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Investigation of variety, typicality and vintage of French and German wines using front-face fluorescence spectroscopy

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Abstract

The potential of front-face fluorescence spectroscopy combined with chemometric methods was investigated for discriminating different wines according to variety, typicality and vintage. A total of 120 wines produced in France and Germany were investigated. Emission (275–450 nm) and excitation (250–350 nm) fluorescence spectra of phenolic compounds were recorded directly on the wine samples using a front-face fluorescence accessory. The emission spectra were characterised by a maximum at 376 nm and a shoulder at 315 nm and the excitation spectra showed two peaks located at about 260 and 320 nm. The shape of the spectra changed with wine samples, varying mainly in the maximum/shoulder intensity. Wine samples were evaluated using principal component analysis (PCA) and classified by factorial discriminant analysis (FDA). 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. These results showed that fluorescence spectroscopic technique may provide useful fingerprints and mainly allow the identification of wines according to variety and typicality.

Keywords: Polyphenol; Tannin; Fluorescence; Chemometry; Authentication

1. Introduction

Nowadays, objective and authentic food information is a major concern of many consumers, and it is gaining importance. Labelling and compositional regulations, which may differ from country to country, have a fundamental place in determining which scientific tests are appropriate for a particular issue. Wines with origin identification are generally high-priced and bring in a higher benefit to the producers than ordinary ones. For consumers having an extensive choice of food commodities, authenticity is a guarantee of safety and eating quality.

Several techniques for assessing the authenticity of labelled food products have been used. These techniques can be classified into two categories. Traditional techniques, such as gas chromatography, capillary gas chromatography of lipid fractions, electrophoretic separation of proteins, focus on the existence or absence of certain chemical compounds in the authentic product [1]. Although these methods provide valuable information on the composition and biochemistry of food products, they are time-consuming, expensive, require highly skilled operators and are not easily adapted to on line monitoring. Hence, an urgent demand exists for rapid, inexpensive and efficient techniques for quality control. A great number of non-invasive and non-destructive instrumental techniques, such as infrared and fluorescence spectroscopic techniques have been developed for the authentication of food products. These analytical tools require limited sample preparation and appear promising. Near-infrared spectroscopy has been used for the determination of physico-chemical parameters of Greek Feta cheeses [2] and for authentication of foods, e.g., identification of different varieties of green asparagus [3] and of different varieties of wheat [4]; differentiation of frozen and unfrozen beef [5]; discrimination of different oils [6]; discrimination between different brands of French Emmental cheeses [7]. Recently, we have shown that fluorescence spectroscopy coupled with chemometric tools is a valuable method for identifying and determining the geographic origin of Emmental cheeses originating from six different countries [8]. Fluorescence spectroscopy can provide

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in a few seconds spectral signatures that can be used as a fingerprint of the food products (dairy products, meat, cereal flours, honey).

Front-face fluorescence spectroscopy provides information on the presence of fluorescent molecules, such as tyrosine, phenylalanine and tryptophan residues in proteins, and their environment in biological samples [9]. The fluorescence properties of aromatic amino acids also have been used to study protein structure and protein interactions in cheese [10]. The emission of tryptophan residues in protein is highly sensitive to its local environment, and is thus often used as an indicator group for protein conformational changes [9]. Using Vitamin A as an intrinsic fluorescent probe, fluorescence spectroscopy can also provide information on the physical state of triglycerides and protein–lipid interactions [11,12].

Polyphenols in wine make up a large and complex family of fluorescent molecules, with diverse structures, properties and sizes (monomers to polymers) [13,14]. The nature and amount of polyphenols are different from one grape variety to another. Further complexity results from reactions of native phenolic compounds of grapes during winemaking and ageing. These compounds are responsible for main sensorial properties of red wines (especially colour and taste, i.e., astringency and to a lesser extent, bitterness). Considering red wine, tannins are important for their astringent sensory properties as well as for their potentially beneficial role in human health.

The objective of the present investigation was to assess the potential of front-face fluorescence spectroscopy using multivariate statistical methods to discriminate 120 wines samples from France (mainly Beaujolais) and Germany (mainly Pfalz) and to identify wines according to variety, typicality and vintage. It appears that fluorescence spectroscopy may give a quick and non-destructive answer to the product authenticity as spectra can be recorded directly on wines.

2. Materials and methods

2.1. Wine samples

A collection of 120 commercial typical and non-typical wines was selected on the basis of labelling and available relevant information (geographical origin, variety, wine process). The collection of 60 red wines includes 60 French wines (30×2 vintages) and 60 German wines (30×2 vintages). As French wines were provided by Société d'Intérêt Collectif Agricole de Recherches EXpérimentales (SICAREX Beaujolais, France), Landwirtschaftskammer Rheinland-Pfalz (Germany) supplied German wines. Thirty French wines and 30 German wines were analysed in 2003 (year 1 in Table 1). In 2004, 30 French wines and 30 German wines were also analysed (year 2 in Table 1).

Typicality was assessed by focus groups with wine chains actors [15]. Forty and 20 French wines were assessed as typical and non-typical (outsider), respectively, whereas 48 and 12 German wines were assessed as typical and non-typical (outsider), respectively (Table 1). The outsiders differed from typical wines according to the geographic origin or/and the variety.

2.2. Fluorescence spectroscopy

Fluorescence spectra were recorded using a FluoroMax-2 spectrofluorimeter (Spex-Jobin Yvon, Longjumeau, France) mounted with a variable angle front-surface accessory. The incidence angle of the excitation radiation was set at 56° to ensure that reflected light, scattered radiation and depolarisation phenomena were minimised. Wine samples were placed in 3 mL quartz cuvette and spectra were recorded at 20 °C. As the emission spectra of phenolic compounds (275–450 nm) were recorded with the excitation wavelength set at 261 nm, the excitation spectra (250–350 nm) were recorded with the emission wavelength set at 376 nm. The slits at excitation and emission were fixed at 3 and 3, respectively. All spectra were corrected for instrumental distortions in excitation using a rhodamine cell in the reference channel.

For each wine, three spectra were recorded on three different aliquots.

2.3. Mathematical analysis of data

In order to reduce scattering effects and to compare samples, the fluorescence spectra were normalised by reducing the area under each spectrum to a value of 1 [16]. Mainly the shift of the maximum and the width changes of the spectra were considered following normalisation.

Principal component analysis (PCA) was applied to the normalised spectra to investigate differences between the wines [10]. PCA transforms the original variables into new axes, or principal components (PCs), which are orthogonal, so mat the data set presented on these axes are uncorrelated with each other. Therefore, PCA expresses the total variation in the data set in only a few PCs and each successively derived PC expresses decreasing amounts of the variance. PCA performed on fluorescence spectra makes it possible to draw similarity maps of the samples and to get spectral patterns [16]. The spectral patterns corresponding to the principal components provide information about the characteristic peaks which are the most discriminating for the samples observed on the maps. While similarity maps allow comparison of the spectra in such a way that two neighbouring points represent two similar spectra, the spectral patterns exhibit the absorption bands that explain the similarities observed on the maps.

Factorial discriminant analysis (FDA) was performed on the PCs resulting from the PCA applied to the fluorescence spectral data (emission spectra or excitation spectra). The aim of this technique was to predict the membership of an individual to a qualitative group defined as a preliminary [17]. For example, a group was created for each type of wine, i.e., typical wine and non-typical wine. FDA could not be applied in a straightforward way to continuous spectra because of the high correlations occurring between the wavelengths.

FDA assesses new synthetic variables called "discriminant factors", which are linear combinations of the selected principal components, and allows a better separation of the centres of gravity of the considered groups. The individual wine samples

Table 1
Collection of the French and German wines analysed in this study

Wine code#	Type	Region	Cultivar	Label	Vintage	Description type	Year of analysis[a]
B01	Typical	Beaujolais	Gamay	AOC	2001	Typical-Beaujolais	1
B02	Typical	Beaujolais	Gamay	AOC	2000	Typical-Beaujolais-Villages	1
B03	Typical	Beaujolais	Gamay	AOC	2000	Typical-Crus	1
B04	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	1
B05	Outsider	Sud-Ouest	Negrette 50%	AOC	2000	*OutsiderCULTIVAR*	1
B06	Outsider	Sud-Ouest	Gamay	VDP	2002	*Outsider REGION*	1
B07	Outsider	Valleedu Rhone	Gamay	VDP	2001	*Outsider REGION*	1
B08	Outsider	Valleedu Rhone	Syrah	VDP	2001	*OutsiderCULTIVAR*	1
B09	Outsider	Savoie	Gamay	AOC	2002	*Outsider REGION*	1
B10	Outsider	Suisse	Gamaret	AOC	2002	*OutsiderCULTIVAR*	1
B11	Outsider	Auvergne	Gamay	VDQS	2002	*Outsider REGION*	1
B12	Outsider	Val de Loire	Gamay	AOC	2000	*Outsider REGION*	1
B13	Outsider	Maconnais	Pinot	AOC	1999	*OutsiderCULTIVAR*	1
B14	Outsider	Pfalz	Dornfelder	Qba	2002	*OutsiderCULTIVAR*	1
B15	Typical	Beaujolais	Gamay	AOC	2000	Typical-Crus	1
B16	Typical	Beaujolais	Gamay	AOC	2000	Typical-Crus	1
B17	Typical	Beaujolais	Gamay	AOC	2001	Typical-Crus	1
B18	Typical	Beaujolais	Gamay	AOC	2000	Typical-Crus	1
B19	Typical	Beaujolais	Gamay	AOC	2000	Typical-Beaujolais	1
B20	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	1
B21	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	1
B22	Typical	Beaujolais	Gamay	AOC	2002	Typical-Coteaux du Lyonnais	1
B23	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	1
B24	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais-Villages	1
B25	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais-Villages	1
B26	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais-Villages	1
B27	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais-Villages	1
B28	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	1
B29	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	1
B30	Typical	Beaujolais	Gamay	AOC	2001	Typical-Beaujolais	1
B31	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	2
B32	Typical	Beaujolais	Gamay	AOC	2001	Typical-Beaujolais-Villages	2
B33	Typical	Beaujolais	Gamay	AOC	2001	Typical-Crus	2
B34	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	2
B35	Outsider	Sud-Ouest	Negrette 50%	AOC	2001	*OutsiderCULTIVAR*	2
B36	Outsider	Sud-Ouest	Gamay	VDP	2003	*Outsider REGION*	2
B37	Outsider	Valleedu Rhone	Gamay	VDP	2002	*Outsider REGION*	2
B38	Outsider	Valleedu Rhone	Syrah	VDP	2002	*OutsiderCULTIVAR*	2
B39	Outsider	Savoie	Gamay	AOC	2003	*Outsider REGION*	2
B40	Outsider	Suisse	Gamaret	AOC	2003	*OutsiderCULTIVAR*	2
B41	Outsider	Auvergne	Gamay	VDQS	2003	*Outsider REGION*	2
B42	Outsider	Val de Loire	Gamay	AOC	2002	*Outsider REGION*	2
B43	Outsider	Maconnais	Pinot	AOC	2002	*OutsiderCULTIVAR*	2
B44	Outsider	Pfalz	Dornfelder	Qba	2003	*OutsiderCULTIVAR*	2
B45	Typical	Beaujolais	Gamay	AOC	2001	Typical-Crus	2
B46	Typical	Beaujolais	Gamay	AOC	2001	Typical-Crus	2
B47	Typical	Beaujolais	Gamay	AOC	2002	Typical-Crus	2
B48	Typical	Beaujolais	Gamay	AOC	2001	Typical-Crus	2
B49	Typical	Beaujolais	Gamay	AOC	2001	Typical-Beaujolais	2
B50	Typical	Beaujolais	Gamay	AOC	2003	Typical-Beaujolais	2
B51	Typical	Beaujolais	Gamay	AOC	2003	Typical-Beaujolais	2
B52	Typical	Beaujolais	Gamay	AOC	2003	Typical-Coteaux du Lyonnais	2
B53	Typical	Beaujolais	Gamay	AOC	2003	Typical-Beaujolais	2
B54	Typical	Beaujolais	Gamay	AOC	2003	Typical-Beaujolais-Villages	2
B55	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais-Villages	2
B56	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais-Villages	2
B57	Typical	Beaujolais	Gamay	AOC	2003	Typical-Beaujolais-Villages	2
B58	Typical	Beaujolais	Gamay	AOC	2003	Typical-Beaujolais	2
B59	Typical	Beaujolais	Gamay	AOC	2003	Typical-Beaujolais	2
B60	Typical	Beaujolais	Gamay	AOC	2002	Typical-Beaujolais	2
D01	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D02	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D03	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1

Table 1 (*Continued*)

Wine code#	Type	Region	Cultivar	Label	Vintage	Description type	Year of analysis[a]
D04	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D05	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D06	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D07	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D08	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D09	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D10	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D11	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D12	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D13	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D14	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D15	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D16	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D17	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D18	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D19	Outsider	Rheinhessen	Dornfelder	QbA	2002	OUTSIDER, other geographic region	1
D20	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D21	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D22	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D23	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D24	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D25	Outsider	Rheinhessen	Dornfelder	QbA	2002	OUTSIDER, other geographic region	1
D26	Typical	Pfalz	Dornfelder	QbA	2002	Typical	1
D27	Outsider	Wiirttemberg	Dornfelder	QbA	2002	OUTSIDER, other geographic region	1
D28	Outsider	Franken	Dornfelder	QbA	2002	OUTSIDER, other geographic region	1
D29	Outsider	Pfalz	Pinot noir	QbA	2002	OUTSIDER, other grape variety	1
D30	Outsider	Pfalz	Cabernet Sauvignon	QbA	2002	OUTSIDER, other grape variety	1
D31	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D32	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D33	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D34	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D35	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D36	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D37	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D38	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D39	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D40	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D41	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D42	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D43	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D44	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D45	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D46	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D47	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D48	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D49	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D50	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D51	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D52	Outsider	Rheinhessen	Dornfelder	QbA	2003	OUTSIDER, other geographic region	2
D53	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D54	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D55	Outsider	Rheinhessen	Dornfelder	QbA	2003	Outsider-other geographic origin	2
D56	Typical	Pfalz	Dornfelder	QbA	2003	Typical	2
D57	Outsider	Wiirttemberg	Dornfelder	QbA	2003	Outsider-other geographic origin	2
D58	Outsider	Franken	Dornfelder	QbA	2003	Outsider-other geographic origin	2
D59	Outsider	Pfalz	Pinot noir	QbA	2003	Outsider-other grape variety	2
D60	Outsider	Pfalz	Cabernet Sauvignon	QbA	2003	Outsider-other grape variety	2

[a] Year of analysis: 1, 2003; 2, 2004.

could be reallocated within the various groups. For each sample, the distance from the various centres of gravity of group was calculated. The sample was assigned to the group where the distance between the centre of gravity was the shortest. Comparison of the assigned group to the real group was an indicator of the quality of the discrimination.

PCA and FDA were performed using XLSTAT-Pro® add-in for Microsoft Excel®.

3. Results and discussion

3.1. Fluorescence spectra of wines

Fluorescence spectroscopy offers several inherent advantages for the characterisations of molecular interactions and reactions. First, it is 100–1000 times more sensitive than other spectrophotometric techniques. Second, fluorescent compounds are extremely sensitive to their environment. For example, tryptophan residues that are buried in the hydrophobic interior of a protein have different fluorescent properties than residues that are on a hydrophilic surface [9]. This environmental sensitivity enables to characterise conformational changes, such as those attributable to the thermal, solvent or surface denaturation of proteins, as well as the interactions of proteins with other food components. Third, most fluorescence methods are relatively rapid.

If absorbance is less than 0.1, the intensity of the emitted light is proportional to fluorophore concentration and excitation and emission spectra are accurately recorded by classical right-angle fluorescence device. When the absorbance of the sample exceeds 0.1, emission and excitation spectra are both decreased and excitation spectra are distorsed. To avoid these problems, a dilution of samples is currently performed so that their total absorbance would be less than 0.1. However, the results obtained on diluted solutions of food samples can not be extrapolated to native concentrated samples since the organisation of the food matrix is lost. To avoid these problems, the method of front-face fluorescence spectroscopy can be used [11].

The fluorescence spectra give information regarding molecules containing conjugated double bounds. Phenolic acids, stilbenes, anthocyanins, flavanols and tannins are the best known fluorescent molecules in wines (Fig. 1). The types and amounts of these molecules vary as a function of the variety and of the maturity of grapes. Wine processing and ageing also have effects on the phenolic compounds. However, wines contain many other compounds (e.g., proteins) that may fluoresce. So a spectrum recorded on a wine sample following, for example, excitation at 261 nm included information on several fluorophores and may be considered as a characteristic fingerprint which may allow the sample to be identified.

The emission spectra of wines made up with Gamay and Dornfelder varieties recorded following excitation at 261 nm are shown in Fig. 2. The emission spectra were characterised by a maximum at 376 nm and a shoulder at 315 nm. In addition, the shape of the spectra changed with wine samples, varying mainly in the maximum/shoulder intensity ratios. Indeed, the spectra of Gamay and Dornfelder wine samples exhibiting the highest instensity at 376 nm also showed the lowest intensity at 315 nm. Considering the excitation spectra of Gamay and Dornfelder recorded for emission at 376 nm, wines made from Dornfelder variety showed larger differences than the wines made from Gamay variety (Fig. 3). The spectra of Beaujolais wines are characterised by a maximum at 260 nm and a shoulder at about 320 nm. In addition, the shape of the spectra changed with wine samples, varying mainly in the maximum/shoulder intensity ratios. Despite the two peaks at about 260 and 320 nm were again observed, the Dornfelder fluorescence spectra reported in Fig. 3b shows larger differences than Gamay ones. As D24 sample spectrum exhibited a broad maximum located at 270 nm and a shoulder at 320 nm, D10 sample spectrum is characterised by a maximum at 315 nm and two shoulders at 330 and 280 nm. The three spectra represented Fig. 3b shows the largest differences observed in the collection and corresponded to three

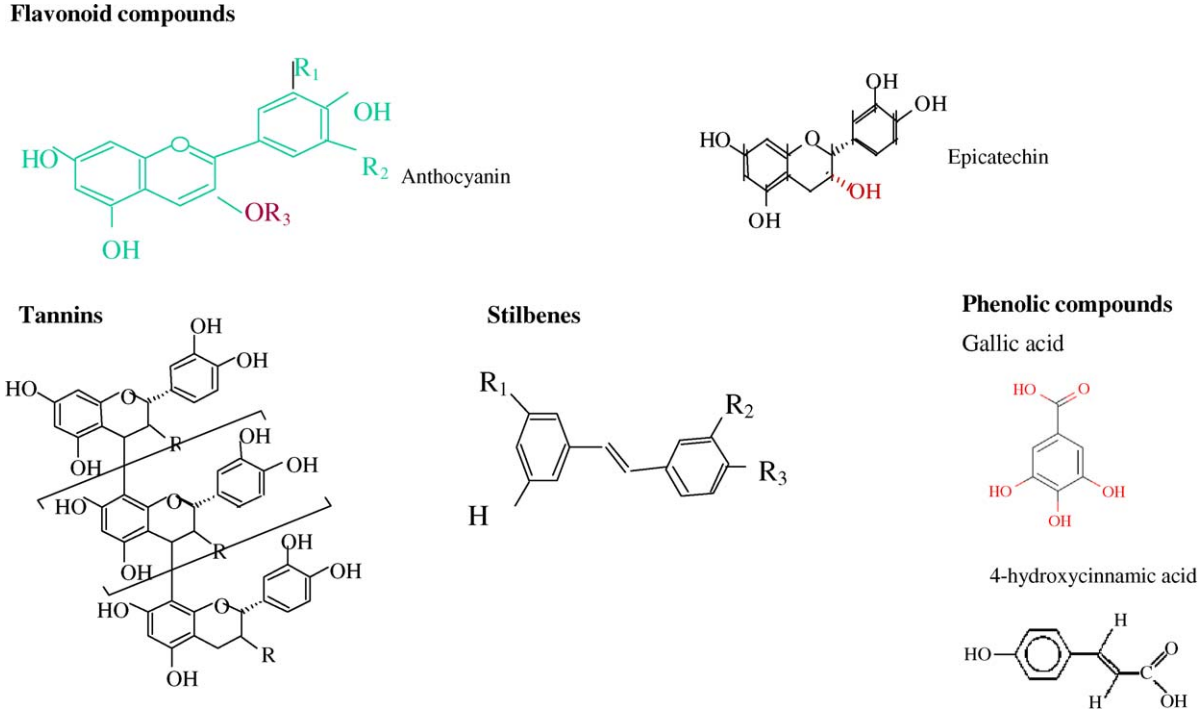

Fig. 1. Potential intrinsic fluorescent probes in wine.

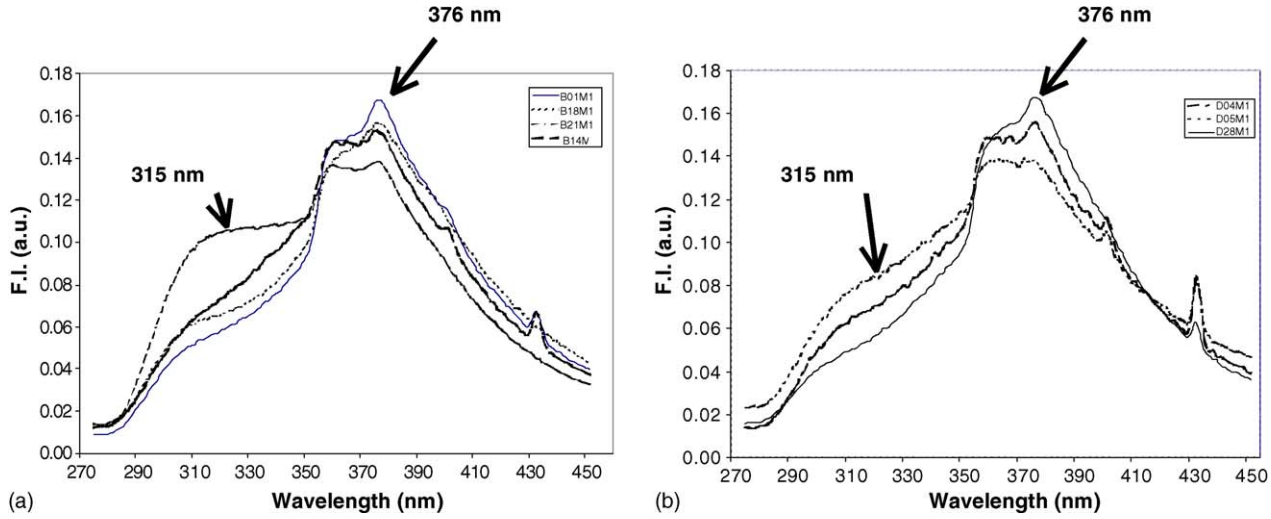

Fig. 2. Emission fluorescence spectra recorded on wine samples from the French (a) and the German (b) collections.

typical Domfelder wines produced in the same region (Pfalz) by wine estate (D10) and wineries (D21, D24). It is concluded that the large differences observed for the spectra originate from the wine manufacturing process. The crossing of the spectra at 295 nm in Fig. 3b could suggest an isobestic point that may come from ionisation of carboxylic groups of phenolic compounds. However, the pH values for D10 (3.88), D21 (3.36) and D24 (3.38) samples did not agree with this hypothesis.

3.2. Multivariate analysis of wine fluorescence spectra

A number of 360 emission spectra was collected for German and French wines. The same figure applied for excitation spectra.

PCA was applied separately on the two collections of 360 normalised spectra. The maps defined by PC1 and PC2 for the PCAs performed on emission and excitation fluorescence data are shown in Fig. 4a and b, respectively. The first two principal components took into account 86.6% (emission data) and 90.3% (excitation data) of the total variance. For the fluorescence excitation data collection, a discrimination of the French and German wine samples was observed. Surprisingly, the fluorescence excitation spectra recorded on wine samples of year 1 superimposed to the ones recorded on wine samples of year 2. This result is surprising since the sensory analysis allowed to discriminate French and German wines analysed year 1 from the ones analysed year 2 [18]. Considering sensory attributes, colour was discriminating the samples according to the year of analysis. The differences between fluorescence and colour results are probably related to the methods, i.e., in the visible range for colour measurements and in the ultraviolet region for fluorescence in this study. Although additional measurements are needed, the results indicate that the excitation spectra may allow to differentiate Gamay wines from Dornfelder wines, whatever the vintage.

A different trend was observed with emission spectra. The PCA similarity map (Fig. 4a) did not show a clear discrimination of German and French wines. But a discrimination of wines analysed year 1 from the ones analysed year 2 was observed for the sole French wines. It is concluded that emission and excitation fluorescence spectra retain complementary and useful

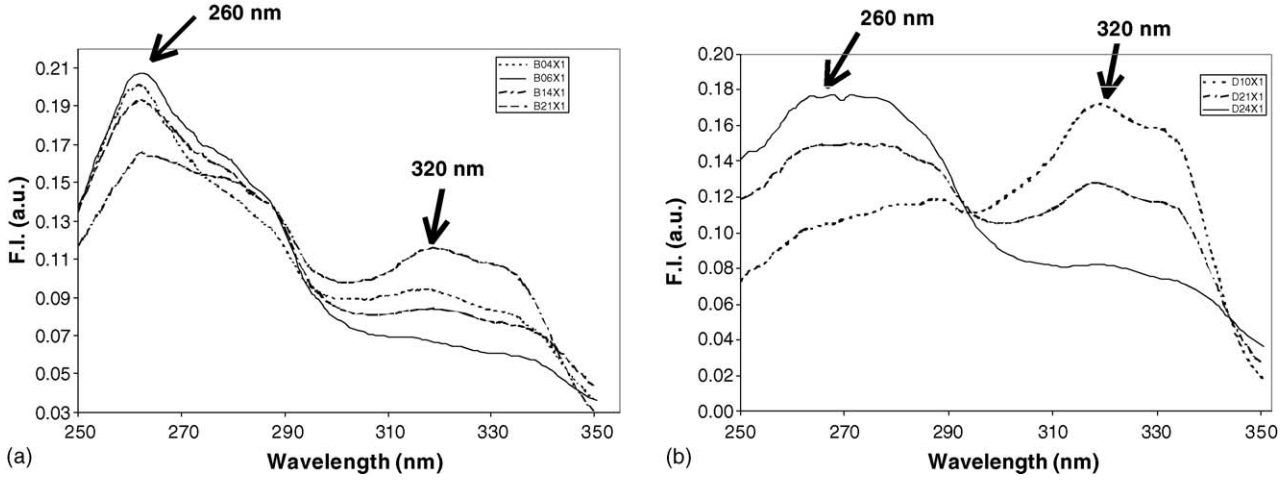

Fig. 3. Excitation fluorescence spectra recorded on wine samples from the French (a) and the German (b) collections.

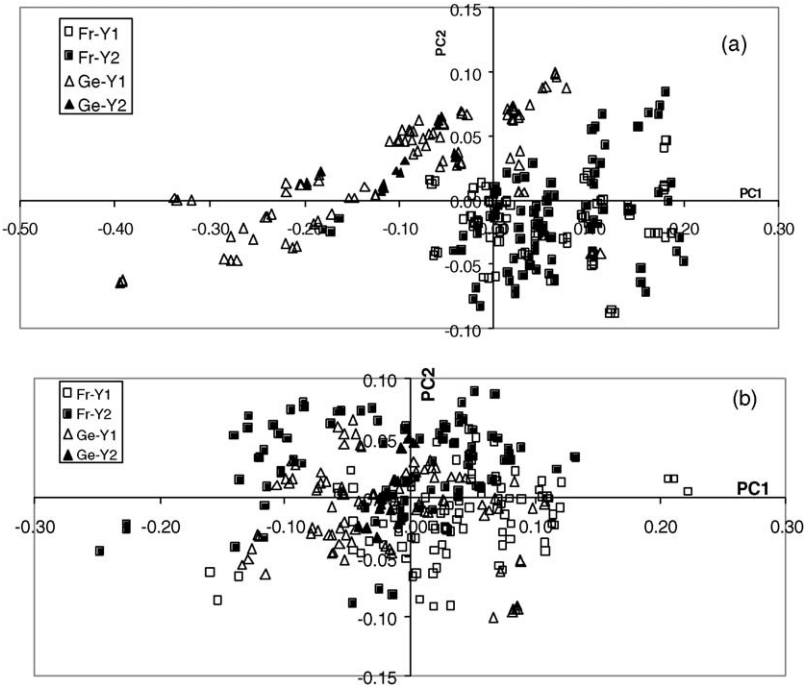

Fig. 4. PCA similarity map determined by principal components 1 and 2 for excitation (a) and emission (b) fluorescence spectra of German (year 1 (△); year 2 (▲)) and French (year 1 (□); year 2 (■)) wines.

information allowing the discrimination of the wine collection. The fluorescence spectrum recorded directly on a wine sample can be considered as a fingerprint.

In a second step, the ability of emission and excitation spectra to differentiate between Gamay and Dornfelder wines was investigated by applying FDA to the principal components of the PCA performed on the excitation fluorescence data or emission fluorescence data. Two groups were created for the investigated wines, i.e., Gamay wines and Domfelder wines. Correct classification amounting to 93.2% and 100% was observed for the emission fluorescence data set and the excitation fluorescence data set, respectively.

The ability of the emission and excitation fluorescence spectra to discriminate between typical and outsider samples was investigated on the subsets formed by Beaujolais data recorded during year 1. PCA was applied separately on the two collections of 90 normalised spectra. The maps defined by PC1–PC2 and PC2–PC3 for the PCAs performed on excitation and emission fluorescence data are shown in Fig. 5a and b, respectively. The plotted principal components took into account 23.0% (emission data) and 96.2% (excitation data) of the total variance. Considering excitation spectra, any discrimination between typical and outsider samples was observed by PCA. The trend appeared different for PCA performed on emission spectra, i.e., the similarity map defined by PC2 and PC3 grossly showing two clusters (typical and outsider). In a second step, the ability of emission and excitation spectra to differentiate between typical and non-typical Beaujolais wines was investigated by applying FDA to

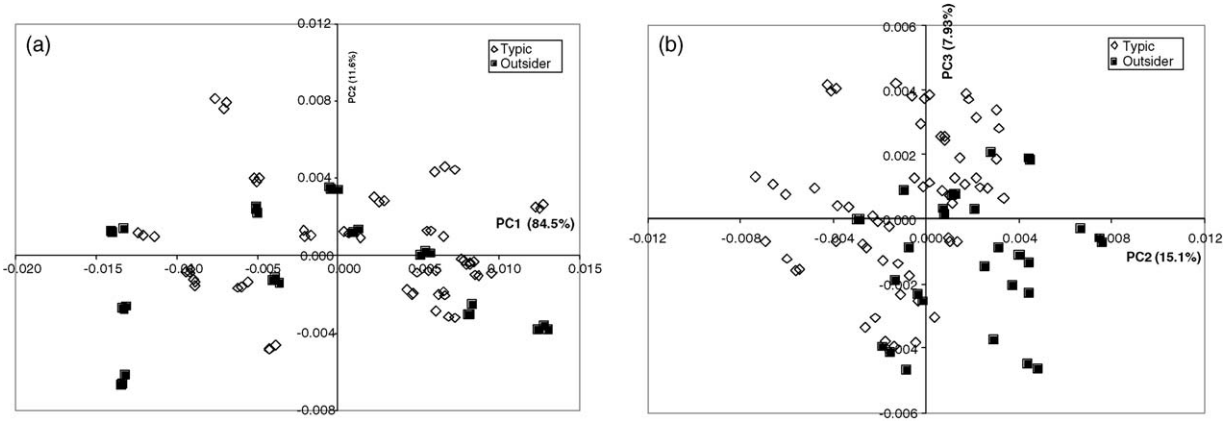

Fig. 5. PCA similarity map determined (a) by principal components 1 and 2 for excitation fluorescence spectra of Beaujolais wines (typic (△); outsider (■)) and (b) by principal components 2 and 3 for emission fluorescence spectra of Beaujolais wines (typic (△); outsider (■)).

the principal components of the PCA performed on the excitation fluorescence data or emission fluorescence data. Two groups were created for the investigated wines, i.e., typical wines and outsider wines. Correct classification amounting to 95% and 87% was observed for the emission fluorescence data set and the excitation fluorescence data set, respectively. FDA results confirm the results shown in Fig. 5: emission spectra allow a better discrimination between typical and non-typical Beaujolais than excitation spectral data.

4. Conclusion

Rapid fluorescence measurements applied directly on wines have been used for monitoring the variety, the typicality and the vintage of a collection of French and German wines. This preliminary study shows that front-face fluorescence spectroscopy combined with chemometrics offers a promising approach for the authentication of wines. The technique is non-destructive, rapid, easy to use and not expensive. It neither needs any particular sample preparation nor special qualification of the personnel. However, these preliminary findings should be confirmed with a larger set of samples and additional wine types. As this wine collection has also been analysed by classical methods, a joint analysis of the fluorescence, sensory and phenolic compounds data sets should allow to investigate the correlations between the different data sets.

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