

FT-NIR Spectrometry Approach for Determining Saffron Origin

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Abstract

Fourier transform near infrared spectroscopy analysis (FT-NIR) of saffron is used for first time in saffron. Its principal advantage is speed analysis, and it does not require sample treatment either. Using Principal Component Analysis (PCA), saffron samples from Spain, Iran and China were clearly differentiated. Other parts of the flower, as the styles, were also analysed being possible its differentiation among the saffron stigmas. The sensitivity for each sample in its own family group, and its specificity, was in both cases 100%.

INTRODUCTION

The technological processes used in the food industry have made very important progress in recent years. This fact combined with the increase in interest by quality on the part of consumers, the ability of laboratories of control, and the regulatory arrangements to which the marketed products have to be adjusted have contributed to the sensibilization toward the control of raw materials, process and finished products. In relation to saffron, one must consider in a special way the composition characteristics and its quality that it is regulated by the ISO 3632 (1993) normative. Parameters such as microscopic analysis, presence of flower residues, humidity, and ash are measured. But most importantly its bitterness, aroma (safranal) and colouring strength, all of which are measured by UV-Vis spectrophotometry at 257, 330 and 440 nm, respectively. Other techniques such as thin-layer chromatography (TLC) or high performance liquid chromatography (HPLC) have been also used to study saffron adulterations.

Infrared spectroscopic technique such as near-infrared (NIR) has been used for exploring the authenticity of many foods. Past applications include establishing the authenticity of foods such as vegetable oils (Lai et al., 1994), olive oil (Bertrand et al., 1999), coffee (Downey et al., 1997), honey (Qui et al., 1999), cheese (Chen and Irudayaraj, 1998), but no references have been found for saffron, although it is very simple, cost-effective, rapid and non-destructive technique. It could serve as potential tool for detecting adulteration or for routine analysis if proper calibration and validation procedures with data acquisition protocols are established. Multivariable analysis is often used in spectrometry to extract information from complex spectra containing overlapping absorption peaks, interference effects and instrumental artefacts from the data collected. The most commonly used multivariable calibration methods are partial least square (PLS) and principal component analysis (PCA). Both these methods are based on data compression and inverse calibration, where is possible to calibrate for the desired component while implicitly modelling the other source of variation (Paradkar et al., 2002). Discriminant analysis is another multivariable procedure commonly used for classification of objects into groups of clusters based on a statistical measure. The success of these methods depends upon the choice of spectral range and the number of variables employed in the calibration model.

The aim of this work was to discriminate saffron samples for first time by their origin based only on differences in their spectra recorded with Fourier Transform Near Infrared (FT-NIR) spectroscopy.

MATERIALS AND METHODS

A Perkin Elmer Spectrum One FT-IR equipment (Norwalk, USA) coupled with a Near Infrared Reflectance Accessory (NIRA) was used for the analysis. Data collection was acquired over a wavelength range of 4000-10000 cm^{-1} and the resolution was set at 16 cm^{-1} . This equipment has a tool that actively standardizes lineshape and wavelength position against a built-in traceable methane reference.

Thirty-two saffron samples from Spain, Iran and China together and styles in power form were analysed by simply placed them on the NIRA window without even needing to remove them from their containers. Spectra were collected in duplicate.

The equipment is as well couple to a computer where the Perkin Elmer software called Spectrum Quant+ is installed for multivariable analysis. In this paper, discriminant analysis was used to classify samples based on their origin country as no calibration curves were done for the moment with any other saffron characteristic.

RESULTS AND DISCUSSION

The near-infrared region was traditionally avoided by the spectroscopists due to the difficult interpretation of band overlapping since acute peaks do not appear in this region of the spectrum and also that it is very difficult to assigned the bands to the different functional groups proved to be due to the numerous overtones and combination bands as it can be seen in Figure 1 for a saffron NIR fingerprint spectra. Thanks to the great advances in data processing technology and computer programming it is possible to carried out some treatment of the spectral information obtained by the instrument. In this case, the spectral data obtained was treated with a principal component analysis using the software Quant+ resulting in Figure 2. It can be observed that styles are clearly differentiated from saffron samples and therefore adulteration with this part of the plant can be positively detected. Within different saffron origin countries it can be seen that are easily distinguish. The PCA graph (Figure 2) shows as well that there is no family overlapping or outliers. The sensitivity for each sample in its own family group, and its specificity, was in both cases 100%. The results were very interesting as no calibration curve was done, being as well the first time that saffron has been analysed with this technique.

In general, NIR spectroscopy and chemometrics are combined to correlate the spectra data with other analyses. Then, for saffron samples it could be very interesting to explore this possibility with parameters such as colouring strength, crocetin esters, picrocrocin, safranal, colorant additions and many others.

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Figures

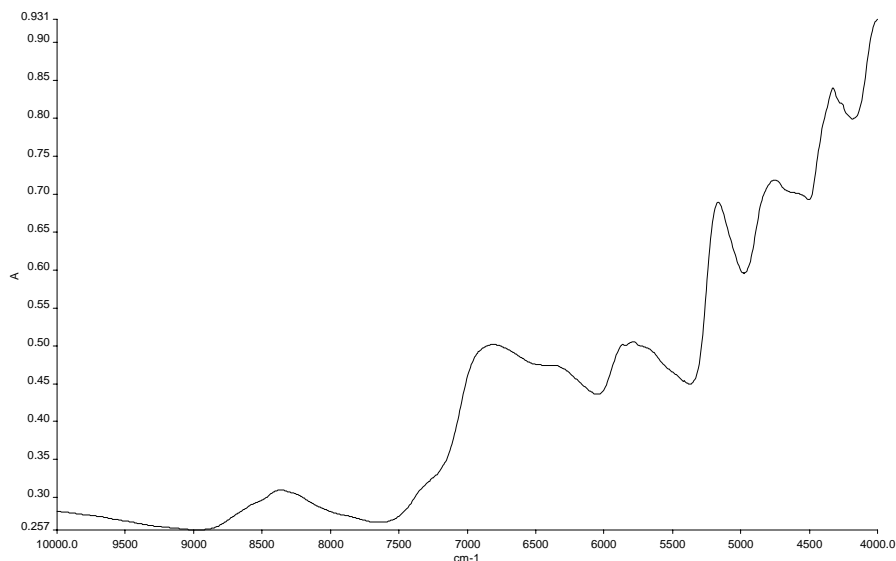


Fig. 1. Saffron NIR spectra fingerprint.

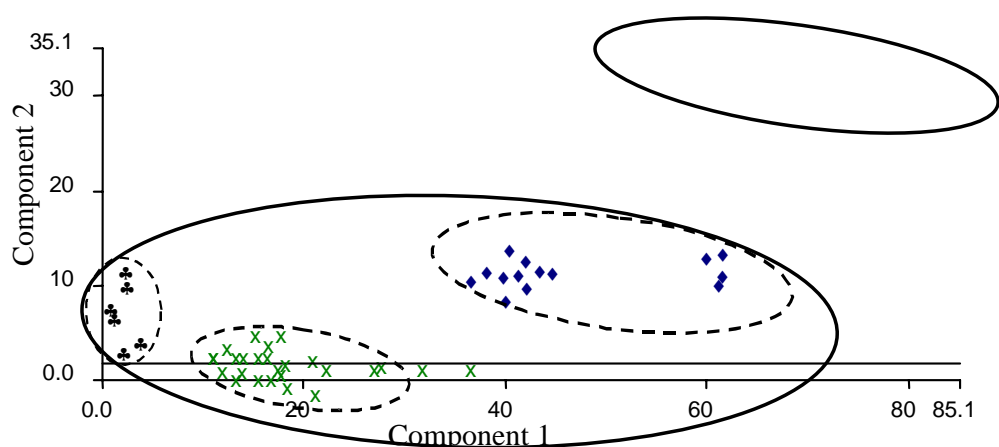


Fig. 2. Principal Component Analysis (PCA) graph for the four analysed families, where “ ” are saffron styles, “•” Chinese saffron, “x ” Iranian saffron and “♦” Spanish saffron samples.