



Research Article

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Prediction of viscosity index of motor oils using FTIR spectral data and chemometrics

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Abstract

In order to ensure the quality of motor oils by measuring viscosity index (VI), regulatory agencies and producers need a more precise, easy and cost effective method for monitoring the qualities. Multivariate data analysis based on Fourier transform infrared (FTIR) spectroscopy was reported in this work as an alternative for measuring viscosity index of motor oils. 27 samples of motor oils of different brands were collected from different regions of Bangladesh. Viscosity index of the samples were first determined by the conventional technique. Savitzky-Golay (S-G), smoothing and mean normalization are the three distinct data preprocessing methods and these were assessed to measure their efficiencies by applying them in developing calibration procedures prior to modeling. Artificial neural network (ANN), principal component regression (PCR) and partial least-square regression (PLSR) were then developed using these processed data for determination of viscosity index of motor oils. Results showed that PCR performed best when it used Savitzky-Golay smoothing data. Performance of PLSR was slightly more than that of PCR ($R^2 \approx 98\%$). PLSR ($R^2 \approx 99\%$) had better predictive performance comparing to ANN ($R^2 \approx 97\%$). Among the calibration techniques studied here, PLSR showed the best prediction results with Savitzky-Golay smoothed FTIR spectral data. The method proposed here to determine viscosity index of motor oils requires less staff dedication, shorter turnaround times and lower expenses than conventional approaches.

Keywords: Motor oil, Viscosity index, FTIR spectral data, Chemometrics.

INTRODUCTION

The main aim of motor oil is to reduce the wear of moving parts, clean and inhibit corrosion and to improve sealing. It also carries away the heat from the moving parts and cools the engine ^[1]. Motor oils may be categorized as mineral or synthetic oils. Applications of mineral-based oils are more common than synthetic oils and they can be used in automobile, jet, aircraft, two and four stroke engines, diesel engines in railroad and truck and marine machinery. These natural oils contain hydrocarbon compounds with substantial amount of undesirable nitrogen and sulfur compounds. Hydrocarbons constitute mixtures of straight and branched chain alkanes, cycloalkanes, and aromatics. Polynuclear aromatic hydrocarbons (PAH) and metal-containing constituents are additives for motor and crankcase oils. Used oils have higher percentage of these compounds than the fresh unused oils ^[2].

Quality control and maintaining various additives blended in motor oils or lubricants is not only important from the automobile and engines prospects, but also from the impact of emissions in the environment. Therefore, automobile sectors and regulatory agencies for monitoring must build up precise methods to effectively follow up and monitor the quality of the motor oils and lubricants and most of the methods follow ASTM (American Standards for Testing and Materials) guidelines. antidiabetic, anti-bacterial, antiplasmodial, antihepatotoxic, anti-oxidant, antimicrobial, immunomodulatory, wound healing and anti-cancerous^[5-11] properties.

Viscosity index (VI) is an arbitrary measure for the change of viscosity, resistance to gradual deformation by shear stress or tensile stress, with variations in temperature. The lower the viscosity index the greater the change of viscosity of the oil with temperature and vice versa. It is used to characterize viscosity changes with relation to temperature in lubricating oil ^[3]. So, it is very important to determine viscosity index to test quality of motor oils. But the traditional determination techniques are sometimes very costly, time consuming and not regarded as environment friendly.

One of the analytical techniques which have been mostly used to monitor quality of lubricating oils is FTIR spectroscopy. It is a fast and nondestructive technique and requires simple sample pretreatment procedure. It can be a qualitative analysis of organic compounds as the characteristic vibrational modes of functional groups are responsible for appearing bands in the infrared spectrum at defined frequencies, which is further, affected by the surrounding functional groups. FTIR spectroscopy can be used for quantitative analysis since the intensities of the bands are proportional to the concentration of the analytes as per to Beer's law [4].

At present, multivariate calibration methods have been used for analyzing various chemical compounds such as foods, wastewater, pharmaceuticals, oils and fuels. The method does not require any separation technique for solutes before their analysis but chromatographic methods [5-17] need separation techniques for sample preparations. The most popular multivariate calibration techniques are principal component regression (PCR), partial least squares (PLS), inverse least squares (ILS) and classical least squares (CLS). Among the different calibration methods existing for multivariate calibration, partial least squares regression (PLS) has been used more frequently because of high-performing calibration models. Software is available and can be readily implemented [14, 18-21].

Partial least squares (PLS) are a reasonable choice to resolve overlapping spectrum [22] and is usually considered as a full spectrum method. Although PLS works in such a manner that measured sample properties are functions of intensities of absorption bands. Small variation from linearity can be acceptable but in case of significant non linearity, PLS tends to provide large prediction errors and therefore needs for more effective models. Inherently ANN is applicable in non linear relationship.

ANN [23] works best if it deals with non-linear dependence between the inputs and outputs for modeling. We can generally expect a network to train quite well depending on the nature of the application and the strength of the internal data patterns. This can be applied to the problems in which the relations may be quite non-linear or dynamic. ANN is an analytical alternative to conventional methods which have limited assumptions of linearity, normality, variable independence etc. Because of capturing many kinds of relationships ANN allows the user to quickly and relatively easily model phenomena which otherwise may be very difficult or impossible to explain. However, this method is more complex computationally than linear methods and is limited to fitting and largely depends on both number and quality of data.

Chemometric model could be a cost effective and rapid alternative to existing chemical methods for determining viscosity index (VI). Multivariate analysis is a chemometric technique to improve the understanding of chemical information and to correlate quality parameters or physical properties to analytical instrument data. FTIR is the instrumental technique used in industrial laboratories because of its simplicity. It demands low cost equipment. It is difficult to perform simultaneous analysis of viscosity index by classical spectrophotometric method because of overlapping spectra. Now, multivariate chemometric methods can be proven the techniques which show best performance in terms of these types of raw samples.

Viscosity index which is one of the key quality parameters of motor oil has been determined by various conventional techniques. But in the recent past, different research work has been done to find out a more fast, effective, cheap and suitable technique to measure this quality parameter in order to identify and overcome all the limitations of the previous conventional methods. NIR, MIR and FTIR spectroscopic techniques were coupled with chemometric classification of motor oils mainly to assess their adulteration [24-29]. Quality parameters of motor oil were predicted by FTIR spectral data and chemometric calibration techniques such as PLSR [11-12, 30-36]. But, spectral data have some instrumental noise and they need to be smoothed before regressions with them. Moreover, calibration models do not perform equally in different types of analysis.

Therefore, the present work aims to apply the multivariate data analysis for determination of the VI of the motor oils by FTIR along with PCR, PLSR and ANN methods. The predictive abilities of such multivariate

calibration models were investigated and successfully compared with each other. The proposed methodology is simple, fast and cost effective. It does not generate hazardous wastes, thus makes it a helpful tool for routine analysis in a quality control laboratory.

Materials and Methods

Sample collection

Total 27 motor oils of different brands investigated in the present work were collected from three large cities: Dhaka, Chittagong and Sylhet in Bangladesh. Total samples consisted of three different groups of "burned oil" corresponding to oils obtained from workshops, "fresh oil", and "refined oil" referring to oil which was obtained from burned oil after running it through a filtration system to remove any insoluble impurities. Fresh motor oils were added to the engine and which run for 5000 km, and drained as "burned oils" for experiment. The oil samples were selected according to the maximum variation in viscosity index. The fresh oil shows high viscosity and high distillation temperature. High viscosity oil is heavy and contains less volatile compounds while used oil contains more volatile components comparing to fresh oil [37].

Assay of viscosity index by reference method

Viscosity index (VI) measures the variation in the viscosity with varying temperatures. The oils which have higher VI have lower viscosity change when subjected to different temperatures. VI reference values were estimated as per the standard method described in ASTM D2270-10 [38].

Spectral data acquisition from FTIR

To record the absorption spectra and their absorbance measurements, a Shimadzu-IR 8400S FTIR spectrometer is used covering wavenumber range 4000 cm^{-1} to 660 cm^{-1} . Resolution is 4 cm^{-1} and for each sample three spectra are obtained. They are then averaged to be a mean spectrum, used in subsequent analysis for giving high signal to noise ratio. At the time of measurements the temperature is kept constant at $20\pm 3^\circ\text{C}$. Steady-state humidity is maintained in the work place, as the FTIR instrument is sensitive to the changes of external environmental.

Light absorbance by sample against wave length (wave number) is the main criteria for spectral data. Each spectrum has a huge number of absorbance values for each wave length. Each wave point is regarded as spectroscopic variable.

Preprocessing of spectral data

Different data preprocessing techniques were investigated to optimize the training and predicting performance of class models. Pre-processing of FTIR spectra is typically the first and crucial step in data analysis. After obtaining spectral data from FTIR, they were preprocessed at first using some transformations. In this study, three smoothing techniques like S-G smoothing [39], MN and SNV [40] were used and their efficiencies were determined.

PCA analysis

PCA most frequently used in chemometrics reduces dimensionality of data through latent variables, principal components (PCs). The main object of PCA is to reduce the dimensionality of a data set which consists of a large number of variables to a smaller number but it retains the variation as much as possible in the data set. PCs are uncorrelated and they are ordered so that first few holds most of the variation present in all original variables. In doing this, measured variables are converted into new variables defined as scores.

Chemometric calibration techniques

Principal components regression (PCR)

PCR is a technique for analyzing multiple regression data that suffer from multicollinearity. It is carried out by two-steps. PCA of spectral data matrix is performed first. The measured variables are converted into new scores on latent variables. Multiple linear regressions (MLR), in the second step, between the scores and measured viscosity index is carried out.

Partial least square regression (PLSR)

The main function of PLS regression is to find the components from X (independent variables) that best predict Y (dependent variable). PLS regression searches for a set of latent vectors that performs a simultaneous decomposition of X and Y with the constraint that these components explain as much as possible of the covariance between X and Y. The step generalizes PCA. It is followed by a regression step where the latent vectors are used to predict Y. Both X and Y as a product of a common set of orthogonal factors and a set of specific loadings are decomposed by PLS regression decomposes [41].

Artificial neural network (ANN)

ANN is a technology that is similar to the human brain and nervous system in learning from experience. In the situations when the problem needs qualitative or complex quantitative reasoning where the conventional statistical and mathematical methods are not enough or the parameters are highly independent and data is intrinsically noisy, incomplete or error prone ANN is more powerful than traditional methods. ANN is an interconnected group of nodes and data processing system based on the structure of the biological neural simulation learned from the data generated experimentally or using validated models [42].

Levenberg-Marquardt back-propagation neural network was used in this study. 10 are number of hidden neurons and sigmoid activation function was used in each training set. Training usually stops when generalization stops improving when indicated by an increase in the RMSE of the validation samples. For model development, validation and test by ANN, spectral data from FTIR and viscosity index of different motor oil samples are considered as raw data for the study. Out of 27 motor oils 18 (eighteen) samples were used for development of the model. Remaining 9 (nine) samples were used to validate the developed model as shown in the Table 1. Root mean squared error (RMSE) and coefficient of determination (R^2) were used in the present study so as to measure the performance of chemometric models. CAMO the Unscrambler software (version 10.3) was used for calibration and validation of PCR and PLSR and all calculations for ANN model were implemented in Matlab (version 2016a).

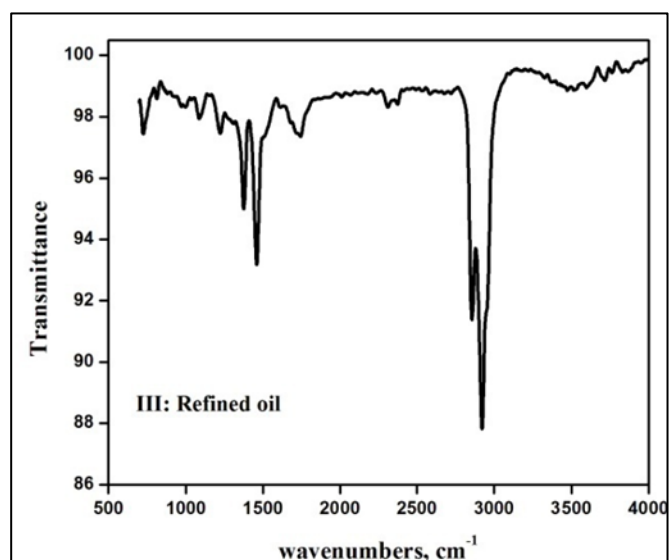
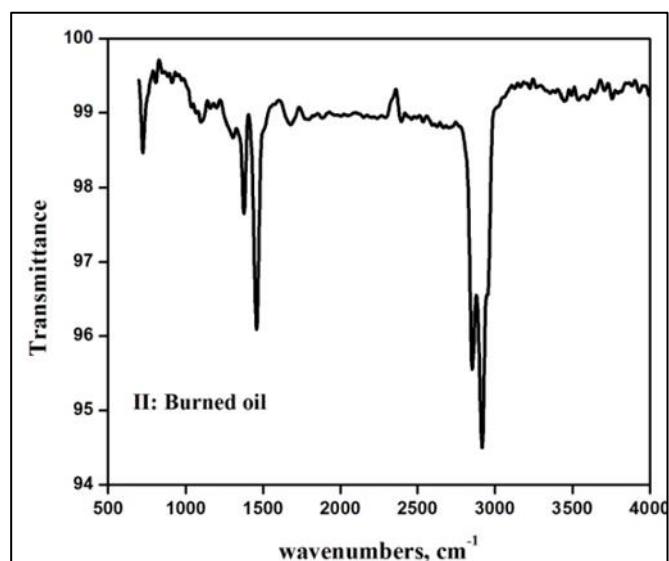
Table 1: Viscosity index for 27 motor oils determined by ASTM method

Sample no.	Viscosity index	Type	Sample no.	Viscosity index	Type
Calibration set			15	102	Burned
1	142	Fresh	16	190	Fresh
2	107	Burned	17	128	Refined
3	116	Refined	18	102	Burned
4	152	Fresh	Validation set		
5	117	Refined	19	114	Refined
6	101	Burned	20	102	Burned
7	123	Refined	21	239	Fresh
8	145	Fresh	22	100	Burned
9	95	Burned	23	159	Fresh
10	114	Refined	24	114	Refined
11	262	Fresh	25	180	Fresh
12	91	Burned	26	102	Burned
13	109	Refined	27	117	Refined
14	139	Fresh			

Results and Discussion

Spectral characterization

FTIR spectra were used for the chemical characterization of fresh, refined, and burned motor oils. Fresh or refined automobile lubricating oils consist of saturated linear and branched chain paraffins. The samples have multiple bands at the 2921–2856 cm^{-1} region, an intense band at 1458



cm^{-1} , and a less intense band at about 1376 cm^{-1} corresponding to the presence of a mixture of hydrocarbons having short length carbon chains and C–H branching vibrations containing –CH– groups in the sample.

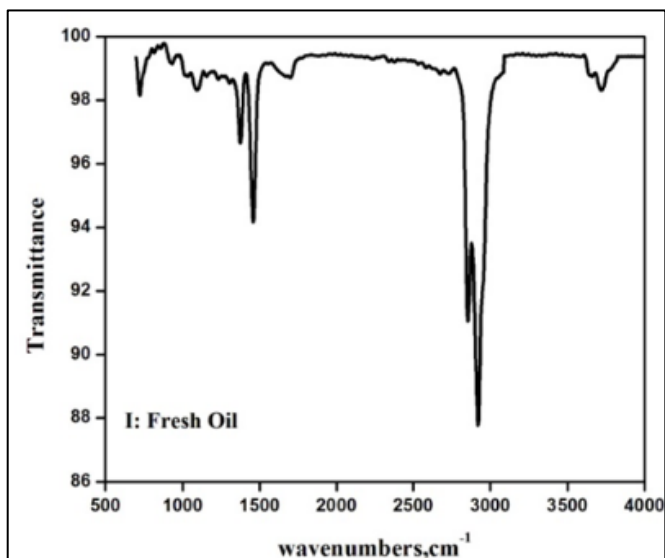


Fig 1: FTIR spectra of fresh oil, burned oil and refined oil.

Lubricating oils are made by using proper additives. Additives are used to enhance the natural properties and to prevent some unexpected properties of the oils. Oxygen-carrying functional groups may be present in fresh oils as friction modifiers or lubricity additives. These are polar molecules consisting of polar and nonpolar functional group and hydrocarbon tails. The spectra comprise the band at 1701 cm^{-1} corresponding to compounds with carbonyl group. Band at 1701 cm^{-1} refers to polymethacrylate in the oil samples which are used as viscosity modifier and pour point depressant additive. Band at 1701 cm^{-1} is used for viscosity index (VI) estimation of lubricating oils.

Several metal compounds are introduced to oils to improve lubricant properties. Zinc dialkyl dithiophosphates (ZDDPs) are organometallic compounds. They are effective antioxidants and included in engine oils. P–O–C bonds of ZDDPs are located at $1090\text{--}920\text{ cm}^{-1}$. Other additives used in industrial, automobile lubricating oils and greases are antioxidants. Fresh oil has absorption band at 3648 cm^{-1} indicating O–H stretching vibrations in monomeric alcohols and phenols. Absence of such bond in burned oil indicates the deterioration of the motor oil.

Calibration with raw spectral data

The viscosity index of 27 motor oils determined by using the Ostwald viscometer and the ASTM (American Society for Testing and Materials) procedure in this study varies from 92 to 262 with average value 131.93 and standard deviation 42.53. FTIR spectral data of absorbance against wavenumber were obtained from FTIR instrument. Calibration models were designed using raw data and preprocessed through S-G smoothing, mean normalization and SNV techniques. Graphical presentation of raw spectral data from FTIR is shown in the Figure 2.

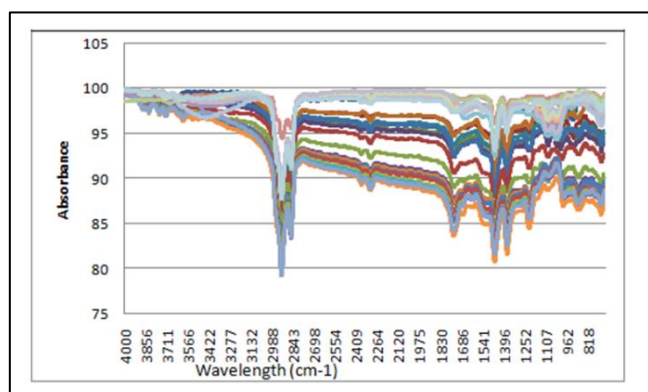


Fig 2 : Raw spectra from FTIR

PCA is performed first, and it shows that PC-1 expresses 56% of the variation whereas PC-2 expresses 17% of the total variation.

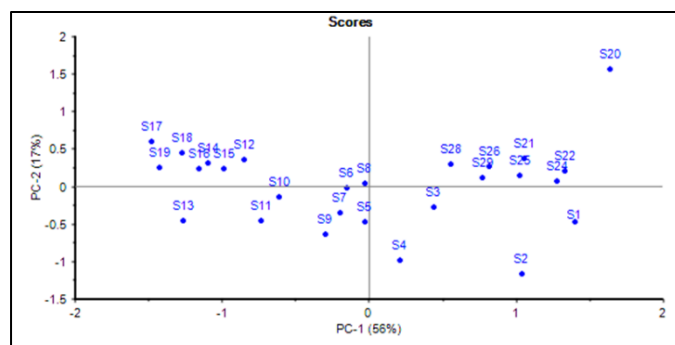


Fig 3: Score plots of raw spectral data

The score plot of PC-1 against PC-2 in the Figure 3 shows the map of motor oil samples. It is clear from the plot that the samples are independently scattered and do not follow any pattern among the independent variables.

Further, an outlier diverges from the overall pattern in a sample. In order to diagnose the data for outlier, influence plot is popularly used. Influence plot is a plotted figure of all samples in a space Hotelling's T^2 in horizontal axis and F-Residuals in vertical axis. From the influence plot as shown in the Figure 4 it can be observed that all samples are within the boundaries (of read lines in the figure) which imply that there is no outlier in the samples under consideration.

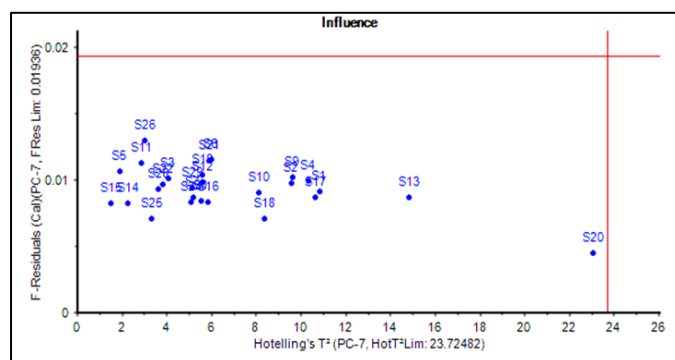


Fig 4: Influence plot of the samples

The Principal component regression (PCR) of raw data for the prediction of viscosity index was developed. The model parameters and the model efficiencies show very poor R^2 value (about 6%) with very high RMSE (40.49). It implies that the PCR can not at all be useable model for predicting viscosity index of motor oil on the basis of raw FTIR spectral data. Partial least square regression (PLSR) has also been developed for predicting viscosity index by spectral data. Here R^2 is approximately 44%, higher than that of PCR, but not yet a good one to use for prediction of viscosity index.

Preprocessing of spectral data

When FTIR spectral data are treated with mean normalization and PCR model is developed, the value of R^2 increases up to 50% percent. On the other hand, PLSR results show that the prediction performance of the model jumped up to 94% when the raw spectral data are treated with mean normalization. When the spectral data are transformed with SNV, and used in PCR, it produces 79% of R^2 value which show much higher than that of raw data. Particularly in this case, PLSR produces the same R^2 (81%) as that of PCR. Finally Savitzky-Golay smoothing filter is performed. It is based on the least-squares fitting of polynomials to segments of the data. Prediction efficiency of PCR has been increased dramatically to approximately 99 percent when FTIR spectral data are smoothed with Savitzky-Golay filtering. This is better than raw data and preferable to the other preprocessing techniques.

In predicted vs. reference plot, the straight line shows the real value of viscosity index of motor oil that should be obtained in the analysis. As shown in the Figures 5 & 6 it is obvious that PLSR with smoothed data using S-G technique is slightly better than that of PCR. Moreover,

PLSR produced about 99 percent of R^2 value, and it is the highest among raw and all treated data.

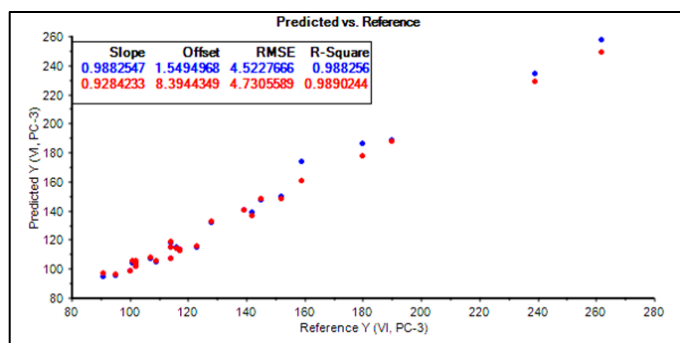


Fig 5: Predicted vs. Reference plots for motor oil samples by PCR

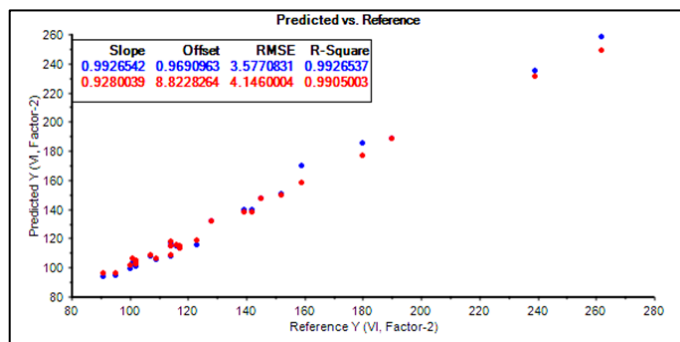


Fig 6: Predicted vs. Reference plots for motor oil samples by PLSR

A comparative picture of performance of PCR and PLSR with raw and treated data is presented in the following Table 2.

Table 2: Model efficiencies of PCR and PLSR with raw and transformed spectral data

Calibration techniques	Raw Spectral data		Mean normalized		SNV		Smoothed with S-G	
	RMS E	R^2	RMS E	R^2	RMS E	R^2	RMS E	R^2
PCR	40.49	0.059	29.58	0.498	19.346	0.748	4.528	0.988
PLSR	31.366	0.435	10.05	0.942	18.28	0.808	3.583	0.993

From the Table 2 it can be shown that PLSR performs slightly better than PCR in all treatments. Both PCR and PLSR show best results when spectral data are preprocessed with S-G smoothing ($R^2 \approx 0.99$). PLSR calibration technique when the FTIR spectral data are smooth with S-G smoothing shows the best result for predicting index number of motor oil.

Table 3: Model efficiencies of ANN with raw and transformed spectral data

Data sets	Raw Spectral data		Smoothed with S-G		Mean Normalized		SNV	
	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2
Calibration(70%)	33.0	0.536	20.26	0.844	27.65	0.485	0.492	0.999
Validation(15%)	26.30	0.059	41.24	0.489	17.71	0.625	11.29	0.943
Test(15%)	31.03	0.166	60.58	0.801	49.32	0.981	31.29	0.931

From the Table 3 it could be seen that for calibration, validation and test data set using ANN, it produces the most significant results when the spectral data are transformed with SNV (93-99%) technique among that

Artificial neural networks (ANN)

In ANN, spectral data points (wavenumbers) are inputs and viscosity indices are outputs. Architecture of the network is in the following Figure 7.

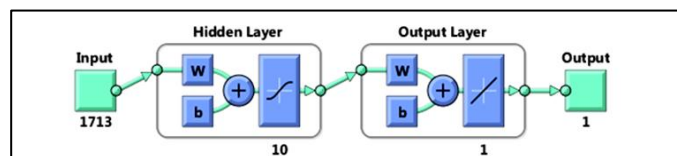


Fig 7: ANN architecture

Here FTIR absorbance against 1713 data points for all motor oils are used as inputs, and viscosity indices of samples measured by Ostwald viscometer are used as outputs for developing the network. 10 hidden layers are used in the network architecture.

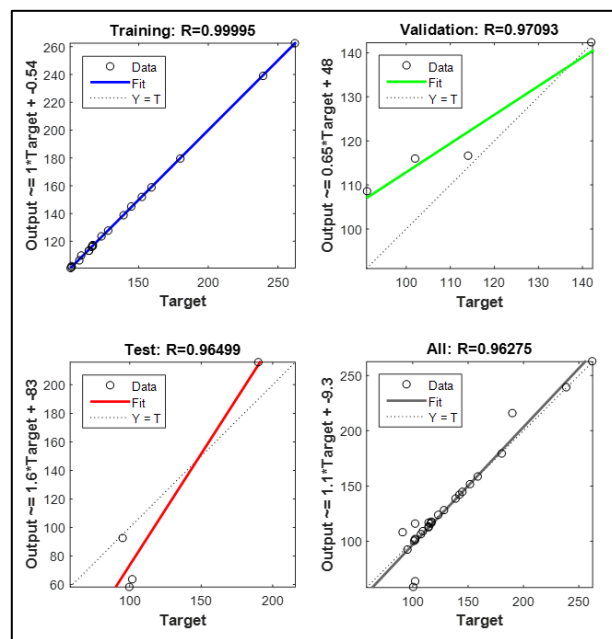


Fig 8: Regression plot of viscosity index against SNV spectra

In case of artificial neural networks (ANN), fitted line is used for prediction of viscosity index of motor oils. The prediction plots as shown in the Figure 8 represent outputs and targets of training, validation, test and overall data by ANN. Dashed line presenting in every plot in the Figure 8 represents the ideal result where the value of outputs equals to targets while the solid line has the meaning of best fitting linear regression line among output and target values. R has an indication of the relationship between outputs and targets. R equal to 1 (one) indicates an exact linear relationship between output and target values where as R close to zero indicates there is no linear relation among the output and target. Model efficiencies of ANN with raw and transformed spectral data are summarized in the Table 3.

of raw (4-54%), S-G smoothed (49-84%) and mean normalized data (48-98%).

Conclusions

In this study PCA was used for dimension reduction of variables, spectral data points. It was also used to have a visual map of samples through score plots. By influence plot we tried to find the outlier in the samples, and it is found that there is no outlier. For preprocessing of spectral data, Savitzky-Golay smoothing, mean normalization and standard normal variate (SNV) were used to smooth the spectral data from FTIR. Savitzky-Golay smoothing shows better predictive efficiency than that of raw data, and mean normalization and standard normal variate (SNV) treated data both with PCR and PLSR. However, SNV shows better results than other treated data for ANN. PCR shows best performance when it used Savitzky-Golay smoothing data. Performance of PLSR is slightly more than PCR. Between ANN and PLSR, the later demonstrated better predictive performance. Among the calibration techniques studied here, PLSR shows the significant prediction results with Savitzky-Golay smoothed FTIR spectral data. Thus, through this study an analytical method is being proposed here for the determination of viscosity index of motor oils with S-G smoothed FTIR spectral information calibrated with PLSR. In proposed chemometrics method no chemical waste is produced as no chemical is used for each sample analysis. It involves no sample preparation hassle. So, there is no sample preparation error in data analysis. The method could be used by motor oil producing companies and quality regulating authorities for monitoring the quality by determining viscosity index on regular basis.

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