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Study of motor oil adulteration by infrared spectroscopy and chemometrics methods

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HIGHLIGHTS

- Adulteration of motor oils is investigated by FT-IR and chemometrics.
- PCA, PLS2-DA and PLSR make possible to discriminate among three types of oils.
- Models predict the amount of oil adulteration with very high accuracy.

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ABSTRACT

Fourier transform infrared spectroscopy (FTIR) coupled to chemometrics techniques was used to investigate high quality motor oils samples adulterated with lower quality oils, like used oils and standard oils. The results showed that Partial Least Squares (PLS) models based on infrared spectra were a suitable analytical method for predicting adulteration of high quality motor oils in the concentration range from 0% to 36% (w/w), with prediction errors lower than 3% (w/w). Partial Least Squares Discriminate Analysis (PLS2-DA) gave good classification results with 100% correct class prediction, in the spectral range of 1800–600 cm^{-1} and concentration range of 0–20% w/w for the two tested oil adulterants in their binary mixtures with the high quality oil. The proposed method can be employed for quality monitoring and control and rapid screening analysis of adulterated motor oils.

1. Introduction

Worldwide directives and legislation for environmental quality have established a set of lower levels for airborne pollutant emissions from combustion. Nowadays, motor manufacturers and fuel companies are investing large amounts of resources in green technologies in order to fulfil the increasingly strict emission requirements. On the other hand, merchandise profit goals using cheap substituent products instead of more expensive higher technological petroleum products has arisen the question about quality authentication. Motor oils, as products of petroleum refinery, are fundamental for optimum car performance [1]. Among the major functions of motor oils are to protect the engine from many physically and chemically related malfunctions like heating, corrosion and contamination [1,2]. As a part of the motor combustion, the motor oils qualities have become increasingly important, not only as motor lubricants, but also because of the impact of the combustion emissions emitted in the environment.

Many products of the petroleum industry, such as heavy crude oils, gasoline, diesel fuel, jet fuel and others are investigated to ascertain for their quality and authenticity, using different chromatographic and spectroscopic methods [3,4]. Instrumental analysis techniques like gas chromatography, high performance liquid chromatography, NMR and Mass spectrometry have been widely used for this purpose, however, these techniques are rather expensive, time-consuming, they require skilled operators and even they can have a high environmental impact.

Infrared spectroscopy has always had a significant place in lubricant analysis to characterize qualitatively its different constituents. Near Infrared Spectroscopy (NIRS) and Mid Infrared Spectroscopy (MIRS) coupled to chemometrics methods have been shown to be powerful techniques for authentication of petrol [5] due to their simple application and robustness, fast performance and cheap sample preparation. With the advent of FTIR spectroscopy, the possibility of developing quantitative methods of lubricant analysis is facilitated. It is because of the inherent spectroscopic power of FTIR instruments, as well as of the advances in sample handling techniques and of the more availability of new chemometrics methods, that quantitative analysis using

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Mid Infrared Spectroscopy MIRS has been greatly facilitated [6]. Despite the fact that motor oils are also among the key products of petroleum industry [7,8], there are not many papers dealing with adulteration studies of oil products [9]. In recent study has been shown that coupling NIRS with chemometrics is suitable for quantitative assessment of food adulteration of virgin olive oils with low quality vegetable oils [10].

Preliminary studies from Balabin et al. [3,11] have revealed the importance of quality control of motor oil adulteration by means of NIR. A large number of chemometric techniques (linear and nonlinear methods like SIMCA, PLS, KNN, MLP and SVM) were used [11] to evaluate the origin of motor oils according to their base stock (synthetic, semi synthetic, and mineral) and to their kinematic viscosity at low (SAE 0 W, 5 W, 10 W, 15 W) and high temperatures (SAE 20, 30, 40, 50). Moreover, the possible differentiation and classification between different types of commercial motor oils using IR Spectroscopy and mathematical data analysis procedures has been shown by Zieba-Palus et al. [9]. PLS quantification has been applied to NIR reflectance spectroscopy for the determination of motor oil contamination in sandy loam [12].

To continue and increase the existing knowledge about motor oil authentication procedures, as a key factor in the identification of possible product adulterations, in this work we propose the use of FTIR coupled to chemometrics methods. The goal of this study is to propose a new procedure to replace traditional laboratory methods, which are relatively slow, inaccurate, and require the use of expensive polluting chemicals by newer methods based on the coupling of IR spectroscopy and chemometrics methods. In particular, FTIR spectroscopy coupled to chemometrics methods, like PCA, PLSR and PLS2-DA, will be tested for discrimination and/or classification of different oil types and for quality assessment and quantification of possible oil adulteration in an easy, accurate and fast way. Therefore, the main objective of this work is to develop and to propose a simple analytical method, based on FTIR and chemometrics methods to determine and to quantify the possible adulteration of highly valued motor oil using low quality oil alternatives.

2. Materials and methods

2.1. Sampling

In these work, three classes of motor oils have been investigated: high quality high priced motor oil (H, synthetic 10W40 motor oil), standard commercial low-cost motor oil (N, commercial oil sold without any indication of its origin or its quality) and finally, used motor oil (U, also sold without being authenticated). These three types of oils were purchased from local market in Morocco and are assumed as being different types and brands. Table 1 shows the motor oils characteristics.

MIR spectra of pure oil samples and of their binary combination in mixtures were measured and used for data analysis. In total, 111 samples were prepared in two sets. A first set (included in Study A) included 61 samples and it was analyzed in order to conduct a classification study about the adulteration of a high quality motor oil (H) with the other two lower quality oil substituent (N and U). The second data set (included in Study B) was composed of 50 samples and it was used for quantification of adulteration of the high quality oil (H) produced by the standard cheap motor oil (N).

2.2. Classification study (Study A)

Sixty samples were prepared in binary mixtures using different binary combinations of the investigated motor oils. The investigated adulteration range was 0–20% in weight (w/w). One first subset of 20 samples was prepared where the high quality oil (H) was adulterated with the standard cheap motor oil (N) and noted as NH oil mixtures group. A second group of 20 samples was composed of binary mixtures between the high quality oil (H) and the used oil (U) and noted as the UH oil mixtures group. And a third group of 20 samples was prepared mixing the standard oil (N) with the used oil (U) and noted as the UN oil mixtures group. All these samples were analyzed by MIR and their corresponding spectra are given in Fig. 1b. Also the pure spectrum of high quality motor oil was included in the data. These 61 samples were preliminary explored in order to discriminate among these three oil mixtures and the pure H spectrum. These 61 samples were further randomly subdivided into 2 new subsets of 46 and 15 samples. The first group of 46 samples (the pure spectrum of high quality was included in this data subset) was used for the calibration of the classification model; and the second group of 15 selected samples was used to validate the model externally.

Table 1
Motor oil characteristics of the three motor oils used in the study (H, N and U).

	Method of analysis: Norm NF EN ISO 3104	
	Kinematic viscosity at 40 °C	Kinematic viscosity at 100 °C
High quality oil H	88.36 mm^2/g	14.07 mm^2/g
Standard oil N	90.29 mm^2/g	11.68 mm^2/g
Used oil U	26.88 mm^2/g	5.78 mm^2/g

2.3. Quantitative study of the adulteration of high quality motor oil (Study B)

Another set of 50 oil mixture samples were prepared for the quantitative study. The selected samples were prepared in binary mixtures (NH) of the standard cheap motor oil (N) and the high quality oil (H), at percentages ranging from 1% to 36% (w/w) of concentration of the standard cheap motor oil. Also pure samples of the two motor oils (N and H) types were considered in the study. The standard motor oil (N) was chosen as the adulterant of the high quality oil because of its easy availability at a considerably reduced price compared to that of the high quality oil (H). During the model calibration, a 0% of adulteration was assumed for the spectrum of the pure sample of high quality oil (H) and a 100% of adulteration was assumed for the pure spectrum of the standard cheap oil (N). The study was repeated considering 3 different calibration scenarios in respect to the included adulterant concentration ranges, i.e. 1–36% (only binary mixtures, NH), 0–36% (pure high quality oil and binary mixtures, H and NH) and 0–100% (pure high quality oil, pure standard cheap oil and binary mixtures, H, N and NH).

Three different spectral ranges data were also tested for each of the above mentioned calibration ranges, i.e. the full spectral range 4000–600 cm^{-1}, the spectral range 3000–600 cm^{-1}; and the spectral range 1800–600 cm^{-1}.

The 50 samples used for the quantitative study were also further randomly subdivided into two subsets, one subset for the model calibration (38 samples) and another subset for the model external validation (12 samples). All samples were kept and analyzed under similar conditions by MIR.

2.4. Acquisition of MIR spectra

A Bruker Vector 22 instrument equipped with a DTGS detector, Globar (MIR) source, and KBr separator was used to record the spectra of all oil mixtures and of pure motor oils. Measurements were taken within the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. All the experimental work reported in this paper has been