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Application of chemometrics and FTIR for determination of viscosity index and base number of motor oils

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ABSTRACT

The viscosity index (VI) and the base number (BN) of motor oils are the most important parameters to be measured in order to assess their performance and service time. Both parameters were simply obtained for virgin and recycled motor oil samples using multivariate calibration based on the FTIR data. Analysis showed that the PLS-1 has outperformed CLS and PCR for the oil parameters prediction. Five and four PLS-1 latent variables were found optimum to obtained the VI and the BN from the FTIR data; respectively. With high accuracy (99–102%) and precision (3–11%), the BN could be determined over the range 4.57–16.45 mg KOH g^{-1} and the VI over the range 96–153. The outputs of the PLS-1 were found comparable to those obtained by the expensive and time-consuming ASTM methods. This developed method is highly recommended for quick monitoring of the motor oil quality parameters.

1. Introduction

Motor oil is vital for maintaining optimum engine performance [1]. Motor oil has many valuable functions, these include: (1) protecting the engine from the effects of heat, pressure, corrosion, oxidation and contamination, (2) providing a fluid barrier between moving parts, reducing friction and wear, (3) cleaning the interior of the engine by removing dirt, wear and combustion contaminants [1,2], and (4) 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, ashless dispersants, zinc dithiophosphate, anti-oxidant/anti-wear, friction modifier, viscosity modifier, antifoam and pour point depressant [2–4].

However, the purpose of detergents in crankcase oils is: (a) to suspend/disperse oil-insoluble combustion products, such as sludge or soot and oxidation products, (b) to neutralise combustion products (inorganic acids), (c) to neutralise organic acids products of oil degradation processes and (d) to control rust, corrosion and deposit-forming resinous species [5,6]. Therefore, it is an important task to assure the motor oil quality. However, the main motor oil physicochemical characteristics are covered under the American Standards for Testing and Materials (ASTM) guides. These are: ASTM D2896 [7], ASTM D445 [8] and ASTM D2270 [9]. The base number (BN) is expressed as mg KOH g^{-1} of additive. It is measured using a potentiometric method (e.g., ASTM D2896 [7]). This test method covers the determination of basic constituents in petroleum products by titration with perchloric acid in glacial acetic acid using a potentiometric titrator. This test method can be used to determine base number up to 300 mg KOH g^{-1}.

For liquids, the viscosity increases as the temperature decreases and vice versa [10]. Variable thickness of oil by viscosity modifiers at low and high temperatures allows the formulation of multigrade oils. The multigrade oils are designed to provide adequate viscosity at high temperatures for engine protection and low viscosity at low temperatures for easy stability. The viscosity index (VI) is used as a measure of oil's response to temperature changes. In addition to affecting the viscosity temperature relationship, viscosity modifiers affect a lubricant's other properties. These include pour point, dispersancy and fuel economy [9].

However, the BN and the VI testing are 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 BN and the VI of motor oil based on the use of the FTIR analysis along with multivariate method was developed and tested. The FTIR spectroscopy is the fastest and cheapest of the spectroscopic tech-

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niques 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 [11,12].

Infrared spectroscopy has always had a place in lubricant analysis to characterise various constituents qualitatively. With the advent of FTIR spectroscopy, the possibility of developing quantitative methods of lubricant analysis has been facilitated [13]. This is because of the inherent computing power of FTIR instruments, advances in sample handling techniques and the availability of new chemometric methods to facilitate quantitative analysis [14]. In subsequent work, an FTIR method for the determination of acid number (AN) in mineral-based lubricants [15,16] was developed. This method is based on the use of differential FTIR spectroscopy to measure carboxylate anion formation (COO^-) upon addition of KOH to oils in which carboxylic acids are present as a result of oxidation. In effect, the Fourier transform infrared-acid number (FTIR-AN) method mimics the acid/base ASTM-AN procedure but is much more rapid and accurate. Reagent-based FTIR analyses of this type have great promise as a means of developing a variety of new methods for analysing important lubricant parameters [15]. In this paper we develop a simple analytical method based on the FTIR and the chemometrics in order to estimate the BN and the VI for motor oil samples.

Recently, multivariate calibration has been applied for analysing 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 [17–28]. 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 [25–28]. 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 classical least squares (CLS), inverse least squares (ILS), principal-component regression (PCR), partial least squares (PLS) and net-analyte signal (NAS) [17–23].

This indicates that the conventional calibration procedures would have a limited application for quantitative determinations. Therefore, the simultaneous determination of these overlapped motor oils requires (a) ASTM methods or (b) the application of a multivariate calibration technique for the resolution of the complex system. The second option was chosen in this study owing to its simplicity, quick and low cost.

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 ASTM 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 [28]: (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 ASTM methods.

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

2. Experimental

2.1. ASTM methods and FTIR analysis

Key American Standards for Testing and Materials (ASTM) chemical methods such as the determination of the BN [7] and the VI [9] were carried out. All tests were carried out in triplicate.

The FTIR spectra were taken using a Shimadzu IR Prestige-21/FTIR-8400S. A small quantity (2 μL) of the sample was deposited with the use of a Pasteur syringe between two well-polished KBr disks (liquid cell), creating a thin film with a spacer of 0.05 mm thickness. Duplicate spectra were collected for the same sample. All spectra were recorded using a Shimadzu IR Prestige-21 Windows Software.

The FTIR spectra of the oil samples were recorded over 400–4000 cm^{-1} range with 20 cm^{-1} interval to end up with 182 points per spectrum. These tests were conducted at the laboratories of the Royal Scientific Society (RSS), Amman, Jordan. The multivariate calculations were carried out using MATLAB (version 7.0). For more validation to our analysis, the multivariate analyses were repeated using UNSCRAMBLER® software and similar results were obtained for all trials.

2.2. Samples

Twenty oil samples were used in the calibration and another ten samples were selected for prediction. These samples were carefully selected among 350 samples that have been monitored in our laboratory at the RSS. The oil samples of the chemometric study were selected according to the following criteria: (a) maximum variation in the BN and the VI, (b) different oil brands and (c) half of the selected samples were virgin motor oils and the other half was recycled motor oils. The chemical analyses that carried out for the oils samples are presented in Table 1. It is worth to mention that the ranges of the BN and the VI in the prediction set were fall within the ranges used in the calibration step (see Table 1).

Independent analyses of the seven motor oil samples by the multivariate calibration and the ASTM methods were carried out. Accordingly, in order to assess the accuracy and precision of the proposed method, the *t*-test and the *F*-test were applied to the results, respectively. The selected seven samples were obtained from different popular oil stations in Amman. Three determinations were carried out for each sample.

2.3. Data analysis

Initially, the spectral absorbances of the motor oil samples were pre-processed in order to improve the quality of the calibration. The following pre-processing steps were carried out: (a) the noise and the negative absorbance values in the spectra were removed or minimised by applying 10-points window Savitzky-Golay [12] filter and (b) the data (the spectra and the reference values) were mean-centred. After gathering the whole data, three different matrices of sizes 20 × 182, 10 × 182 and 7 × 182 which represent the calibration, validation and real mixtures, respectively, were developed. Two separate vectors collecting from the calibration (20 × 1) and the validation (10 × 1) reference values of the BN and the VI were also obtained. At the start, the simple CLS model was applied to the data and the regression matrix ($\mathbf{K}$) was calculated as [12]: $(\mathbf{C}^t\mathbf{C})^{-1}\mathbf{C}^t\mathbf{A}$, where $\mathbf{C}, \mathbf{A}$, t are the matrix of reference values of the BN and the VI, matrix of all samples measured at 182 wavenumbers and t stand for transpose. The prediction of the reference values were obtained as [12,23]: $(\mathbf{KK}^t)^{-1}\mathbf{K}^t\mathbf{A}_{un}$, where $\mathbf{A_{un}}$ represent the spectra of the unknown samples. The accuracy and the precision of the CLS model for quantifying the VI and the BN were estimated by comparing the obtained data with the outputs of the ASTM methods.

Table 1
Chemical analysis of 30 motor oil samples by reference methods.[a]

Sample no.	Base number[b] (mg KOH g^{-1})	Viscosity index[b]	Status[c]
Calibration set[d]			
1	12.16	109	Virgin
2	11.36	139	Recycled
3	5.83	103	Virgin
4	7.28	101	Recycled
5	6.14	150	Virgin
6	6.34	97	Recycled
7	10.43	96	Virgin
8	12.97	136	Recycled
9	6.61	128	Virgin
10	6.61	126	Recycled
11	11.75	98	Virgin
12	6.54	105	Recycled
13	10.78	96	Virgin
14	13.29	101	Recycled
15	11.24	104	Virgin
16	8.14	128	Recycled
17	11.19	104	Virgin
18	8.07	153	Recycled
19	16.45	102	Virgin
20	4.57	98	Recycled
Validation set[d]			
21	11.12	128	Virgin
22	11.13	98	Recycled
23	9.56	99	Virgin
24	8.44	98	Recycled
25	8.28	144	Virgin
26	11.59	120	Recycled
27	10.40	122	Virgin
28	6.79	134	Recycled
29	6.14	109	Virgin
30	11.46	158	Recycled

[a] ASTM D2896 [8] and ASTM D2270 [10] were applied to obtain BN and VI, respectively.
[b] Average of three trial (R.S.D. < 3% in all cases).
[c] The status of the motor oil was evaluated according to Al-Ghouti and Al-Atoum's procedure [3].
[d] Samples: 1–20 used for calibration and 21–30 were left for validation.

Inverse calibration models including the PCR and the PLS-1 were applied separately to the spectral data and the general equation that used in the prediction was [12]: $\mathbf{c}_{\text{un}} = \mathbf{pA}$, where $\mathbf{p}$ is the calibration vector that estimated for each parameter using the PCR and PLS-1 algorithms and $\mathbf{c}_{\mathbf{un}}$ is the concentration of the unknown samples. The multivariate analysis was applied over the whole range (400–4000 cm^{-1}) using 182 points per spectrum. No attempt was made to select sub-regions, for the whole range as the case in many published papers [12,28]. Detection of outliers or clusters in the samples was employed by the graphical representation of the most important principal-component factors [28].

Finally, the best calibration model among the CLS, PCR and PLS-1 was used to find the BN and the VI for the new motor oil samples. The results of the PLS-1 method were statistically compared with the highly accurate ASTM methods outputs. The economical analysis was also involved in this study.

3. Results and discussion

The FTIR spectra of the motor oil samples were recorded over the range (400–4000 cm^{-1}) and are illustrated in Fig. 1. For more clear FTIR graphics, the full spectra are divided into three regions: 3050–2750, 1800–1500 and 1300–600 cm^{-1}. The spectra of the motor oils were strongly overlapped within the entire spectral region and no certain wavenumber can be found.

3.1. Multivariate calibration

Before running the multivariate calibration, a univariate calibration at certain informative spectral points was tested. A number of wavenumbers were carefully selected from the motor oil spectra where a large spectral change with reference values (either BN or VI) is observed and the results are shown in Fig. 2. For the VI, the largest variation in the spectral data was observed at: 721, 821, 860, 981, 1381, 1460 and 1701 cm^{-1} (see Fig. 2). The maximum variation was observed at 1701 cm^{-1} where absorbance value was

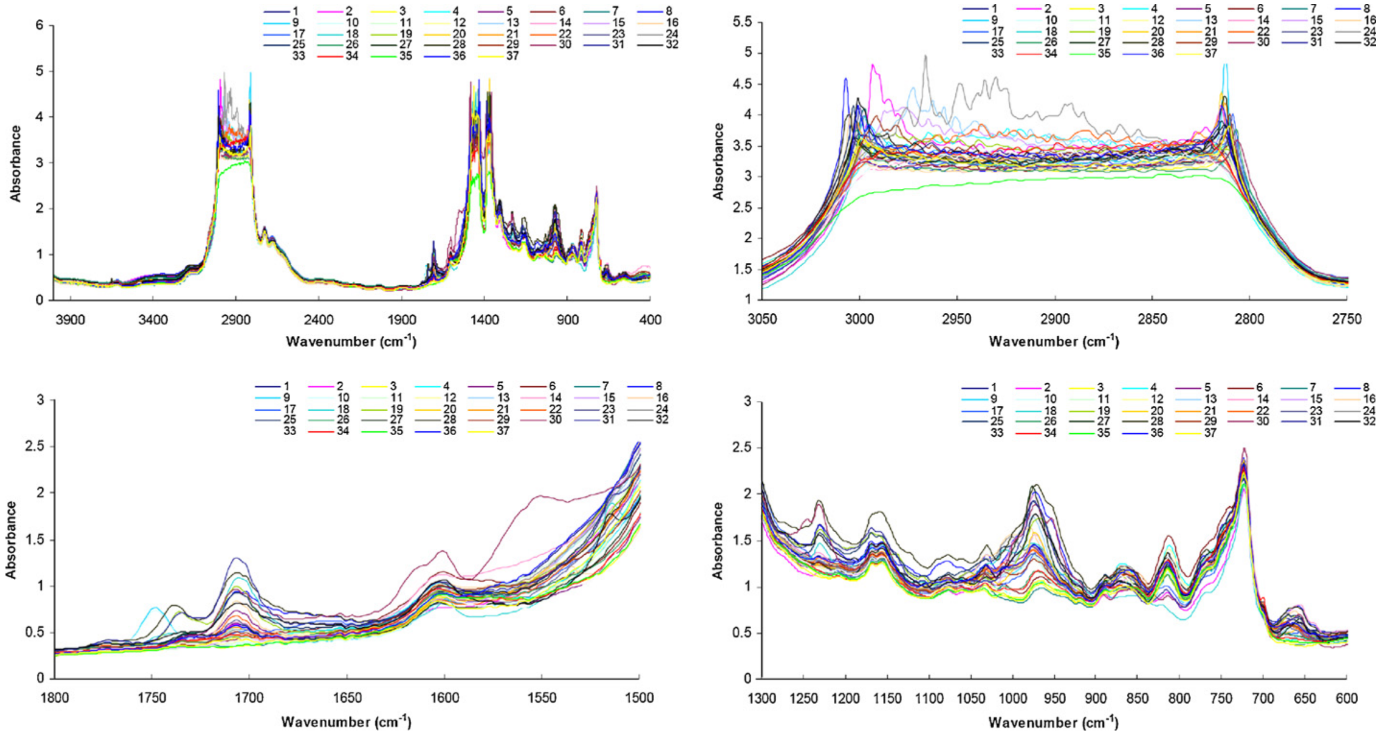

Fig. 1. Fourier transform infrared spectra of the motors oils.

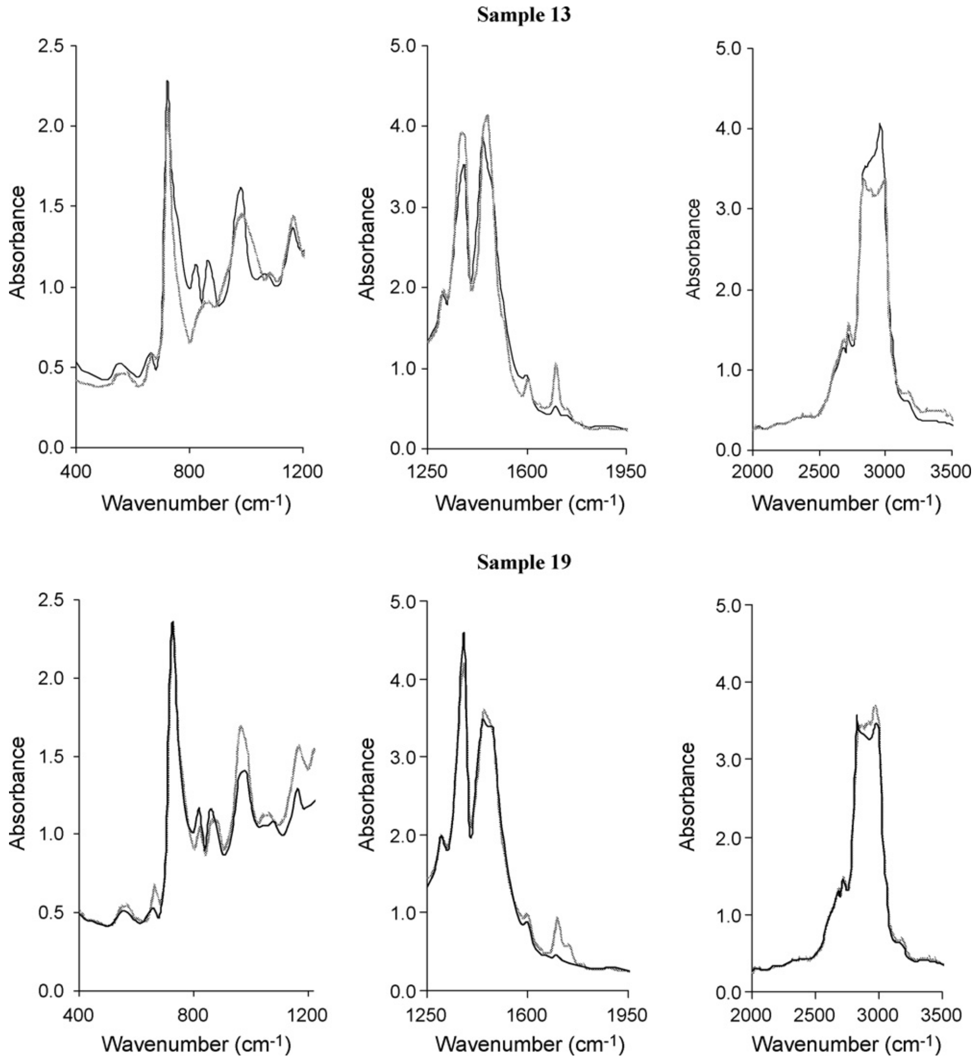

Fig. 2. FTIR spectra of the sample 13 (solid line, VI = 96) and sample 18 (dashed line, VI = 153). and the sample 19 (dashed line, BN = 16.45) and sample 20 (solid line, BN = 4.57).

increased from 0.54 (VI = 96) to 1.07 (VI = 153). Accordingly, the univariate calibration (the VI versus absorbance at 1701 cm^{-1}) could be carried out at this informative wavenumber. For the BN value, the largest variations were noted at 657, 723, 813, 972, 1355, 1483, 1604 and 1710 cm^{-1} with maximum variation at 1710 cm^{-1}. The univariate calibration at 1701 cm^{-1} for the VI and 1710 cm^{-1} for the BN were constructed from the calibration samples and used to predict the corresponding values in the validation set. Poor correlation values were obtained (0.4221–0.5316) for both parameters and the failure of this calibration was attributed to non-selectivity of the wavenumbers used in the calibration.

3.2. *Determination of the VI and the BN in the validation set*

From the chemometric point of view, the calibration matrix of the high condition number is suffering from high collinearity and cannot be trusted for producing a high calibration quality [28]. For example, the correlation coefficient between absorbance values taken at 1720 and 1721 cm^{-1} for the calibration samples was 0.9202. The condition number of the calibration matrix was very high (23,000) and quite far away from 30, the collinearity-limit set by the chemometricians [29]. This situation necessitates the decomposition of these matrices in order to eliminate the collinearity and unwanted information that would retard the useful calibration. Using the PLS-1 or the PCR methods, the unwanted (or redundant) data in the calibration matrix can be eliminated while keeping those of importance for the BN or the VI. The spectral data were subjected to three chemometric methods (CLS, PCR and PLS-1) in order to find the VI and the BN and the results are shown in Table 2.

As can be noted in Table 2, the performance of the CLS was disappointed for both oil parameters as indicated from high R.S.D. values. Probably, the CLS is the first choice that may come to the analyst's mind in order to calibrate the non-selective systems and this back to the successful application of this model to many FTIR data [28,29]. One essential condition that should be held to apply the CLS is that all components (parameters) should be known beforehand and included in the calibration phase. Accordingly, one should not expect a high prediction power for the CLS in real systems where many unexpected interferences are present. For the PCR, five factors were found to be optimum for the calibration and the estimating oil parameters in the unknown samples. For the PLS-1, five (for the BN) and four (for the VI) latent variables were found to be optimum to generate the best calibration vector for each parameter. The optimum factors and latent variables for the prediction were determined at minimum error of the perdition in the validation set. The results presented in Table 2 indicate that the CLS has a limited application for estimating the BN and the VI from the non-selective 182 spectral points. The PLS-1 has outperformed the PCR and CLS for accurate estimation of oil parameters and this is obvious from

Table 2
Calibration of spectral data by CLS, PCR and PLS-1 for finding VI and BN of motor oil samples.

Model	Calibration set (20 samples)		Validation set (10 samples)	
	VI	BN (mg KOH g^{-1})	VI	BN (mg KOH g^{-1})
CLS	105.2(17.3)	114.2(32.1)	100.2(14.6)	126.5(37.3)
PCR	101.2(12.2)	98.3(8.6)	100.2(12.0)	106.2(17.3)
PLS-1	99.9(5.4)	99.6(3.8)	98.8(9.8)	105.3(10.9)

Average recovery (R.S.D.).
The range of BN in the samples was (4–16 mg KOH g^{-1}) and range of VI was 96–153. For all methods, 182 points were selected to represent the informative regions. 4 PCR factors were used to calibrate BN and VI in the oil samples. 4-PLS-1 and 5-PLS-1 were selected to calibrate VI and BN, respectively.
Outlier samples were detected using principal-component analysis prior chemometric analysis.

the good recoveries and the low R.S.D. values given in Table 2. Simply, the PLS-1 was able to extract useful information and free of noise from the 182 points and this advantage is not available in the CLS methods which assumed a linear relationship between solute concentration in the mixture and the absorbance at each wavenumber. The most important types of nonlinearities that encountered in chemical analysis are [28,29]: (a) curvature in concentration-response function, (b) shift in the position of the absorption band and (c) change in the width of the absorption bands. In fact, the first type of nonlinearities is the most common in chemical analysis and often found in multi-component systems, the case that we have in this study.

3.3. Outliers problem

Detecting outliers and careful selection of the informative spectral bands are necessary to improve the calibration power of the PLS-1 [23,28]. Principal-component analysis was used to detect outliers in calibration, validation, new samples and to view the clustering in samples. Using the PCA, seven non-zero eigenvalues (1.120, 0.0018, 0.0011, 0.0008, 0.0006, 0.0005 and 0.0001) were found after decomposing the calibration matrix of the standard mixtures. As can be noted from the magnitudes of the eigenvalues, the data matrix of both systems can be well-represented using the first two eigenvectors. The statistical analysis revealed that 97% of the total variances in both systems can be presented by the first two eigenvalues. The scatter plot of the PC1 (first principal component or score vector against the PC2 (second principal component or score vector) reveals evident pattern in the oil samples and facilitate detection any potential outlier(s). The PC1-PC2 plot was depicted in Fig. 2 for both systems.

As clearly indicated in Fig. 3, the plot shows two clusters. However, the PCR could not differentiate between the virgin and recycled motor oil samples. For more information about virgin and recycled engine oil differentiation, please see Ref. [2].

3.4. Determination of the BN and the VI in the new samples

For more practical application, the proposed analytical method was applied for the determination of the BN and the VI in seven new oil samples collected from different local stations. For each sample, the target parameters were carefully estimated using the ASTM standard methods and the optimised PLS-1 method. Five determinations were carried out for each individual motor oil sample. The results were given in Table 3.

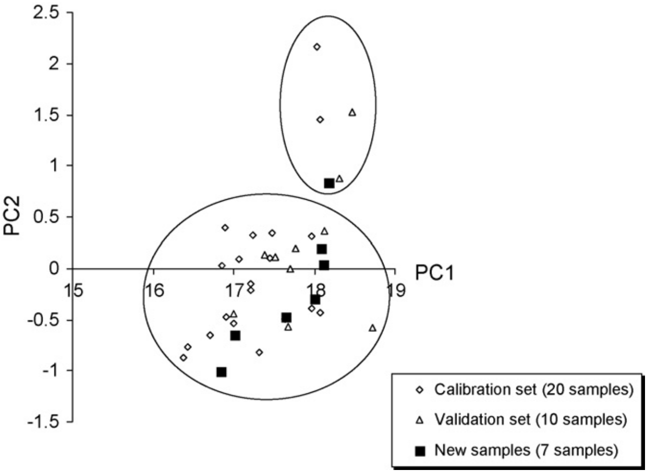

Fig. 3. PC1–PC2 plot for the oil samples.

As clearly indicated in Table 3, the FTIR-PLS-1 method is an effective method in estimating the important motor oil quality parameters without the need for running expensive analyses like those involved in the ASTM methods [7–9]. The results of the t-tests indicate that no significant difference between the ASTM methods and the proposed method for determination of the BN and the VI. The F-test indicated that both methods are having similar precision. It is worth mentioning that the proposed method can be applied for the virgin and the recycled oils which would give a wide applicability of the current method in the motor oil analysis. So it can be concluded that the PLS model for the FTIR data treatment are adequate for the routine control of the motor oil quality. Fig. 4 shows the comparison between the data found by the PLS-1 model and those found by the reference ASTM procedure. It can be seen

Table 3
Analysis of new oil samples using ASTM methods and FTIR-PLS-1 method ($n = 5$) $t(0.05, 8) = 2.31$, $F(0.05, 4, 4) = 9.605$.

Sample	BN (mg KOH g^{-1})				VI			
	ASTM D2896	PLS-1	*t*-Test	*F*-test	ASTM D2270	PLS-1	*t*-Test	*F*-test
1	9.15	8.12	1.2	4.2	125	119	0.6	5.3
2	10.25	10.19	2.0	5.3	134	135	0.9	2.3
3	7.16	7.51	0.6	1.2	100	109	1.4	5.6
4	5.59	5.60	0.9	0.9	122	126	2.1	4.6
5	6.16	5.95	1.2	2.3	104	97	2.1	2.3
6	12.30	11.92	1.4	1.9	109	111	0.6	1.6
7	6.17	6.33	0.3	3.6	132	128	0.7	1.8

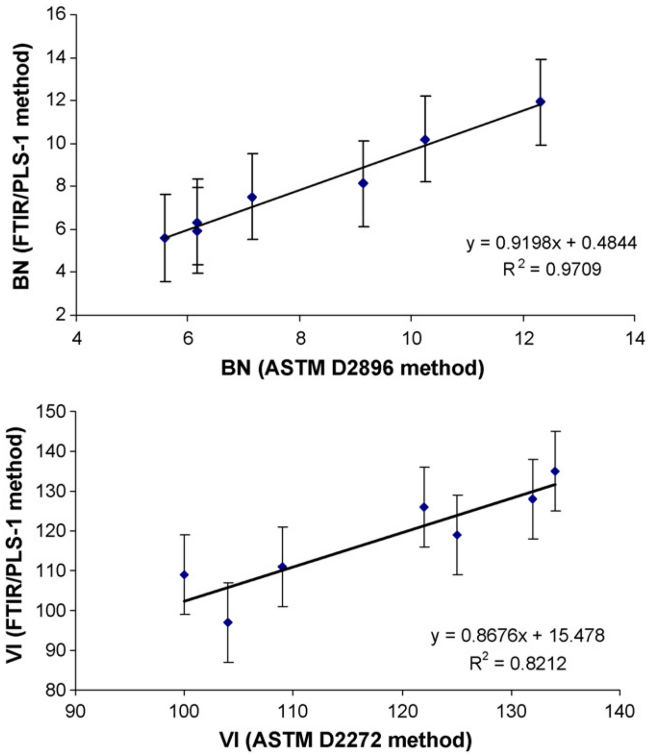

Fig. 4. Comparison between data found for motor oils BN and VI prediction by means the treatment of FTIR data using the PLS-1 model and those found by the reference ASTM procedure.

that the PLS model gives by far more accurate results and strongly precise results.

4. Conclusion

The viscosity index (VI) and the base number (BN) of motor oils are the most important parameters to be measured in order to assess their performance and service time. In this study, the multivariate calibration offered a simple and accurate determination of the VI and the BN for the motor oils without the need for running expensive standard methods. The PLS-1 applied to the FTIR data can be used to find the BN (4–16 mg kg^{-1}) and the VI (96–153) for the motor oils with a good accuracy and precision. The results obtained herewith are expected to be useful for determination and routine tests purposes.

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