



# Determination of the peroxide value in extra virgin olive oils through the application of the stepwise orthogonalisation of predictors to mid-infrared spectra



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## ABSTRACT

The potential of stepwise orthogonalisation of predictors (SELECT) coupled with multivariate calibration methods and pre-processing tools was examined to develop reliable and parsimonious regression models based on Fourier-transform mid-infrared (FT-MIR) spectroscopy for the prediction of peroxide value in extra virgin olive oils. The comprehensive calibration methodology proposed also involved the study of the structure of noise present in data, the preliminary detection of anomalous objects, and the appropriate construction of calibration sets. The improvement achieved through the application of feature selection was particularly remarkable when SELECT-Ordinary Least Squares (OLS) was applied on first-derivative spectra. In this case, a high-quality OLS model was obtained, providing a predictive ability similar to that achieved by full spectrum approaches (after noise removal and signal pre-processing) and with no significant signs of over-fitting (4.9, 5.3 and 5.2% root-mean-square errors of the residuals obtained in calibration, cross-validation and external prediction, respectively), but considerably improved properties in terms of model parsimony and interpretability. In fact, it should be noted that only 12 relevant predictors from a total of 408 original wavenumbers were selected to model peroxide value, which meant a very notable compression rate. The quality of the results obtained encourages the feasibility of implementing a FT-MIR based calibration strategy similar to that proposed in routine analysis for the assessment of other critical quality parameters for olive oil.

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## 1. Introduction

From a quality assurance standpoint, the determination of peroxide value (PV) is one of the most important quality control measurements for olive oil because it is an indicator of the primary oxidation status of the product. This parameter measures the concentration of primary oxidation products, mainly consisting on hydroperoxides that are not stable and decompose producing secondary oxidation products such as ketones and aldehydes that are responsible for off-flavour development (Guillén & Cabo, 1999, 2000). Oxidative processes involving the formation of hydroperoxides can occur during processing or storage through auto-oxidation and photo-oxidation (Choe & Min, 2006; Inarejos-García, Gómez-Rico, Desamparados Salvador, & Fregapane, 2010). The higher the PV the lower olive oil oxidative stability, with the consequent detrimental effect on quality.

However, despite the importance of PV as a quality index, the official method established by the European Union for its determination (Commission Regulation (EEC), 1991) is laborious, time consuming, requires the use of organic solvents and, even more importantly, its accuracy depends strongly on experimental conditions (Van de Voort, Ismail, Sedman, Dubois, & Nicodemo, 1994). The relevance of PV as an olive oil quality parameter justifies the need for reliable, fast and non-destructive techniques, as well as a high degree of automation to facilitate implementation in industrial routine analyses in order to provide near-real-time measurements for assessing olive oil quality and quality changes.

In this context, vibrational spectroscopy has been widely applied in recent decades as an alternative analytical tool suitable for application in the field of food quality. Traditionally, near-infrared spectroscopy (NIR) was more extensively applied than Fourier-transform mid-infrared (FT-MIR) spectroscopy for quality assurance and characterisation purposes. However, FT-MIR has attracted great interest in recent years. This fact is largely related to the recent instrumental and technical developments in MIR spectroscopy together with its potential advantages over NIR for food

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analysis (higher sensitivity, selectivity and high-quality spectral information). FT-MIR spectroscopy, combined with multivariate data analysis, has emerged as a rapid and powerful tool for quantitative and qualitative analysis of foodstuffs (Downey, 1998; Karoui, Downey, & Blecker, 2010; Sun, 2008; Wilson & Tapp, 1999). In terms of olive oil quality assurance the potential of MIR spectroscopy for classification and authentication purposes has been examined, including approaches aimed at classifying oils according to their geographical origin (Gurdeniz, Ozen, & Tokatli, 2010; Hennessy, Downey, & O'Donnell, 2009), and at discriminating oils from different botanical origins and varieties (Lerma-García, Ramis-Ramos, Herrero-Martínez, & Simó-Alfonso, 2010; Sinelli et al., 2010). Moreover, FT-MIRS has been applied to detect and quantify the adulteration of extra virgin olive oil with other edible oils (Maggio, Cerretani, Chiavaro, Kaufman, & Bendini, 2010; Vlachos et al., 2006), and for monitoring oxidative stability (Krichene et al., 2010; Navarra et al., 2011). Likewise, a number of previous studies have reported the feasibility of using FT-IR to monitor various quality parameters in edible oils such as free fatty acidity (Iñón, Garrigues, Garrigues, Molina, & De La Guardia, 2003), fatty acids and triacylglycerols (Dupuy, Galtier, Ollivier, Vanloot, & Artaud, 2010), and the anisidine value (Guillén & Cabo, 2002). Nevertheless, despite the rapid growth of research and reporting on MIR spectroscopy based methods for the characterisation of virgin olive oils, very few studies have focused on the development of calibration models to predict the PV of olive oils (Bendini et al., 2007; Maggio et al., 2009). Furthermore, it has to be noted that even the few studies that have explicitly addressed the modelling of PV of olive oils based on MIR measurements have reported relatively low predictive abilities, mainly due to the limited sensitivity associated with the use of attenuated total reflection (ATR) IR spectroscopy for calibration purposes and to the relatively large error inherent in the reference method, and also because they have not focused specifically on the need to perform suitable data pre-processing prior to calibration.

The actual applicability of MIRS in the assessment of olive oil quality parameters depends crucially on the reliability of the multivariate calibration models constructed, which would be limited not only by the error of the reference technique used to measure the response variable, but also by a number of potential problems associated with MIR signals (interferences, overlapping and signal saturation effects, risk of chance correlations and overfitting, systematic variation unrelated to the response and multicollinearity). Thus, the application of suitable chemometric techniques is obligatory to manage and resolve all these limitations (Gabrielsson & Trygg, 2006; Zeaiter, Roger, & Bellon-Maurel, 2005).

Standard methods for calibration of infrared spectra, such as partial least-squares (PLS) regression, are often applied using the full set of available spectral variables. However, when particular hypotheses are met (e.g. very small random independent error in the spectra), a well-performed variable selection prior to the calibration step can greatly improve the selectivity of a regression model, thus providing more robust, reliable and parsimonious models, and simplifying data analysis and interpretation, in relation to full-spectrum approaches (Forina, Lanteri, Cerrato-Oliveros, & Pizarro-Millán, 2004; Pizarro, González-Sáiz, Esteban-Díez, & Orío, 2011; Xiaobo, Jiewen, Povey, Holmes, & Hanpin, 2010).

All in all, the present study aimed to show the effectiveness of using a comprehensive stepwise calibration methodology to properly tackle and overcome certain major problems normally encountered in multivariate calibration. This study will show how the application of such a calibration strategy enabled the development of an improved and reliable calibration model, based on selected reduced fingerprints of the olive oil samples, in order to

provide near real-time predictions of the PV, which is essential for controlling the degree of oxidation/rancidity of extra virgin olive oils.

The main strength and novelty of the calibration approach proposed resides in integrating, in the same methodology, different data processing steps involving various critical stages that need to be considered in a calibration procedure: (1) an analysis of the structure of the noise present in data; (2) outlier detection and removal; (3) application of the Duplex algorithm to guarantee the representativity of the training and test sets; and (4) the application of SELECT (stepwise orthogonalisation of predictors) method (Forina, Lanteri, Casale, & Cerrato-Oliveros, 2007) to extract from FT-IR extra virgin olive oils a minimum number (maximum parsimony) of significant predictors. A comparison is provided of the results yielded by the constructed PLS models based on a full-spectrum approach (testing different spectral pre-processing methods to optimise model performance) and the optimal models constructed after variable selection.

As an important contribution to this study, it should be noted that the SELECT method was preferred due to the potential advantages it offers in spectroscopic applications. In fact, SELECT, applied for calibration purposes, does not only focus on the selection of variables displaying high correlations with the response but, thanks to its stepwise decorrelation procedure, it also avoids the presence of redundant information in the subset of selected significant predictors (Casale et al., 2012; Pizarro, Esteban-Díez, González-Sáiz, & Forina, 2007). The present study also aimed to show and exploit the benefits that this powerful feature selection technique can offer to improve regression performance.

## 2. Experimental

### 2.1. Extra virgin olive oil samples

The data set used comprised a total of 126 authentic extra virgin olive oils from 15 of the most recognised Spanish Protected Designations of Origin (PDOs), all obtained from the 2008–2009 harvest and supplied by reliable sources, including the Supervisory Councils of the different PDOs, certified mills producing PDO extra virgin olive oils and specialised stores. In accordance with the denomination “extra virgin olive oil”, and as established by the Regulation (EC) no. 1234/2007, the superior category olive oils used in this study were obtained directly from olives and processed solely by mechanical means. Special care was taken to ensure that the samples in the calibration set spanned the whole range of variation of the PV potentially encompassed by high quality protected Spanish extra virgin olive oils.

To minimise oxidation and hydrolysis rate, all the samples were stored at 4 °C in amber glass bottles and dark conditions until the analyses were carried out. Since the quality of olive oil decreases with storage time, thereby giving rise to changes in multiple quality parameters including PV, all analyses were completed within two months after receiving the samples.

### 2.2. Reference analyses

The PV of the oil samples was determined in accordance with the analysis method set out in Commission Regulation (EEC) No 2568/91 of 11 July 1991. Thus, the PV was measured as the quantity of substances in the sample, expressed as milliequivalents of active oxygen per kilogram (mEq O<sub>2</sub>/kg), which oxidise potassium iodide under the testing conditions. The PV range covered by the calibration samples ranged from 3.4 up to 18.2 mEq O<sub>2</sub>/kg.

The precision of the method was evaluated studying repeatability and inter-day precision at two different PV levels (6.7 and

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