USE OF ATTENUATED TOTAL REFLECTION FOURIER TRANSFORM INFRARED SPECTROSCOPY AND PRINCIPAL COMPONENT ANALYSIS FOR THE ASSESSMENT OF ENGINE OILS[**]

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Attenuated total reflection Fourier transform infrared spectroscopy coupled with principal component analysis was used to investigate expensive and low-priced engine oil samples. A total of 174 oil samples of 15 commercial brands (expensive and low-priced) was successfully differentiated into five viscosity grades. The percentage of successful clustering of these oils ranged from 70.6 to 100%. The viscosity grades of oils of each commercial brand were also successfully distinguished for 10 different commercial brands. The successful clustering for this ranged from 72.5 to 100% for the 159 studied oil samples. Moreover, 15 low-priced oil samples of five commercial brands were assessed with 100% accuracy.

Keywords: *Fourier transform infrared spectroscopy, principal component analysis, engine oils, adulteration.*

ИСПОЛЬЗОВАНИЕ ИК-ФУРЬЕ-СПЕКТРОСКОПИИ С ОСЛАБЛЕННЫМ ПОЛНЫМ ОТРАЖЕНИЕМ И МЕТОДА ГЛАВНЫХ КОМПОНЕНТ ДЛЯ ОЦЕНКИ КАЧЕСТВА МОТОРНЫХ МАСЕЛ

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Для исследования различных проб моторного масла использованы инфракрасная спектроскопия с преобразованием Фурье и ослабленным полным отражением в сочетании с методом главных компонент. На пять классов вязкости дифференцированы 174 образца масла 15 дорогих и недорогих коммерческих марок. Процент успешной кластеризации масел 70.6—100 %. Определены классы вязкости масел для 10 различных торговых марок. Успешная кластеризация составила от 72.5 до 100 % для 159 изученных проб масел. С точностью 100 % определены 15 образцов недорогих масел пяти торговых марок.

Ключевые слова: *инфракрасная спектроскопия с преобразованием Фурье, метод главных компонент, моторные масла, фальсификация.*

Introduction. Engine oil, motor oil, and lubricant oil are simply different terms used to represent the lubricant used for the inner components of automobile combustion engines for reducing friction and wear. Engine oils comprise a base oil and many additives [1, 2]. Modern engine oils separate and lubricate the moving parts of an engine by forming a layer around the motor parts to reduce friction between them, thereby also reducing engine wear. Most oils contain detergents to remove impurities and deposits. Moreover, they cool the engine parts, which reduces energy loss [3–5]. The composition of engine oils depends on their

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base stock (mineral, semi-synthetic, or fully synthetic) and the desired performance [3–9]. The oil additives are usually mixed in particular ratios with engine oils to enhance their performance. These additives may include metallic detergents, ashless dispersants, antioxidants, anti-wear substances, friction modifiers, viscosity modifiers, antifoaming agents, and pour point depressants [8–11]. In recent years, owing to environmental concerns such as increased pollution, global warming, climate change, and waste disposal, the quality of engine oils has become significantly important. Due to the presence of relatively expensive oils in the market, greedy sellers or manufacturers have resorted to the adulteration of the expensive engine oils for financial gain [5, 7, 12]. Replacing expensive oils with cheaper ones is considered to be the most common adulteration behavior. Mixing expensive oils with different ratios of low-priced oils is another form of adulteration [5].

Oil adulteration can be uncovered by testing the viscosity, flash point, or base number. Anti-wear or antioxidant additives, such as zinc dialkyldithiophosphate (ZDDP) and polyisobutylene succinamide, may also be a measure of oil authentication [13]. Several analytical techniques such as atomic spectroscopy and Fourier transform infrared (FTIR) spectroscopy have been reported in the literature for the detection oil adulteration. Despite the large number of the publications dealing with different aspects of engine oils, limited studies focused on engine oil quality control using infrared (IR) spectroscopy have been published. For instance, FTIR and atomic absorption spectroscopy were used to differentiate between expensive and low-priced oils [7]. Near-IR spectroscopy (NIRS) and mid-IR spectroscopy coupled with chemometric methods have been proven to be powerful techniques for lubricant authentication, which are highly recommended for the quick monitoring of the parameters that determine engine oil quality [8]. Common instrumental analysis techniques such as gas chromatography, high-performance liquid chromatography, nuclear magnetic resonance spectroscopy, and mass spectrometry have been widely used for analyzing engine oils [14]. Such techniques are rather expensive and time-consuming and might have a high environmental impact. The advent of FTIR spectroscopy has facilitated the possibility of developing quantitative methods for lubricant analysis. Chemometric tools such as principal component analysis (PCA) are used to enhance the sensitivity of spectroscopic techniques by studying the full spectra of the studied samples. Bassbasi et al. used FTIR spectroscopy coupled with chemometric methods for analyzing high-quality 10W-40 engine oil that is adulterated with low-quality oil [12]. NIRS coupled with multivariate analytical algorithms have been used to evaluate the efficiency of different methods for engine oil classification based on their base stock (mineral, synthetic, or semi-synthetic) and kinematic viscosity at low and high temperatures. The results showed that partial least squares (PLS) regression based on the IR spectra represents a suitable analytical method for obtaining the extent of adulteration in high-quality engine oils in the concentration range from 0 to 36% (w/w), with prediction errors being lower than 3% (w/w). PLS discriminant analysis provided good classification results with 100% success in class prediction in the spectral range of 1800–600 cm^{-1} and in the concentration range of 0–20% w/w for the two tested oil adulterants in their binary mixtures with the high-quality oil. The proposed method can be employed for the quality monitoring and control and rapid screening analysis of adulterated engine oils [12]. Time-resolved fluorescence spectroscopy was implemented for classifying engine oils based on their viscosity grade [6]. FTIR spectroscopy has also been utilized for identifying the engine oil additives, such as ZDDP and polyisobutylene succinamide, along with other parameters such as the specific gravity, kinematic viscosity, flash point, and total base number [13]. In this work, attenuated total reflection (ATR)-FTIR spectroscopy coupled with PCA will be used for the assessment of different engine oils based on the commercial brand and the viscosity grade (Table 1). In contrast to transmission (used in [8]), ATR is a very simple, reproducible, and accurate analysis method, and has informative bands in the ranges of 1100–1800 and 2600–3100 cm^{-1}.

Experimental. Engine oil samples of 15 commercial brands available in the Jordanian market were collected, and their corresponding viscosity grades were noted. In many cases, oils from two different batches of each grade of a given commercial brand were obtained. The studied brands were chosen based on popularity and price. The samples were purchased directly from the exclusive importers in Jordan. The studied samples are listed in Table 2. All IR measurements were performed in the ATR mode of a Bruker Alpha FTIR spectrometer equipped with a deuterated triglycine sulfate detector and a zinc selenide window. All FTIR spectra were collected in triplicate in the range 4000–600 cm^{-1} with a resolution of 4.0 cm^{-1} against air as the background. Three samples of each oil listed in Table 2 were studied using ATR-FTIR spectroscopy as explained above. Each sample was IR scanned in triplicate and then averaged so that it can be used for PCA. All collected spectra were background corrected. For data processing and analysis, MATLAB 7.0.4 (MathWorks, MA, USA) with PLS Toolbox 4.0 (Eigenvector Research Inc., WA, USA) software was used. Several data sets were created whenever spectral signature comparisons were needed.

Results and discussion. *Assessment of oils based on the commercial brands.* This assessment aims to examine the ability of ATR-FTIR spectroscopy coupled with PCA to differentiate among the oils of different commercial brands having similar viscosity grades. Four different viscosity grades were chosen for the study: 0W-20, 5W -20, 5W-30, and 10W-40. Four oils of three commercial brands of the 0W-20 grade were studied (Ati Realy, Veedol [two batches], and Totachi). The FTIR spectra in the range 3550–600 cm^{-1} for these samples are shown in Fig. 1, which indicates that all oil samples have almost identical spectral features. The bands in the range 2850–2960 cm^{-1} are attributed to symmetric and asymmetric stretching vibrations of the C–H bond in CH_2 and CH_3. The bending vibrations of CH_2 and CH_3 groups appear in the range 1200–1500 cm^{-1}. The band at 722 cm^{-1} also corresponds to the hydrocarbons. The FTIR spectra also show the presence of additives. The bands at 1744 (C=O), 1228 (C–O), 1169, and 1154 cm^{-1} can be attributed to the presence of viscosity modifiers that belong to the polymethacrylate family. The bands at 660 and 970 cm^{-1} are assigned to the P=S and P–O–C vibrations in ZDDP. Nevertheless, differentiating among the oil samples based on a visual investigation of the spectra is very complicated and difficult especially for a large number of oil samples. Hence, PCA was used to distinguish among these samples. The FTIR spectral data of the above samples were arranged in a two-dimensional data set (12 columns×1666 rows) and saved in a Microsoft Excel file prior to conducting PCA. When applying PCA, only the first few principal components (PCs) are usually examined. More than 99% of the total variation in the data set were captured within the first 5 PCs. The best PCA score plot obtained in terms of the successful clustering of the oil samples that belong to same oil brand is shown in Fig. 2. This plot was constructed using PC4 and PC5, which account for only ~3.5% of the total variation in the data set. This reflects the high similarities among the spectra expressed by the earlier PCs. In general, samples having identical composition and hence identical spectra tend to form an independent cluster in the PCA score plot. The greater the distance between two clusters, the higher is the difference in their compositions. In Fig. 2, four well-resolved clusters can be clearly recognized, with each cluster representing a particular commercial brand. Samples 1–3 belong to Ati Realy, which is a low-priced oil, samples 10–12 belong to Totachi, and the Veedol samples of each batch number formed two additional independent clusters. The obtained PCA score plot suggests that the assessment of the oils of different commercial brands of the 0W-20 grade is possible. The other grades (5W-20, 5W-30, 20W-50, and 10W-40) were also analyzed in the same manner. For these analyses as well, almost no significant spectral differences were noted through the visual investigation. Therefore, PCA was applied to the spectral data sets of all commercial brands of each viscosity grade. The resulting PCA score plots for these grades showed almost complete differentiation of each commercial brand, as summarized in Table 1. However, for grade 20W-50, the successful clustering was about 70% obtained using 42 oil samples; this might be explained based on the fact that the additives used in manufacturing oils of this grade are less diverse from those used in manufacturing oils of the other grades. The PCA score plots of these grades were described in Table 1. Based on the results in Table 1, the assessment of engine oils of different commercial brands of a given viscosity grade was successfully achieved using FTIR spectroscopy coupled with PCA. The resulting PCA score plots can be used as calibration models for identifying engine oil samples in the future.

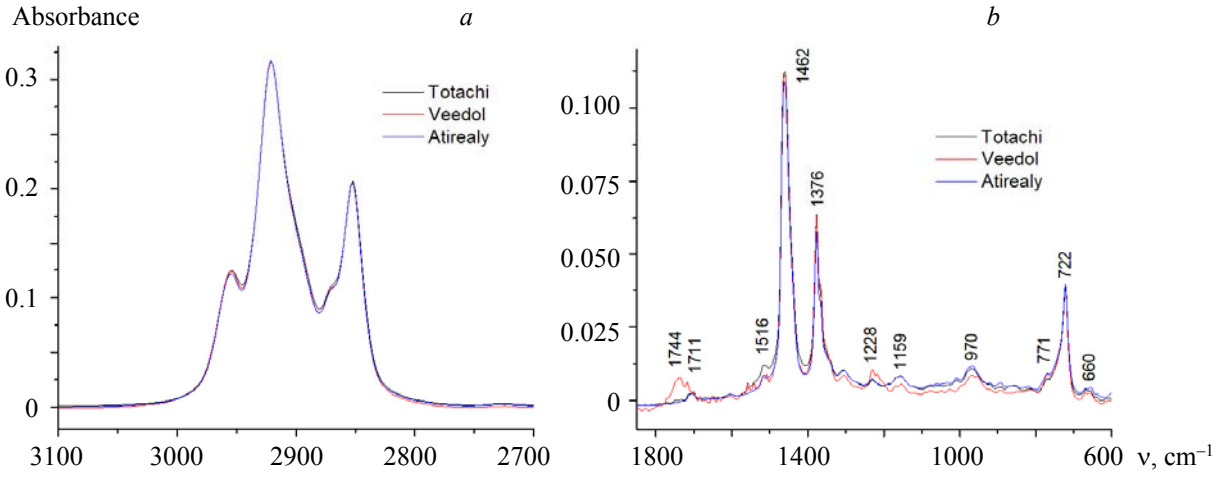

Fig. 1. The FTIR spectra of 0W-20 engine oils in the range 2700–3100 (a) and 600–1850 cm^{-1} (b).

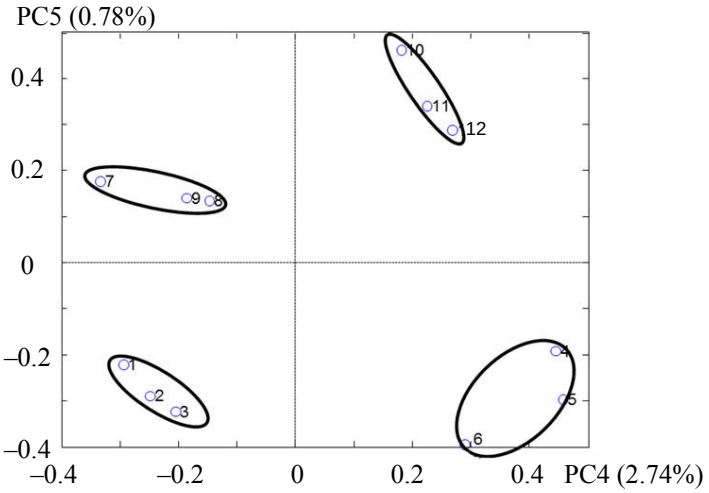

Fig. 2. The PCA score plot applied to the data set containing the FTIR spectral data for the studied engine oils of grade 0W-20: samples 1–3 (Ati Realy [low-priced]), samples 4–6 (Veedol), samples 7–9 (Veedol), and samples 10–12 (Totachi). The two clusters of Veedol are from different batches.

TABLE 1. Details of the Studied Engine Oils and the Percent of Successful Clustering According to their Commercial Brands

Grade	Commercial brand	Number of samples	PCs used in the PCA score plot	% of successful clustering
0W-20	Ati Realy, Veedol*, Totachi,	12	PC4, PC5	100
5W-20	Liqui Moly*, Veedol, Ford*, Totachi*	21	PC3, PC4	100
20W-50	Liqui Moly*, Veedol*, Totachi*, Zinol, Meguin, Rexco, Atlantic, Valvoline, Mobile special*, Shell	42	PC3, PC6	70.6
5W-30	Shell*, Mobile, Ford, Totachi*, Valvoline, Veedol*, Liqui Moly, Meguin*	36	PC4, PC5	92.3
10W-40	Mobil*, Madrid*, Ford, Totachi*, Valvoline, Shell* Zinol*, Wurth*, Veedol*, Arco, Liqui Moly*, Meguin*	63	PC5, PC6	98.6

*Two different batch numbers were studied, with three samples from each batch being used.

Assessment of oils based on the viscosity grade. For the purpose of quality control, a question to be addressed was whether the differences in the viscosity grades of oils of a given commercial brand can be identified using the proposed method. In an attempt to answer this question, the available grades of some oils in the Jordanian market have been studied in this section. Table 2 lists the studied brands and their viscosity grades. Once again, the collected FTIR spectra for all studied grades were visually inspected. The FTIR spectra of oils of grades 20W-50, 5W-20, 5W-30, and 10W-40 of Liqui Moly are displayed in Fig. 3. In general, the spectra reveal almost identical features except for the spectra of the 5W-20 grade, which shows an additional broad band extending from 3000 to 3700 cm^{-1}. This band may be attributed to the N–H stretching in polyisobutylene succinimide, an additive that serves as a dispersant, which disperses carbon soot and prevents sludging in engine oils. The presence of polyisobutylene succinimide also causes an additional band to appear at 1640 cm^{-1}, which corresponds to the N–H bending vibration. Nevertheless, since no clear visual differences can be detected in the FTIR spectra, PCA was employed. Spectral data of all samples of the different grades of Liqui Moly were concatenated in a single data set of 21 columns and 1666 rows. The best resulting PCA score plot (Fig. 4) was obtained upon using PC1 and PC4, which account for about 96% of the total variation in the data set. Figure 4 illustrates that the PCA score plot shows six well-resolved clusters. Each cluster in the plot represents a particular viscosity grade of Liqui Moly. Different batches of the same grade were clustered independently. Samples 1–3 and samples 4–6 are from two different batch

TABLE 2. The Studied Engine Oil Samples Categorized According to their Viscosity Grade

Commercial brand	Viscosity grade	Number of samples	% of successful clustering
Shell	5W-30* 20W-50* 10W-40*	18	100
Mobil	20W-50* 5W-30 10W-40*	15	100
Ford	10W-40 5W-30 5W-20*	12	91.6
Totachi	5W-20* 20W-50* 5W-30* 10W-40* 0W-20	27	92.6
Valvoline	10W-40 20W-50 5W-30	9	89
Zinol Wurth	10W-40* 20W-50 10W-40*	9 6	100 100
Liqui Moly	5W-30 5W-20* 10W-40* 20W-50*	21	100
Meguin	20W-50 5W-30* 10W-40*	15	100
Veedol	5W-20 20W-50* 5W-30* 10W-40* 0W-20*	27	72.5

*Two different batch numbers were studied, with three samples from each batch being used.

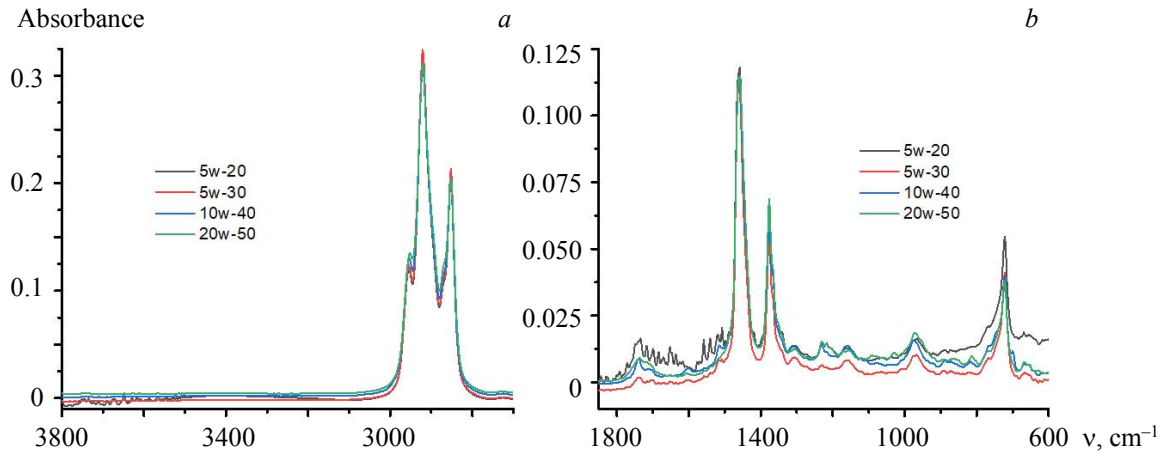

Fig. 3. The FTIR spectra of the different viscosity grades of Liqui Moly in the range 2700–3800 (a) and 600–1850 cm^{-1} (b).

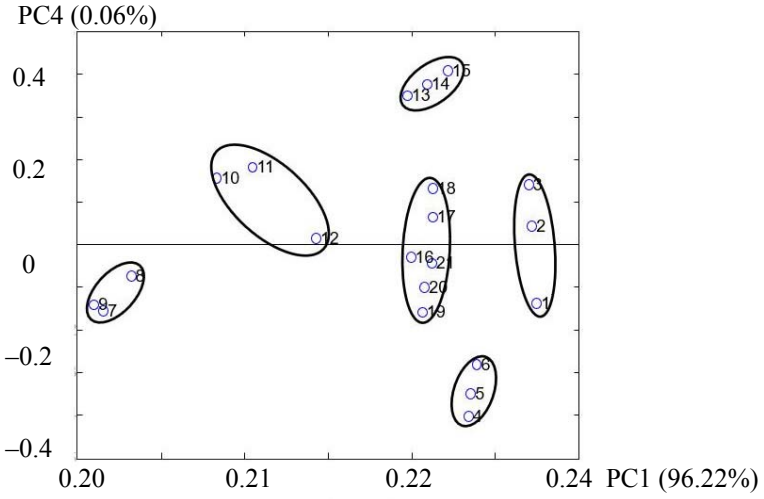

Fig. 4. The PCA score plots applied to the data set containing the FTIR spectral data for the studied engine oils of Liqui Moly of grades (samples 1–3) 20W-50, (samples 4–6) 20W-50, (samples 7–9) 5W-20, (samples 10–12) 5W-20, (samples 13–15) 5W-30, (samples 16–18) 10W-40, and (samples 19–21) 10W-40.

numbers of the viscosity grade 20W-50 of Liqui Moly. The two batches from grade 5W-20 also formed two separate clusters (samples 7–9 and samples 10–12), samples (13–15) from the grade 5W-30 were also clustered in a standalone cluster, while all samples from grade 10W-40 (samples 16–21) were clustered in almost a single cluster although they belonged to two different batches. This PCA score plot was successful in identifying 100% of the studied samples of Liqui Moly according to the viscosity grade. Very close clustering scenarios for identifying the viscosity grades were also obtained for the rest of the studied oils, as can be seen in Table 2.

Low-priced oils. One of the objectives of this study is to differentiate among expensive and low-priced oils. This can be achieved by identifying a special FTIR feature for the low-priced oils that distinguishes it from expensive oils. As reported above, the low-priced oils were easily distinguished from the other expensive oils of the same grade due to the formation of independent clusters in the PCA score plots. Each low-priced oil used in this study has the same viscosity grade as displayed in Table 3. Therefore, the viscosity grade assessment was not conducted for the low-priced oils. Hence, the FTIR spectra of the low-priced oils spectra were compared with each other to confirm whether they contain the same oil under different commercial brands; especially, these oils were produced and imported from the same country. Figure 5 shows the FTIR spectra for the five low-priced oils. The spectra are almost identical with very slight variations in the characteristic bands of some additives. Therefore, the spectral data of these oils were used in constructing a data set of dimensions of 5 columns×1666 rows to be used for PCA. The best resulting PCA score plot was obtained using PC2 and PC3, as displayed in Fig. 6. Successful clustering of the five oils was achieved using only less than 0.1% of variation in the data set. For additional investigation, loading plots were created to evaluate the contribution of the wavenumbers to the PCA score plots. For example, Figs. 7a and b represent the loadings on PC4 and PC5 shown in Fig. 2, respectively, while Figs. 7c,d represent the loadings on PC2 and PC3 shown in Fig. 6, respectively. The loading plots display the wavenumbers that are considered to be responsible for the assessment of oil samples based on the viscosity grade or commercial brand.

TABLE 3. The Studied Low-Priced Engine Oil Samples

Commercial brand	Viscosity grade	Number of samples	% of successful clustering
Rexco	20W-50	3	100
Ati Realy	0W-20	3	100
Atlantic X	20W-50	3	100
Madrid Max	10W-40	3	100
Arco	10W-40	3	100

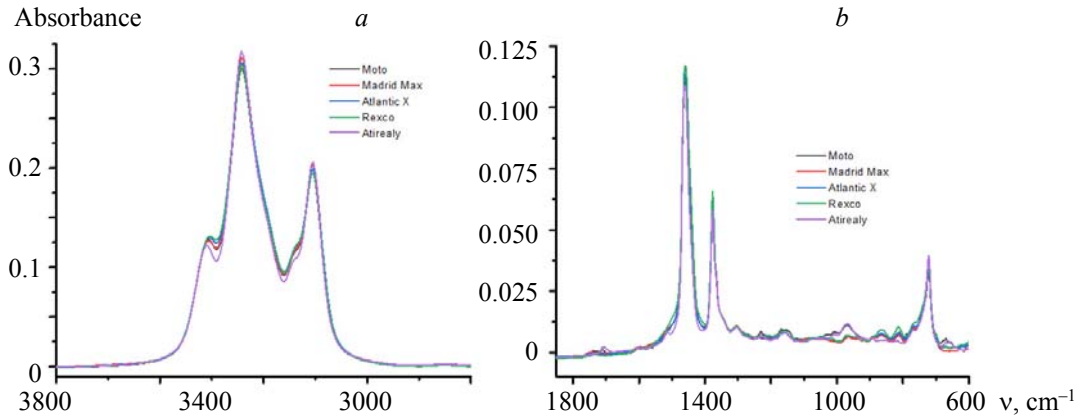

Fig. 5. The FTIR spectra for the five low-priced oils in the range 2700–3100 (a) and 600–1850 cm^{-1} (b).

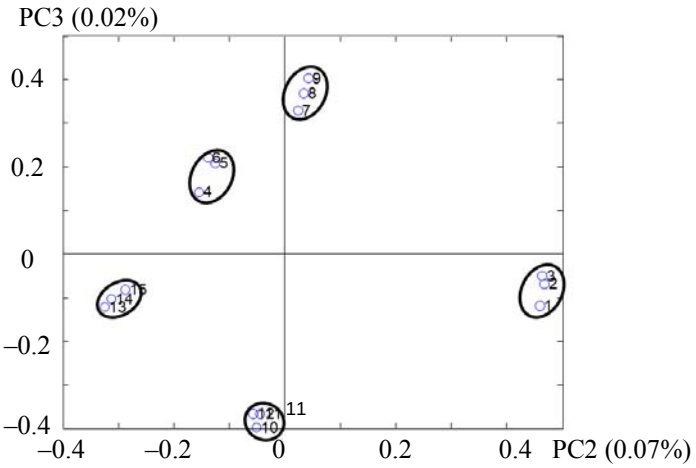

Fig. 6. The PCA score plots applied to the data set containing the FTIR spectral data for the low-priced engine oils of (samples 1–3) Ati Realy (0W-20), (samples 4–6) Atlantic X (20W-50), (samples 7–9) Madrid Max (10W-40), (samples 10–12) Moto (10W-40), and (samples 13–15) Rexco (20W-50).

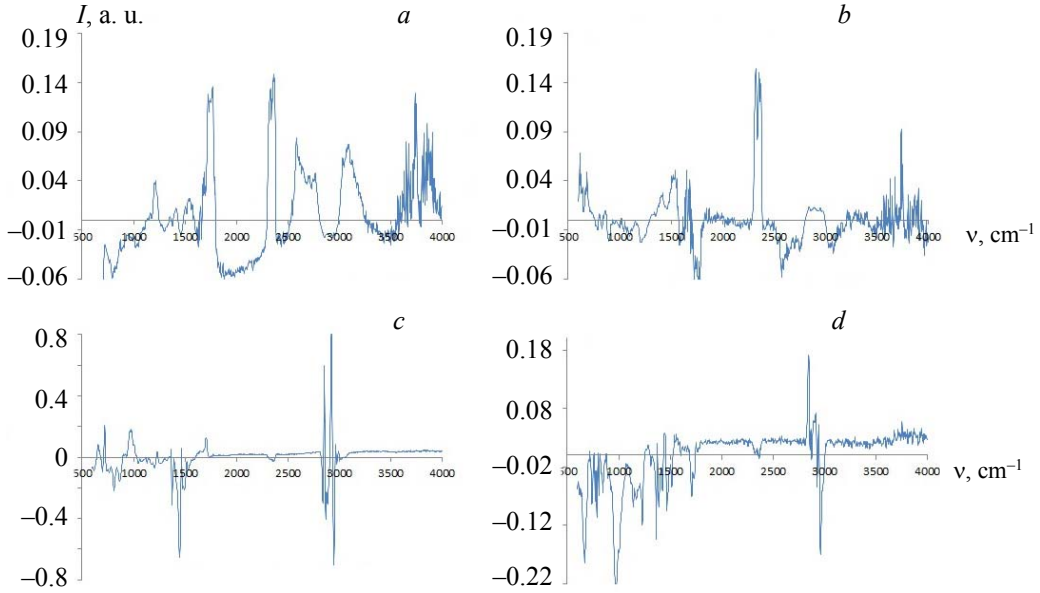

Fig. 7. The loadings on PC4 (a) and PC5 (b) used in Fig. 2, and PC2 (c) and PC3 (d) in Fig. 6.

As shown in Fig. 7, the loadings on each PC used for creating the PCA score plots showed relatively weak contribution for specific wavenumbers in the assessment process. This result was also found for the remainder of the obtained PCA score plots. Thus, PCA is capable of revealing the differences between viscosity groups of the studied samples but cannot provide the wavelength-specific differences and, hence, the physicochemical origin of those differences.

Conclusions. Visual investigation of the FTIR spectra of all studied oils revealed no significant differences, requiring PCA to be implemented. The oils were classified based on two criteria: commercial brand and viscosity grade. The resulting PCA score plots enabled the differentiation among oils of different commercial brands used in this study. Low-priced oils were also identified based on the formation of corresponding independent clusters in the PCA score plots. The different viscosity grades of oils of a specific commercial brand were also successfully differentiated using the proposed method. The assessment of the oils based on the viscosity grade is also important for quality control.

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