Discrimination of Saffron from different producing countries by Mid- Infrared Spectroscopy

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The objective of the present work was to examine the possibility to discriminate saffron from different countries, especially from Greece, Iran, Italy, and Spain using mid-infrared spectroscopy and multivariate analysis.

250 saffron samples (harvested in 2006), from Greece (40 samples), Iran (87 samples), Italy (60 samples) and Spain (63 samples) were extracted by diethylether using ultrasound assisted extraction in an ultrasound water bath at the fixed frequency of 35 kHz.

The FT-IR spectra of extracts were collected using ZnSe window. 20 μL of the extract were placed twice on ZnSe window. The solvent was air-dried and a thin layer of the sample was formed. The spectra were collected against the pure ZnSe window background. Spectra were collected and manipulated using the OMNIC (ver. 7.3) software supplied from the manufacturer of the spectrometer.

The spectra were truncated to 1869 data points. Factor analysis using principal component analysis and discriminant analysis of the spectra and their second derivatives were analyzed by SPSS ver. 14.0.

Factorial principal component analysis was applied to different spectral regions of the spectra and their second derivative, as well. Then the PC with eigenvalue- one criterion were used for discriminant analysis. The best discriminatory approach was achieved in the spectral region 2000- 700 cm^{-1} using the second derivatives of the spectra where 93.6% of original grouped cases were correctly classified. The correct classification rates for saffron sample from Greece, Iran, Italy, and Spain were 90.0%, 89.5%, 96.7% and 98.4%, respectively.

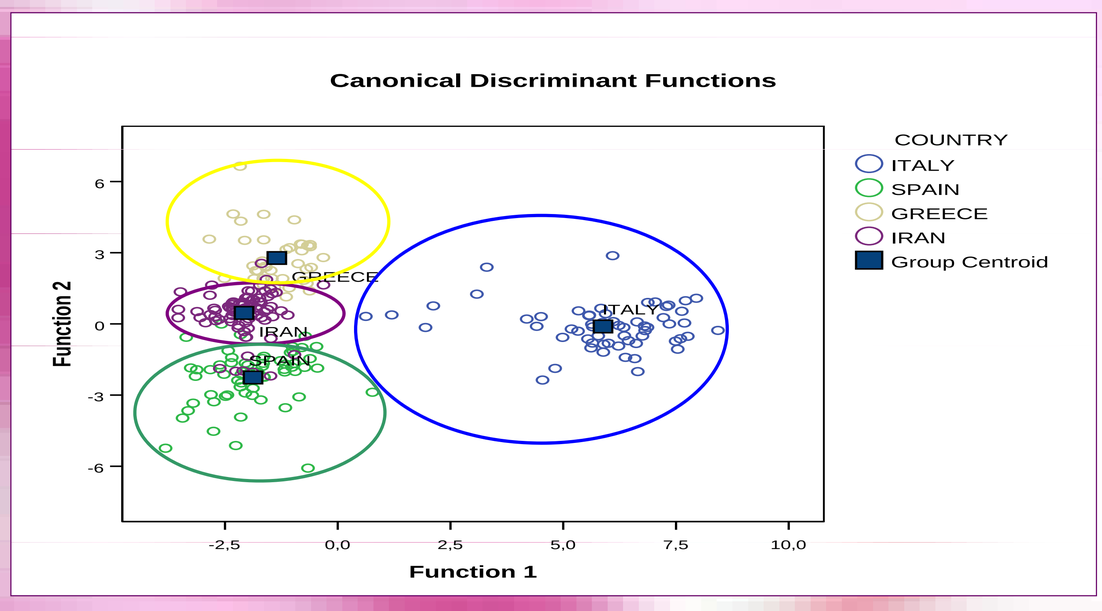

***Table**. The main peaks of the FT-IR spectra of aromatic extracts and their assignments*

Wavenumbers (cm-1)	Assignments
~3400	-OH
3010	stretching vibration of -C-H
2920	out-of-phase $-CH_2-$ stretching
2851	in-phase $-CH_3$ stretching
1736 (Greek, Spanish, Iranian samples)	-C=O
1746 (Italian samples)	ester carbonyl functional group of triglycerides
1670	carbonyl functional group of safranal
1461	$-CH_2-$ and $-CH_3$ deformation.
~1372	-OH bending vibration, -C-O-H in-plane bending vibration, $-CH_3$ in-plane bending vibration,
1263	-OH in-plane bending
1166	stretching vibration of the -C-O ester
1098-1021	skeletal vibration of C-OH and C-O-C of pyranosyl ring of sugars

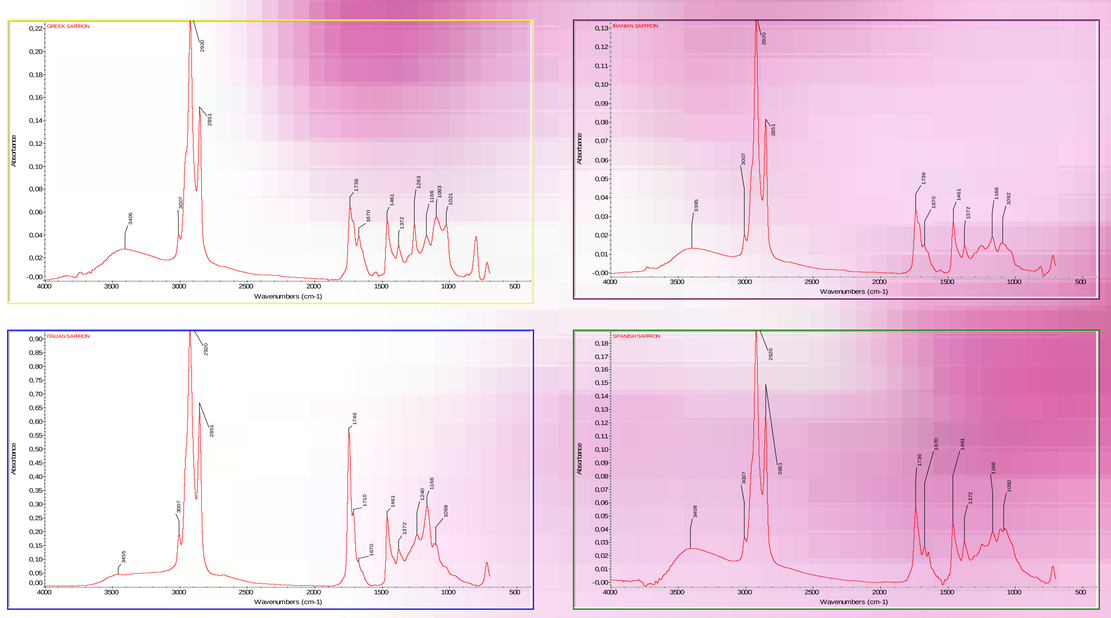

***Figure.** FT-IR spectra of saffron aromatic extracts from samples originated from Greece, Iran, Italy and Spain.*

Italian samples tend to differentiate better from the samples of the three other countries. This is justified by the fact that Italian samples are coming from Sardinia island, where a process called "feidatura" takes place before drying, during which the stigmata are wetted with extra virgin olive oil [1]. The remaining samples are located closely but in well distinguished areas. This tendency could be explained by the dehydration process that it is used in each country, which affects the profile of their aroma compounds. Many researchers have investigated how the different treatments used during the dehydration process reflect to the volatile content and coloring strength [2-4].

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2. M. Carmona, A. Zalacain and G. L. Alonso. The chemical composition of Saffron: color, taste and aroma. Ed. (Bormarzo, 2006), 1st ed., Chap. 3, p. 59- 62.
3. C. D. Kanakis, D. J. Daferera, P. A. Tarantilis and M. G. Polissiou, J. Agric. Food. Chem. 52, 4515, (2004).
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