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Analytical Methods

Classification of brandies and wine distillates using front face fluorescence spectroscopy

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ABSTRACT

This study demonstrates the use of front face fluorescence spectroscopy and multivariate data analysis for differentiating brandies from wine distillates. Owing to the low price of the wine distillates, they are sometimes used for the counterfeiting brandies. For this reason, there is a need for a rapid method for drink authentication to reassure consumers and protect regional designations. Total luminescence and synchronous scanning fluorescence spectra were recorded followed by a classification of samples using principal component analysis (PCA) and hierarchical cluster analysis (HCA). Both PCA and HCA carried out on the emission spectra (360–650 nm) recorded at excitation wavelength 350 nm and synchronous fluorescence spectra (200–700 nm) collected at wavelength interval 90 nm provide very good differentiation between the two spirit classes. Less good classification was obtained using excitation spectra (225–425 nm) obtained at emission wavelength 440 nm. These results indicate that the front face fluorescence spectroscopy offers a promising approach for the authentication of brandies.

1. Introduction

Brandy is a spirit drink produced from wine spirit, whether or not blended with a wine distillate distilled at <94.8 vol.%, provided that that distillate does not exceed a maximum of 50% by volume of the finished product. This spirit is aged for at least one year in oak receptacles or for at least six months in oak casks. Wine spirit is a spirit drink produced by the distillation at <86 vol.% of wine or wine fortified for distillation or by the redistillation of a wine distillate at <86 vol.%. Wine spirit shall not contain added ethanol of agricultural origin (Regulation (EC) No 110/2008).

In Slovak Republic there are two types of these spirits: "wine distillates" are less expensive, and can be legally produced using wine distillates diluted with ethanol from other sources, whereas "brandy" is more expensive and should contain ethanol from grape. Brandy has to be aged for a certain period in oak casks to obtain characteristic taste, flavour and colour. Traditional techniques utilised to analysis of brandy, such as gas chromatography–mass spectrometry (Caldeira, Pereira, Climaco, Belchior, & Bruno de Sousa, 2004), high-performance liquid chromatography (Canas, Belchior, Spranger, & Bruno-de-Sousa, 2003) and capillary electrophoresis (Panossian, Mamikonyan, Torosyan, Gabrielyan, & Mkhitaryan, 2001), focus on the determination of a certain marker compounds in a test product followed by a comparison of the values obtained with those previously documented for authentic product. This approach is often time-consuming, expensive, requires highly trained staffs and the range of compounds, which must be quantified to ensure authenticity, is continuously increasing. In the last few years, there has been an increasing need to develop rapid, inexpensive and effective analytical methods, as well as requiring low sample manipulation. These demands lead to an approach based on food matrix characterisation as a whole and spectroscopic methods combined with chemometric techniques have been studied for this purpose.

While there has been a notable growth for near-infrared (Barboza & Poppi, 2003; Pontes et al., 2006) and Fourier transform infrared (Lachenmeier, 2007; Palma & Barroso, 2002) spectroscopy, there has been little research carried out using either UV–VIS absorption or fluorescence spectroscopy in spirit drink authentication applications. Recent work using UV–VIS absorption spectroscopy dealt with discriminating 100% agave tequilas from other types of tequila (Barbosa-García et al., 2007).

A review (Christensen, Norgaard, Bro, & Engelsen, 2006) has revealed that the application of fluorescence spectroscopy for direct analysis of food has increased during the last decade, probably due to the wide-spread use of multivariate data analysis tools.

Front face fluorescence spectroscopy has demonstrated its feasibility to classify Swiss honeys from seven different floral sources (Karoui, Dufour, Bosset, & De Baerdemaeker, 2007). This method has also been used for the determination of the geographical origin of milk (Karoui, Martin, & Dufour, 2005) and cheeses (Karoui, Bosset, Mazerolles, Kulmyrzaev, & Dufour, 2005; Karoui, Dufour, et al., 2005). Within the area of cheese ripening, the studies concluded

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that fluorescence spectroscopy is suitable to discriminate each ripening stage (Karoui & De Baerdemaeker, 2007).

The potential of front face fluorescence spectroscopy combined with principal component analysis (PCA) and factorial discriminant analysis (FDA) has been investigated for discriminating different wines according to variety, typicality and vintage. PCA performed on the whole collection of excitation spectra allowed a good discrimination between French and German wines. Using FDA, correct classification of typical and non-typical Beaujolais amounting to 95% was observed for the emission fluorescence data set (Dufour, Letort, Laguet, Lebecque, & Serra, 2006).

Synchronous scanning fluorescence spectra and multivariate data analysis (nearest neighbour method and linear discriminant analysis) have been used for classification of differently stored beer samples (Sikorska, Górecki, Khmelinskii, Sikorski, & De Keukeleire, 2006) and of different beers from different breweries (Sikorska, Górecki, Khmelinskii, Sikorski, & De Keukeleire 2004). Synchronous scanning fluorescence spectra are also useful for detection of adulteration of virgin olive oil (Poulli, Mousdis, & Georgiou, 2007).

The aim of this paper is to show that front face fluorescence spectroscopy and multivariate statistical methods (principal component analysis and hierarchical cluster analysis, HCA) can be used for distinguishing between commercial samples of brandies and wine distillates. It appears that front fluorescence spectroscopy may give a quick and non-destructive answer to the product authenticity as spectra can be recorded directly on samples.

2. Materials and methods

2.1. Samples

The studies were performed on 16 brandies (B) from three different producers (B_1, $n = 8$; B_2, $n = 4$; B_3, $n = 4$) and 30 wine distillates (D) from five different producers (D_1, $n = 12$; D_2, $n = 10$; D_4, $n = 4$; D_5, $n = 2$; D_6, $n = 2$). Four brandies were acquired directly from the manufacturers; other samples were purchased from the local supermarkets. Brandy B_1, a traditional Slovak product from the Small Carpathian viticultural region, is made of the grape using a classic method of ageing wine spirit in small 300 l oak barrels for a minimum 5 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.

Wine distillates are produced using wine spirits diluted with ethanol from other sources. They are frequently mixed with sugar, brandy aroma and caramel. Wine distillates D_1 contain honey and colourants (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.

2.2. Fluorescence spectroscopy

Fluorescence spectra were recorded using a Perkin–Elmer LS 50 Luminescence spectrometer equipped with a Xenon lamp and a variable angle front-surface accessory. The incidence angle of the excitation radiation was set at 56°. Samples were placed in 10 mm × 10 mm × 45 mm quartz cell. Excitation and emission slits were both set at 5 nm.

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 5 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 5 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.

Fluorescence measurements were done in triplicate for each sample.

The spectrometer was interfaced 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. Mathematical analysis of data

PCA and HCA were applied to the fluorescence spectra to investigate differences between the samples. 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 recognising the data structure. PCA decomposes a data matrix with n rows (samples) and p columns (variables) into the product of a scores matrix, with n rows (samples) and $d < p$ columns (principal components, PCs), and a loadings matrix, with $d < p$ rows (PCs) and p columns (variables). The scores are the positions of the samples in the space of the principal components and the loadings are contributions of the original variables to the PCs. All PCs are mutually orthogonal, and each successive PC contains less of the total variability of the initial data set. Usually, only a limited number $d < p$ of PCs are retained, as the variability in the others is due to noise. This reduces the dimensionality of the data considerably, enabling effective visualisation, classification, and regression of multivariate data (Geladi, 2003).

HCA is an unsupervised pattern recognition method detecting natural grouping in data. Objects are grouped in clusters in terms of their similarity. The initial assumption is that the nearness of objects in the space defined by the variables reflects the similarity of their properties. There are diverse possibilities and rules used to measure distances (in various metrics in multidimensional space), form and linkages among individual clusters. 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 (Otto, 1999).

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

Recently, total luminescence spectroscopy (TLS) has been applied to obtain emission spectra over a range of excitation wavelengths in the form of Excitation–Emission matrices (EEM contour maps), which allowed to obtain more detailed information than that obtained using conventional mono dimensional fluorescence (Poulli, Mousdis, & Georgiou, 2005; Sikorska et al., 2006).

Total luminescence spectra of the brandy and wine distillate are shown in Fig. 1 as contour maps. In general, spectral features and fluorescence intensity values of all brandies are typical of brandies of similar origin and nature. Brandy total luminescence contour