



Prediction of Kinematic Viscosity in Motor Oil Using FTIR coupled with Partial Least Squares Regression

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Abstract

This study focuses on the quantification of the kinematic viscosity motor oil by the use of mid-infrared spectroscopy with chemometrics. Fifty (50) samples of motor oils in kinematic viscosity which varied between 71.84 and 137.31mm²/s were subjected to infrared analysis. The aim was to develop a calibration model for the prediction of viscosity in motor oil by using Fourier transform-infrared spectroscopy. The spectral transmissions of all samples were obtained in the spectral range of 600–4000 cm⁻¹. Ten latent variables were found optimum to obtain the kinematic viscosity from the FTIR data. The values obtained for correlation coefficient and root mean square errors of prediction were 0.99 and 0.49, respectively. The outputs of the PLS-1 were found comparable to those obtained by the expensive and time-consuming methods. This developed method is highly recommended for quick monitoring of the motor oil quality parameters.

Keywords: Motor oil, kinematic viscosity, FTIR and PLS

1. Introduction

Motor oil is vital for maintaining optimum engine performance [1]. 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 [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 [3]. The kinematic viscosity of motor oils is the most important parameter to be measured in order to assess their performance and service time [4]. However, the kinematic viscosity testing is in general slow and time-consuming and it is generally expensive in testing. In this work, a procedure for simple and accurate determination of the kinematic viscosity of motor oil based on the use of the Fourier transform-infrared (FTIR) analysis along with multivariate method was developed and tested. The FTIR spectroscopy is the fastest and cheapest of the spectroscopic techniques used by scientists for identification purposes. It is based on the measurement of well-defined and usually sharp characteristic fundamental frequencies associated with specific functional groups [5, 6]. FTIR has been applied to oil quality control [7]. 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

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ely different components [8-9].

Recently, multivariate calibration has been applied for analyzing many chemical systems including wastewater, foods, drugs formulations, oils and fuels without the need for separation of solutes prior to their analysis as the case in chromatographic analyses [10–11]. Multivariate calibration is an effective calibration method in which the chemical information (absorption, emission, transmission, etc.) of a set of standard mixtures recorded at different variables (wavenumbers) are related to the concentration of the chemical compounds present in the mixtures [12]. The popular calibration way used in chemical analysis is the univariate calibration in which the chemical information of a set of solution recorded at one variable (i.e. wavenumber) is related to the solute concentration in the solution. The most applied multivariate methods are principal-component regression (PCR) and partial least squares (PLS) [13]. The ultimate purpose of the multivariate calibration methods is to find useful relationships between one set of the cheap FTIR measurements and the expensive and lengthy reference motor oil measurements. The obtained relationships are then used to obtain motor oil quality parameters quickly and with a good accuracy. Many problems can be raised and affected the calibration quality of the multivariate calibration which includes [12]: (a) non-selectivity problems, (b) the collinearity problem, (c) the optimum number of the calibration samples and the informative spectral regions and (d) the outlier problem. Proper treating of these problems would be necessary to end up with a high calibration power and accurate determination of the motor oil quality parameters and to avoid the tedious application of the reference methods.

Therefore, the aim of this work is to apply the chemometrics for a simple and accurate determination of the kinematic viscosity of the motor oils using FTIR along with the PLS-1 calibration. The results obtained are expected to be useful for determination and routine tests purposes.

2. Materials and Methods

2.1. Motor Oil Sampling

After a survey on the quality of lubricating oils for machinery engines and machines in the Moroccan company, fifty (50) samples of motor oils were collected. Just after collection all samples were analyzed by FTIR in a range from 4000 to 600 cm^{-1} and by the method of the reference for determination of viscosity. A set of 35 samples was selected randomly to build up the calibration model while the other 15 samples were used for the validation purpose.

2.2. Kinematic viscosity and FT-MIR Analysis

Determination of kinematic viscosity was made according to the International Standard Organization [14]. FTIR spectra are obtained using a Vector 22 Bruker FTIR Spectrophotometer equipped with an attenuated total reflectance accessory (ATR single-reflexion, Diamond, incident angle 45°), DTGS detector, Globar (MIR) source, and KBr Germanium separator with a resolution of 4 cm^{-1} at 98 scans. Spectra are scanned in the absorbance mode from 4000 to 600 cm^{-1} and the data are handled with OPUS. Analyses are carried out at room temperature. The background is collected before each sample and measured. Before the chemometric analyses (PCA and PLS), the data were pre-processed by taking first derivative of the absorbance spectra for the baseline removal using the Savitzky-Golay method with a second order polynomial and 40 smoothing points. The PCA and PLS regression were performed using the Unscrambler version 10.1.

2.3. PCA and PLS Regression

PCA was carried out to detect the presence of any spectral outliers in the spectral data prior to develop a prediction model using PLS regression. Primarily, PCA is a feature reduction mathematical procedure that can be useful to provide basis for the other multivariate linear regression analyses such as the PLS regression [15]. It reduces the dimensionality of the data and forms a $n \times p$ covariance matrix, where n is the number of spectra of the oil samples analyzed and p represents the absorbance values. In PCA, the Eigen spectra and their respective eigenvalues are calculated. The numbers of components in the data are then reduced to a smaller group of principal components, termed as PCAs [16]. PLS is a supervised analysis. It is based on the relation between the signal intensity and the characteristics of the sample [17]. Interference and overlapping of the spectral information may be overcome by using powerful multicomponent analysis such as PLS regression. PLS [18] allows a sophisticated statistical approach using spectral region rather than unique and isolated analytical bands. The first step is to perform a calibration model. This involves collecting a set of reference calibration samples containing all expected chemical and physical variations that will be predicted later.

PLS attempts to maximize the covariance between two data blocks X and Y . PLS searches for the factor subspace most congruent to both data blocks, and its predictions are usually better than using other multilinear regressions (MLR) methods such as MLR, especially when a large number of collinear variables are present in the X data block. A new matrix of weights (reflecting the covariance structure between the X predictors and Y response variables) is calculated which provides rich factor interpretation and information for each latent variable independently.

The evaluation of the errors in the calibration is estimated by computing the standard error of calibration (SEC) after comparing the real concentration with the computed one for each component. The SEC is calculated using Equation 1.

$$SEC = \sqrt{\left(\frac{\sum_{i=1}^N (C_i - C'_i)^2}{N-1-p} \right)} \quad 1$$

where C_i coefficients are the known values, C'_i are the calculated values, N is the number of samples, and p is the number of independent variables in the regression optimized by cross validation. The standard error of prediction (SEP) gives an estimation of the prediction performance during the step of validation of the calibration equation (Equation 2).

$$SEP = \sqrt{\left(\frac{\sum_{i=1}^M (C_i - C'_i)^2}{M} \right)} \quad 2$$

where C_i is the known value, C'_i is the value calculated by the calibration equation, and M is the number of samples in the prediction set. Another useful parameter is the relative error of prediction (REP %) that shows the predictive ability of the model. This is calculated from Equation 3.

$$REP\% = \sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{\sum_{i=1}^n (y_i)^2}} \times 100 \quad 3$$

Quality assessment of the obtained results is discussed by comparing predicted and measured values, both for calibration and validation data sets. All chemometrics calculations were performed by using the Unscramble X software version 10.1 from CAMO (Computer Aided Modeling, Trondheim, Norway). The predictive ability of the model is also expressed by the calculation of the bias and the square of correlation coefficient (R^2) usually called Q2 in the prediction. Regression coefficients are the numerical coefficients expressing the link between the predictor variations and the response variations. The bias is the systematic difference between predicted and measured values. The bias is computed as average value of the residuals. The residual is the measure of the variation which is not taken into account by the model. The residual for a given sample and a given variable is computed as the difference between observed value and fitted (projected or predicted) value of the variable on the sample.

3. Results and Discussions

3.1. Typical FTIR Spectra of motor oil

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 2960 cm^{-1} arising from symmetric and asymmetric stretching vibrations of methylene ($-\text{CH}_2$) and methyl ($-\text{CH}_3$) groups [19]. The second cluster of bands is in the spectral region between 1200 and 1500 cm^{-1} , which are attributed to the vibrations of ($-\text{CH}_2$), ($-\text{CH}_3$) and aliphatic ($-\text{COC}-$) groups. The last cluster of spectral bands is observed in the region of 722 cm^{-1} .and is due to vibrations of cis-HC=CH- [20].

3.2. Principal Component Analysis

Previous studies indicate that PCA is a useful tool for the identification of spectral outliers in the absorbance spectra of the samples and can be employed to increase the quality of the prediction model [21]. The PCA was performed on the (first derivative pretreated) absorbance spectra of all motor oil samples ($n = 50$) which enabled to detect one spectral outlier in the data (as circled in Figure 2). The absorbance spectra of these samples (spectral outlier) was included in the preliminary calibration model (not shown) but excluded from the PLS analysis performed to develop a final calibration model (as described next).

The data set contained 50 samples including one spectral outlier identified using PCA (Figure 2). After excluding the spectral outliers, the remaining 49 samples were randomly split into two sets. One (calibration set) set of samples ($n = 34$) was used for constructing MIR-PLS calibration model and the second set ($n = 15$) was used for the validation of the calibration model (hereafter, referred as the validation set).

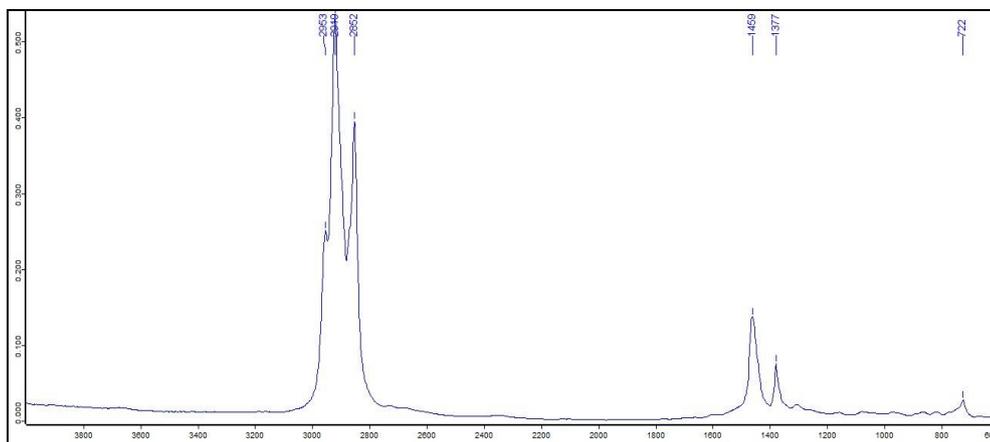


Figure 1. FTIR Spectra of the Oil Samples in the Spectral Range 4000-600 cm⁻¹

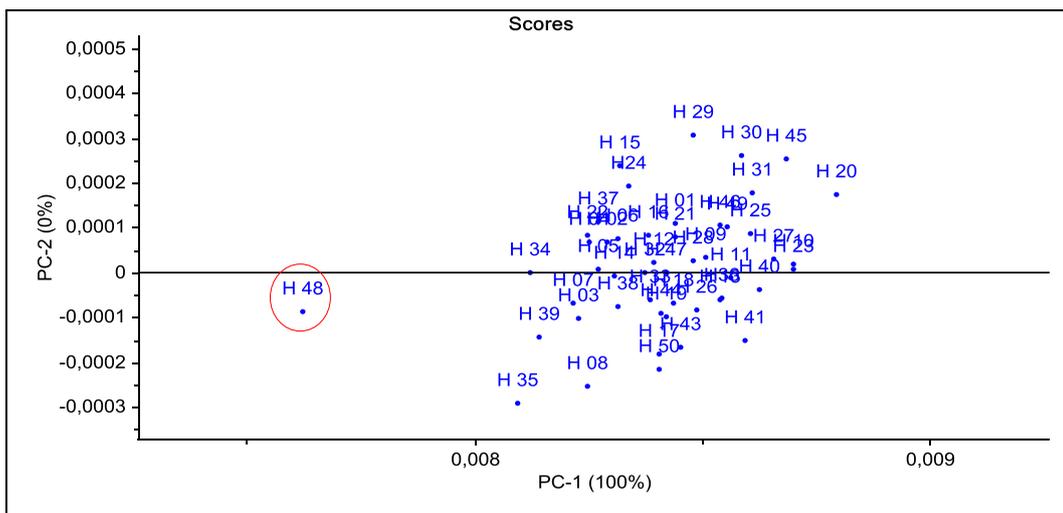


Figure 2. Principal Component Analysis (PCA) Performed on the (First Derivative Pre-treated) Absorbance Spectra of all Motor Oil Samples (n = 100) The Red Filled Circle is the Spectral Outlier in the Oil Samples

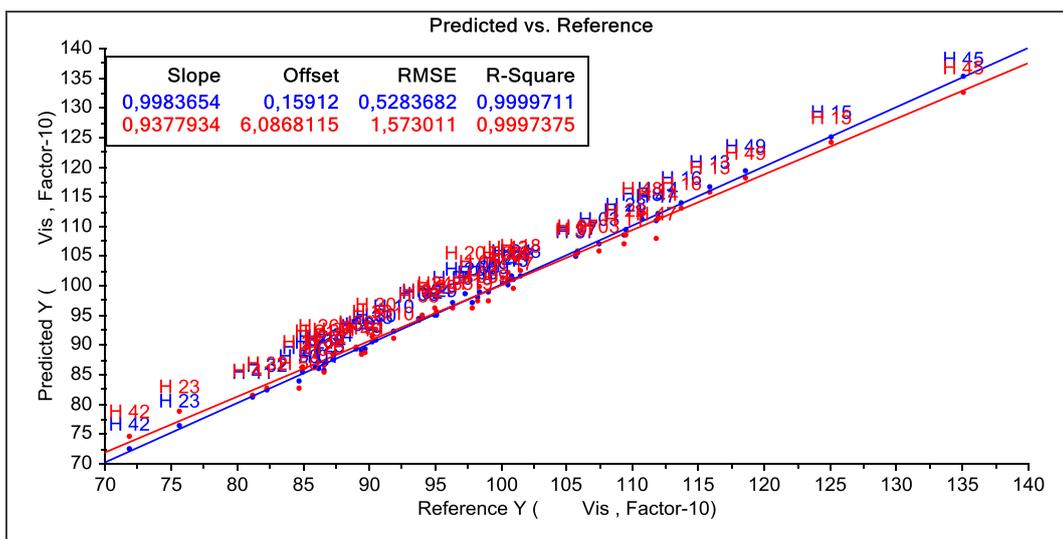


Figure 3. Plot of the Predicted and Measured Values for Kinematic Viscosity, obtained from the Final PLS Model Developed from the MIR Spectra

3.3. PLS Modeling

The PLS model is built by considering the spectra of motor oil at frequency region of 3000–600 cm⁻¹ where X variables and the Y variables are associated to the kinematic viscosity. The PLSR models are evaluated using coefficient of determination (R²) in the calibration, root-mean-square error of calibration (RMSEC) and cross validation (RMSECV). The per-

formance of the PLSR models on the independent validation set is evaluated using R^2_p and root mean square errors of prediction (RMSEP). The results show the robustness of the model to determine the kinematic viscosity for 34 samples of motor oils, as can be seen in Figure 3. The PLS model is validated by a full cross validation. The obtained statistical parameters RMSEC, RMSECV, and R^2 are summarized in Figure 3. The coefficient of determination (R^2) of 0.99, RMSEC of 0.52, and RMSECV of 1.57 can be considered satisfactory.

3.4. Validation of MIR-PLS Model

The validity of the resulting preliminary and the developed calibration model based using the set of 34 samples, were tested using a validation set of the unknown motor oil samples (Table 1). The prediction equation obtained from the final calibration model ($n = 34$; Figure 3) was applied to the validation set in order to calculate the statistical parameters related to the estimation of kinematic viscosity in unknown samples. The obtained results are given in Tables 1 and 2.

Table 1. Prediction of Kinematic Viscosity of External Validation

Samples	Y-Predicted	Y-Reference
1	85,79	86,31
2	98,82	98,37
3	98,03	98,26
4	86,76	86,75
5	101,07	101,06
6	97,05	97,88
7	94,91	94,99
8	85,6	86,65
9	85,29	84,98
10	90,86	90,53
11	90,39	90,36
12	104,82	105,69
13	86,65	86,72
14	99,94	100,58
15	100,88	100,64

Table 2 shows clearly that the FTIR-PLS method is an effective method for the determination of kinematic viscosity in motor oil. The results indicate that there is no significant difference between the reference methods and the proposed one. Therefore, the PLS model for the FTIR data treatment appears to be an appropriate approach to predict the kinematic viscosity in motor oil.

Table 2. Statistical Parameters Carried Out by External Validation on PLS

External validation	LVs	R_p^2	RMSEP	Bias	REP%
	10	0.994	0.497	-0.188	0.532

4. Conclusions

PLS-R calibration models developed in the 71.84 and 137.31 mm^2/s calibration range, gave less than 2% relative error for external validation samples. Therefore, we can conclude that the FTIR spectra of motor oil can be properly modeled by PLSR using first derivative of the absorbance spectra for the baseline removal using the Savitzky-Golay method, with a second order polynomial and 40 smoothing points as initial data pretreatments. This study had also underlined that the spectral region 3000–600 cm^{-1} was useful for good predictions of kinematic viscosity. FTIR spectroscopy coupled with chemometrics techniques is reported as an adequate method for the determination of viscosity in motor oil, without any previous sample pretreatment and any destructive sampling manipulation. Therefore, the proposed spectroscopic method provides a convenient alternative in terms of time and solvent saving for routine analysis of large number of samples. This approach can be considered fast, clean, and affordable methodology.

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