

# Optical spectral signatures of liquids by means of fiber optic technology for product and quality parameter identification

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Absorption spectroscopy in the wide 200–1700 nm spectral range is carried out by means of optical fiber instrumentation to achieve a digital mapping of liquids for the prediction of important quality parameters. Extra virgin olive oils from Italy and lubricant oils from turbines with different degrees of degradation were considered as 'case studies'. The spectral data were processed by means of multivariate analysis so as to obtain a correlation to quality parameters. In practice, the wide range absorption spectra were considered as an optical signature of the liquids from which to extract product quality information. The optical signatures of extra virgin olive oils were used to predict the content of the most important fatty acids. The optical signatures of lubricant oils were used to predict the concentration of the most important parameters for indicating the oil's degree of degradation, such as TAN, JOAP anti-wear index, and water content. [DOI: 10.2971/jeos.2009.09005]

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## 1 MOTIVATION

One of the most important issues in many industrial applications is the possibility of measurements performed in real time without any sample withdraw, which is the so-called control online. Absorption spectroscopy carried out in various spectral bands is a valuable diagnostic tool that is frequently used for laboratory testing of different products. The intrinsic characteristics of optical fibers together with the large supply of optical fiber components dedicated specifically to spectroscopy, make it possible the implementation of moderate cost devices for the analysis of the product to be made online.

This work presents a method of analysis for liquids capable of

comparing similar samples in order to predict relevant quality parameters that are usually measured by means of bulky and expensive laboratory equipment. Absorption spectroscopy in the wide 200–1700 nm spectral range is carried out by means of optical fiber instrumentation to demonstrate the feasibility of the online approach. According to the minor differences in the chemical composition, each sample is identified by its absorption spectrum, which is considered a unique spectral fingerprint, as if it were a product signature. Then, the spectral data were processed by means of Partial Least Square (PLS) analysis looking for a correlation with the concentration of the most important quality parameters.

In order to demonstrate the potential of this method, which has an application in many industrial sectors, two types of very different liquids were considered as 'case studies', such as extra virgin olive oils (EVOOs) produced in Italy, and lubricant oils with different degree of degradation coming from big machineries. The wide range absorption spectra of EVOOs allowed to predicting nutritional factors such as the most important fatty acids, while the spectral signature of lubricant oils showed a significant correlation with parameters of wear identification.

A good fitting between predicted and true values was achieved, demonstrating that cheap micro-optic technologies and multivariate data analysis can provide a tool for low-cost product characterization.

## 2 SAMPLES ANALYZED

### 2.1 Extra virgin olive oils

Italian EVOOs bearing labels of certified area of origin are characterized by distinctive taste and exceptional nutritional properties [1, 2]. These peculiarities derive from the kind of olives used and the traditional, low-mechanization production means [3, 4]. New methods and technologies are envisaged for qualifying and certifying these oils, to protect both producers and consumers. A library of 40 oil samples from the 2005–2006 harvesting was considered. They were produced in the Sicilia region, that is the deep South of Italy. These oils have distinctive tastes and nutritional characteristics. Attention was paid to the prediction of fatty acids, especially the fraction of oleic and palmitic acids [5, 6]. Reference data of these fatty acids were available. The reference data were measured by means of a conventional gas-chromatography detector. Oleic acid is the most important monounsaturated fatty acid, and is considered a fundamental nutritional factor, since it decreases the levels of total plasma cholesterol, thus reducing the incidence of coronary heart diseases [7]. Palmitic acid, a saturated acid, is responsible for tissue resistance to insulin, thus inducing obesity and hypertension [8].

### 2.2 Lubricant oils

The lubricant oil is a key element in the proper functioning of industrial machinery such as turbines, compressors, and presses. The condition of the oil becomes irreversibly degraded due to machine operation, and needs to be monitored frequently so as to avoid structural damage to the machinery. Furthermore, lubricant oil status is an indication of the correct machinery operation, since any wrong functioning impairs the chemical-physical properties of the oil [9, 10]. Currently, according to a regularly-programmed operational schedule, oil samples are manually drawn and sent to specialized laboratories, where they are analyzed by conventional analytical instrumentation. In order to minimize manual sampling and to reduce the number of costly laboratory analyses, a rapid online alert by means of low-cost sensors would be advisable. A collection of 27 lubricant oils was considered. These samples came from three different types of turbines: 6 samples were from an aeronautic-type gas turbine (TGAD), 6 sam-

ples were from a steam turbine (TV), and 15 samples were from a gas turbine (TG). They were both mineral-paraffin and polyester-synthetic oils belonging to various brands, such as Mobil, AGIP, Chevron, Shell, and Castrol. The predicted parameters were those indicating oil wear or wrong functioning, such as: the presence of water, which is usually due to defective gaskets, the oil acidity, expressed by the total acid number (TAN), the JOAP anti-wear index, and the presence of phosphorous. All the oils were previously analyzed in the Mecoil laboratory using ASTM standard methods [11] and reference data were available.

## 3 ABSORPTION SPECTROSCOPY

The instrumentation for absorption spectroscopy made use of an optical fiber-compatible source, and of optical fiber spectrometers as detectors. For both liquids, the source was a deuterium-halogen lamp by Micropack Inc., model DH-2000-BAL [12]. EVOOs were analyzed by means of two spectrometers by Ocean Optics Inc., models HR4000 and NIR512, operating in the UV-VIS and NIR ranges, respectively [13]. Lubricant oils were analyzed by means of a single spectrometer by Instrument Systems, model Spectro 320 [14]. The liquid sample under test was contained inside a 10 mm-pathlength quartz cuvette [15]. Two standard multimode optical fiber strands, with a 200  $\mu\text{m}$  core diameter, were used for connecting both source and detector to the cuvette holder, which was equipped with collimating and focussing optics so as to perform transmission measurements efficiently. An empty cuvette was used as reference for absorbance evaluation. The dynamic range of this experimental set-up was 0÷6 absorbance units.

Figures 1 and 2 show the measured absorption spectra of the entire collection of EVOOs and lubricant oils, respectively, in the UV-VIS and NIR ranges.

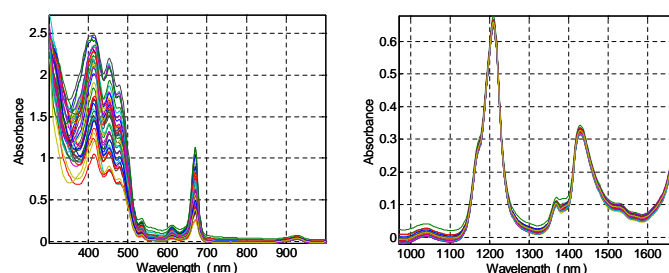


FIG. 1 Absorption spectra of the entire collection of extra virgin olive oils in the UV-VIS (left) and NIR (right) spectral bands.

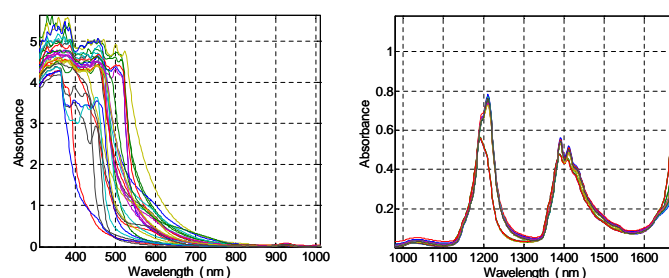


FIG. 2 Absorption spectra of the entire collection of lubricant oils in the UV-VIS (left) and NIR (right) spectral bands.

Analysis	Parameter	Central wavelength (nm)	R <sup>2</sup>	SECV
EVOO	Oleic acid	500	0.826	3.4%
	Palmitic acid	1150	0.930	2.3%
Lubricant oil	Phosphorus	1250	0.991	230 ppm
	JOAP index	1170	0.999	2.4
	TAN	840	0.830	0.18 mg KOH /g
	Water	1140	0.876	68 ppm

TABLE 1 Results of spectral data processing, reporting the central wavelength of the 500 nm width optimal spectral window, together with R<sup>2</sup> and the SECV for all analyzed liquids.

## 4 DATA PROCESSING

In both cases the source data for the analysis were the absorption spectra, arranged as rows of a data matrix, in which each row represented a different sample and each column a different wavelength. The original data were firstly integrated with a boxcar integration algorithm, achieving both data compression and spectra noise reduction. The spectral resolution of the integrated data was 5.1 nm for EVOO spectra and 4.2 nm for lubricant oil spectra. A further spectra smoothing was made using a 5-point mobile average.

For each quality parameter to be fitted, an optimal spectral band was selected using the Moving Window Partial Least Square Regression (MWPLSR) [16]. A spectral window of preset width was "moved" along the working spectral band, making at each position a cross-validated PLS regression [17]. Then an optimal position was chosen according to the goodness of fit, which was evaluated looking at the determination coefficient (R<sup>2</sup>) and the Standard Error of Cross Validation (SECV).

The determination coefficient, R<sup>2</sup>, is the ratio between the variance of the predicted values and the variance of the true values (which is always higher). It ranges between 0 and 1, and the fit is as better as the R<sup>2</sup> is closer to 1. This is evaluated using all samples for model calibration.

The Standard Error of Cross-Validation, SECV, is the root mean square error between the true and the predicted values in a Cross-Validation run. The Cross-Validation is a procedure in which the samples are divided into  $N$  subsets. The values of the fitted variable for the  $N^{th}$  subset are predicted using the other  $N - 1$  subsets for model calibration.

Three sizes were tested for the moving window: 500, 600 and 700 nm. In any case the 500 nm window gave the best results.

Using PLS only did not give, however, fully satisfactory results, because the influence of the single parameter was often masked by the so-called *systematic noise*: i.e. the interference due to chemical or physical factors which are of no interest for the analyses.

In order to remove, or at least reduce, the influence of systematic noise, the Orthogonal Signal Correction (OSC) [18] technique was applied to the optimal spectral window. OSC uses the PLS regression to find the spectral features linked to the

latent factors which are uncorrelated to parameter to be fitted, and subtract them from the spectra.

We employed OSC to remove systematic noise from the spectra of both EVOOs and lubricants, then a single-factor PLS regression was used to predict the various quality parameters. A single OSC factor was sufficient to improve the fit for both EVOO and lubricant spectra.

## 5 PREDICTION OF QUALITY PARAMETERS

Table 1 summarizes the results of spectral data processing, reporting the central wavelength of the 500 nm width optimal spectral window, together with R<sup>2</sup> and the SECV.

For EVOOs, the prediction of palmitic acid fraction was excellent and it was very good also for oleic acid fraction. The UV spectral band was mostly informative for the prediction of oleic acid, while palmitic acid was better predicted by using the NIR spectrum. Figures 3 and 4 show the PLS regression plots correlating the true and predicted values of the oleic and palmitic acid fractions, respectively.

For lubricant oils the prediction was excellent for phosphorus content and JOAP anti-wear index, while it was very good also for water content and TAN. The NIR spectral band above 1000 nm was mostly informative for the prediction of water, phosphorus and JOAP index, while the optimal region for TAN was shifted towards the visible spectral region.

Figures 5–8 show the PLS regression plots correlating the true and predicted values of lubricant oil quality parameters.

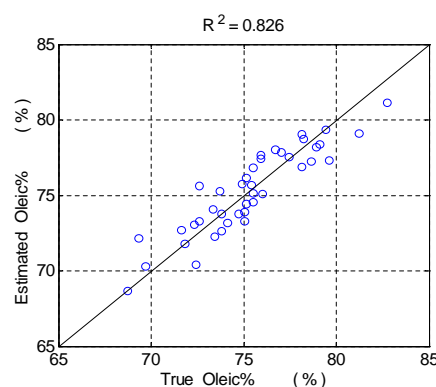


FIG. 3 PLS regression plot correlating the true and predicted values of oleic acid fraction in extra virgin olive oils.

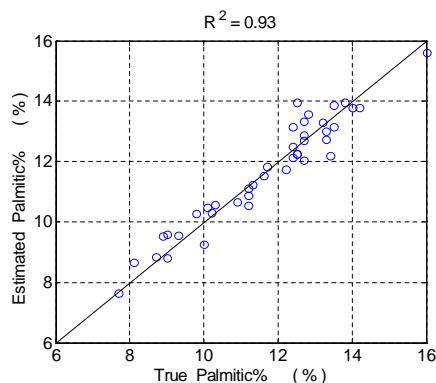


FIG. 4 PLS regression plot correlating the true and predicted values of palmitic acid fraction in extra virgin olive oils.

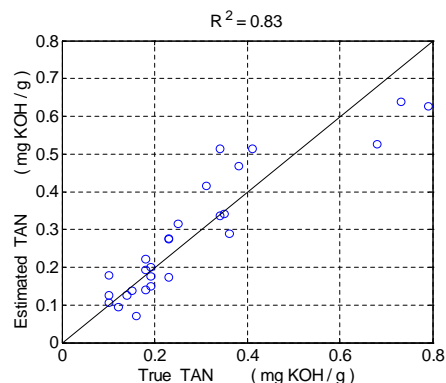


FIG. 6 PLS regression plot correlating the true and predicted values of TAN in lubricant oils.

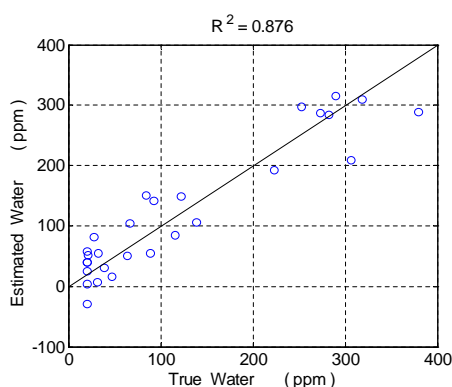


FIG. 5 PLS regression plot correlating the true and predicted values of water content in lubricant oils.

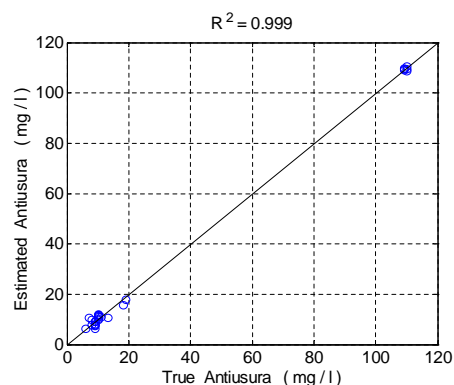


FIG. 7 PLS regression plot correlating the true and predicted values of JOAP anti-wear index in lubricant oils.

## 6 CONCLUSIONS

Absorption spectroscopy in a wide spectral range, complemented by a multivariate data processing, was used to predict important quality parameters of different liquids such as EVOOs and lubricant oils, in order to demonstrate the potentials of optical spectroscopy for product characterization. The optical spectrum is in practice like a product fingerprint, from which to extract quantitative information of selected quality parameters. While conventional techniques make use of several instruments for the measurements of those parameters, optical spectroscopy allows for their assessment by means of a single instrumentation. In addition, given that all measurements were performed by means of compact optical fiber-based instruments, this work demonstrates the possibility of implementing online devices for continuous monitoring.

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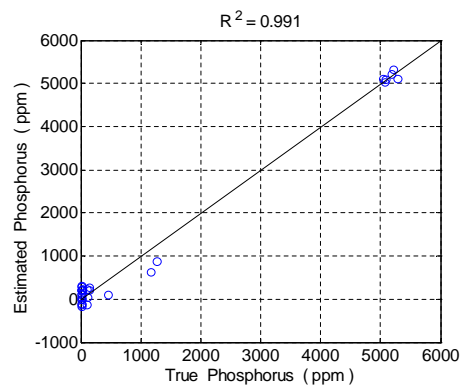


FIG. 8 PLS regression plot correlating the true and predicted values of phosphorous content in lubricant oils.

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