

CLASSIFICATION AND QUALITY CONTROL OF LUBRICATING OILS BY INFRARED SPECTROSCOPY AND CHEMOMETRIC

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ABSTRACT :

FT-IR coupled to chemometrics techniques was used to investigate the quality control of engine lubricating oils SAE 30 of gear and machines in industries. The results showed that Partial Least Squares Discriminate Analysis (PLS2-DA) gave good classification results with 100% correct class prediction. The proposed procedure is fast, non-destructive, simple and easy to operate. This developed method is highly recommended for quick monitoring of the oil's quality, and it is another application of FTIR-chemometrics method for quality control of lubricating oils.

Keywords: lubricating oils, quality control, FT-IR, PLS-DA, Chemometrics.

1. INTRODUCTION

Motor oil is vital for maintaining optimum engine performance¹. Motor oil has many valuable functions, these include: protecting the engine from the effects of heat, pressure, corrosion, oxidation and contamination, providing a fluid barrier between moving parts, reducing friction and wear, cleaning the interior of the engine by removing dirt, wear and combustion contaminants^[1-2], and cooling an engine by increasing heat dissipation, further reducing wear and preventing the entry of contaminants. Motor oil mainly consists of two materials, which are the base oil and chemical additives. Various types of additives are blended with base oil according to its grade and specific duty such as metallic detergents, ash less dispersants, zinc bithiophosphate, anti-oxidant/anti-wear, friction modifier, viscosity modifier, antifoam and pour point depressant^[2-3].

FT-IR recently applied to oil control quality^[4]. Average infrared spectroscopy (MIRS) combined with chemometrics methods is an emerging technique of analysis to verify the authenticity of oils due to its simplicity, speed and ease of sample preparation. Infrared spectroscopy has always had a place in lubricant analysis to characterize qualitatively different components^[5-6]. These methods applied will replace traditional methods long and even unable to accurately

determine the rate of adulteration of oils and requiring the use of expensive chemicals and pollutants. These traditional methods for control quality include the determination of kinematic viscosity at 40 ° C and 100 ° C^[7], the sulfated ash^[8], pour point^[9], flash point^[10], density^[11], TBN (total base number)^[12], and the content water^[13].

In this context, an important part of this work was primarily carried out the study on the quality of engine lubricating oil of SAE 30 gear and machines. This end, we conducted an experimental study focuses on the analysis of fifty samples of SAE 30 motor oil on the one hand, by physicochemical analyses lubricants and secondly, by chemometrics methods (PCA and PLS-DA) combined with infrared spectroscopy Fourier transform (FTIR) to evaluate its quality. The goal of this paper is therefore, to investigate the potential of PLS2-DA method, coupled to MIR spectroscopy technique, as an alternative analytical tool for non-destructive and fast for the quality control of lubricating oils SAE 30.

2. Experimental

2.1-Sampling

After a survey on the quality of lubricating oils for machinery engines and machines in the Moroccan phosphates company, we got a set of 50 samples, Drums and cans of lubricants were randomly sampled. The sampling was done using a pipette or a syringe. Containers for samples collected using bituminous fluid containers were tightly closed; preferably we chose vases or bottles with wide collar that could be sent to the laboratory within the premises of a liter, wide open, for lubricants, greases and bitumen products. The work had two types of analysis, physico-chemical analysis of lubricants and chemometrics methods, PCA and PLS-D combined with infrared spectroscopy Fourier transform (FTIR).

2.2- Physic-chemical lubricants analysis

In this study, the physico-chemical lubricants analysis of 50 samples includes the determination of kinematic viscosity^[7] at

40 ° C & 100 ° C, the determination of sulfated ash^[8], the determination of pour point^[9], the determination of point light^[10] in an open cup, the determination of density^[11], the determination of TBN^[12] and the water content^[13].

2.3-Acquisition of means infrared (MIR) spectra

A Bruker Vector 22 equipped with a DTGS detector, Globar (MIR) source, KBr and Ge separator was used to acquire spectra using infrared. Measurements were taken within the range 4000 cm⁻¹ at 400 cm⁻¹ at a resolution of 4 cm⁻¹ and 98 scans was taken.

2.4- Chemometrics methods

2.4.1- Principal component analysis (PCA)

PCA allows determining the main features of the spectra, to compare them and to highlight links between the descriptive variables (the absorbance at different wavelengths) ^[14]. PCA projects the cloud of points in a representation space of small dimensions. It calculates new variables called principal components that are linear combinations of the starting absorbance. Since the objective of the analysis is simplification, choose the size of the representation space by making a compromise between two conflicting goals; take a low dimensional space and keep a maximum variance explained. The selection of optimal number of components in PCA and of latent variables in PLSR is done using the lowest prediction error in cross validation (leaving-out-one sample at a time) related to the PRESS_k, the sum of squares prediction error for the model which includes k factors (components), and optimal prediction of y values for the external validation samples not included in the calibration step. The model giving the lowest relative prediction errors in external validation is finally chosen.

2.4.2- Partial least Square Discriminate PLS-DA

The partial least squares discriminate analysis method, PLS-DA, ^[15] usually is applied. This technique finds the components or latent variables which discriminate as much as possible between two different groups of samples from their FT-IR spectra (X block) according to their maximum covariance with a target class defined in the y data block. It attempts to describe whether a spectrum of a sample belongs or not to a particular class, consisting of zeros and ones. According to the number of simultaneously regressed y vectors two different PLS-DA approaches are possible. In case of only one class is modelled at a time the method is the ordinary PLS1-DA. When several classes are simultaneously modelled at the same time, the PLS2-DA modified method

can be used ^[16]. For the classification study (Study A) in this work PLS2-DA, was used. All data (Physic-chemical lubricants analysis and FTIR spectra) acquired were developed by The Unscrambler software version X (Camo, Norway) for the purposes of PCA and PLS2-D algorithms.

3. Results and discussions

3.1- Physico-chemical and MIR analysis of lubricants:

3.1.1- Physico-chemical analysis of lubricants:

We investigated the characteristics of fifty samples of SAE 30 engine oil, the results allow us to conclude that the studied oils have a density value, which is an average of 895.5 kg/m³ and a kinematic viscosity value at 40 and 100 ° C respectively, which is an average of 96.40 and 11.16 mm² / s, a sulfated ash content is an average of 1.92%, a base number (TBN), which is on average 15.9 mg (KOH) / g, a flash point and flow which are respectively averaged 231 ° C and -27 ° C and a water content of 0%. Based on these results, we can consider that the majority of studied oils conform to the specifications of this industry, except the samples 16, 17, 18, 28, 29, 30, 31, 40, 41, 42, 43 and 48 which have values in base index (TBN) and kinematic viscosity that do not respect this conformity intervals in the technical file of SAE 30 oil. So we can classify our samples into three groups: conform Group (Con), non-conforming group with high viscosity values (NC1) and non-conforming Group to low viscosity (NC2).

3.1.2 Spectral features:

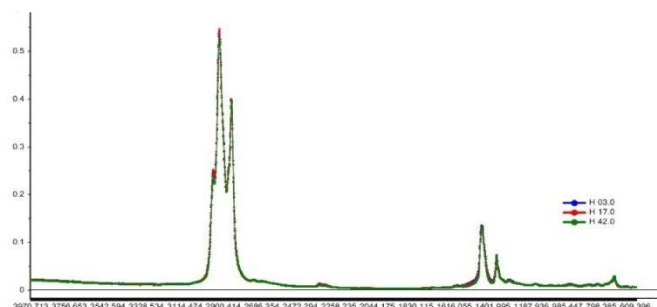


Figure 1. ATR-MIR spectra of the oil samples in the spectral range 4000-600 cm⁻¹

In Figure 1, all experimental spectra are dominated by three clusters of spectral bands. The first group of spectral bands are observed in the spectral region between 2850 and 2920 cm⁻¹ arising from symmetric and asymmetric stretching vibrations of methylene (-CH₂) and methyl (-CH₃) groups [17] . The

second cluster of bands is in the spectral region between 900 and 1500 cm^{-1} , which are attributed to the vibrations of (-CH₂), (-CH₃) and aliphatic (-COC-) groups. The last cluster of spectral bands is observed in the region of 723 cm^{-1} and is due to vibrations of cis-HC=CH- [18].

3.2- Chemometric Evaluation

3.2.1-Principal Component Analysis (PCA):

After analyzing of 50 samples of SAE 30 motor oil, Principal Component Analysis with full cross validation was applied to the first data set of 50 classification samples (see Materials and Methods section) exploring the full acquired data.

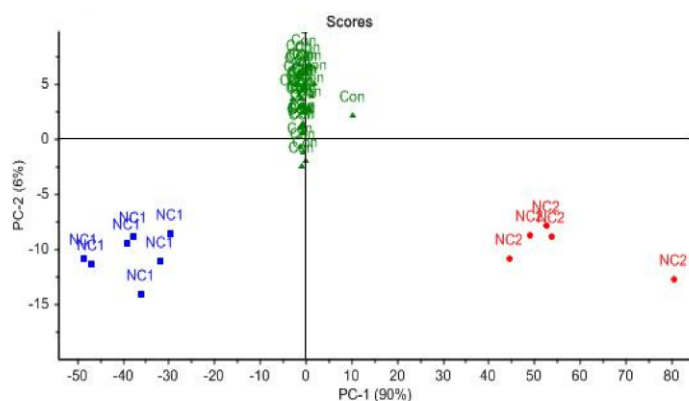


Figure 2. PCA scores plot (PC1 vs. PC2) in the analysis of the FTIR spectra.

The PCA model with three components already explained 99% of the total data variance (PC1 captured 85%, PC2 captured 6% and PC3 captured 3% of the variance respectively). PC1 vs. PC2 scores plot of the spectra of the first data set given in Figure 2, distinguished three major clusters of samples according to conformity: conform group (Con), non-conforming group with high viscosity values (NC1) and non-conforming group with low viscosity (NC2).

3.2.2- Partial least square discriminate PLS-DA

This PLS2-DA model was built considering the FTIR spectra as X variables, while the Y variables were associated with the three different conformity classes (one different y variable for each conformity class, with 1 or 0 depending on whether it belongs or not to the considered data group). The model obtained in this way was able to discriminate among the three conformity classes (Con, NC1 and NC2), as it can be seen from the PLS2-DA scores plot in Figure.3.

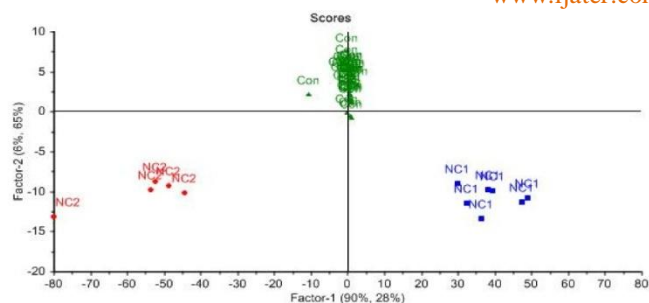


Figure 3. PLS2-DA scores plot (LV1 versus LV2) in the analysis of the FTIR spectra.

The first PLS2 latent variable (LV1) explains 90% of Y variance and 28% of X variance and discriminates between the type of non conformity of oil NC1 and NC2). The second PLS2 latent variable explains a rather high percentage of variance of y (6%) based only on a small amount of variance in X (65%), related with the amount and type of conformity.

Table 1 shows the calculated figures of merit of the results obtained by the PLS2-DA model using the calibration samples subset (see Material and Methods section). A correlation between measured and predicted classes (R² around 0.96 and 0.95 in all cases) and low prediction errors (RMSEC between 0.06 and 0.08) were obtained. When the previously obtained PLS2-DA model was applied to classify the oil validation samples subset (see Material and Methods section) a low prediction error (RMSEP) between 0.09 and 0.12 were also obtained.

Classes ^a	Figures of merit ^b		
	R ² _c	RMSEC	RMSEP
Con	0.96	0,0841	0,1228
NC1	0.96	0,0647	0,1127
NC2	0.95	0,0690	0,0992

Table 1: Figures of merit achieved by PLS2-DA discrimination of the three different types of motor oil samples (Con, NC1 and NC2).

^a Investigated classes by PLS-DA.

^b Reported model figures of merit: R²_c – R-square in calibration; RMSEC-Root Mean Squared Error in Calibration; RMSEP-Root Mean Squared Error in external validation.

3.3- Predicting conformity of new samples:

In this section, we will keep five samples: three conform (2, 11 and 22) and two not conform (29 and 42). We will make a model without the five samples, and then we will predict their conformity (with external validation) to make sure that our model is perfect.

From the graph of the scores, we note that the samples are separated into three groups: conform group and two non-

conform groups (NC1 et NC2), and after quality prediction of the five samples we found the following results:

Table 2. Results of the classification of motor oil binary samples for the prediction of samples not used in calibration (external validation data set).

Echantillons	Classe conform 1:		Classe 2: NC1		Classe 3: NC2	
	y-predicted	y-reference	y-predicted	y-reference	y-predicted	y-reference
H 02	0,9395	1,000	0,0572	0,000	0,0033	0,000
H 11	0,9099	1,000	0,0724	0,000	0,0177	0,000
H 22	0,9397	1,000	-0,1505	0,000	0,2108	0,000
H 29	0,0544	0,000	0,9163	1,000	0,0293	0,000
H 42	-0,1489	0,000	0,1487	0,000	1,0001	1,000

Table 2 shows that for the 5 validation samples; we note that the samples 2, 11 and 22 are conform, the sample 29 is not conform with a low viscosity value (NC1), and the sample 42 is not in conform with a high viscosity value (NC2). A 100% correct classification was achieved, i.e. all oil spectra of the validation data set were correctly matched to the three corresponding classes. In Table 1, the predicted values by the PLS2-DA model are always very close to 1. These results confirm that the predictive ability of the developed PLS2-DA model was very good. Therefore, it was concluded again that FTIR spectroscopy together with the application of chemometrics PLS2-DA method can be used to discriminate conformity of motor oils.

4. Conclusion

In this study, FTIR spectroscopy coupled to chemometrics techniques like PLS2-DA and PCA was reported as an adequate method for the quality control of lubricating oils SAE 30 according to kinematic viscosity at 40 ° C & 100 ° C, without any previous sample pretreatment and without any sample destructive manipulation. Both PCA and PLS2-DA chemometrics methods were able to discriminate accurately to what class belongs a particular conformity of motor oil sample. In this method samples were classified into three groups: conform group (Con), no conform group with high values in viscosity (NC2) and no conform group with low viscosity values (NC1). In one hand by physicochemical analysis, on the other hand by chemometrics methods (PCA and PLS2-DA) combined with Fourier transform of infrared spectroscopy (FTIR). Such chemometrics treatment of spectral data results faster and more simple and convenient than the usually applied classical one. Good estimations of class were given by PLS2-DA technique which was used in Achieved prediction results, with very low errors.

5. References

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