The feasibility of near infrared spectroscopy for olive oil quality control

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Introduction

Commission Regulation (EEC) Nº 2568/91,[1] amended by Regulation (EC) Nº 656/95 of 28 of March 1995,[2] defines the characteristics of olive oil and olive-residue oil and the revelant chemical and organoleptic methods of analysis. According to those regulations, virgin olive oils are defined as extra virgin olive oil, virgin olive oil, current virgin olive oil and lamp virgin olive oil. In the main olive oil-producing countries, such us Italy, Greece and Spain, millions of tons of olive oil are analysed every year. However, the huge amount of time, personnel, equipment, reagents etc., needed to analyse olive oil according to the above-mentioned EEC regulations, mean that, in practice, only a few methods are used to classify virgin olive oils. The most common analytical methods used by the olive oil sector are reflected in Table 1. Other methods, such as moisture, total polyphenols content, oxidative stability, etc. are also important for the assessment of the nutritional and technological quality of oils.

Table 1. Chemical and organoleptic characteristics of olive oil as defined by Regulation EEC Nº 2568/91 amended by Regulation EC Nº 656/95.

	Free acidity (%)	Peroxides (meq O_2 kg^{-1})	K_{270}	Panel test score
Extra virgin olive oil	max. 1.0	max. 20	max. 0.20	min. 6.5
Virgin olive oil	max. 2.0	max. 20	max. 0.25	min. 5.5
Current virgin olive oil	max. 3.3	max. 20	max. 0.25	min. 3.5
Lamp virgin olive oil	min. 3.3	min. 20	min. 0.25	max. 3.5
Refined olive oil	max. 0.5	max. 10	max. 1.20	—
Olive oil	max. 1.5	max. 15	max. 1.00	—
Crude husk olive oil	min. 2.0	—	—	—
Refined husk olive oil	max. 0.5	max. 10	max. 2.50	—
Husk olive oil	max. 1.5	max. 15	max. 2.00	—

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Near infrared (NIR) technology has been used for the analysis of different chemical characteristics of vegetable oils.[3–5] With respect to olive oil, most of the work done has been related to authentication problems.[6,7] However, there is no information relating to NIR calibration equations for the prediction of chemical and sensorial parameters of olive oils.

The objective of this current work is to study the feasibility of using NIR spectroscopy for the prediction of: free acidity (*FA*), peroxides value (*PV*), extinction coefficients at K_{270}, K_{232}, K_{225}, total polyphenols content (*TPF*), oxidative stability (*OS*), moisture (*H*) and sensorial panel test scores (PTS).

Material and methods

Samples

Two sets of samples were used. Set I was provided by an olive oil co-operative and has 104 samples of virgin oils, representing finished commercial oils produced at the co-operative. Set II was provided by an olive oil research station and has 67 samples of virgin olive oils taken on the way out from the decanter.

Reference analyses

FA, *PV*, K_{270}, K_{232} and PTS were determined according to the EEC regulations.[1,2] *H* was determined by following the norm UNE 55020.[8] TPF was determined by the Folin–Ciocalteu method.[9] K_{225} was calculated by the measurement of the extinction coefficient at 225 nm.[10] *OS* was determined according to the norm UNE 55116 by using the automatic Rancimat method.[11]

Instrumentation and software

A scanning monochromator, NIRSystems model 6500 (NIRSystems Inc., Silver Spring, MD, USA), with spinning module, was used to measure folded transmission spectra from 400 to 2498 nm every 2 nm. The analysis was carried out using a sample cell of 0.1 mm pathlength (Reference IH-0345). Two spectra were recorded for each sample and the average spectrum was used to obtain the calibration equations. All manipulations and processing of the spectra were carried out with the ISI NIRS 3 software v. 3.11 (Infrasoft International, Port Matilda, PA, USA).

Chemometric methods

Modified partial least squares (PLS) was used to obtain regression equations for all the analytical parameters. The PLS method performs a principal component analysis (PCA) decomposition in such a way that the reference data is used for an optimal decomposition of the NIR data and it then performs the regression equations. The modified partial least squares (MPLS) method standardises residual values before calculating the next regression term. All the equations were obtained using a standard normal variate (*SNV*) and detrending method and different derivative math treatments.

The methodology for the development and validation of NIR calibrations has been recommended by different authors.[12–14] The statistics used to select the best equations were the coefficient of determination (r^2) and the standard error of cross-validation (*SECV*).

Results and discussion

Tables 2 and 3 give the chemical and organoleptic characteristics analysed from the two sets of samples. According to the *FA* values and panel test scores it can be seen that the samples cover a broad range of virgin olive oil types, from extra virgin to lamp virgin oils.

Using both sets of samples, a number of calibration equations were developed and the best equations, in terms of *SECV* and r^2, were selected (Table 4). The high r^2 values (> 0.9) obtained for the pre-

Table 2. Mean, standard deviation and range of analytical values (Set I).

Variable	Mean	*SD*	Range
FA (%)	2.06	1.61	0.43–9.14
PI (meq kg^{-1})	9.31	3.01	4.38–14.82
K_{270}	0.17	0.05	0.10–0.41
K_{232}	1.69	0.15	1.41–2.13
Panel score	4.76	1.48	2.20–7.12

Table 3. Mean, standard deviation and range of analytical values (SET II).

Variable	Mean	*SD*	Range
FA (%)	2.52	2.72	0.14–10.50
PI (meq kg^{-1})	6.74	4.04	3.62–29.50
K_{270}	0.13	0.04	0.10–0.25
K_{232}	1.56	0.13	1.24–1.98
K_{225}	0.13	0.12	0.03–0.51
TPF (ppm)	172.1	176.2	36.0–733.0
OS (h)	69.7	43.5	15.2–211.0
H (%)	0.23	0.10	0.04–0.55

Table 4. NIR calibration statistics for the prediction of chemical and organoleptic characteristics of virgin olive oil.

Variable	Mean	Range	*SD*	*SECV*	r^2
FA (%)	1.98	0.44–7.30	1.56	0.06	0.99
PV (meq kg^{-1})	9.09	4.38–14.82	2.66	1.55	0.66
K_{270}	0.16	0.10–0.36	0.04	0.02	0.78
K_{232}	1.67	1.41–1.99	0.12	0.07	0.64
K_{225}	0.10	0.03–0.30	0.06	0.02	0.93
TPF (ppm)	146.1	36.0–733.0	140.2	43.2	0.90
OS (h)	68.04	15.20–211	40.98	9.10	0.95
H (%)	0.22	0.12–0.43	0.08	0.04	0.76
Panel score	4.88	2.20–7.10	1.46	0.50	0.88

diction of *FA*, K_{225}, *TPF* and *OS* confirmed that NIR has an excellent ability to predict these analytical parameters. The polyphenol values and the oxidative stability are not included as recommended methods by the EEC,[1,2] but they are of great importance for the sensory and nutritional quality and the shelf-life of the olive oils. In addition, the bitter taste of virgin olive oils is correlated to the PFT values.[10]

The precision of the equations for *PV* ($r^2 = 0.66$, *SECV* = 1.55 meq kg^{-1}) and K_{232} ($r^2 = 0.64$, *SECV* = 0.07) is limited by the standard error of the reference method and also by the changes in the oxidative state of the samples from the time that the reference analysis was done to the time when the NIR spectrum was recorded. The low *SECV* values obtained for the prediction of two important analytical parameters, K_{270} and K_{225}, despite the low mean reference values of the calibration samples (0.16 and 0.10) should be highlighted. Those results indicate that the compounds could be responsible for the absorbance at 270 and 225 nm are less influenced, by the storing conditions and manipulation of the samples which take place before the NIR analysis, than the compounds detected by the *PV* and K_{232} methods.

H is also of critical importance at the olive oil processing plant and the equation obtained, ($r^2 = 0.76$; *SECV* = 0.04%) was also accurate.

It is of paramount importance for the olive oil sector to find methods that can asses the sensory properties of the virgin olive oil. At present, sensory evaluation is done by a trained panel. However, that is too costly and there are important intra- and inter-panel variations. The equation obtained for the prediction of the panel test scores accounts for 88% of the existing variation in organoleptic characteristics of the oils.

Conclusions

Many analytical methods can be used to classify virgin olive oils according to the categories defined by the EEC regulations. However, all of them are tedious, need trained personnel, sophisticated equipment and use a large amount of chemicals.

NIR can provide a technically and scientifically attractive method for the quality control of the virgin olive oil marketed in Europe. In less than five minutes NIR could provide a chemical and sensorial evaluation of the oil.

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