10 nm. For $\Delta\lambda$ = 30 nm, the fluorescence intensity of bands increased, changes in their relative intensities were noted, and maxima were blue-shifted to 407 and 460 nm, respectively. At increased $\Delta\lambda$, the first band was shifted to 405 and 399 nm and the second one to 452 and 435 nm for $\Delta\lambda$ = 40 and 60 nm, respectively. The further increase of intensity and band broadening was apparent for $\Delta\lambda$ = 70 nm, resulting in only one band with maxima at 400 nm. The banding intensity increases at higher $\Delta\lambda$ values. The shape and intensity of the fluorescence maxima varied from one mixed wine spirit to another. For example, the maximum fluorescence intensity for sample D_1 and D_2 was observed at excitation wavelength 396 nm ($\Delta\lambda$ = 95 nm) and 391 nm ($\Delta\lambda$ = 85 nm), respectively.

Generally, the fluorescence maxima shift to shorter wavelengths with increasing $\Delta\lambda$ for both brandy and mixed wine spirit. Brandies give a longer wavelength less intensive fluorescence band, while mixed wine spirits give a shorter high intensive band.

The shape and intensity of the synchronous fluorescence spectra of caramel depend on the difference between excitation and emission wavelengths $\Delta\lambda$ (Fig. 2c). For $\Delta\lambda$ = 10 nm, two bands with maxima at 420 and 478 nm are observed. At increased $\Delta\lambda$, the first band was shifted to 407, 404 and 400 nm and the second one to 460, 453

and 435 nm for Δλ 30, 40 and 60 nm, respectively. For Δλ = 70 nm, only one band with maxima at 399 nm was recorded. Comparison shows that the maxima observed for caramel at different Δλ-values are consistent with the respective maxima in mixed wine spirits.

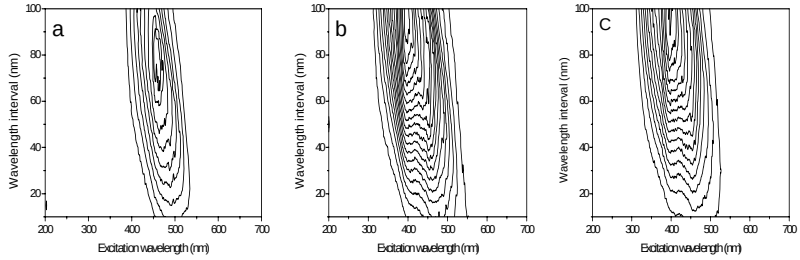

Fig. 2. Contour plots of total synchronous fluorescence spectra of brandy (a), mixed wine spirit (b), and caramel (0.750 g L^{-1} in ethanol:water, 40:60, v/v) (c). Contours join the points of equal fluorescence intensity.

3.3. Multivariate analysis of excitation and emission spectra

The PCA was carried out separately on the excitation and emission spectra to investigate differences between samples. The best classification was achieved using excitation spectra (225–460 nm) recorded at emission wavelength 470 nm or emission spectra (400-650 nm) recorded at excitation wavelength 390 nm. The fluorescence spectra showed different shapes. The width of excitation spectra was larger for mixed wine spirits than those for brandies. Mixed wine spirits had higher fluorescence intensity regardless of wavelength but they were also more heterogeneous in this respect. Excitation and emission spectra obtained for the mixed wine spirit at the excitation/emission wavelength pair 390/470 nm are similar to those of caramel. Moreover, the absorption spectrum is in good agreement with that of caramel in the wavelength range 325–600 nm.

The PCA output indicates that the first PC (PC1) has the largest eigenvalue at 38.0 and accounts for 82.6% of the total variance in the collected data. The second PC (PC2) has next largest eigenvalue at 7.8 and accounts for 17.0% of the data variation. The remaining PCs account for 0.4% of the variation. According to the eigenvalue results displayed in the *scree plot* (eigenvalue *vs* number of eigenvalues), only the first two PCs were used for the purpose of PCA illustration. The variances of the subsequent components are similar and correspond to experimental noise, scatter band residuals and baseline fluctuations. The general guideline in PCA applications is to select those PCs which account, cumulatively, for at least 80% to 90% of the data variation. Cumulatively, the first two PCs from the collected data account for 99.6% of the total variance indicating that two PCs appear sufficient to explain the structures in the data. The similarity map defined by the PC1 and PC2 of the PCA performed on excitation spectra allowed a good discrimination of beverages (Fig. 3a). Spectral pattern associated with the PCs provide the characteristic wavelengths that may be used to discriminate between spectra. The spectral pattern associated with the PC1

exhibited a positive peak around 280 nm and a broad positive peak between 350–450 nm corresponding to caramel. The spectral pattern associated with the PC2 exhibited positive peaks at 250 and 300 nm (results are not presented). While a discrimination of the brandy and mixed wine spirit samples was achieved with excitation data collection, a different trend was observed with emission spectra. The PC1 has an eigenvalue at 40.2 and accounts for 87.4% of the total variance in the collected data. The PC2 has an eigenvalue at 5.7 and accounts for 12.4% of the data variation. Cumulatively, the first two PCs from the collected data account for 99.8% of the total variance indicating that two PCs appear sufficient to explain the structures in the data. Although the PCA similarity map defined by the PC1 and PC2 did not lead to a clear discrimination of beverages, a general trend pointing out the brandies and mixed wine spirits was observed on the map (Fig. 3b). Brandies B_1 constitute one subgroup, while brandies B_2 and B_3 constitute another subgroup. Finally, there is a group of mixed wine spirits.

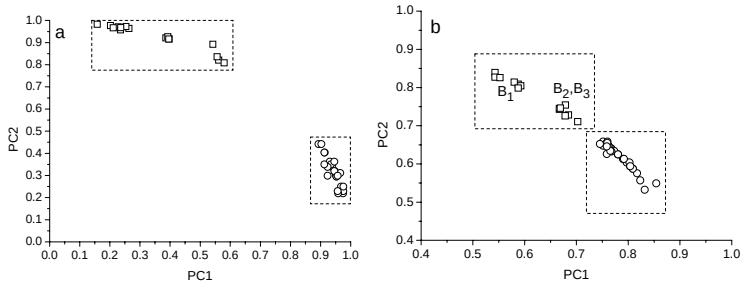

Fig. 3. Principal component analysis similarity map (score plot) determined by principal component 1 (PC1) and principal component 2 (PC2) for excitation fluorescence spectra recorded at emission wavelength 470 nm (a) and emission spectra recorded after excitation at 390 nm (b) on brandy (□) and mixed wine spirit (o) samples.

In a second step, HCA was carried out separately on the excitation and emission spectra in order to evaluate the number of subsets of similar samples appearing in the complete data set. For the sake of simplicity, a reduced number of samples were included in the figures, but from them we can clearly recognize the clustering common to all the samples. The evaluation of the above mentioned excitation spectral region provided two main clusters (Fig. 4a). All mixed wine spirits are linked together in the first main cluster. This main cluster is heterogeneous enough but consists of various small groups of very similar products. For instance most of the mixed wine spirits from producer 1 (D_1) is found as such in one subgroup with 97% of similarity among them. All brandies are linked together in the second main cluster. One subcluster is constituted of B_1 (brandy from producer 2) with 98% of similarity. Another subcluster is constituted of B_2 and B_3 with 95% of similarity among them and 90% in relation to B_1. Fig. 4b shows the results from HCA concerning the emission spectra. The dendrogram shows that the brandies are well separated from the mixed wine spirits. The first main cluster contains mixed wine spirit samples, while the second one contains brandy samples. Mixed wine spirits form three smaller groups. One small group is constituted of samples D_2 with 98% of similarity among them and by sample

D_5 with 92% of similarity with the samples D_2 of this group. Another group is constituted of D_2, D_4 and D_6 with 96% of similarity among them and 88% in relation to the group of D_1. Samples D_1 show a similarity of 94% to each other. Brandy samples form three small subclusters of the second main cluster corresponding to three different producers. One subcluster is constituted of B_1 with 95% of similarity. Another subcluster is constituted of B_2 and B_3 with 96 % of similarity among them and 73% in relation to B_1.

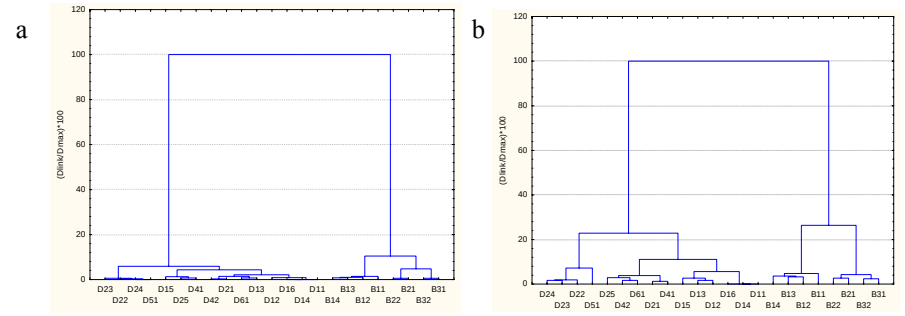

Fig. 4. Hierarchical cluster analysis dendrogram using Manhattan distance for excitation fluorescence spectra recorded at emission wavelength 470 nm (a) and emission spectra recorded after excitation at 390 nm (b) on brandies (B) and mixed wine spirits (D).

3.4. Multivariate analysis of synchronous fluorescence spectra

PCA was applied separately on synchronous spectra measured at $\Delta\lambda$ 10–100 nm. The best classification was achieved using fluorescence spectra recorded at $\Delta\lambda = 80$ nm. The synchronous fluorescence spectra showed different shapes. The width of synchronous spectra was larger for mixed wine spirits than those for brandies. Mixed wine spirits had higher fluorescence intensity regardless of wavelength but they were also more heterogeneous in this respect. Synchronous fluorescence spectra of brandy, mixed wine spirit and caramel (E 150a) obtained at $\Delta\lambda = 80$ nm confirmed an earlier assignment of the band.

Figure 5a shows that the plot of the first two PCs lead to a good discrimination of beverages according to origin. The PC1 has an eigenvalue at 38.6 and accounts for 84.0% of the total variance. The PC2 has an eigenvalue at 7.2 and accounts for 15.6% of the data variation. Cumulatively, the first two PCs from the collected data account for 99.6% of the total variance. The spectral pattern (Fig. 5b) associated with the PC1 presented a positive peak at 280 nm, a broad positive peak between 320–460 nm and a negative peak at 550 nm. The spectral pattern associated with the PC2 exhibited a negative peak at 250 nm and a positive peak around 500 nm.

Applying HCA to fluorescence spectra recorded at $\Delta\lambda = 80$ nm, the dendrogram shows that the mixed wine spirits are well separated from brandies (Fig. 6). The first main cluster contains mixed wine spirit samples only, while the second one contains brandy samples. Mixed wine spirits cluster consists of various small groups of very similar products. One small group is constituted of samples D_2 with 99% of similarity among them and by sample D_5 with 95% of similarity with the samples D_2 of this

group. Another group consists of D_1 with 96% of similarity among them and 80% in relation to the previous group (D_2, D_4, D_5, and D_6). Brandy samples form three small subclusters of the second main cluster corresponding to three different producers. One subcluster is constituted of B_1 with 97% of similarity. Another subcluster is constituted of B_2 and B_3 with 95 % of similarity among them and 86% in relation to B_1.

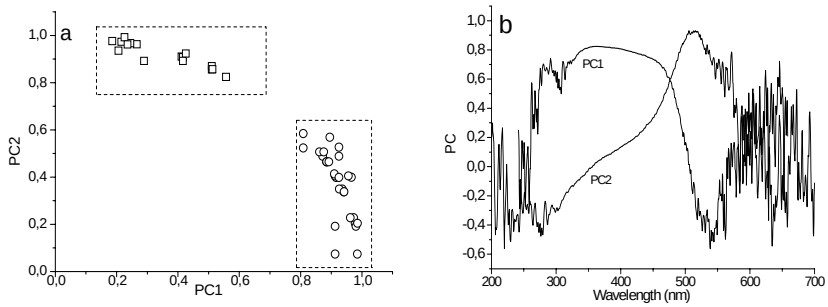

Fig. 5. Principal component analysis similarity map (score plot) determined by principal components 1 (PC1) and principal component 2 (PC2) (a) and spectral pattern (loading) corresponding to PC1 and PC2 (b) for synchronous fluorescence spectra recorded at $\Delta\lambda$ = 80 nm on brandy (□) and mixed wine spirit (o) samples.

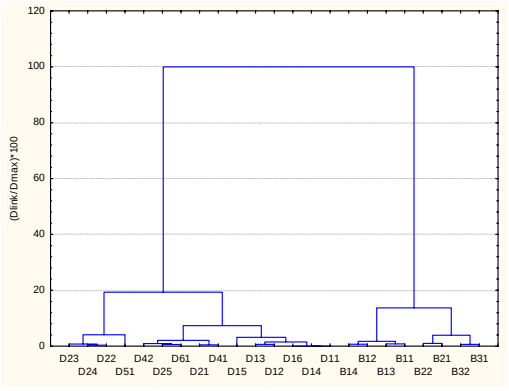

Fig. 6. Hierarchical cluster analysis dendrogram using Manhattan distance for synchronous fluorescence spectra recorded at $\Delta\lambda$ = 80 nm on brandy (B) and mixed wine spirit (D) samples.

Finally, a supervised pattern recognition method, LDA, was applied to fluorescence spectra recorded at $\Delta\lambda$ = 80 nm to classify samples according to their origin. LDA starts with number of objects whose group membership is known. A basic problem in LDA is deciding which variables (excitation wavelengths) should be included in the analysis. In stepwise discriminant function analysis, a model of discrimination is built step-by-step (forward or backward). Specifically, at each step all variables are reviewed and evaluated (Fischer's statistics—F to enter and F to remove values) to determine which one will contribute most to the discrimination between groups. This variable will then be included in the model, and the process

starts again. After performing backward LDA, a classification function was obtained for individual analyzed beverages containing five variables (excitation wavelengths): 280, 388, 396, 402, and 498 nm, which provide 99.6% correct predictions for brandies and wine distillates samples

These results show that complete synchronous spectra are not required to discriminate between beverages. Instead of them, fluorescence intensity could be measured at selected wavelengths.

4. Conclusions

This study shows that brandies and mixed wine spirits can be discriminated using differences in their fluorescence spectra. Differentiation between samples was accomplished by multivariate data analysis methods (PCA, HCA, and LDA). Comparison of the results obtained from multivariate data analysis indicated that better classification was obtained from synchronous fluorescence spectra than from the excitation/emission fluorescence spectra. Right-angle fluorescence spectroscopy offers a promising approach for the authentication of brandies as neither sample preparation nor special qualification of the personnel are required, and data acquisition and analysis are more simple when compared to front-face technique.

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