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FTIR Spectrometry with PLS Regression for Rapid TBN Determination of Worn Mineral Engine Oils

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Abstract: The TBN (Total Base Number) parameter is generally recognized by both engine oil processors and engine manufacturers as a key factor of oil quality. This is especially true for lubricating oils used in diesel and gas engines, which are exposed to relatively high temperatures and, therefore, require more effective protection against degradation. The FTIR spectrometry method together with a multivariate statistical software helped to create a model for the determination of TBN of worn motor oil SAE 15W-40 ACEA: E5/E7, API: CI-4. The best results were provided using a model FTIR with Partial Least Squares (PLS) regression in an overall range of 4000–650 cm^{-1} without the use of mathematical adjustments of the scanned spectra by derivation. Individual spectral information was condensed into nine principal components with linear combinations of the original absorbances at given wavenumbers that are mutually not correlated. A correlation coefficient (R) between values of TBN predicted by the FTIR-PLS model and values determined using a potentiometric titration in line with the ČSN ISO 3771 standard reached a value of 0.93. The Root Mean Square Error of Calibration (RMSEC) was determined to be 0.171 mg KOH.g^{-1}, and the Root Mean Square Error of Prediction (RMSEP) was determined to be 0.140 mg KOH.g^{-1}. The main advantage of the proposed FTIR-PLS model can be seen in a rapid determination and elimination of the necessity to work with dangerous chemicals. FTIR-PLS is used mainly in areas of oil analysis where the speed of analysis is often more important than high accuracy.

Keywords: oil analysis; engine oil; lubricants; FTIR spectrometry; total base number (TBN); partial least squares (PLS)

1. Introduction

Lubrication oil is particularly important to maintain optimum performance and reliability of a combustion engine. Therefore, it is necessary to monitor the condition of the oil in order to avoid excessive wear or failure of important parts of the lubricating device. Oil analysis (OA) finds its application in this area. Based on the results of the oil analysis, it is possible not only to predict and prevent an emergency, but also to optimize lubricant change intervals. The application of OA in practice is thus beneficial from the point of view of operational safety, economic, and other environmental reasons.

Observation of chemical and physical parameters of the lubricating oils being used is mainly based on standardized analytical procedures allowing us to obtain overall information about the lubricant condition. Nevertheless, these procedures are time-consuming and require many sophisticated

laboratory procedures that are difficult to perform automatically and require a wide scale of laboratory equipment.

In relation to the above, infrared spectrometry, primarily the infrared spectrometry with Fourier transformation (FTIR spectrometry), play a more and more important role in the area of lubricant analysis [1,2]. This analytical tool allows for obtaining a spectral image of base oil and other constituents such as additives, contaminants, and degradation products. A level of wear of motor oils can be determined using differential spectroscopy from the spectra of original and worn oils. Thanks to this, it is possible to relatively evaluate the content of oxidation, nitration, and sulfation products; the volume of water, fuel, and cooling agent; and the depletion of anti-oxidation additives [3,4].

Advances in FTIR spectrometry have also brought new and complex mathematical and statistical methods into the software of spectrometers. The simplest spectral quantitative analysis assumes a validity of the Lambert–Beer principle, i.e., a linear correlation between absorbance (or transmittance) and concentration of measured analytes (under constant experimental conditions). If these assumptions are not met, the quantitative FTIR analysis uses matrix calculations and statistics that are more sophisticated, and selected spectral parts of the whole spectra are being evaluated. This allows us to determinate such parameters of lubricants (as well as fuels and other products) that can be primarily defined as physical-chemical ones, i.e., it is not possible to assign a specific spectral band to them (e.g., viscosity, viscosity index, flashpoint, octane, or cetane numbers, etc.) [5–11].

Advanced mathematical-statistical methods that allow compression of an extensive matrix of spectral data and the creation of regression calibration models for the prediction of evaluated quality parameters of lubricants into one or more groups based on similarities of their variables are usually included in the software of FTIR spectrometers. The most common are usually methods of principal component analysis (PCA) [12], partial least squares (PLS) regression [13], principal component regression (PCR) [14], and discriminant analysis (DA) [15].

Among routine tests performed in order to monitor the condition of the engine oil, we can mention the measurement of the Total Base Number (TBN), which describes a total volume of alkaline compounds that contribute to a so-called alkaline reserve of the lubricants. Carriers of this alkaline reserve are usually detergents on a basis of sulfonates, phenolic, calcium salicylates, magnesium salicylates, or barium salicylates, i.e., additives used in order to neutralize acid decay products appearing during fuel combustion or acid products of oxidation degradation of the oil while these products are the main source of dangerous corrosion of engines [16]. Apart from the detergents, dispersants and some anti-abrasion additives also play a role in the neutralization of acids. Wolak [17] proposed a model based on changes in TBN in oil engines under operating conditions that can be used to predict the behavior of engine oil during use.

TBN determinates a volume of a perchloric acid defined as an amount of mg KOH that is necessary for neutralization of all basic components present in 1 g of a sample (mg KOH.g^{-1}). TBN values decrease during motor oil usage. An acceptable limit is about 50% of the TBN of new oil. The decrease of the TBN is directly linked to a level of oil wear. A volume of acid components in the oil, i.e., slightly acidic components being partly in new oil and partly being produced during a combustion process and oil oxidation, is characterized by a Total Acid Number (TAN) [18,19]. A principle of determination of both parameters is a titration definition based on a potentiometric determination of an equivalence point.

Al-Ghouti et al. [20] have dealt with the possibility of application of the FTIR spectrometry and chemometrics to the determination of a viscosity index and TBN of motor oils. Both parameters can be obtained for new and worn motor oils with the use of a multi-dimension calibration based on FTIR spectrometry data. This work has proved that PLS provides more exact results than PCR and a classic method of least squares (CLS) in terms of prediction of oil parameters. With a high accuracy (99–102%) and precision (3–11%), the FTIR technique allows us to determine the TBN over the range of 4.57–16.45 mg KOH.g^{-1} and VI over the range of 96–153. Results obtained through FTIR-PLS were comparable to those obtained using the expensive and time-consuming ASTM D2270-04 and D2896-07a

methods. Determination of TAN and TBN in motor oils using the FTIR spectrometry has also been described by Van de Voort et al. [21] and Li et al. [22].

A possibility of usage of the FTIR spectrometry as an alternative method for checking oils and fuel is quite extensively described in other works [23–27]. Adams et al. [28] used the FTIR analysis to monitor antioxidants and to determine the TAN in synthetic turbine oils that are being used in military aircraft engines. A two-dimension IR correlation analysis has been used for examination and interpretation of observed trends in a spectrum, i.e., the dynamics of a growing volume of acid products of thermo-oxidation reactions and the depletion of anti-oxidation additives, as well as functional properties and wears of the engine. In addition, Rivers et al. [29] proposed an FTIR regression model for determining the TAN of used engine oils in aviation engine oils. Caneca et al. [11] applied FTIR spectrometry in connection with MLR (multiple linear regression), PCR, and PLS for prediction of the viscosity of motor oils suitable for diesel engines. The proposed calibration model allowed us to predict the viscosity with RMSEP = 3.8 mm^2.s^{-1} and a relative average error of 3.2%. Marinović et al. [30] focused on the development of an FTIR-PLS model for a fast and precise simultaneous determination of the following parameters of used motor oils: density, viscosity, and pour point. The authors have stated that a spectral region and a number of main components are the main criteria for the construction of a good calibration model. The following spectral regions have been identified as suitable ones: 4000–3097 cm^{-1}, 1864–1552 cm$^{-1,}$ and 1320–665 cm^{-1}. Excluded spectral regions did not contain any spectral data or they were ranges showing absorbance higher than 1.5 a.u.

The TAN is also one of the most important observed parameters of crude oil [31]. Regular supplies of crude oils during a three-year period were used to develop and test a partial least-squares multivariate model for determining the TAN based on near-infrared spectra (NIR) [32].

A proposal of a methodology of analysis of an adulterate petrol using the FTIR spectrometry and multi-dimensional calibration has been described by Al-Ghouti et al. [27]. Experimental results have shown that density value, distillation temperature, and FTIR spectrometry in connection with multi-dimension methods without a need to use a chromatographic separation and other expensive techniques, such as octane number definition, may serve as suitable tools to distinguish clean motor petrol from diluted petrol or other fuels.

Liu et al. [33] developed a compact moisture-content monitoring system based on the visible-near-infrared (Vis-NIR) spectroscopy with PLS regression and backpropagation neural network algorithms, which was shown to be able to determine the moisture content in lubricating oil in a fast, simple, and accurate way.

In companies with a large fleet of high-volume diesel (HVD) vehicles, the maintenance strategy [34] is often based on OA. The speed of obtaining OA results is often more important than their accuracy. The aim of this work is to present the creation of a calibration PLS regression model from FTIR-ATR spectroscopic data for the rapid determination of TBN mineral engine oils SAE 15W-40, ACEA: E5/E7, API: CI-4. This type of lubricant is used in HVD motors.

2. Materials and Methods

2.1. Oil Samples

Two hundred and fifty samples of a worn mineral engine oil SAE 15W-40, ACEA: E5/E7, API: CI-4 have been taken. This type of engine oil was being used in engines of a 3-axle transporter TATRA T-810. It uses a liquid-cooled supercharged six-cylinder diesel engine Renault DiX7 240-EC01. Individual samples were taken in a mileage range of 200–15,000 km.

The properties (quality) of engine oils are given by the ACEA and/or API specifications. ACEA E5/E7 means that it is the stable motor oil and stay-in-grade oil that provide effective control with respect to piston cleanliness and bore polishing. It further provides excellent wear control, soot handling, and lubricant stability. It is recommended for highly rated diesel engines meeting Euro I, Euro II, Euro III, Euro IV, and Euro V emission requirements and running under severe conditions,

e.g., extended oil drain intervals according to the manufacturer's recommendations. It is suitable for engines without particulate filters, and for most of the Exhaust Gas Recirculation (EGR) engines and most engines fitted with the selective catalytic NOx reduction systems. API CI-4 is an engine oil designed for high-speed four-stroke diesel engines, requiring compliance with emission standards (with EGR).

2.2. TBN Determination

For each sample of the worn motor oil, the TBN was determined in accordance with ČSN ISO 3771 [35] standard using potentiometric titration with the use of automatic titrator DL 25 (Mettler Toledo). The sample of the oil was dissolved in a water-free mixture of chlorobenzene and concentrated acetic acid, and then it was potentiometrically titrated by a 0.1 M solution of perchloric acid in ice-cold acetic acid (with a 2:1 ratio). For an indication of an equivalency point, a glass measurement electrode and a calomel comparison electrode with a water-free salt bridge were used. The value of the TBN is specified as mg KOH.g^{-1} of the oil sample. For used engine oil, the standard deviation of the TBN determination according to this methodology is 0.04 mg KOH.g^{-1} and the relative standard deviation (RSD) is 0.5%.

2.3. Acquisition of IR Spectra and Data Processing

Infrared spectra were recorded by an FTIR spectrometer Nicolet iS10 (Thermo Scientific) equipped with deuterated triglycine sulfate detectors (DTGS) and a horizontal attenuated total reflectance (ATR) with ZnSe crystal. The device is equipped with OMNIC software that allows setting parameters of the spectrometer controls the measurement itself, and runs subsequent operations with the spectra. MIR spectra of the motor oil samples were collected over the spectral range 4000–650 cm^{-1}. Measurement parameters: resolution 4 cm^{-1}, number of spectrum accumulations 64.

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

3. Results and Discussion

For purposes of designing an FTIR model in combination with multivariate methods for determination of the TBN of samples of the SAE 15W-40 motor oil, 250 samples of the worn motor oil were used, their spectra were collected, and reference TBN values were determined by a potentiometric titration following the ČSN ISO 3771 standard.

Figure 1 shows the spectrum of fresh SAE 15W-40 mineral oil over the entire wavelength range 4000–650 cm^{-1}. The main spectral bands correspond to the primary functional groups present in this type of engine oil. Infrared bands with peaks at 2953, 2915, and 2847 cm^{-1} correspond to CH valence vibrations of saturated n-alkyl groups. The deformation vibrations of the CH bonds exhibiting a band with a peak at 1459 cm^{-1} and 1379 cm^{-1} belong to the CH$_2$, and CH$_3$ groups. The spectral band is associated with the P-O-C bond and P = S bond of Zinc Dialkyl Dithiophosphate (ZDDP), which is used as the most effective antioxidant, and peaks at about 970 cm^{-1} and 656 cm^{-1}, respectively. The frequency of 723 cm^{-1} on the spectrum corresponds to the vibrations of the CH bonds of the long carbon chains. Zzeyani et al. [36] publish that during the operation of the lubricating oil, the evolution of these bands can be used as an indicator of lubricant degradation.

In many of the multivariate analysis techniques, it is important to pre-process the data [12]. The TQ analyst software used allows us to normalize variables entering the model before calibration by using a function of average centering, i.e., it is not necessary to consider intercept. The software calculated an average spectrum that was then deducted from individually measured spectra. In parallel, an average TBN was calculated and then deducted from individual TBN values of a calibration row. Subsequently, methods of multivariate statistical analysis were applied to these normalized matrices.

Calibration is a process used to create a mathematical description of the correlation between a measure marked as a signal and a measure determining a property of the measuring system. The found

correlation is then used to estimate unknown values of the measured parameter (in this case TBN) for measured values of the signal (absorbance). The dependence of the signal on properties of the measuring system may have various strengths. For calibration, it is favorable if a small change of the properties causes a big change of the signal. It means that the calibration is sensitive to the properties change [14].
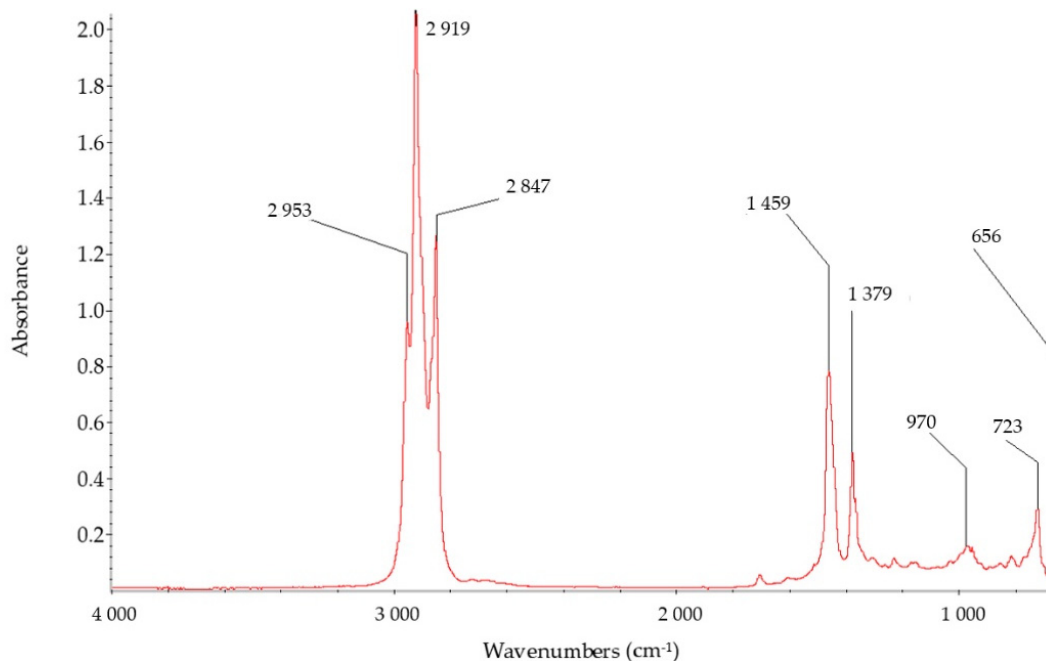

Figure 1. Infrared spectra of engine oil in the spectral range 4000–650 cm^{-1}.

Based on the analysis of results of already published works [11,28,29], PLS and PCR regressions were used to construct calibration models.

During optimization of the calibration models for determination of TBN using FTIR spectrometry, isolated engine oils were successively identified; these are oils with incorrectly determined reference TBN value or with a deviation in a measured spectrum. These outliers have been identified using Chauvenet's test [37] and, in the case of the PLS calibration model, also Leverage's diagnostics [37]. After isolated results and poor-quality spectra had been excluded, 210 samples in the TBN range 8.999–10.700 mg KOH.g^{-1} were used. This set was then distributed into two sub-groups of samples—200 calibration samples that were used for the construction of a calibration model, and 10 samples that were used to test the prediction ability of the defined model.

An important phase of construction of the calibration model is the identification of fundamental spectral information in obtained spectra of engine oils, i.e., the selection of a specific part of the spectrum that will then be used for calculation. Suitable spectral regions for the construction of the calibration model were identified by Statistical Spectra diagnostics [37]. The highest correlation between change of spectral information and change of TBN value was recorded in the whole range of spectral region 4000–650 cm^{-1}. The absorption matrix then contained 837 data points at a resolution of 4 cm^{-1}. When constructing calibration models FTIR-PLS and FTIR-PCR, a mathematical description of the correlation between the matrix (200 × 837) of spectral information of calibration samples and a unit vector that characterize values of the TBN calibration standards was prepared. During creation of calibration PLS and PCR models, the matrix of spectral data was transformed using PCA from original variables into a lower number of latent variables—principal components (PCs) that are linear combinations of original absorbances and mutually do not correlate.

Furthermore, a calibration model for a spectral range 1780–650 cm^{-1}, i.e., matrix of range (200 × 283), was tested. In this spectral region are all additives that are related to the alkaline reserve of

the engine oil. In the case of oil degradation, the products of oxidation (the attachment of oxygen to hydrocarbons contained in the oil, band 1660–1,00 cm^{-1}—carbonyl bonds), nitration (the attachment of nitrogen oxide, 1610–1650 cm^{-1}—the nitro groups), and sulfation (the attachment of sulfur dioxide, band 1150 cm^{-1}—the sulfation/oxidation groups) are located in this spectral region [17]. In all cases, these are acidic products that reduce TBN.

The calibration model for determination of alkaline reserve in worn oils was created without any mathematical adjustments and with adjustment of spectra using 1st and 2nd derivations. These adjustments contribute to a higher response of the spectral information.

Table 1 shows an overview of the results of individual calibration FTIR-PLS models based on used adjustments of spectra and used spectral range. Models using a PCR did not show satisfactory results, since they are not presented in this work.

Table 1. Results of calibration and validation of determination of the TBN using the FTIR-PLS regression in different spectral ranges.

Spectral Range	PLS				
	PCs	R	RMSEC (mg KOH.g^{-1})	RMSEP (mg KOH.g^{-1})	RMSECV (mg KOH.g^{-1})
4000–650 cm^{-1}					
Not adjusted	9	0.93	0.171	0.140	0.193
1st derivation	6	0.90	0.189	0.123	0.220
2nd derivation	9	0.91	0.178	0.164	0.372
1780–650 cm^{-1}					
Not adjusted	4	0.90	0.193	0.124	0.194
1st derivation	3	0.87	0.206	0.136	0.186
2nd derivation	5	0.91	0.182	0.139	0.372

As can be seen in Table 1, the most satisfactory results of calibration were obtained using the PLS algorithm applied to a classic spectral record in a zone of wavenumbers 4000–650 cm^{-1}.

A correlation coefficient (*R*) [16,23] characterizing the quality of the calibration model should be as close as possible to a value 1. The following formula (1) is used to calculate the correlation coefficient,

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

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 is a total number of calibration samples.

Dependency with a correlation coefficient of 0.95–0.99 is considered highly significant, with a correlation coefficient of 0.80–0.94 as very significant, and with a correlation coefficient of 0.50–0.79 as moderately significant. If the coefficient has a value lower than 0.50, the correlation is considered insignificant. The correlation (see Figure 2) between TBN values predicted using the FTIR-PLS model with 9 PCs and values obtained via potentiometric titration reached a very significant level (R = 0.93).
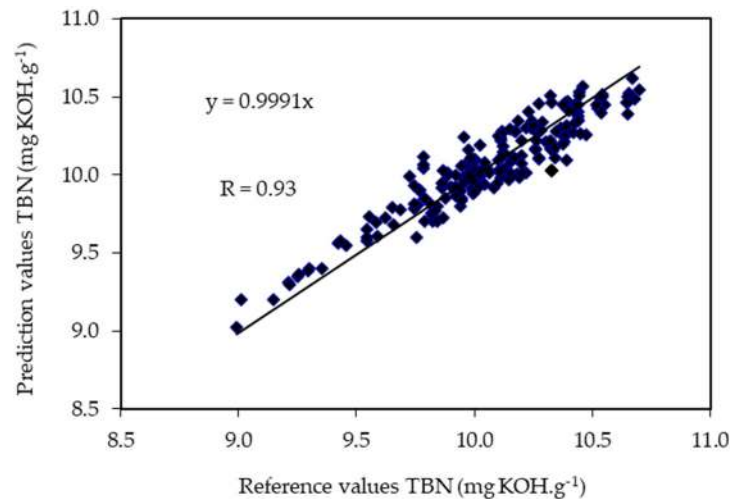
Figure 2. Regression dependency between values of TBN predicted by an FTIR-PLS model and values determined by a standardized ČSN ISO 3771 method.

To determine an optimal number of principal components, PRESS (Prediction Residual Error Sum of Square) (2) diagnostics [13] was used, i.e., sum of squares of differences between TBN values (c_{ie}) predicted by the FTIR-PLS model and real TBN (c_{ir}) values that were determined by a standardized method on the number of the PCs used for calibration. The optimal number of the PCs is selected in the minimum of the PRESS.

$$PRESS = \left[\sum_{i=1}^{m_c} (C_{ie} - C_{ir})^2 \right]^{0,5} \sim \ min \tag{2}$$

PRESS diagnostics tested a change of the value of the RMSECV (Root Mean Square Error of Cross- Validation) [13] when the calibration model was extended to another of the PCs (see Figure 3). Adding a component that represents important spectral and chemical information causes reduction of the RMSECV parameter to a minimum, a value of which stabilizes or starts to grow when another component is added.
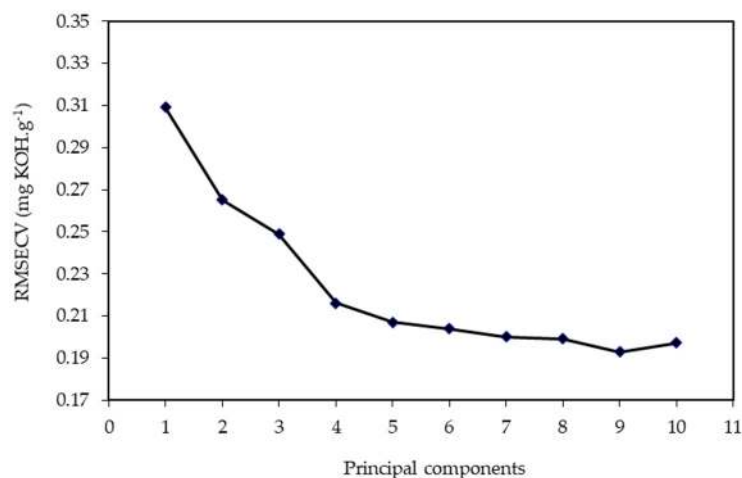

Figure 3. RMSECV depending on the number of principal components.

PRESS diagnostics reached its minimum at value RMSECV = 0.193, i.e., with the use of 9 principal components. Adding another component into the model causes a predicted residual error to grow to a

value of 0.197 (see Figure 3), i.e., noise in data was included in the model. RMSEC (Root Mean Square Error of Calibration) reached a value of 0.171 mg KOH.g^{-1}.

A very significant correlation ($R = 0.90$) between the predicted TBN values of the FTIR-PLS model with four PCs and the TBN values according to the standardized method was recorded in the spectral range 1780–650 cm^{-1}. This spectral region is called the "fingerprint region" of the chemical bond or sample being studied. Molecular vibrations are unique to each compound in this region, so this region is crucial for the accurate characterization of a chemical compound. By comparing the spectra of fresh engine oil and worn engine oil in the area of fingerprint FTIR spectra, several changes can be observed in the infrared bands. The bands with a peak at 1172 and 1156 cm^{-1} belong to the sulfonate detergent tension bands [38,39], and the bands with a peak at 970 cm^{-1} and 656 cm^{-1} belong to the ZDDP. RMSEC was 0.193 mg KOH.g^{-1} and RMSEP = 0.124 mg KOH.g^{-1} for ten external samples. Figure 4 shows the spectra of engine oil samples with different TBN values in the spectral range 1780–650 cm^{-1}.
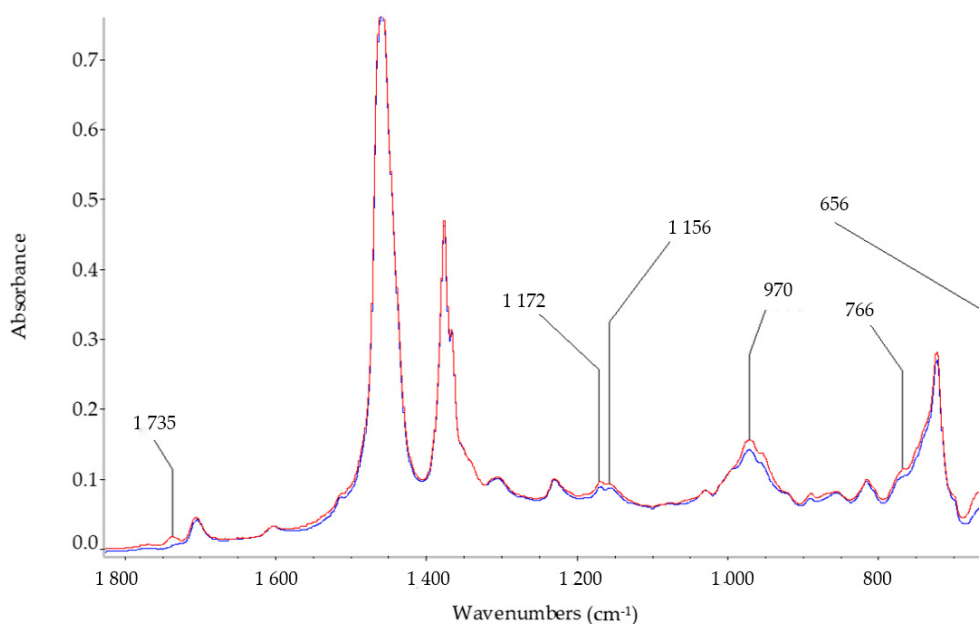

Figure 4. The spectra of engine oil with different TBN values in the spectral range 1780–650 cm^{-1}.

In order to define a suitable calibration model, validation of the model with 10 external lubricants with a known TBN value was carried out. As can be seen in Table 1, the value of the calibration error RMSEC [13,26] for all models did not significantly differ from RMSEP (Root Mean Square Error of Prediction) [13,26].

Although both tested spectral areas (4000–650 cm^{-1}) and (1780–650 cm^{-1}) show a very significant correlation (R = 0.91) between predicted and real TBN values where the spectral information in data was highlighted using the 2nd derivation, cross-validation did not confirm the robustness of these models (see Table 1).

TBN values predicted by the best FTIR-PLS model were then statistically compared by QC Expert software against results obtained by a standardized method. A paired t-test ($\alpha = 0.05$) proved that differences between referential and predicted values were not statistically significant, and F-test has proved that both methods show a similar accuracy.

However, it should be noted that the real samples of engine oils used to construct the calibration models were in very good condition. Therefore, it is necessary to continuously supplement the FTIR-PLS model with additional calibration samples and thus extend the calibration range of TBN determination.

4. Conclusions

This work presents possibilities of the determination of TBN of a worn mineral motor oil SAE 15W-40 ACEA: E5/E7, API: CI-4 that is used in supercharged diesel engines of the TATRA T-810 transporter using an FTIR spectrometry method combined with the use of the multivariate software. Based on a study of information sources, regression methods PLS and PCR were tested for the development of models for the determination of the TBN using an FTIR spectrometry method. During the construction of calibration models, it came out that in an initial phase of the model construction it is important to identify isolated standards, i.e., samples of the motor oil with an insufficient scan of spectra or with incorrectly determined measured quality parameter using the standardized method.

For the determination of TBN in samples of worn-out mineral motor oil SAE 15W-40, FTIR-PLS was proposed as the most suitable model, which works with a data set in the whole spectral range of 4000–650 cm^{-1}. The spectral data were compressed into new 9 PCs. The recorded spectra were not subsequently adjusted by derivation. A correlation coefficient between TBN predicted by the model and TBN determined using potentiometric titration in accordance with a ČSN ISO 3771 standards reached a value of 0.93, which is considered to be a very significant correlation. The RMSEC reached a value of 0.171 mg KOH.g^{-1}, RMSEP = 0.140. Very significant correlations (R = 0.90) between the TBN reference values and the predicted FTIR-PLS values were achieved also for the spectral range of 1780–650 cm^{-1}.

The main advantage of the proposed methodology of determination of the TBN using the FTIR spectrometry in connection with a PLS regression can be seen primarily in its speed (sample analysis takes about one minute) and absence of work with dangerous chemicals.

The developed FTIR spectrometry method equipped with the multivariate mathematical-statistical software allows us to replace a standardized method of monitoring degradation of oil fillings during operation and to provide adequate results in a much shorter period of time, which allows us to discover the real status of the device and accept relevant corrective measures much faster.

In further research, the authors will focus on the design and validation of the FTIR model in conjunction with multidimensional methods for determining other important lubricant parameters (e.g., kinematic viscosity, dynamic viscosity, viscosity index, flash point, etc.), for which the determination of these parameters by standardized methods is lengthy. Methodologies for determining these parameters in worn engine oils of various SAE and API, ACEA specifications will be verified.

Nomenclature

ACEA	Association des Constructeurs Européens d Automobiles
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
CLS	Classic Least Squares
DA	Discriminant Analysis
EGR	Exhaust Gas Recirculation
FTIR	Fourier Transform Infrared
HVD	High-Volume Diesel
OA	Oil Analysis
PCA	Principal Component Analysis
PCR	Principal Component Regression
PCs	Principal Components
PLS	Partial Least Squares
PRESS	Prediction Residual Error Sum of Square
RMSEC	Root Mean Square Error of Calibration
RMSECV	Root Mean Square Error of Cross-Validation
RMSEP	Root Mean Square Error of Prediction
RSD	Relative Standard Deviation
SAE	Society of Automotive Engineers
TAN	Total Acid Number
TBN	Total Base Number
Vis-NIR	Visible-Near-Infrared
ZDDP	Zinc Dialkyl Dithiophosphate

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