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Application of FT-IR spectroscopy to the characterisation and classification of wines, brandies and other distilled drinks

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Abstract

FT-IR spectra were employed for the differentiation and classification of wines and brandies during their ageing process, as well as for the characterisation and differentiation of distilled drinks from several producing countries. The FT-IR spectra have enabled the differentiation of the six scales of ageing of sherry wine. A good linear regression fit (regression coefficient = 0.995) has been obtained between ageing scale and the data of the FT-IR spectrum. In the case of Brandy of Jerez, it has been possible to differentiate the three degrees of ageing and to devise a system of classification by means of linear discriminant analysis, with a reliability of 83%. The application of the regression by partial least squares has allowed us to obtain a regression between the degree of ageing and the data of the FT-IR spectrum (correlation coefficient = 0.986). Lastly, Spanish, French and South African brandies, as well as cognacs and armagnacs have been characterised, and a complete differentiation of the latter two types from the rest of the samples of distilled drinks has been obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: FT-IR spectroscopy; Wine; Spirits; Differentiation

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1. Introduction

The application of spectroscopic techniques in the study of the origin and differentiation of food and drink products has developed considerably in recent years. The advantage of these techniques lies in the almost complete lack of sample preparation required, which makes them especially rapid to apply.

In order to develop methods of classification and differentiation, the spectra are treated with chemometric techniques that permit their characterisation, and subsequently the construction of models. Recently a review has been made of the application of this methodology to foodstuffs [1]. Using this methodology, it has been possible the determination of the authenticity and origin of wines of Slovenia by IRMS and SNIF-NMR, in combination with techniques of principal components analysis (PCA) and linear discriminant analysis (LDA) [2].

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Other non-spectroscopic techniques as the aromatic index [3], solid-phase microextraction-gas chromatography-mass spectrometry of volatile compounds [4] and combination of gas chromatography and high performance liquid chromatography [5] have been also used for wine and spirits classification with good results. For these techniques some kind of sample handling is needed. Even FT-IR has been used for classification of red wine cultivars, however phenolic wine extracts were used to obtain the spectra, therefore a suitable prior extraction method was needed [6].

On the other hand, in recent years, methods have been under development for the determination of compounds of interest in wines by means of the analysis of mid-infrared spectra. Among the compounds analysed is ethanol [7] and others found in considerably lower concentrations, such as sugars and organic acids [8]. FT-IR has also been used coupled to HPLC to determine sugars, alcohols and organic acids [9]. These proven techniques can be employed in the qualitative analysis of wine, since the differences in the composition of wines and distilled drinks of different ages or of different geographical origins should be reflected in the IR spectra.

This study presents the results of the application of chemometric techniques to the FT-IR spectra obtained from samples of wines, brandies and other distilled drinks. PCA, LDA and partial least squares regression (PLS) have been applied for the determination of the origin of various distilled drinks, and in the characterisation of the ageing of sherry wines and brandies of Jerez (from Spain).

In the case of wines, samples corresponding to the ageing of Fino sherry wine have been studied. This ageing process is carried out in wooden casks with the participation of yeasts and for a period of not less than 3 years. It takes place in a system of scales or 'criaderas' through which the wine is progressively transferred, blended and aged. Because each scale consists of a very large number of casks, the particular content of each one of these may, to a certain degree, be different from other casks of the same scale, producing slight variations in the ageing. These variations tend to be eliminated when the wine progresses to the following scale, since the total volume of wine is homogenized before passing to the next scale. Nevertheless, it is particularly interesting to determine rapidly if any of the casks or scales that comprise the system is ageing at a rate different from that of the rest.

In the case of the Brandy of Jerez, the system of ageing is similar to that described for sherry wine, apart from the yeasts being absent. For both sherry wine and Brandy of Jerez, chemical compounds that present significant variations during the course of the product's passage through the system of scales have previously been determined [10,11].

The final set of samples analysed consists of a variety of spirit drinks produced from the distillation of wines. The differences in the original wines and in the systems of distillation and ageing give rise to differences in the final products. In this study, it has been investigated whether these differences are reflected in the FT-IR spectra.

2. Experimental

A WineScan FT-120 instrument was employed to obtain the IR spectra. No prior preparation of the sample was carried out, apart from that which the equipment itself performs i.e. filtration and thermostatisation at 40 °C. Thermostatisation was done to obtain reproducible IR spectra. The only temperature allowed by the instrument is 40 °C.

The system enables the recording of the IR spectrum of a sample between the wavelengths of 926–5012 cm^{-1}, divided into 'pin numbers' (PN) from 240 to 1249. The effect of this is to provide a total of 1009 individual wavenumbers for each sample. However, the zones between 400 and 445 PN and between 770 and 940 are not taken into account in this type of study since they cover the absorbance of water and only constitute a source of noise in the spectrum. The spectra are obtained in duplicate for each sample and the mean of the two measurements is used.

The samples analysed correspond to Fino sherry wine of different degrees of ageing, all obtained from the same single ageing batch of 'criaderas and solera'. The brandies and other distilled drinks comprised samples acquired commercially, apart from the brandies of Jerez, which were supplied by the Regulatory Commission of the Specific Denomination of Brandy de Jerez. Fig. 1 presents the spectra obtained for a Fino sherry wine, for a Gran Reserva Brandy de Jerez, and for a Cognac.

The PCA, LDA and PLS have been applied to the data of FT-IR spectra by means of the data treatment programs Minitab version 10.0 and Unscrambler 7.5.

First and second derivatives of the spectra were also used in the chemometric studies. Worse results were obtained, therefore, all the chemometric studies were done using the original spectra.

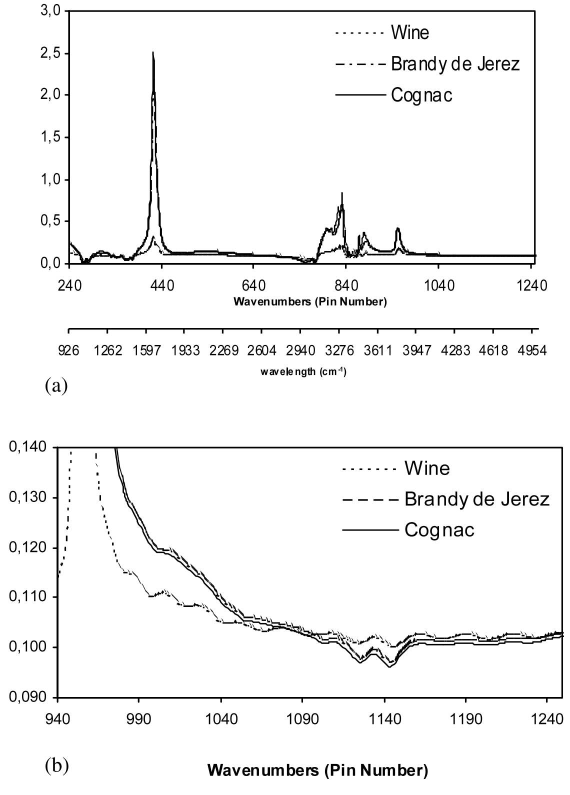

Fig. 1. (a) Full FT-IR spectra of a 'Fino' sherry wine, a 'Gran Reserva Brandy de Jerez' and a Cognac. (b) Magnified zone of the FT-IR spectra.

3. Results and discussion

3.1. Analysis of different degrees of ageing of Fino sherry wines

The set of samples consisted of three samples of each of the six scales or levels of the ageing batch. Each sample was taken from a different cask.

The application of the PCA to these samples, utilizing all the wavenumbers provided, including those corresponding to the absorbance of water, did not produced differentiation between the samples corresponding to the various degrees of ageing. In addition, the PN that contribute most to the first principal component (PC1) are those corresponding to the absorption band of water; this explains the lack of separation between the samples. If the same analysis is performed excluding the PN where the absorption of water is recorded, the distribution presented in Fig. 2a is obtained. In this figure, a clear differentiation is observed between the different scales of ageing. In this case, the percentage of total variance explained by PC1 reaches 90%.

The absorbance in each zone of the spectrum varies markedly; specifically for the quantitative determination of parameters, the zone mainly used is the region between 240 and 770 PN. Particular zones in this interval have been proposed, for example, to quantify ethanol [7].

When the same PCA is performed using only the PN values below 770 as variables, we obtain the distribution shown in Fig. 2b. The differentiation between degrees of ageing is perfect when only these wavenumbers are used, and the groups are seen to be completely differentiated. Obviously, PC1 is related to the ageing process, whereas PC2 recorded another reasons of differences between the samples.

In contrast, if the analysis is performed with the PN values above 940, the classification obtained is considerably less clear. The groupings correspond generally to the degree of ageing but in a less well-defined way compared with the analysis using PN of less than 770.

Utilising the PN values below 770, a PLS regression was performed in order to correlate the age of the wine in the ageing batch sampled and

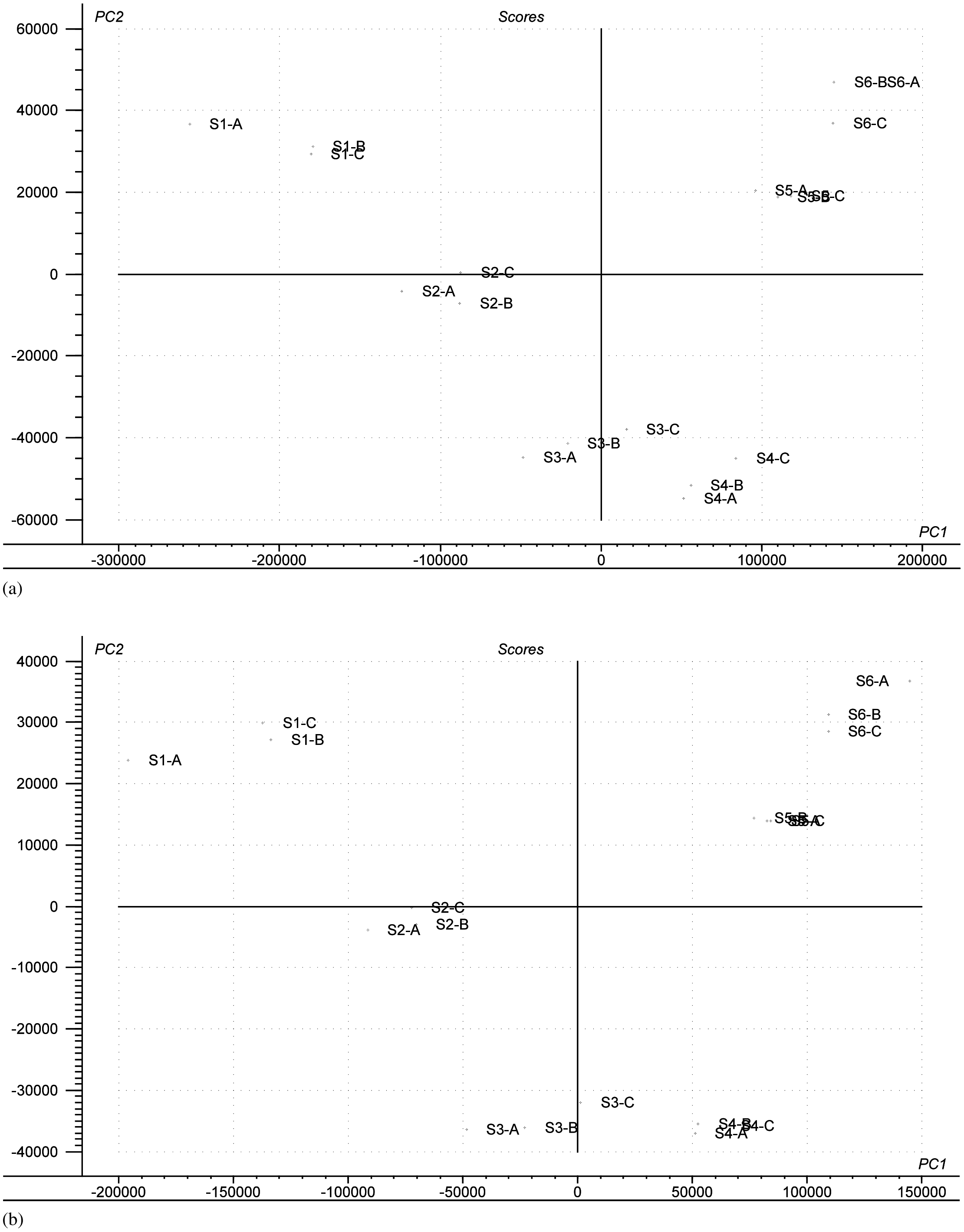

Fig. 2. (a) Distribution in the factorial space (PC1, PC2) for ‘Fino’ sherry wines obtained using the PN 240–400, 445–770, 940–1249. (b) Distribution in the factorial space (PC1, PC2) for ‘Fino’ sherry wines obtained using the PN 240–400, 445–770.

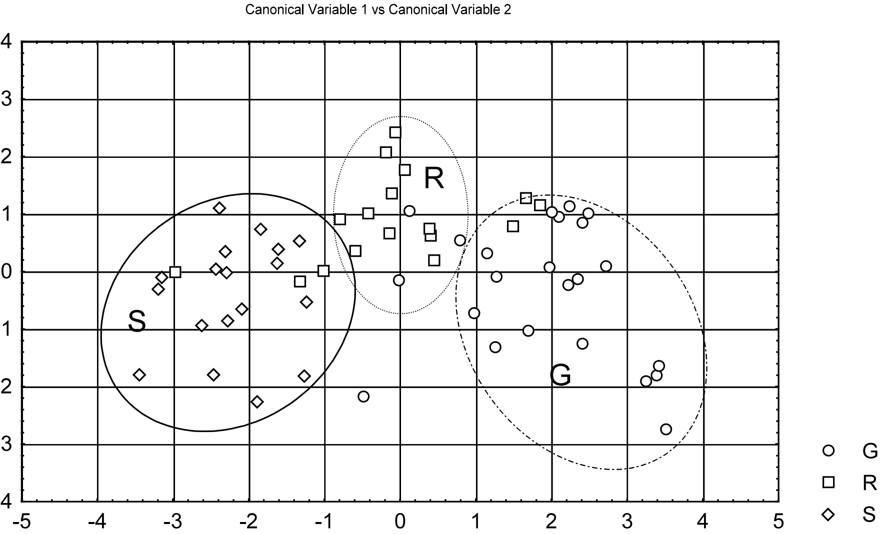

Fig. 3. Distribution in the canonical space derived from the LDA for 'Brandies de Jerez' obtained using the PN 240–400, 445–770, 940–1249.

the FT-IR spectra of the samples. Four factors were used. The resulting coefficient of correlation was 0.995.

From these results, it can be concluded that the use of the IR technique to measure the spectra between PN of 240 and 770 provides sufficient information to differentiate the degrees of ageing of Fino sherry wine. However, if PN values above 940 are employed, the differentiation is not sufficient to separate the successive degrees of ageing.

3.2. Application to the ageing of brandies of Jerez

The samples of these brandies of Jerez correspond to the three categories of ageing recognised officially for aged brandies by the D.E. Brandy of Jerez: Brandy Solera (S) with a minimum of 6 months of ageing, Brandy Solera Reserva (R) with more than 1 year of ageing, and Brandy Solera Gran Reserva (G) with more than 3 years of ageing. In all cases, the samples corresponded to commercially available brandies. The numbers of samples analysed were 23 samples of category S, 14 of category R, and 22 of category G.

The PCA obtained with the participation of the full range of PN showed three large groupings. The first one is formed by most of the samples corresponding to category G, while the other two groups are formed by the samples of categories R and S. But none of the groups provide a clear differentiation between the samples.

Consequently, and with the aim of determining the wavenumbers that are most significant for the evolution of the ageing process in brandy of Jerez, a LDA of the data was performed. A leave-one-out technique was used to obtain the theoretical classification of the samples based on the canonical variables. The presence of two large groups can be observed (Fig. 3), corresponding to the brandies of category G and of category S, respectively. In other words, the least and the most aged are separated into their respective groups. However, most of brandies of category R, with an intermediate degree of ageing, are situated between these two groups.

The most influential range of wavenumbers in this case is found in the zone of PN below 770, as is found for the ageing of sherry wine. Therefore, to characterise brandies of Jerez by their length of ageing, it is necessary to record the FT-IR spectra in this zone. When these measurements are made, the degree of ageing of the sample can be determined with a probability of correct classification of 83%. On this point, it should be emphasised that this percentage is similar to that recorded in a previous study. In that study, a series of analytical parameters including phenolic compounds (14 in total) and short-chain organic acids (6 in total) were used [10,11]. This spectroscopic technique, therefore provides a similar degree of reliability to that obtained employing as variables the results of the chromatographic analysis of the polyphenols and organic acid of brandies.

Lastly, a PLS regression was performed on the samples employing the age expressed as months kept in barrel as the objective variable. The result of the PLS regression was a coefficient of correlation of 0.986, taking the full range of PN available. Twelve factors were needed to reach this coefficient of correlation. It should be noted here that, according to the regulations of the Regulatory Commission of the Specific Denomination, the months of ageing of each category of brandy correspond to the minimum period for which it must be kept in barrel, but in certain wineries, the periods of ageing applied to particular products are substantially longer than the minimum stipulated. This may explain why 12 factors were needed to get 0.986 as correlation coefficient.

3.3. Application to distilled drinks

The application of the technique to other spirit-based drinks was performed for a series of drinks produced from aged distillates. In this case, the samples were obtained commercially, and corresponded to 12 Spanish brandies from different regions (E), 4 French brandies (F), 9 cognacs (C), 4 armagnacs (A) and 4 South African brandies (S). This particular part of the study is directly relevant to the other main field of application of qualitative analytical methods in enology, the characterisation of the origin of specific products. It must be said in this case that the full set of samples included products both of different geographical origins and of different characteristics. Some of the samples, such as the cognacs and armagnacs, belong to the same denomination of origin, while for others, the common characteristic is the country of origin—Spain, France or South Africa. Specifically within the subset of 11 samples originating from Spain, a total of 6 production zones are represented. The effect of this is that a complete classification of the samples analysed cannot be expected.

As in the preceding case, the first analysis was conducted using together the full set of spectral information available after eliminating the absorption zone of water. There was no clear differentiated except in the case of the group formed by the armagnacs and cognacs.

If the same analysis is performed utilising the wavelength region below 770 PN, it can be seen that the classification obtained is very similar to the preceding one.

However, when the PCA is performed utilising the wavenumbers of more than 940 PN, the result is clearly different (Fig. 4). The samples corresponding to the cognacs can be observed clearly differentiated from the rest of the samples. The same occurs with the armagnacs, although in this case there are three Spanish brandies those present great similarities with this group of samples. The remaining samples present groupings closely related to their origins, although the different production zones within the same country produce groupings of small numbers of cases, in comparison with those obtained for the cognacs and armagnacs.

Overall, it can be concluded that, in the case of drinks produced from distillates, the application of the technique with wavelengths above 940 PN enables the characterisation of the group of samples analysed in function of their origin, permitting the clear differentiation of samples corresponding to specific denominations of origin.

4. Conclusions

Given the speed and simplicity of analysis, and the differentiation results it provides, FT-IR can be considered an interesting technique for the characterisation of both wines and brandies, and consequently for application in the quality control of the production of these products.

Ethanol and sugars have a high response in the IR spectra. So, samples with different concentrations of ethanol and sugars will have different

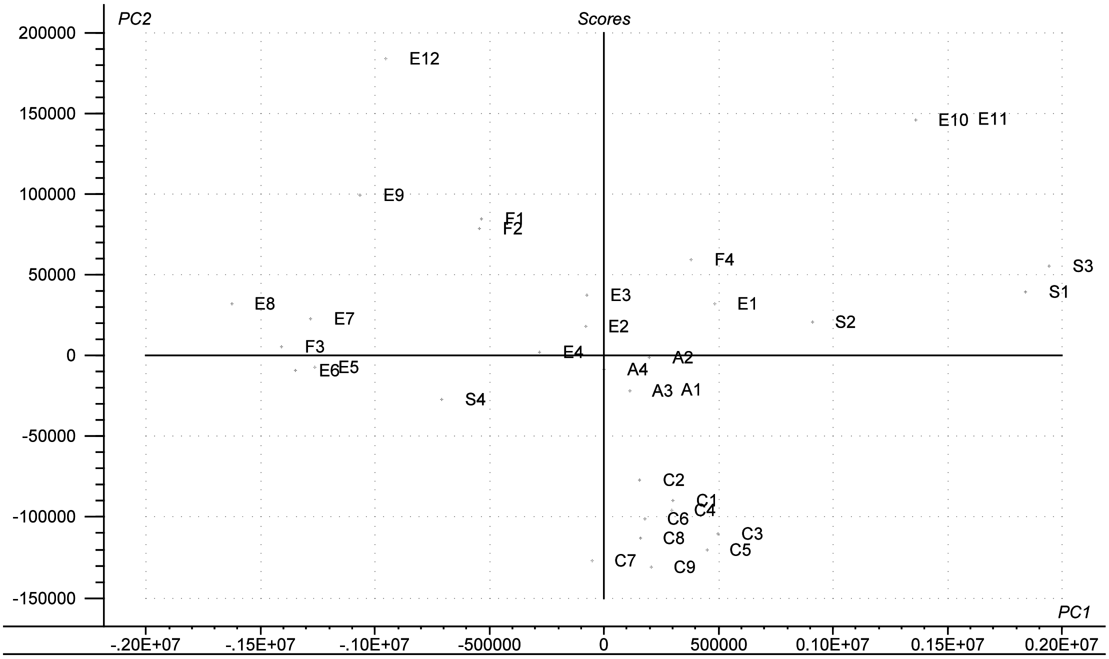

Fig. 4. Distribution in the factorial space (PC1, PC2) for spirits obtained using the PN 940–1249.

spectral zones to be used as fingerprints in characterisation studies. As it occurs in the results presented in this work.

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