


Article

Application of FTIR-ATR Spectrometry in Conjunction with Multivariate Regression Methods for Viscosity Prediction of Worn-Out Motor Oils

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Abstract: Viscosity is considered to be a key factor in the quality of lubrication by oil and engine manufacturers and is therefore one of the most monitored parameters of lubricants. FTIR (Fourier-transform infrared) spectrometry in combination with Partial Least Squares (PLS) and Principal Component Regression (PCR) was therefore proposed and tested as an alternative to the standardized method for determining the kinematic viscosity at 100 °C with an Ubbelohde capillary viscometer (CSN EN ISO 3104) of worn-out motor oil grade SAE 15W-40. The FTIR-PLS model in the spectral region of 1750–650 cm⁻¹ with modification of the spectra by the second derivative proved to be the most suitable. A significant dependence of R = 0.95 was achieved between the viscosity values of 190 samples of worn-out motor oils, which were determined by a standardized laboratory method, and the values predicted by the FTIR-PLS model. The Root Mean Square Error of Calibration (RMSEC) parameter reached 0.148 mm²s⁻¹ and the Root Mean Square Error of Prediction (RMSEP) parameter reached 0.190 mm²s⁻¹. The proposed method for determining the kinematic viscosity at 100 °C by the FTIR-PLS model is faster compared to the determination according to the CSN EN ISO 3104 standard, requires a smaller amount of oil sample for analysis and produces less waste chemicals.

Keywords: oil condition monitoring (OCM); motor oil; lubricants; FTIR spectrometry; kinematic viscosity; Partial Least Squares (PLS) regression; Principal Components Regression (PCR)



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1. Introduction

Motor oil is important for maintaining optimum engine performance [1,2], reducing fuel consumption [3–5] and emissions [6]. During its operation in the engine, it is exposed to considerable oxidation, high temperature, pressure and the penetration of unwanted contaminants from external environment. These factors affect the formation of degradation products in motor oil and lead to the loss of additives. In addition to the actual chemical aging of the oil, it is also degraded by residues of imperfectly burned fuel, condensed water or coolant penetrating through leaks, metal abrasive particles from the engine [7]. Furthermore, small dust impurities and contaminants from gritting materials on the maintenance of roads in the winter months, which are sucked in from the environment when driving with a clogged air filter, have an effect on the deterioration of the oil [8,9]. Motor oils in diesel engines are heavily contaminated with soot. Jakobiec et al. [10] state that soot generated in the engine can cause hard sludge, high lubricant viscosity or oil gelling. According to Ziólkowska [11], soot particles tend to agglomerate, and it is the main cause of motor oil gelling at high temperatures.

Oil and engine manufacturers consider viscosity to be a key factor in lubrication quality. It is stated in the literature [8,12] that in the case of large-volume compression ignition engines (CI), a range of viscosity change of ±20% compared to the viscosity of

new oil is usually allowed to ensure lubrication. The quantity that allows to evaluate the change in the viscosity of the lubricant depending on the change in temperature is the viscosity index. The higher the viscosity index value, the less the viscosity changes with temperature.

Therefore, large viscosity changes can occur during motor oil operation. Products of thermo-oxidative degradation and soot in oil have an effect on the increase in viscosity. Oxidation of the oil is accompanied by its darkening, increase in its acidity and viscosity, odour and discharge of insoluble oxidation products [13]. The increase in viscosity can also be caused by the penetration of coolant into the oil due to an operational accident of the engine. The increase in motor oil viscosity also occurs when the base oil has a high evaporation rate, so that more volatile fractions decrease during operation. This is reflected in increased oil consumption and the unfavourable composition of exhaust emissions [14,15].

On the contrary, the decrease in the viscosity of the operated oil is due to the dilution of the oil with fuel, the depolymerization of polymer additive used as a viscosity index modifier, or also due to cracking of the oil under thermal stress [16]. Soot is formed in a significant amount in oil cracking, contributing to increasing the viscosity of the motor oil.

Exhaust after-treatment and regeneration systems can contribute to increased fuel supply to the motor oil. As many as tens of percent of unburned fuel penetrates the motor oil of cars in urban traffic due to incomplete regeneration of the DPF filter [17,18]. Frequent cold starts, i.e., driving in city traffic or a fault in the injector, will also cause the oil to be diluted with fuel and this may lead to a reduction in the viscosity of the lubricant. Too low oil viscosity means that the lubricating film is too thin and has a low load capacity.

In order to increase the safety and reliability of vehicles, the economy of operation, and also for environmental reasons [19,20], there are currently requirements for continuous oil condition monitoring (OCM), especially for large-volume engines. The OCM [21] is usually part of maintenance plans. Traditional analysis of motor oils consists of a combination of standardized physical and chemical methods that require a variety of laboratory instruments. Standard operating procedures are often time consuming, require environmentally problematic solvents and agents, and therefore new alternatives are sought. For example, the Spectro FDM Q600 Fuel Sniffer (Fuel Dilution Meter) was developed in collaboration with the US Navy to determine the dilution of motor oil with petrol, diesel and other hydrocarbons. This device uses a built-in surface acoustic wave sensor to measure the concentration of fuel vapours present in the atmosphere above the oil sample [22]. Different types of sensors are also designed to monitor viscosity [23,24]. A simple, inexpensive and reliable capacitive sensor as an indicator of the end of life of motor oils was proposed by Heredia-Cancino et al. [25]. This sensor measures the permittivity of the oil samples used, which correlates with their oxidation, nitration and sulfation. An overview of lubricant condition sensors for online machine condition assessment was published by Zhu et al. [26]. Hujo et al. [1] designed laboratory test equipment suitable for monitoring the efficiency of oil filters and evaluating the technical life of motor oils.

Differential FTIR spectroscopy is currently commonly used for the purposes of OCM—monitoring the thermal and oxidative degradation of motor oil, reducing the content of additives and the penetration of contaminants into the oil filling. With the development of information technology and the expansion of spectrometer software with multivariate mathematical and statistical software, predictive models have recently begun to develop from which several quality parameters of crude oil [27,28], lubricating oils [29] and fuels [30,31] can be obtained from a single spectrum, which can have both chemical and physical nature (e.g., viscosity, viscosity index, density, octane number, cetane number, etc.). The most common multivariate methods for evaluating entire spectral regions include Principal Components Analysis (PCA) [32], Partial Least Square (PLS) [33], Interval-PLS (iPLS) and Principal Components Regression (PCR) [34].

Viscosity [5], Total Base Number (TBN) [35] and Total Acid Number (TAN) [36] are motor oil parameters that are evaluated for both new and used motor oils. For this reason, FTIR chemometric models have been proposed as an alternative to the standardized

determination of TBN and TAN by potentiometric titration, which is time consuming and requires the preparation of reagents [37–39]. Another possibility for the determination of TBN and TAN is the thermometric determination according to ASTM D8045, therefore Macián et al. [40] verified the possibility of an alternative determination of the thermometric determination of these parameters based on FTIR in combination with chemometrics. De Rivas et al. [41] developed predictive models for the determination of TAN oils (SAE 50) used in aircraft turbine engines using IR data and PLS Regression, Projection Pursuit Regression (PPR), Support Vector Machines (SVM), Linear Models (LM) and Random Forest (RF).

In the case of new lubricants for various applications, Pinheiro et al. [29] tested the possibilities of using advanced chemometric methods in conjunction with FTIR spectroscopy to determine their selected quality parameters. No multivariate method gave satisfactory results when predicting kinematic viscosity at 40 °C and 100 °C. Hirri et al. [42] achieved excellent results in the validation of the FTIR-PLS model in the range of 3000–600 cm^{-1} for the prediction of kinematic viscosity from derived spectra of new lubricating oils intended for machine motors and machines. Braga et al. [43] compiled and validated the FTIR-PLS model to determine the viscosity index of new lubricating oils from 81 different manufacturers/brands in Brazil.

For the purpose of predicting the kinematic viscosity at 40 °C of used TURBO SAE 15W-40 motor oils, which are suitable for CI engines, Caneca et al. [44] tested the use of FTIR spectrometry in conjunction with multiple linear regression (MLR), PCR and PLS regression. The MLR calibration model proved to be the best in the spectral range 650–4000 cm^{-1} , which made it possible to predict the viscosity with a relative standard deviation (RSD) of 3.2% from the spectra. Marinovic et al. [45] discussed the development of the FTIR-PLS model for fast and accurate simultaneous determination of lubricant parameters for gas engines and turbines: density, viscosity and pour point. These wavenumber regions were identified as suitable spectral regions: 4000–3097 cm^{-1} , 1864–1552 cm^{-1} , 1320–665 cm^{-1} . The excluded spectral regions did not contain any spectral data or were ranges showing absorbance higher than 1.5 a.u. According to the authors, the spectral region and the number of principal components (PCs) are the main criteria for the construction of a good calibration model.

FTIR spectrometry in conjunction with PLS (iPLS) has also been used to quantify the penetration of contaminants (petrol, ethylene glycol and water) into lubricating oils [46] and to examine the adulteration of high-quality motor oils with used or lower quality oils [47]. A large number of chemometric methods have been used to classify motor oil according to the origin of the base oil (synthetic, polysynthetic and mineral oil) and according to the relationship between oil viscosity and winter temperatures (SAE 0W, 5W, 10W, 15W) and high summer temperatures (SAE 20, 30, 40, 50) [48]. The summer viscosity number is determined by the kinematic viscosity at 100 °C, i.e., approximately the operating temperature of the motor oil.

The aim of this paper is to present the methodology of design and validation of FTIR model in conjunction with PLS and PCR regression for rapid determination of one of the most important parameters of motor oils—kinematic viscosity at 100 °C ($KV_{100\text{ °C}}$). The proposed methodology for determining the viscosity of motor oils from the Infrared (IR) spectrum in conjunction with powerful mathematical and statistical software is an alternative to the standardized method for determining the kinematic viscosity at 100 °C with an Ubbelohde capillary viscometer. The methodology is designed to determine $KV_{100\text{ °C}}$ of motor oils of the grade SAE 15W-40, which are the best-selling motor oils in most of Europe and, due to the weather conditions in this geographical area, are sufficient for most users of turbo-diesels.

2. Materials and Methods

2.1. Oil Samples Used for Construction and Verification of the Calibration Model

A total of 230 samples of worn-out MAXIMA RLD SAE 15W-40 mineral motor oil (Renault Trucks Oils, Saint-Priest, France) were taken, which was operated in turbo-diesels of TATRA T-810 transporters cooled by liquid. Oil sampling was performed in the range of 200–15,000 km per oil fill. The MAXIMA RLD 15W-40 is a high-quality motor oil recommended for high performance diesel engines meeting Euro I–Euro V emission standards. It is suitable for engines without particulate filters and for most engines with exhaust gas recirculation (EGR) and most engines equipped with the systems of selective catalytic reduction of NO_x.

2.2. Determination of Kinematic Viscosity at 100 °C

The kinematic viscosity at 100 °C was measured for samples of worn-out motor oils in accordance with the CSN EN ISO 3104 standard [49]. The principle of the method used is to measure the flow time of a given volume of motor oil sample between the lines in a calibrated Ubbelohde capillary; the viscosity is given by the product of the flow time and the capillary constant. The capillary tube size 1C (capillary constant 0.03 mm²s⁻¹) is used for the standard analytical range 6–30 mm²s⁻¹. The measurements were repeated twice for each sample and the difference in results must not exceed ±0.5%. Calibration of viscosity capillaries was verified with petroleum oils with a certified viscosity value at 100 °C.

2.3. IR Spectrum Acquisition and Data Processing

Infrared spectra of 230 samples of worn-out oils were recorded on a Nicolet iS10 spectrometer (Thermo Scientific, Inc., Waltham, MA, USA) using the attenuated total reflectance (ATR) with a ZnSe crystal. Measurement parameters: spectral range 4000–650 cm⁻¹, resolution 4 cm⁻¹, number of spectrum accumulations 64. The new background spectrum was obtained before measuring each sample to reduce baseline shifting and ambient variations. Steady-state humidity was maintained in the workplace, as the FTIR instrument is sensitive to the changes of external environmental.

The obtained data were processed by TQ analyst version 8 (Thermo Scientific, Inc., Waltham, MA, USA), QC Expert version 2.5 (Trilo-Byte, Pardubice, Czech Republic), and by Microsoft Excel.

3. Results and Discussions

3.1. Development of Calibration FTIR-ATR Model

FTIR calibration model for determination of kinematic viscosity at 100 °C (KV_{100 °C}) of worn-out motor oils, i.e., the procedure of conversion of IR absorption information into viscosity values obtained by laboratory reference method according to CSN EN ISO 3104 [49], was developed by the frequently used regression methods—PLS [50] and PCR [51].

Prior to the creation of calibration models, the experimental data were normalized by the Mean Centering function [52]. This is a procedure that calculates the average spectrum; it was subtracted from the individual measured spectra. In parallel, the average KV_{100 °C} values were calculated and these average values were subtracted from the values measured by the standardized method. The resulting normalized (unitless) matrix and normalized vector were used to construct calibration models.

A set of 230 samples of worn-out motor oils was used to construct the calibration model. Using Spectrum Outlier diagnostics [52], outliers (a total of 25) were removed during the creation of the calibration model; these were motor oils into which coolant had penetrated as a result of an operational accident and oil samples for which the viscosity value was inaccurately determined. The Spectrum Outlier diagnostics calculates the Mahalanobis distance of the spectrum of each oil calibration sample from the average spectrum and then looks for the spectra that are most different from the other calibration samples. The diagnostics uses the Chauvenet's test [52] to assess whether the difference is significant. The remaining set of 205 standards with a kinematic viscosity in the range

of $11.340\text{--}14.855\text{ mm}^2\text{s}^{-1}$ was subsequently divided into two subsets, i.e., 190 calibration samples and 15 samples testing the predictive ability of the calibration model.

Figure 1 shows the IR spectra of oils with different kinematic viscosity values in the entire measuring range. The decrease in the viscosity value of oils was mainly affected by the penetration of fuel into the oil filling, which is manifested by an increase in the height of the spectral band with a maximum at 811 cm^{-1} belonging to out-of-plane bending = C–H vibrations of aromatics. The cause of the increase in viscosity may be the products of thermal oxidation reactions manifested in the spectrum by valence vibration of the carbonyl group–C=O with a maximum at 1745 cm^{-1} ; this was not proven in the present case. The spectral bands with peaks at 2952 , 2920 and 2853 cm^{-1} correspond to the CH valence vibrations of saturated n-alkyl groups. Symmetric and asymmetric deformation vibrations of CH bonds exhibiting a band with a peak at 1461 cm^{-1} and 1377 cm^{-1} belong to the CH_2 and CH_3 groups. According to Al-Ghouti and Al-Atoum [53], the band with a peak at 1706 cm^{-1} is shown by polymethacrylate, which is used in motor oils as a viscosity modifier and a pour point depressant. The most effective antioxidant and anti-abrasion additive Zinc Dialkyldithiophosphate (ZnDDP) is manifested in the spectrum by a band with a peak at 974 cm^{-1} (P–O–C bond) or at 660 cm^{-1} (P=S bond).

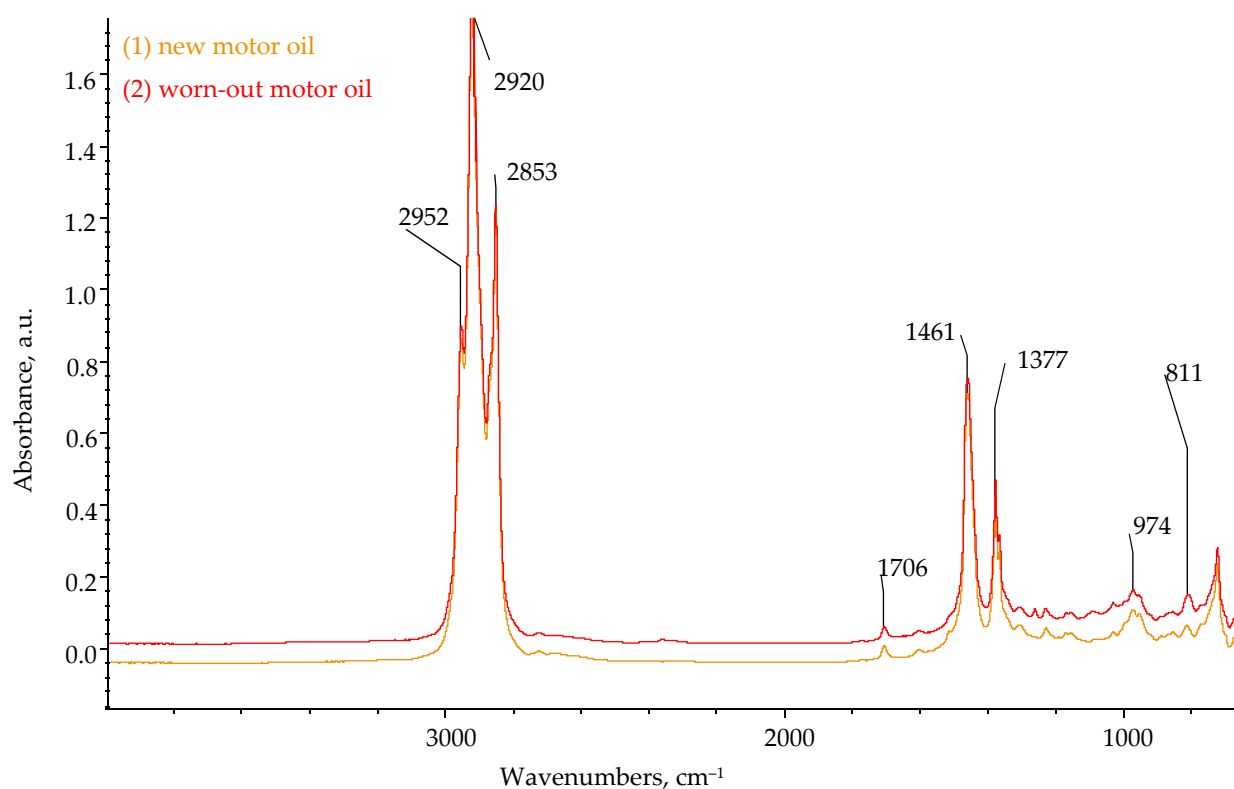


Figure 1. FTIR spectra in the measured range $4000\text{--}650\text{ cm}^{-1}$, (1) new motor oil with $\text{KV}_{100\text{ }^\circ\text{C}} = 13.950\text{ mm}^2\text{s}^{-1}$, (2) worn-out oil with $\text{KV}_{100\text{ }^\circ\text{C}} = 10.743\text{ mm}^2\text{s}^{-1}$.

An important step in creating a calibration model is to identify the essential spectral information in the measured spectra of motor oils used for calibration, i.e., to select the part of the spectrum that will be used for the calculation. The diagnostics of statistical spectra [52] identified the highest correlation between the change in spectral information and the change in $\text{KV}_{100\text{ }^\circ\text{C}}$ in the wavenumber range of $1750\text{--}650\text{ cm}^{-1}$. The absorption matrix thus contained 275 data points at a resolution of 4 cm^{-1} . In the area of the so-called fingerprint [54], in addition to the spectral bands already mentioned which are related to the change in viscosity, there are also indistinct spectral bands belonging to detergent-dispersant additives, which are calcium and magnesium salts of organic acids; alkylthiophosphates, sulfonates, phenolates [46]. Among other things, these additives play

an important role in neutralizing acidic fuel combustion products or acidic products of oxidative degradation of oil. Thus, the increase in oil viscosity caused by the oxidation products of oil degradation may correlate with the loss of these additives. The change in viscosity was apparently not affected by soot contamination of motor oil, which is reflected in an overall shift of the spectrum to higher absorbances in the region of about 2000 cm^{-1} ; this spectral region did not significantly correlate with the change in kinematic viscosity. A correlation of $R = 0.34$ between $KV_{100\text{ }^\circ\text{C}}$ and soot in worn-out motor oils operated in large-volume diesel engines was published in [55].

When creating the FTIR-PLS and FTIR-PCR calibration models, a mathematical description of the dependence between the spectral data matrix X (190×275) of the calibration samples and the matrix Y , i.e., the unit standard vector of samples of used motor oils with determined values of $KV_{100\text{ }^\circ\text{C}}$ according to CSN EN ISO 3104, was created. During the creation of calibration PLS and PCR models, the matrix of spectral data was transformed by Principal Components Analysis (PCA) [50] from the original variables to a significantly smaller number of latent variables—Principal Components (PCs), which in the present case are linear combinations of original absorbances at 4 cm^{-1} and are mutually uncorrelated, i.e., the basic characteristic of each PCs is its degree of variability-of variance. Therefore, the real calibration result is not only affected by the height or the area of the bands, but also the slope and curvature of the spectrum. It was the substantial change in the spectrum due to the penetration of the coolant into some of the samples of monitored oil fillings that caused the evaluation of these spectra by program diagnostics as atypical spectra (outliers) and therefore unsuitable for creating calibration models.

The PRESS (Prediction Residual Error Sum of Square) diagnostics was used in TQ analyst to determine the optimal number of principal components [39].

The criteria for selecting a suitable calibration model are the Root Mean Square Error of Calibration (RMSEC) [33,42] and the Correlation Coefficient (R) [39]. Equation (1) is used to calculate RMSEC and Equation (2) is used to calculate the Correlation Coefficient,

$$RMSEC = \sqrt{\frac{\sum_{i=1}^m (c_{ie} - c_{ir})^2}{m_c}} \quad (1)$$

$$R = \frac{\sum_{i=1}^m (c_{ir} - \bar{c}_r)(c_{ie} - \bar{c}_e)}{\sqrt{\sum_{i=1}^m (c_{ir} - \bar{c}_r)^2 \sum_{i=1}^m (c_{ie} - \bar{c}_e)^2}} \quad (2)$$

where: c_{ie} is a predicted value of an i -th calibration sample, \bar{c}_e is an average predicted value, c_{ir} stands for a value of a parameter of the i -th calibration sample defined based on a standardized method, \bar{c}_r is an average value of the parameter determined using a standardized method and m_c is a total number of calibration samples.

The Correlation Coefficient R indicates the strength of the regression dependence between the laboratory values and the values predicted by FTIR spectrometry; it should be as close to one as possible.

Table 1 provides an overview of the results of the proposed calibration models according to the spectrum adjustments used and the regression method used. Table 1 shows that the FTIR calibration model using PLS regression compared to PCR gives better results. This can be attributed to the fact that in the case of PLS regression, the determination of the number of PCs and the regression and rotation of the transformed matrices are performed simultaneously. In contrast, in PCR, the spectral information is first used to calculate PCs, and in the next step a mathematical description is created as the dependence of PCs on $KV_{100\text{ }^\circ\text{C}}$. It follows that PCs are also used to construct the model, which can describe the source of variability in data that are not related to viscosity.

Table 1. Results of FTIR-PLS/PCR regression models for kinematic viscosity prediction at 100 °C.

Spectral Range 1750–650 cm ⁻¹	PLS			PCR		
	PCs	R	RMSEC (mm ² s ⁻¹)	PCs	R	RMSEC (mm ² s ⁻¹)
not adjusted	7	0.89	0.197	10	0.88	0.204
1st derivation	5	0.88	0.197	10	0.85	0.186
2nd derivation	10	0.95	0.148	10	0.47	0.372

As can be seen from Table 1, the adjustment of the spectra by the second derivation, which leads to the enhancement of the spectral bands [56], had a positive impact on the construction of the FTIR-PLS calibration model in the spectral range 1750–650 cm⁻¹. A significant dependence of R = 0.95 was achieved between the viscosity values determined by the standardized laboratory method according to CSN EN ISO 3104 and the values predicted by FTIR-PLS calibration models and RMSEC = 0.148 mm²s⁻¹ (see Figure 2).

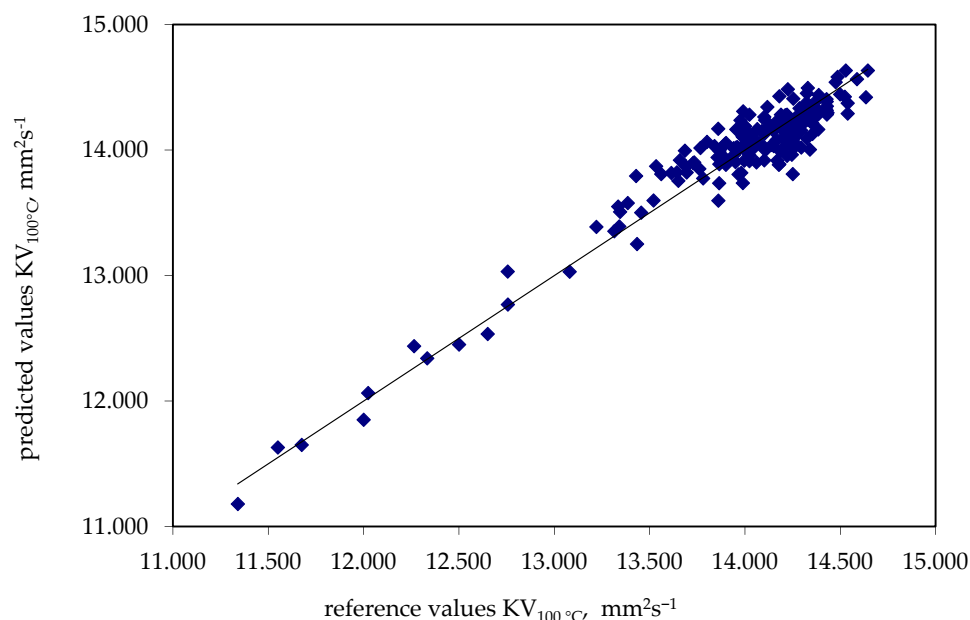


Figure 2. Regression dependence between kinematic viscosity values at 100 °C predicted by FTIR-PLS model and determined by the standardized method; the regression line equation is $y = 0.8774x + 1.7230$, $R = 0.95$

Given that 190 calibration standards and 275 wavenumbers were used to construct the calibration model, it was not the case that the correlation arose from overfitting (precising spectral data by derivation until they lose real information value) of too many wavelengths with a small number of samples. The spectral information contained in the 275 data points was compressed into ten principal components (PCs), which are linear combinations of the original absorbances at given wavenumbers and are uncorrelated to each other. The optimal number of PCs was determined by PRESS diagnostics in the minimum of RMSECV (Root Mean Square Error of Cross Validation) [39]; adding another component after this point does not improve the performance of the method, but on the contrary reduces it.

The proposed calibration model must be continuously supplemented by other standards—motor oils, the composition of which will correspond to the matrix of worn-out motor oils and the range of their values KV_{100 °C}.

3.2. Validation of the Calibration Model

A portion of the sample set with viscosity reference values (15 motor oil samples) was left outside the calibration set and used for initial verification of the calibration equations.

Validation of the calibration models was selected based on the RMSEP (Root Mean Square Error of Prediction) value [45,51]. Equation (3) was used for the calculation.

$$RMSEP = \sqrt{\frac{\sum_{i=1}^m (c_{iev} - c_{irv})^2}{m_v}} \quad (3)$$

where: c_{iev} is a predicted value of an i -th validation sample, c_{irv} stands for a value of a parameter of the i -th validation sample defined based on a standardized method, m_v is a total number of validation samples.

The RMSEP of reliable calibration is usually not much larger than RMSEC [12]. In the case of validation of the FTIR-PLS model without spectrum adjustment, the value of $RMSEP = 0.179 \text{ mm}^2\text{s}^{-1}$; in the case of the model with spectrum adjustment by the 1st derivative, the value of $RMSEP = 0.182 \text{ mm}^2\text{s}^{-1}$; and in the case of the best calibration model with spectrum adjustment by the second derivative, the value of $RMSEP = 0.190 \text{ mm}^2\text{s}^{-1}$. For all predictive models for determining viscosity at $100 \text{ }^\circ\text{C}$, the RMSEC differed only minimally from the RMSEP error expected in future predictions.

Table 2 presents the results of testing the predictive ability to determine $KV_{100 \text{ }^\circ\text{C}}$ by the best FTIR-PLS model (using the adjustment of the spectra of the second derivatives) on fifteen external samples of motor oils. This model provided a relative standard error of prediction 2.3%.

Table 2. Results of external validation of the best FTIR-PLS model.

Validation Sample	Measured $KV_{100 \text{ }^\circ\text{C}}$ (mm^2s^{-1})	Predicted $KV_{100 \text{ }^\circ\text{C}}$ (mm^2s^{-1})	Standard Deviation (mm^2s^{-1})
1	14.275	14.107	0.119
2	14.219	14.111	0.076
3	14.534	14.370	0.116
4	13.890	14.110	0.156
5	14.032	13.837	0.138
6	14.125	14.275	0.106
7	14.032	13.850	0.129
8	14.610	14.455	0.110
9	13.900	13.750	0.106
10	12.550	12.320	0.163
11	11.720	11.600	0.085
12	13.540	13.290	0.177
13	12.010	12.211	0.142
14	14.250	14.480	0.163
15	14.000	14.249	0.176

The viscosity values predicted by the best FTIR-PLS model, constructed from the data points of the spectra adjusted by the second derivative (for the wavenumber range $1750\text{--}650 \text{ cm}^{-1}$), were further statistically compared with the results obtained by the standardized method. Based on the paired t -test ($\alpha = 0.05$), it was shown that the differences between the reference and predicted values are not statistically significant. The F-test confirmed that both methods have similar accuracy.

Due to the fact that the quality of the engine oil is affected by the operating conditions and the technical condition of the vehicle, there may be significant changes in its physical and chemical properties. For this reason, the predictive ability of the proposed calibration model should be continuously verified by real samples of operated oils, for which the kinematic viscosity was determined by the standardized method.

4. Conclusions

In transport companies with a large fleet of diesel vehicles and in military repair companies, the maintenance strategy is often based on the OCM. The speed of obtaining OCM results is often more important than their accuracy.

Therefore, the paper presents the methodology of FTIR-PLS/PCR models for the prediction of kinematic viscosity at 100 °C of worn-out SAE 15W-40 motor oils, recommended for high-performance diesel engines.

As an alternative to the standardized determination of $KV_{100\text{ °C}}$ of worn-out oils by the Ubbelohde capillary viscometer according to CSN EN ISO 3104, FTIR spectrometry in conjunction with PLS regression proved to be the best. The presented results show that it is important to identify the following for the design of a robust FTIR multivariate model: deviating oil samples—outliers; the spectral range that most strongly correlates with the change in viscosity; number of PCs that include variability in spectral data associated with viscosity and test the adjustment of spectra by derivatives. The predictive power of the FTIR regression model needs to be validated by an independent set of oil samples for which the viscosity value was determined by a standardized method.

The benefit of the proposed and verified methodology presented in the article is a relatively simple way of determining the kinematic viscosity (i.e., ‘physical’ quantity) from the infrared spectrum. This spectrum can also be used not only for qualitative and quantitative analysis of chemical composition, but also for the determination of other ‘non-chemical’ quantities; a multivariate model must be available for them, created from a sufficient amount of quality data. The paper presents a methodology for determining $KV_{100\text{ °C}}$, but the process of creating a model is generally applicable to a number of other quantities (viscosity index, TBN, TAN, flash point, etc.). The possibility to obtain the values of as many quantities as there are robust FTIR-multivariate models available from a single spectrum is of particular practical importance. This approach can replace several sophisticated laboratory instruments with a single FTIR spectrometer.

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