T.R.
EGE UNIVERSITY
Graduate School of Applied and Natural Science

QUANTITATIVE DETERMINATION OF BINARY AND TERNARY OF BIODIESEL/DIESEL, MINERAL OIL AND SOLVENT MIXTURE WITH CHEMOMETRIC APPROACH

MSc THESIS

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Chemistry Department

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Aslıhan YILMAZ tarafından Yüksek Lisans tezi olarak sunulan "***Quantitative Determination of Binary And Ternary of Biodiesel/Diesel, Mineral Oil And Solvent Mixture With Chemometric Approach***" başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve **15.05.2019** tarihinde yapılan tez savunma sınavında aday oybirliği/~~oyçokluğu~~ ile başarılı bulunmuştur.

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15 / 05 / 2019

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ÖZET

BİODİZEL/DİZEL, MİNERAL YAĞ VE ÇÖZGENLERİN İKİLİ VE ÜÇLÜ KARIŞIMLARININ KEMOMETRİK YAKLAŞIMLA NİCEL TAYİNİ

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Enerji Piyasası Düzenleme Kurumu’nun getirmiş olduğu düzenleme ile günümüzde dizel yakıtına en az % 0,5 (V/V) oranında biyodizelin harmanlanması zorunlu hale gelmiştir. Ayrıca, biyodizel, mineral yağ ve çözgen karışımları standart akaryakıt kalitesine benzetilerek araçlarda kullanılması, yakıtlarda sahteciliğe yol açmıştır. Gerek yakıtların gerekse mineral yağlar gibi maddelerin yapısının karmaşık olmasından ötürü, karışımların eş zamanlı tayinleri bilinen kromatografik yöntemlerle pahalı ve zaman alıcıdır. Kromatografik analizlerin aksine, daha hızlı, daha az örnek gerektiren spektroskopik teknikler ile kemometrik tekniklerin birleştirilmesi kompleks karışımların analizi için avantaj sağlamaktadır.

Bu tez çalışmasında dizel/biyodizel, mineral yağ ve çözücünün ikili ve üçlü karışımlarının tayinine yönelik yöntem geliştirilmeye çalışılmıştır. Hazırlanan karışımların Fourier Dönüşümlü Kızıl Ötesi (FTIR) spektrometresi ile spektrumları alındı ve spektral verilere, kısmi en küçük kareler yöntemi (KEK) uygulandı. Kalibrasyon ve validasyon sonuçlarına bakıldığında KEK yöntemi, biyodizel/dizel, mineral yağ ve çözücü karışımlarının eş zamanlı analizine olanak tanımaktadır.

Anahtar sözcükler: Kısmi en küçük kareler yöntemi, biyodizel, mineral yağ, FTIR

ABSTRACT

QUANTITATIVE DETERMINATION OF BINARY AND TERNARY OF BIODIESEL/DIESEL, MINERAL OIL AND SOLVENT MIXTURE WITH CHEMOMETRIC APPROACH

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MSc in Chemistry

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In 2018, with the regulation introduced by the Energy Market Regulatory Authority, it has become obligatory to blend biodiesel at least 0.5 % (V / V) to diesel fuel. In addition, simulating standard fuel quality the use of biodiesel, mineral oil and solvent mixtures in the vehicles has led to counterfeiting of fuels. Because both structure of the fuels and the mineral oils are complex, simultaneous determinations of the mixtures are expensive and time consuming by known chromatographic methods. In contrast to chromatographic analyzes, combining chemometric techniques with faster, lesser sample spectroscopic techniques is advantageous for the analysis of complex mixtures.

In this thesis, it was aimed to develop the method for the determination of the binary and ternary mixtures of diesel / biodiesel, mineral oil and solvent. The spectra of the prepared mixtures with Fourier Transform Infrared (FTIR) spectrometry were taken and the partial least squares method (PLS) was applied to the spectral data. The PLS method allows simultaneous analysis of biodiesel / diesel, mineral oil and solvent mixtures, based on calibration and validation results.

Keywords: Partial least square, biodiesel, mineral oil, FTIR

PREFACE

Due to the technological improvements instrumental analysis technics have gained vital importance, nowadays. Especially, so low level analyte amounts can be determined in complex structured matrices. However, before instrumental analysis there are many steps such as sampling, preparation and selecting suitable method. Chemometric methods, which contributes chemical science, have developed with the knowledge of statistic, math and computer sciences. These methods allow us mathematical analysis of signals come from equipment, before and after chemical analysis. Beyond the classical methods, using with the spectrometric technics provides an opportunity to determine without need preparing sample. Thus means time, money and energy saving.

In this paper, Partial Least Square Algorithm, which allows multivariable statistics analysis, is implemented on chemical data come from Fourier Transform Infrared Spectroscopy- Attenuated Total Reflectance (FTIR-ATR) spectrometry and is tried to improve quantitative analyze method for complex compounds such as biodiesel, diesel and mineral oil.

In introduction part consists fuels and fraud of it, analysis sample on this field and basic of chemometrics. In procedure part shows data sets for preparing of samples synthetically. Finally, in findings and results is showed sample analysis, data collection and chemometric analysis and explained some suggestions according to findings.

Lastly, my advice to one who wants to study in chemometric, should learn fundamental statistic and linear algebra.

İZMİR

15/05/2019

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SYMBOLS AND ABREVIATIONS

Symbols	**Explanation**
°C	Tempeture unit
ʎ	Wavelenghts
ѵ	Wavenumbers
w/w %	mass percent
v/v %	percent by volume

Abreviations

API	American Petrolum Institute
ASTM	American Society of Testing and Materials
EPA	Environmental Protection Agency
EN	European Norm
ISO	International Organization for Standardization
TSE	Turkısh Standards Institution

1. INTRODUCTION

1.1 Basic Definition of Fuels

Fossil fuels are originated from the decayed and fossilized remains of plants and animals that lived millions of years ago. Fuels can be divided by their physical properties and can also be classified as the natural and artificial fuels. Natural solid fuels are wood, coal, etc. and their secondary products are coke and charcoal. **Petroleum** is the primary liquid fuel and its derivatives include diesel (gasoil), gasoline, kerosene, naphtha and ethanol. Natural gas constitutes another class of fuel and its secondary products are hydrogen, propane, methane, etc. (Chaudhuri, 2011).

Petroleum is probably the most important substances in modern society since it is extensively used as fuel to satisfy the demands of an energy-dependent civilization and also provides raw materials for the industry. The petroleum is derived from the Latin petra and oleum words meaning rock oil and refers to hydrocarbons that occur widely in the sedimentary rocks.

Petroleum is a naturally occurring mixture of hydrocarbons in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen and some metals (ASTM, 2012). Raw petroleum, also known as crude oil, is a mixture of light, simple hydrocarbons such as methane, ethane, propane, butane, and pentane, along with other paraffinic, naphthenic, and aromatic hydrocarbons which are the main ingredients of organic industry. A number of products including solvents, lubricating oil, asphalts, coke and waxes are derived from refining crude oil.

Crude petroleum has minimal value but when refined it provides high-value liquid fuels, solvents, lubricants, and many other products. According to American Petroleum Institute (API) gravity, crude oil is referred as light, medium or heavy depending on its sulfur content. API gravity of light crude oil is greater than 40, while it is within 15-40 for medium and less than 15 for heavy crude oil (Vempatapu and Kanaujia, 2017). Since it is a mixture of compounds with a wide range of boiling points, petroleum can be separated in the refinery systems.

The fuels obtained from all the refining streams are required to comply with certain regulatory requirements. Among them, gasoline and diesel are the automotive fuels which are extensively used for transportation.

Gasoline is a mixture of aliphatic and aromatic hydrocarbons in a range of C4-C12 with the boiling range of 30-225°C. Its composition depends on the origin of the crude oil. Diesel fuel is generally used in the agricultural equipment, automobiles and public transport. Its composition is similar to gasoline only the carbon numbers are higher, typically within the range of C10-C19. The boiling points of the components vary in the range of 180-370°C.

Biodiesel is considered as an alternative fuel for industry by the Environmental Protection Agency (EPA) and the American Society of Testing and Materials (ASTM) and it is becoming more popular since it is produced from renewable resources (Bağcıoğlu, 2011). It can be produced from animal fat and vegetable oil combined with an alcohol in the presence of a homogeneous catalyst.

Biodiesel contains the mono alkyl esters of long chain fatty acids derived from renewable lipid sources. In addition, petroleum diesel is a mixture of hydrocarbon molecules which is derived from crude oil and barely contains oxygen while biodiesel includes up to 10-12% weight of oxygen which allocates complete combustion diminishing hydrocarbon and carbon monoxide emission. But, high oxygen content results in nitrogen oxides (NOx) emissions (Agarwal et al., 2006).

Biodiesel is commonly used as blends with conventional mineral diesel fuel since its physical and chemical properties are similar to petro diesel (Pimentel et al., 2006). In France, for example, biodiesel is marketed in a volume fraction of 5% in petro diesel blends while in the US, energy legislation has mandated the use of at least a volume fraction of 2% (Foglia et al., 2005) along with 0.5% volume fraction proposed in Turkey (EPDK, 2017).

Mineral oil is a distillation by-product of petroleum and this colorless oil is used in medicine as a laxative and as an emollient (Viswanathan, 2016). In addition to personal care products mineral oil is nevertheless used in illegal adulteration of fuel.

White spirit is a solvent including complex hydrocarbon mixtures with various components (C7-C14), mostly aliphatic and aromatic hydrocarbons with a distillation range of 150-215°C (Lam, 1992). White spirit is also used for adulteration in fuel as a thinner to obtain same viscosity with original fuel.

1.2. Adulteration in Fuel

Because of the great variation in prices, increased fuel prices and regular tax payments, liquids fuels are probably one of the most forged products. Consumer who intensely uses fuel especially in agriculture and transportation sectors has used mineral oil contained illegal addition substance such as solvents, unlicensed production of biodiesel/diesel and do not comply with corresponding standard requirements and caused very dangerous problems when they consumed.

It is clear that consumption of fraud mineral oil for fuel leads to vehicle fires, explosions, accidents and fatality due to mineral oil being flammable. This situation establishes a risk in terms of safety concerns. On the other hand, using fraud fuel would lead to loss in tax revenue and illegal profit resulted from tax-evasion. Additionally, forged products can be made either by mixing recycled or discarded residual oils with solvents such as white spirit, toluene, hexane, thinner which are used as paint thinner in dying industry or base and vegetable oils with solvents to give the similar viscosity to diesel (KMO, 2014).

According to 2010 data of Ministry of Environment and Urbanization published by Petroleum Industry Association (PETDER), 44.873 tons of residual mineral oil was collected in Turkey and the rest of the oil, which is about 205.127 tones, was not recorded (PETDER, 2011). Similarly, 2015 Annual Report has indicated that there is a significant gap in Turkey between the quantity of mineral oil supplied to the market and amount consumed. This difference reflects that large amount of mineral oil might have been used to adulteration of the fuel.

Another concern in adulteration is the addition of raw fatty oil to the biodiesel blends. The use of raw vegetable oils can cause carbon deposition, injector blocking, and incomplete combustion because of their high viscosities, low volatilities, and polyunsaturated character, as well as its gum formation characteristic because of oxidation and polymerization (Soares et al., 2008).

Due to possibility of addition of this inexpensive raw material in excess than the legally prescribed amounts, it is necessary that diesel/biodiesel blends must be correctly determined according to quality standards and regulations. Physical-chemistry studies of the properties of diesel mixtures with pure vegetable oils with grades that range up to 5% (w/w) were already addressed by the literature (Oliveira et al., 2007).

Considering the difficulties to work with rather complex matrices, it is crucial to develop a fast, reliable and practical method for the determination of adulteration of fuels with mineral oil and solvents.

1.3. Analysis Methods Used in Adulteration

Owing to complexity of the composition of fossil fuels and their products, fuel adulteration has been extensively studied by a number of researchers. Standard methods accepted today are ISO, EN, and ASTM covering various parameters for testing of fuels. Although, these methods are applied to monitor adulteration of gasoline and diesel fuels, there is not any test specifically designed to measure the adulteration of petroleum products.

The quality assurance (QA) and control (QC) procedures are crucial in monitoring and ensuring the quality of the fuels. Table 1.1 lists the regulatory standards related to the QA/QC of finished petroleum fuels. In addition, some non-standard and laboratory developed methods in accordance with the required applicable norms are also being used in the industry.

Table 1.1 Regulatory standards related to the QA/QC of petroleum fuels

Parameter	**Standard**
Cetane number	ISO 5165, EN 15195, EN 16444, ASTM D6
Cetane index	ISO 4264, ASTM D976
Density	ISO 3675, ISO 12185
Aromaticity/PAHs	EN 12916, ASTM D1319
Sulfur content	ISO 20846
Flash point	ISO 2719, ASTM D93
Kinematic viscosity	ASTM D445, ISO 3104

In the petroleum test laboratories, all these methods must have been developed and proficiency testing programs have to be applied. Any deviation in the test results is taken into account as an indication for a change in the composition and may be considered as the adulteration. Primary evidence of the adulteration in gasoline is obtained from physico-chemical tests including the density, distillation, octane number and vapor pressure (Vempatapu et al., 2017).

However; these tests ought to be confirmed with data obtained from spectroscopic and chromatographic techniques. There are few reports concerning high performance liquid chromatography (HPLC) methods for adulteration. A former study describes a HPLC-UV method for the determination of kerosene in gasoline (Dhole and Ghosal, 1995). Another HPLC-UV method coupled with chemometric classification and multivariate calibration was reported for the detection of triacylglycerols used for diesel adulteration with vegetable oils (Brandao et al., 2012).

Gas chromatography (GC) coupled with flame ionization detector (FID) is commonly used for detailed hydrocarbon analysis, in particular. Adulteration of gasoline samples with organic solvents has been investigated by comparing the physico-chemical parameters with the data from GC-FID system and hierarchical clusters analysis has been employed for improving the detection of the type and relative proportion of solvent (Wiedemann et al., 2005).

Although the solvent adulteration in gasoline is difficult to detect due to its presence in unadulterated gasoline, their presence can be easily monitored through disproportionate analysis by GC-FID (Vempatapu et al., 2017). Detailed hydrocarbon analyzer (DHA) was designed for straight-run hydrocarbon fractions using single 100 m long capillary column (Blomberg et al., 2002).

Recently, two-dimensional gas chromatography (GC-GC) has been popular for the petroleum analysis due to the improved resolution. A detailed characterization of gasoline samples adulterated with solvents or kerosene has been accomplished via using GC-GC-FID system (Degodoy et al., 2008).

However, there a few chromatographic methods developed for adulteration of diesel samples probably due to the increased complexity of the sample as it contains much more hydrocarbons isomers from various classes (Vempatapu et al., 2017). On the other hand, gas chromatography coupled to mass spectrometry becomes a powerful tool for petroleum analysis. In addition, chemometrics has been utilized for identifying the adulteration in conjunction with GC-MS.

Alberici et al. have proposed a method for detecting adulteration in gasoline, diesel and biodiesel which is free of sample preparation steps (2010). The technique was termed “easy ambient sonic-spray ionization mass spectrometry” and suitable for hyphenation and onsite analysis.

Another application of this method was reported for fingerprinting of gasoline, kerosene and diesel samples where the aromatic compounds containing nitrogen have been considered as the markers for the sample (Haddad et al., 2012). The admixtures of gasoline/kerosene and gasoline/diesel have been characterized with great accuracy.

In the emission or fluorescence spectroscopy, the analyte concentration has been determined by using intensity of emission in visible region. Applications also include the synchronous fluorescence spectroscopy (SFS) to characterize the fuels and lubricants (Parta et al., 2002) and for adulteration studies have been conducted to detect the kerosene in commercial automotive fuels (Taksande et al., 2006). The SFS analysis has also be combined with multivariate calibration to detect adulterant in diesel (Corgozinho et al., 2008).

The use of nuclear magnetic resonance spectroscopy (NMR) in fuel analysis was reviewed by Silva et al. (2011). The standard methods, ASTM D5292 and ASTM D4808, include high and low-resolution NMR, provide compositional information but, it can also be used for the adulteration studies. Structural information can be also obtained by Fourier transform infrared spectroscopy (FTIR) (Gallignani et al., 1993). The standard methods used in diesel adulteration have been summarized in Figure 1.1.

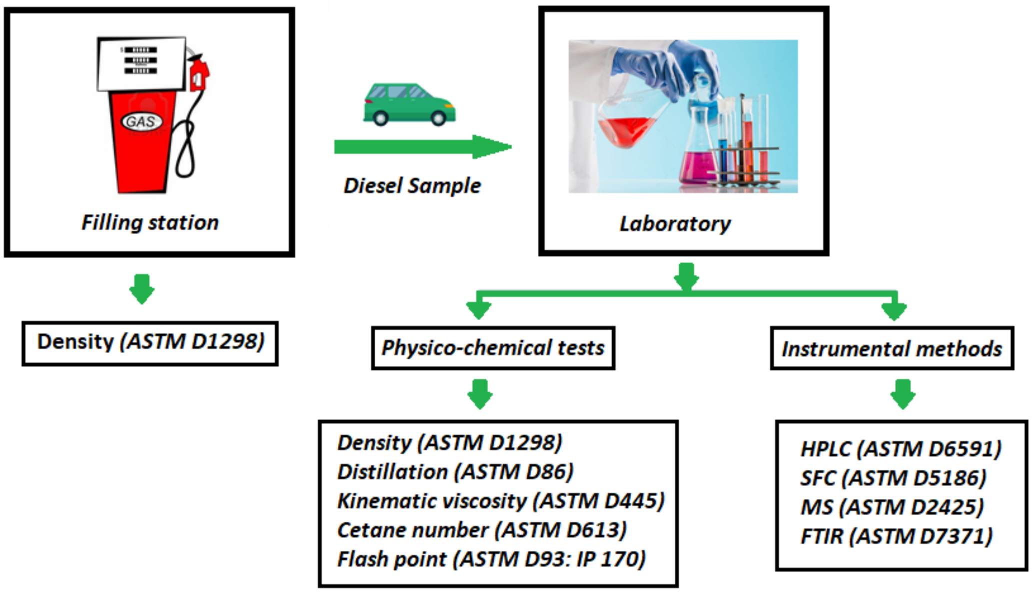

Figure 1.1. The standard methods used in diesel adulteration (Vempatapu et al., 2017).

In the analysis of fuel samples like gasoline and diesel, generally vibrational spectroscopic techniques such as infrared (IR) and near infrared (NIR) are used in combined with multivariate analysis (Oliveira et al., 2007). These techniques are more popular since they provide a fast and practical way for an accurate analysis without any sample pretreatment step. A few reports can also be encountered recently for the analysis of biodiesel.

Gasoline is usually adulterated with naphtha, kerosene, diesel and other cheap solvents (Vempatapu et al., 2017). The detection of this adulteration is a difficult task since the solvents used for forging purposes are also the natural components of the gasoline. Therefore, it requires a huge effort to reveal the composition profile of the samples for further comparison with unadultereated gasoline to detect the adulteration. A fast and reliable method to screen the gasoline samples can be accomplished with the aid of multivariate chemometric techniques combined with IR (Teixeira et al., 2008).

Near infrared (NIR) measurements have also been coupled with multivariate classification methods for the adulteration studies (Al-Ghoutia et al., 2008; Balabin et al., 2010; Khanmohammadi et al., 2012). Table 1.2 summarizes the methods based on infrared measurements for adulteration studies.

Table 1.2 Analytical methods based on infrared measurements for adulteration studies

Sample Type/ Adulterant	**Technique**	**Data Analysis**	**References**
Diesel/biodiesel blends/Vegetable oil	FTIR and FT-Raman	PLS, PCR, ANN	Oliviera et al., 2007
Gasoline/ diesel oil, kerosene, turpentine spirit or thinner	FTIR	MLR	Teixeira et al., 2008
Super motor gasoline/ regular motor gasoline	NIR	MLR	Al-Ghoutia et al., 2008
Classification of refinery or process type gasoline	NIR	LDA, QDA, RDA, SIMCA, PLS, KNN, SVM, PNN, ANN-MLP	Balabin et al., 2010
Diesel /Soybean and Corn Biodiesel blends	FTIR and IRMS	PCA, HCA, SVM	Santos et all., 2017
High quality engine oil / Lower quality engine oil	VIS-NIR	PCA and PLS	Srata et all., 2019

*PLS: Partial least square regression, PCR: Principal component regression, ANN: Artificial neural network, MLR: Multivariate linear regression, LDA: Linear discriminant analysis, QDA: Quadratic discriminant analysis, RDA: Regularized discriminant analysis, SIMCA: soft independent modeling of class analogy, KNN: K-nearest neighbor, SVM: support vector machines, PNN: probabilistic neural network, MLP: multilayer perceptron HCA: hierarchical clustering analysis.

1.4. The Aim of the Thesis

Fuel adulteration is a serious problem in many countries and therefore, development of a method for detecting any adulteration in fuels was considered to be main task. However, it is difficult to analyze with traditional methods since biodiesel, diesel and mineral oil have long chain hydrocarbon derivatives with similar chemical structure. Chromatographic methods are both costly and time consuming since they require sample pretreatment. On the other hand, spectroscopic methods can be coupled with chemometrics to analyze complex mixtures in spite of overlapping peaks obtained. These techniques provide us a rapid fuel authentication and quality control.

The aim of this thesis is to develop a simple, fast, efficient and inexpensive analytical method to certify the quality and authenticity of the fuels. Likewise, a new chemometric method using alternative analytical techniques to screen the presence of solvent, mineral oil and biodiesel in fraud fuel samples becomes indispensable and recommended for routine applications in quality-control monitoring programs, which is the objective of this research. Next section gives the basic information on chemometry and infrared spectroscopic analysis.

1.5. Overview of Chemometric Analysis

In 1971, the term “kemometri” in Swedish was first coined a Swedish professor Svante World and in English it is equivalent to “chemometrics” (Kiralj et al., 2006). The International Chemometrics Society was founded afterwards by S. Wold and Bruce Kowalski two pioneer scientist in the field. Over the last two decades, chemometrics has opened many alternatives for analytical method improvement along with development of various software programs and high-dimensional hyphenated apparatus. Today, chemometrics has an important place in analytical chemistry.

Chemometrics is a potent tool for complicated chemical structures such as petroleum products analyzed by optical spectroscopy. By definition, chemometrics is an interdisplinary application by using of mathematical and statistical methods combined with useful information from chemical analysis through powerful software tools. Chemometric analysis has also included handling, interpreting and processing of chemical data to providing the maximum amount of chemical information (Khanmohammadi et al., 2012).

The application of various chemometric techniques usually involves quantification, classification or discrimination so called multivariate methods by using data measured from a number of samples. The objective of these multivariate data analysis is to find out all the variations by revealing relationships between the samples and variables in the data matrix and to compose new latent variables. By this means, a mathematical model is set up by multivariate data analysis with known samples. Finally, unknown samples can be predicted by the proposed model. This method is schematically described in Figure 1.2.

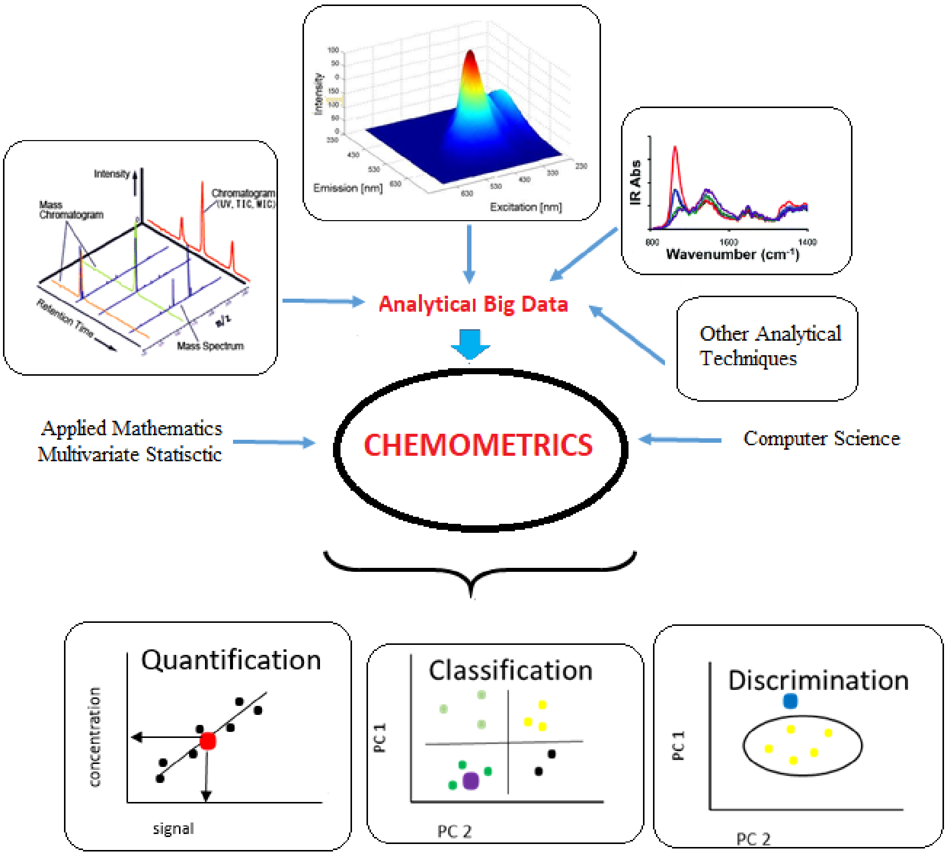

Figure 1.2 Contexts of Chemometrics (Brereton et al., 2018)

In this context, chemometrics take part analytical chemistry in terms of design of experiments, calibration and signal processing. Also, chemometrics include more complex calculations not calculated with calculator. Along with developing computer science, many software such as Minitab, Matlab and PLS Toolbox are used to make the chemometric calculations (Brereton et al., 2018).

In mixture of one or more compound, the analysis of these compounds both without pretreatment and simultaneously analysis is one of the basic problem in analytical chemistry and others branches. Although for the analysis of mixed samples spectroscopic and chromatographic techniques have been used, these techniques are not adequate to for very low quantities and in some situations, multiple component interaction of analytes with each other. Therefore, the sensitivity of the methods and accuracy of the results are tried to be increased by subjecting the data obtained from the classical analytical devices to various mathematical algorithms. Basic information about multivariate calibration techniques are given below.

1.5.1 Principles of the Multivariate Calibration

In analytical chemistry, several applications are associated with a mathematical model giving relationship between properties of sample and instrumental signals. To determine this relationship, we need calibration and prediction. Therefore, the samples are prepared at various concentration levels of certain chemical contents and their instrument responses are recorded. Then the model is used to predict concentration of unknown sample.

The main objective of a chemometrics model is to the estimation of parameter from a limited number of measurements. Since the measurements are costly, the reduced number of experiment is desired. While the responses to be estimation are referring to dependent variables, concentration levels are called independent variables (Brereton et al., 2018). In the present thesis, the responses are the absorbance values obtained via FTIR spectra corresponding to concentration levels of a series of fuel blends.

During calibration, a correlation of the measured concentrations of sample and the system property is searched and generally, one response taken from instrument is correlated to concentration of the only one component in a sample which is called as ***univariate calibration*** (Bağcıoğlu, 2011). For example, in chromatographic or spectroscopic studies absorption at a wavelength or a peak area is related with the concentration of one component in a sample. This relationship is expressed with a mathematical model as below;

$$\mathbf{Y} = \mathbf{X} \cdot b \qquad (1\text{-}1)$$

In this expression, classic calibration or inverse calibration can be if the model is linear. When instrumental signal is a function of concentration in classic calibration, concentration is a function of instrumental signal in inverse calibration. Therefore, in Eq. 1-1, **Y** is the vector of absorbance at single wavelength and **X** is a vector of concentration of one component in a number of samples. This situation is valid at classical calibration technique. In inverse calibration technique, this formula is vice versa. That is, as the spectral signal is written into **X-**vector form in rows, the corresponding component concentration is written into **Y**-vector form in rows. The scaler “*b*” is often called “regression coefficient” or “b-coefficient”, which are estimated with X and Y parameters, and can be calculated by the least square procedure the following equation where the X^T is the transpose of the concentration vector.

$$\hat{b} = (X^T X)^{-1} \cdot X^T \cdot Y \qquad (1\text{-}2)$$

After determining *b*, prediction is performed for the unknown samples. In the case of single component, it is enough to assess only one signal point. But, in the analysis of two or multi component system is needed to more than one signal points. The technique that correlated multiple responses of instrument to properties of a sample is known as ***multivariate calibration*** (Conzen, 2006). The aim of multivariate calibration techniques is to develop a model for the determination of mixture component with acquired signals from various instrument types. Multivariate calibration has several advantages over univariate calibration;

- It allows for the simultaneous analysis of all components in a mixture quickly and in an economic way using a single spectrum.
- If there are either outliers or the presence of unknown interfering components in the sample, they may cause wrong prediction of the quantity. Multivariate calibration can recognize this outlier or interference and overcome this challenge without any need for sample preparation step. Selecting more variables by multivariate calibration minimizes the time and effort spent during the eliminating of the interferences (Bağcıoğlu, 2011).
- Instrumental signal from the concentration data can include noise. When multiple signal measurements are received, uncertainty in of the results is reduced.

In multivariate calibration techniques is used either classical calibration or inverse calibration technique. Additionally, it can be apply the full spectrum. Therefore, vectors become matrix.

Multivariate calibration methods contain such as Classical least square (CLS), Inverse least square (ILS), Principal component analysis (PCA) and Partial least square (PLS) algorithms. We choose PLS calibration method, which is so effective on analyzing collinearity data, in this study.

1.5.2 Partial Least Square (PLS)

Unlike traditional calibration, it models both structure of X and of Y. To perform analysis with PLS for a mixture both data structures must be correlated with each other. It can apply to data which are strongly collinear, noisy, and a lot of X-variables, and also simultaneously model various response variables (Wold, 2001). PLS originally was introduced about 1975 by Herman Wold in the field of econometrics for modelling chains of matrices. It called path model (Wold, 1982) Around 1980, Svante Wold and Harald Martens has modified the ordinary PLS model due to reason ordinary model was difficult to apply data from science and technology which is a calibration technique for relating two data matrices, dependent (Y) and independent (X) variables, by a multivariate model.

In PLS, measurements are taken from a large number of samples and data matrices including response and concentrations is written for mathematical representation and their eigenvectors called factors or principal component are generated. These eigenvectors contain all information about analyzed system and they be used for calibration and prediction instead of original spectra. Actually, the eigenvectors obtained are the linear combination of the original variables, representing the degree of variation of the maximum variation in the data set. Furthermore, new orthogonal variables which are not correlated each other are obtained. This process known as decomposition thereby number of variables in the large data set is reduced.

In PLS, eigenvectors or principal components (PCs) generated from data matrices are sorted in descending order. Due to the first PC contains most of variations in data matrices and the rest PCs also contain the remaining variation it is important that most of the variance is explained by the least number of factors. This has a significant result for the assessment of the spectrum. The lower PCs mainly qualify the important changes in spectral structures, whereas the higher PCs represent the disturbing part of the instrumental noise. Thus, number of optimum PCs are of vital for the quality of PLS model.

If too few PC is selected, predictive power of the model may be insufficient. This is called as under fitting. If number of PCs is too large, this is resulted in overfitting.

Mathematically, absorbance data matrix X and concentration data matrix Y is decomposed producing a matrix of scores, T, U and loadings P, Q, respectively. The model equation for PLS are given in Equations 1.3 and 1.4 for absorbance and concentration data matrix, respectively.

$$X = T\,P^T + E \qquad (1\text{-}3)$$

$$Y = U\,Q^T + F \qquad (1\text{-}4)$$

The aim of PLS is to model all the components comprising X and Y so that the X block residuals, E, and Y block residuals, F are roughly equal to zero. An inner relationship that links the score of the X block with the scores of the Y block is also established.

$$U = T\,W \qquad (1\text{-}5)$$

Equation 1-5 is advanced by considering the related inner relationship. Latent vectors are calculated for both blocks separately and thus the inner relation is developed by exchanging the scores T and U with an iterative method. After the model calculated, combination of the equations 1-3, 1-4 and 1-5 give a matrix of PLS-calibration coefficients $\hat{B}$ for each component in Y.

$$\hat{B} = P\,(P^T P)^{-1}\,W\,Q^T \qquad (1\text{-}6)$$

$$\hat{Y} = X\,B \qquad (1\text{-}7)$$

By using Equations 1-6, Y-variables of new samples are predicted. T, U, W, P and C are calculated via a PLS-Calibration algorithm described. The score, T and U, include the information about samples and their similarities and or dissimilarities with regard to investigated system. For obtaining a good fit for predicted component of new sample PLS model validation is an important stage. Validation method allows to identification of outliers and especially permits the optimum number of PCs. The closeness between the value predicted by the model and the actual value indicates the precision of the model.

There are three figures of merit for assessment errors of estimated model. They are root mean square error of calibration (RMSEC), the root mean square cross validation (RMSECV) and the root mean square error of prediction (RMSEP). RMSECV gives an idea about the closeness between the concentration values estimated by calibration model and accepted true values for the calibration samples used to obtain the model parameters.

$$\text{RMSEC= } = \sqrt{\frac{1}{m-2}\sum_{i=1}^{m}(y_{\mathrm{i}} - \hat{y}_{\mathrm{i}})} \qquad (1\text{-}7)$$

The best model is the one which has the lowest error in prediction. One of the validation types is cross validation which is used leave-one-out cross validation carried out by predicting *m* calibration models, where removed each of m calibration samples one by one. Namely, after a sample has been removed from the calibration data set, model has set up by remaining samples. Removed sample is analyzed in the model and calculated error of analysis for this sample. Until all calibration samples are removed from calibration data set once, this process is repeated and RMSECV is calculated.

$$\text{RMSECV} = \sqrt{\frac{1}{m}\sum_{i=1}^{m}(y_{\mathrm{i}} - \hat{y}_{\mathrm{i}})} \qquad (1\text{-}8)$$

To calculate RMSEP, the validation samples (test set) are prepared and analyzed independently from calibration sample. In the developed calibration model, the signal values of the validation samples are replaced and the concentration values are estimated.

$$\text{RMSEP} = \sqrt{\frac{1}{m}\sum_{i=1}^{m}(y_{\mathrm{i}} - \hat{y}_{\mathrm{i}})} \qquad (1\text{-}9)$$

The symbols in the above equations indicate that y_i is accepted the true value, $\hat{y}_i$ is concentration value estimated by model, m is a sample number for used calibration data set or validation data set and the notation i indicates the ith sample.

1.5.3 Principles of the Infrared Spectroscopy (IR) Techniques

IR Spectroscopy also known as Vibrational Spectroscopy is a branch of molecular spectroscopy examining interactions between electromagnetic radiation and matter. This technique deals with vibrational transition in the molecule.

Substance to be analyzed absorbe infrared radiation and vibrational or rotational energy states of molecules is excitation. As a result, spectrum given information about its functional groups is obtained. IR spectrum is a characteristic for each molecule because different functional groups absorb in different frequencies IR radiation.

IR region consist of three region be part of Near Infrared Region (NIR), Middle Infrared Region (MIR), Far Infrared Region (FIR). Spectral region of MIR is divided into as functional region (4000-1500 cm^{-1}) and fingerprint (1500-500 cm^{-1}) and all bands observed in fingerprint region are specific for the molecule. The structure of molecules is identified by considering the stretch bands in this region.

Table 1.3 Regions of Infrared Spectroscopy (Skoog, 2016)

Infrared Regions	**Range Wavelengths (ƛ, µm)**	**Range Wavenumbers (v, cm^{-1})**
Near (NIR)	0.78 to 2.5	12800 to 4000
Middle (MIR)	2.5 to 50	4000 to 200
Far (FIR)	50 to 1000	200 to 10
Most used	2.5 to 15	4000-670

Another application of IR technique is quantitative analysis. The technique measures the absorption, transmission, or reflection of MIR radiation caused by the interaction of the dipole moment of the molecule with the IR radiation. Measured property, absorbance, is linearly correlated to the concentration of chemical compound. This absorption abides Beer Law, thus permitting quantitative information (Bunaciu et al., 2016).

The signal generated by the detectors in the IR absorption spectrometers is generally weak probably due to poor resolution and therefore, the sensitivity is low. To improve the signal to noise ratio is necessary to take more than one measurement which costs a lots of time. The interferences setting which is called Michelson interferometer has been developed for solving this issue where the measurement results are collected as interferogram and mathematical Fourier transform formula are applied on the results to improve S/N ratio. This technique is called Fourier Transform IR spectrometer (FTIR) as given in Figure 1.3.

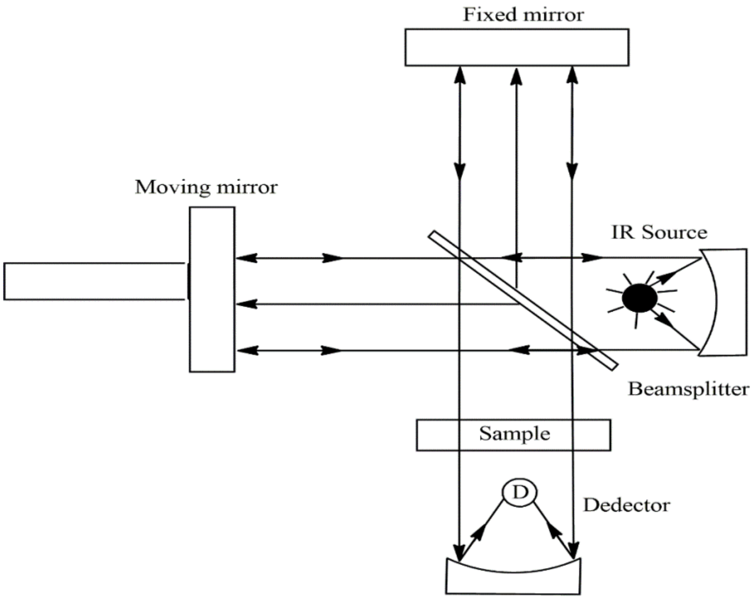

Figure 1.3 Instrumentation of FTIR Spectroscopy.

FTIR spectroscopy can be coupled with various equipment such as attenuated total reflectance (ATR) used identification and quantification about several analytes. Recently, FTIR-ATR technique has become popular in analytical chemistry due to the no sample preparation and its robustness, reliability and quickness. The clearest advantage is that very few amount samples can be used in this technique and it is important for the green chemistry.

2. MATERIALS AND METHOD

2.1 Instrumentation and Procedures

Spectroscopic analysis with a chemometric approach of mixture of biodiesel, diesel, mineral oil and solvent was maintained by using a Perkin Elmer Spectrum One FTIR spectrometer equipped with Universal Attenuated Total Reflectance (UATR). Operational conditions and specification of instrumentation are given Table 2.1.

Table 2.1 Operational conditions and specification of FTIR-ATR

Specification of FTIR-ATR	
Source	MIR (8000-30) cm^{-1}
Beam splitter	OptKBr
Detector	$LiTaO_3$
Interferometer	Improved Michelson interferometer
Accessory	Universal ATR (Diamond/ZnSe Crystals)
Operational conditions	
Spectral Region (Wavenumber)	4000-650 cm^{-1}
Spectral Resolution	4 cm^{-1}
Accumulation	4 Scans

All FTIR spectra were recorded taking background before every measurement and at 23 ± 1 °C was studied.

2.2 Chemical Reagents

Diesel fuel was obtained from fuel service station in Trabzon, TURKEY. Mineral oil, biodiesel, toluene, hexane, xylene and white spirit was supplied from manufacturer in İzmir. Biodiesel has been obtained from EPDK licensed company and complies with TS EN 14214: 2012 + A1: 2014 standard.

2.3 Procedures

2.3.1 Preparation of Binary Blends of Biodiesel and Diesel

As issued by EPDK, the regulation about biodiesel mixing to diesel must have at least 0.5 % (V/V). Therefore, the working range of 0.00 % (V/V) to 10.00 % (V/V) was chosen for the biodiesel. For this purpose, 50.0 mL of samples were prepared in a beaker by mixing biodiesel and diesel in definite proportions as given in Table 2.2. The blends were mixed with the magnetic bar to obtain a homogeneous mixture.

Table 2.2 Percent Composition of Binary Blends of Biodiesel and Diesel

Calibration Data Set			**Independent Validation Data Set**		
No	**Biodiesel (v/v %)**	**Diesel (v/v %)**	**No**	**Biodiesel (v/v %)**	**Diesel (v/v %)**
1	0.00	100.00	**1**	0.25	99.75
2	0.50	99.50	**2**	1.50	98.50
3	1.00	99.00	**3**	3.00	97.00
4	2.00	98.00	**4**	5.00	95.00
5	4.00	96.00	**5**	7.00	93.00
6	6.00	94.00	**6**	9.00	91.00
7	8.00	92.00			
8	10.00	90.00			

2.3.2 Ternary Blends of Biodiesel, Mineral Oil and Solvent

Ternary blends of biodiesel, mineral oil and solvent were prepared synthetically in order to analyze non-fuel products used as fuel. Mixture of toluene, xylene and hexane in equal mass percentages is used as a solvent. Ternary blends were prepared in various mass ratios to be 10.00 g of final mass. All ternary blend percentages are shown in Table 2.3

Table 2.3 Percentages of Ternary Blend of Biodiesel, Mineral Oil and Solvent

Calibration Data Set							
No	**Biodiesel (w/w %)**	**Mineral Oil (w/w %)**	**Solvent (w/w %)**	**No**	**Biodiesel (w/w %)**	**Mineral Oil (w/w %)**	**Solvent (w/w %)**
1	0.53	88.41	11.05	**21**	18.35	63.28	18.37
2	1.99	91.80	6.21	**22**	0.00	60.23	39.77
3	5.05	87.75	7.20	**23**	0.00	80.15	19.85
4	1.50	88.52	9.97	**24**	69.90	0.00	30.10
5	11.02	74.18	14.81	**25**	29.56	70.44	0.00
6	16.12	59.85	24.03	**26**	19.90	80.10	0.00
7	20.12	63.75	16.12	**27**	15.07	84.93	0.00
8	0.00	74.98	25.02	**28**	0.00	100.00	0.00
9	0.00	69.72	30.28	**29**	100.00	0.00	0.00
10	24.62	55.12	20.27	**30**	20.33	79.67	0.00
11	27.76	34.01	38.23	**Independent Validation Set**			
12	35.27	25.53	39.20	**1**	2.08	91.56	6.36
13	41.90	28.02	30.08	**2**	1.98	91.82	6.21
14	29.76	34.46	35.78	**3**	7.99	82.05	9.96
15	42.90	28.00	29.10	**4**	0.81	94.61	4.58
16	14.84	69.82	15.34	**5**	21.82	61.75	16.44
17	34.00	31.10	34.89	**6**	29.92	39.75	30.33
18	37.86	29.97	32.17	**7**	42.55	51.95	5.50
19	25.56	37.87	36.57	**8**	8.41	51.50	40.09
20	43.01	43.99	12.99	**9**	59.79	20.21	20.00

As shown in the Table 2.3, concentration of biodiesel was changed from 0.00 % to 100 % (w/w), mineral oil from 0.00 % to 100 % (w/w), and solvent from 0.00 % to 40.09 % (w/w).

2.3.2 Ternary Blends of Biodiesel, Mineral Oil and White Spirit

White Spirit is one of the most commonly used as an adulterant therefore; it was used in this study in the preparation of ternary blends. All blends were prepared as described section 2.3.1 and the details were given in Table 2.4.

Table 2.4 Percentages of Ternary Blend of Biodiesel, Mineral Oil and White Spirit

<table>
<tr><th colspan="8">Calibration Data Set</th></tr>
<tr><th>No</th><th>Biodiesel (w/w %)</th><th>Mineral Oil (w/w %)</th><th>White Spirit (w/w %)</th><th>No</th><th>Biodiesel (w/w %)</th><th>Mineral Oil (w/w %)</th><th>White Spirit (w/w %)</th></tr>
<tr><td>1</td><td>0.51</td><td>80.40</td><td>19.09</td><td>17</td><td>35.21</td><td>32.43</td><td>32.35</td></tr>
<tr><td>2</td><td>2.17</td><td>91.61</td><td>6.22</td><td>18</td><td>47.83</td><td>26.02</td><td>26.15</td></tr>
<tr><td>3</td><td>5.01</td><td>87.92</td><td>7.07</td><td>19</td><td>37.98</td><td>40.56</td><td>21.46</td></tr>
<tr><td>4</td><td>1.55</td><td>88.37</td><td>10.08</td><td>20</td><td>25.92</td><td>37.11</td><td>36.97</td></tr>
<tr><td>5</td><td>10.90</td><td>73.92</td><td>15.19</td><td>21</td><td>41.71</td><td>45.47</td><td>12.82</td></tr>
<tr><td>6</td><td>16.05</td><td>59.65</td><td>24.30</td><td>22</td><td>18.30</td><td>63.32</td><td>18.39</td></tr>
<tr><td>7</td><td>19.98</td><td>63.94</td><td>16.07</td><td>23</td><td>0.00</td><td>60.45</td><td>39.55</td></tr>
<tr><td>8</td><td>0.00</td><td>74.64</td><td>25.36</td><td>24</td><td>0.00</td><td>79.62</td><td>20.38</td></tr>
<tr><td>9</td><td>0.00</td><td>70.13</td><td>29.87</td><td>25</td><td>70.07</td><td>0.00</td><td>29.93</td></tr>
<tr><td>10</td><td>24.60</td><td>54.87</td><td>20.53</td><td>26</td><td>29.94</td><td>70.06</td><td>0.00</td></tr>
<tr><td>11</td><td>29.52</td><td>41.34</td><td>29.14</td><td>27</td><td>19.96</td><td>80.04</td><td>0.00</td></tr>
<tr><td>12</td><td>36.07</td><td>24.09</td><td>39.85</td><td>28</td><td>15.11</td><td>84.89</td><td>0.00</td></tr>
<tr><td>13</td><td>41.84</td><td>28.47</td><td>29.69</td><td>29</td><td>0.00</td><td>100.00</td><td>0.00</td></tr>
<tr><td>14</td><td>28.78</td><td>34.84</td><td>36.38</td><td>30</td><td>0.00</td><td>0.00</td><td>100.00</td></tr>
<tr><td>15</td><td>42.50</td><td>27.63</td><td>29.86</td><td>31</td><td>100.00</td><td>0.00</td><td>0.00</td></tr>
<tr><td>16</td><td>14.75</td><td>68.92</td><td>16.33</td><td>32</td><td>20.30</td><td>79.70</td><td>0.00</td></tr>
<tr><th colspan="8">Independent Validation Data Set</th></tr>
<tr><th>No</th><th>Biodiesel (w/w %)</th><th>Mineral Oil (w/w %)</th><th>White Spirit (w/w %)</th><th>No</th><th>Biodiesel (w/w %)</th><th>Mineral Oil (w/w %)</th><th>White Spirit (w/w %)</th></tr>
<tr><td>1</td><td>8.13</td><td>81.76</td><td>10.11</td><td>5</td><td>41.79</td><td>53.00</td><td>5.22</td></tr>
<tr><td>2</td><td>0.85</td><td>94.83</td><td>4.32</td><td>6</td><td>8.50</td><td>50.74</td><td>40.76</td></tr>
<tr><td>3</td><td>21.26</td><td>63.64</td><td>15.10</td><td>7</td><td>59.93</td><td>20.08</td><td>19.99</td></tr>
<tr><td>4</td><td>29.94</td><td>40.02</td><td>30.04</td><td></td><td></td><td></td><td></td></tr>
</table>

The general procedure is given in Figure 2.1. IR Spectra of all prepared blends were recorded by FTIR-ATR. Their spectrum was exported to Excel program (MS Office 2016, Microsoft Corporation) in order to organize the data and draw plots. Calibration set and independent validation set were analyzed by Minitab 18.

Calibration sets were used built for calibration model and the independent validation set were used to determine the predictive power of these model. To obtain optimum number of principal component was chosen leave one out cross validation and by using these components were attempt the model. After fitting model, independent validation set was predicted by model and RMSEP was calculated.

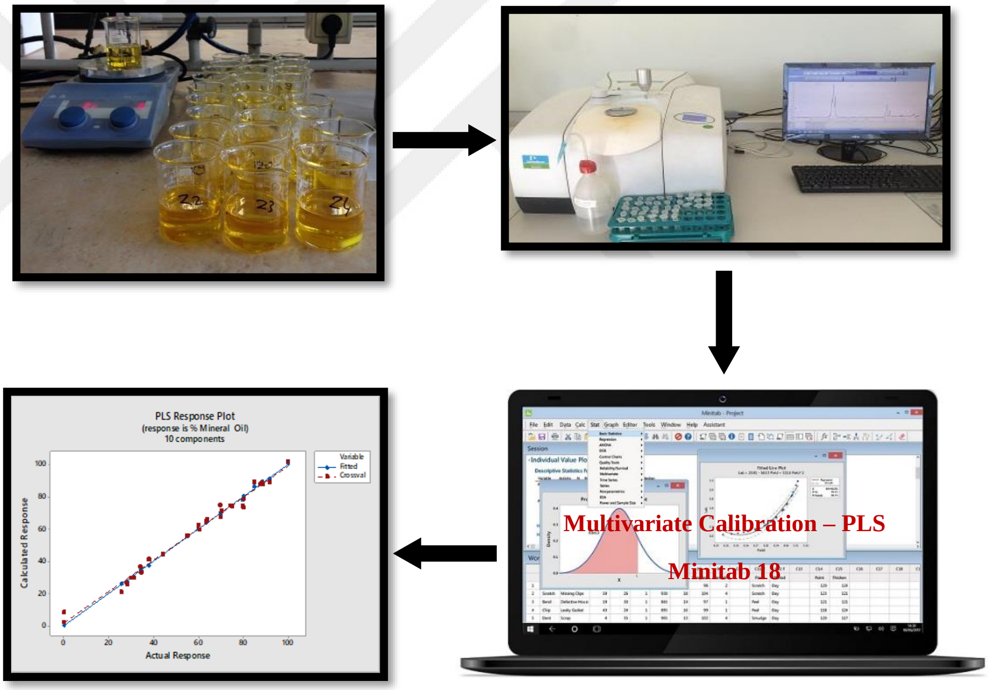

Figure 2.1 Graphical representation of steps followed during study

3. RESULTS AND DISCUSSION

Biodiesel is emerged as an alternative fuel source. Since biodiesel has higher viscosity, flash point, density, and lower cold-filter plugging point than petro diesel, their binary blends are used. Hence, it is important of analysis that binary mixture. Here, we focused on to develop a method based on FTIR-ATR and PLS techniques to detect the amount of biodiesel in diesel. Then, ternary blends of biodiesel, mineral oil and solvent were determined quantitatively.

3.1 Analysis of Binary and Ternary Blends of Biodiesel, Diesel, Mineral Oil, Solvent and White Spirit

Initial studies were conducted to analyze binary mixture of biodiesel-diesel and the pure spectra of biodiesel and diesel are given in Figure 3.1.

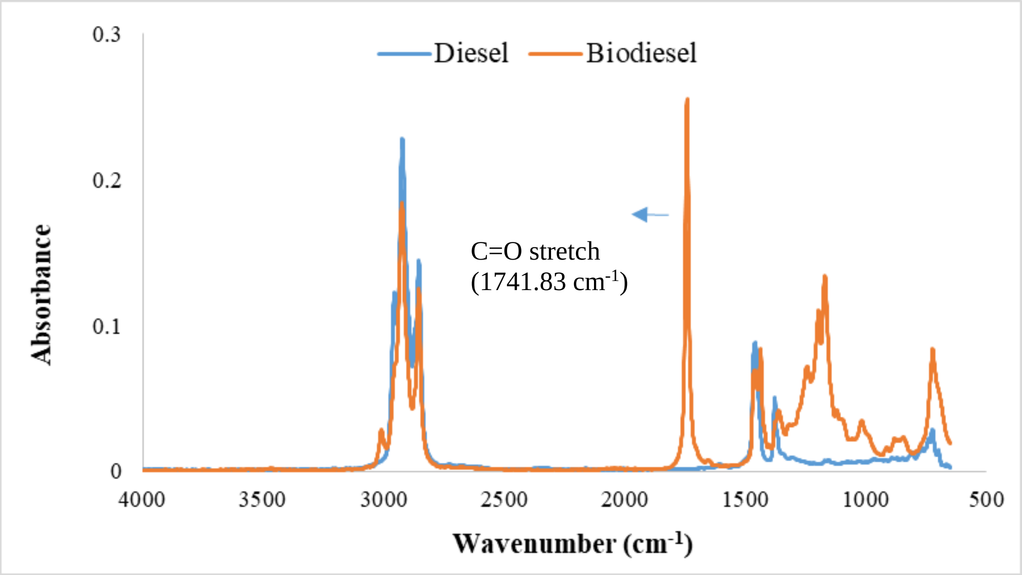

Figure 3.1 FTIR-ATR spectrum of pure form of biodiesel and diesel.

As can be seen in Figure 3.1, biodiesel and diesel have different spectral features due to carbonyl peak belonging to biodiesel in 1741.83 cm^{-1} and differences in the fingerprint region. Therefore, the wavenumbers between 1800-1692 cm^{-1} and 1327-940 cm^{-1} were chosen as the working range for calibration. Figure 3.2 shows the superimposed spectra of all blends.

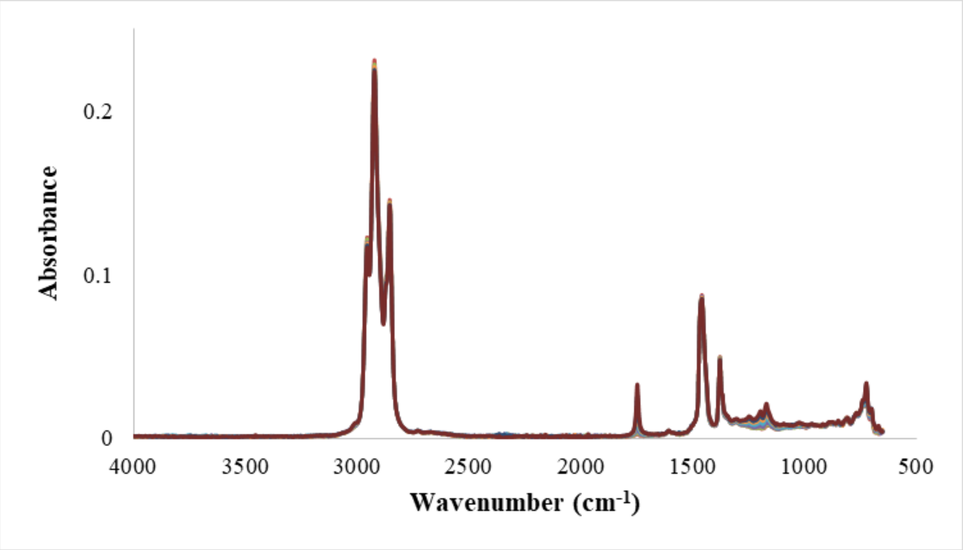

Figure 3.2 FTIR-ATR spectra of all binary blends of biodiesel-diesel

As can be seen full spectrum, prepared blends in different percentage of biodiesel and diesel give rise to the variability especially in the region of 1800 - 1692 $cm^{-1}$and 1327-940 cm^{-1} wavenumber. The peaks nearly overlap in the remainder region. These apparent variations are used for the chemometric model since they include qualitative information about amount of binary blends.

Using concentration of binary blends and their absorbance value, multivariate calibration model was developed with PLS. Actual vs predicted concentration values were calculated by developed PLS model, which calibration data set and independent data set given Table 2.2, were shown in Figure 3.3.

As shown from Figure 3.3, there is a good correlation between actual and predicted biodiesel because regression coefficients, R^2, values of biodiesel and diesel is very close to 1 and this correlation is linear. Developed PLS models for biodiesel/diesel blends have high R^2 values but this does not only the parameter evaluating predictive power of method. The methods of RMSEC and RMSEP values were also taken into consideration for the performance of model. In this context, we applied the PLS/FTIR-ATR model to independent test set for validation.

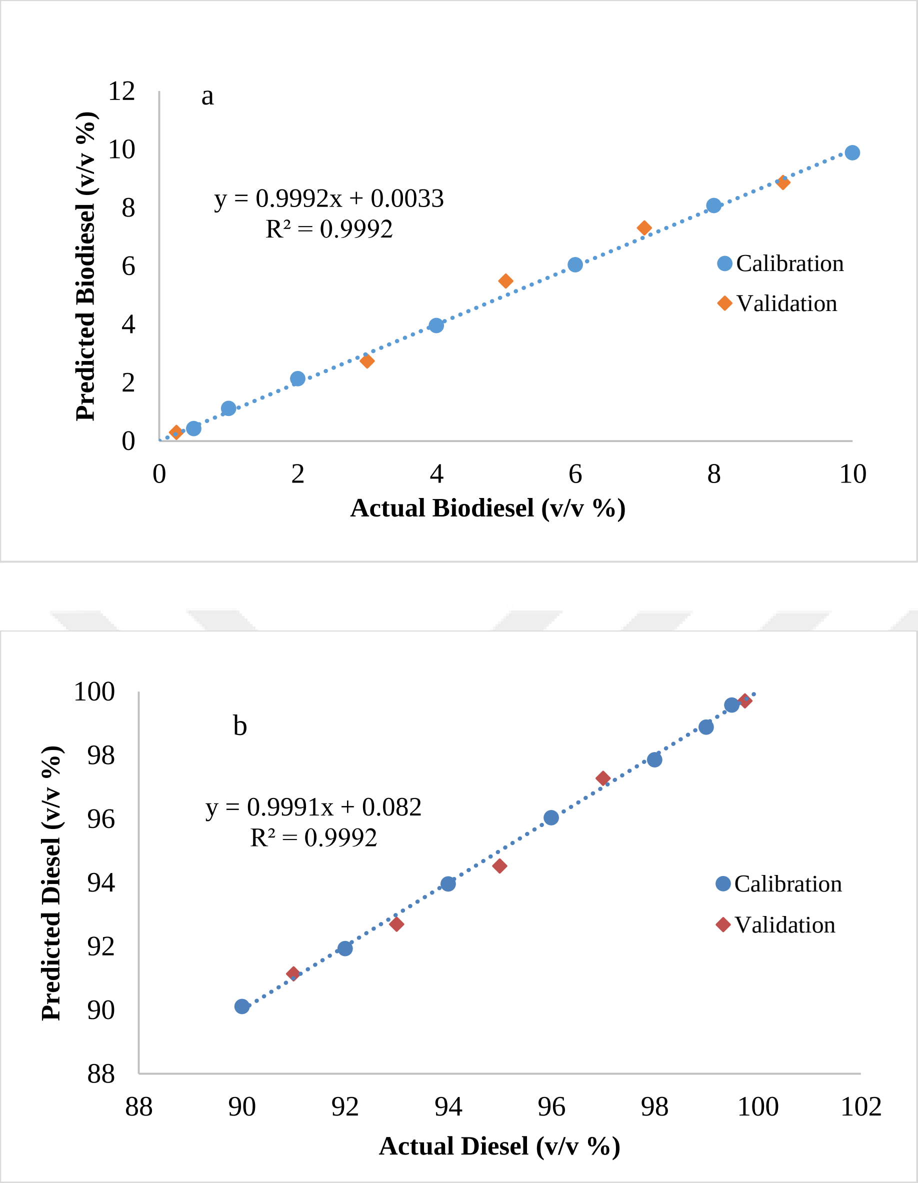

Figure 3.3 Actual versus predicted plot of a) biodiesel and b) diesel analyzed with PLS

Statistical parameters for the PLS model are given in Table 3.1.

Table 3.1 Statistical parameters of model developed with PLS-FTIR/ATR for biodiesel and diesel

Working Spectral Region	**1800-1692 cm^{-1} and 1327-940 cm^{-1}**	
Optimum PC Number 2	**Biodiesel (w/w %)**	**Diesel (w/w %)**
R^2	0.9992	0.9920
RMSEP	0.29	0.29
RMSEC	0.12	0.12

The data given in Table 3.1 indicates that the PLS models developed for both biodiesel and diesel have high R^2 and low RMSEP values. In addition, RMSEC and RMSEP values were found to be satisfactory as they are close to each other. Figure 3.4 shows, residual values of biodiesel are within the error limits at 95 % confidence level. Hence, the model developed was proven to be well fitted for the quantitative determination of biodiesel in diesel/biodiesel of binary blends.

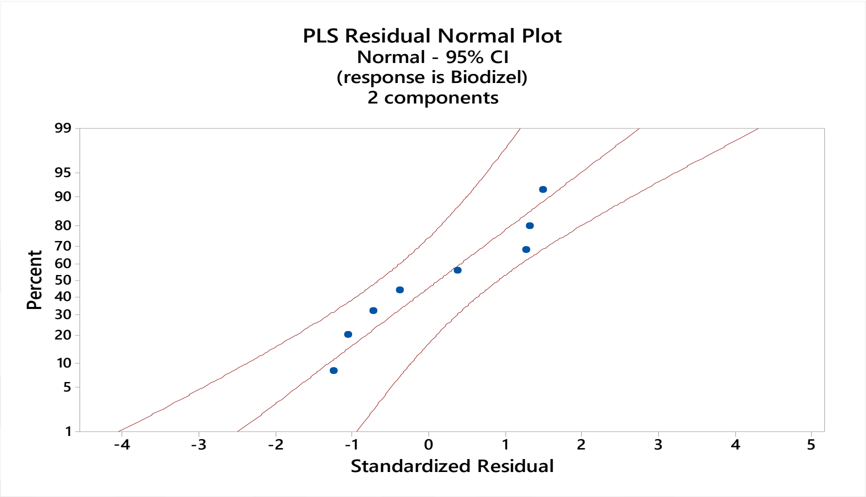

Figure 3.4 PLS Residual Normal Plot of Biodiesel

In the second part of experimental studies, ternary blends of biodiesel, mineral oil and solvent and first of all, FTIR spectra of all three components were recorded individually and given in Figure 3.5.

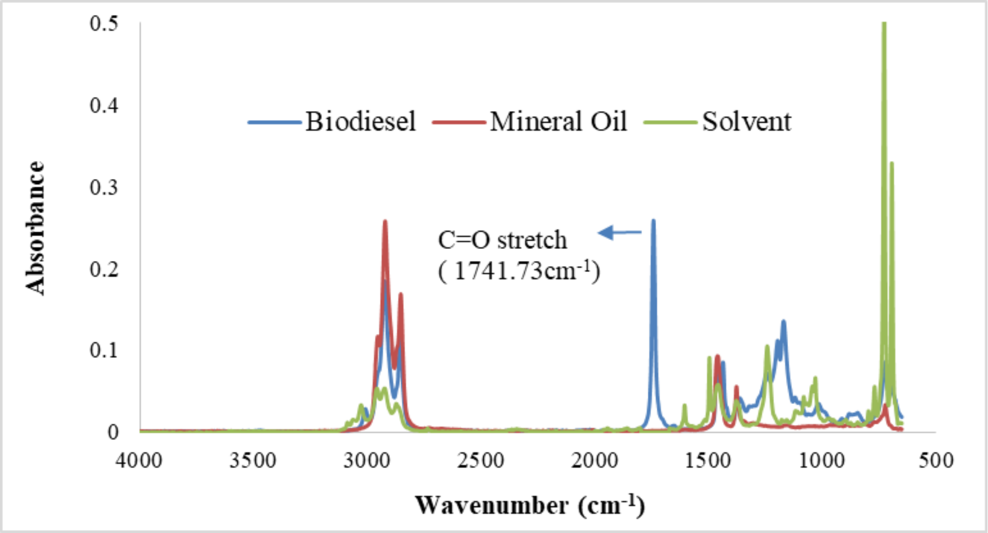

Figure 3.5 FTIR-ATR spectrum of pure form of biodiesel, mineral oil and the solvent.

As shown in Figure 3.5, biodiesel, mineral oil and solvent nearly have same spectral properties. While biodiesel and mineral oil have almost identical absorbance values in the range of 3000-2800 cm^{-1}, absorbance of solvent is lower. Furthermore, the carbonyl peak is apparently seen in 1741 cm^{-1}.

For PLS modelling, it is extremely important to choose spectral regions where each component in blend gives different stretching peak because of its ability to interpret source of variation. Thus, mixtures of different amounts of biodiesel mineral oil and solvent were prepared in order to the PLS modelling and the spectra of these mixtures were given in Figure 3.6.

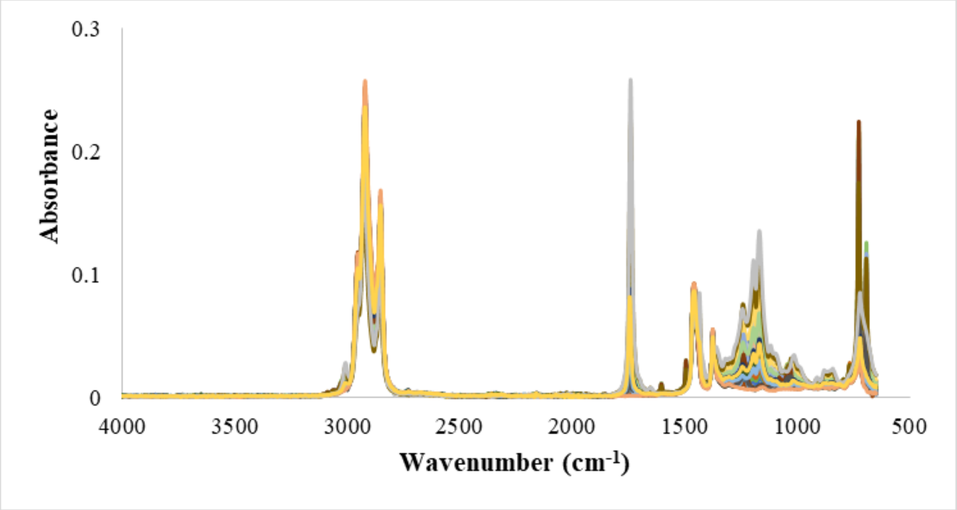

Figure 3.6 FTIR ATR spectra of all blends of biodiesel, mineral oil and solvent

According to Figure 3.6, the variations in the peaks in the regions of 3000-2850 cm^{-1} and 1800-500 cm^{-1} reflects the change in their concentrations. Since Minitab 18 program only allows the analysis of a certain number of variables, due to the limitations occurred in column number of the data sheet, we had to choose the number of variables which reflects the variability within the data. First of all, in 3000-2850 cm^{-1}, 1750-1375 cm^{-1} and 750-630 cm-^{1} regions of wavenumber have been chosen to set up the PLS model. Principal component number which explains the variability above the 90% was found to be 4. In Figure 3.7 the calibration graphs drawn for calibration and validation data sets plotted against the actual values versus the predicted values.

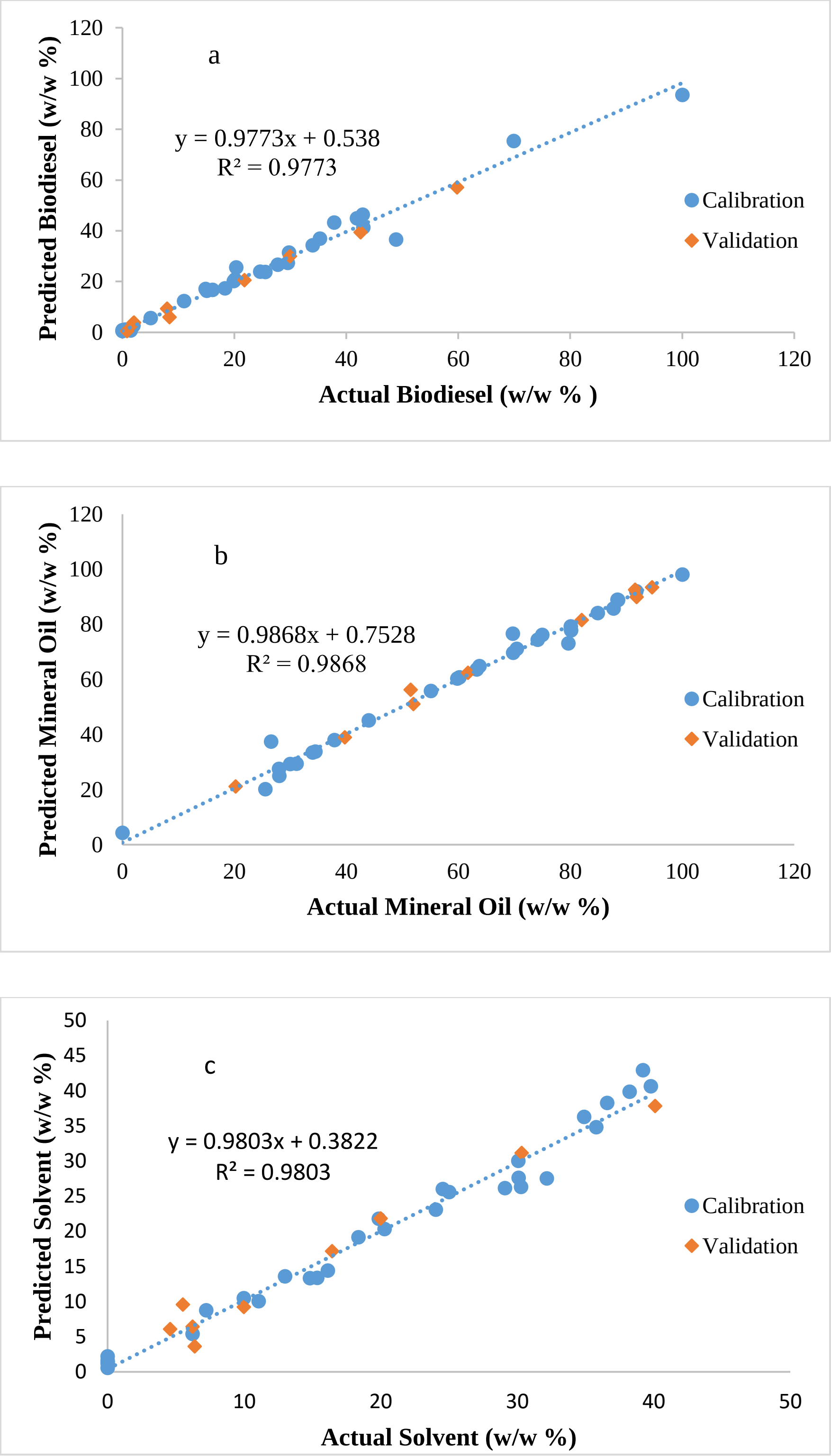

Figure 3.7 a) Actual versus predicted plot of a) biodiesel, b) mineral oil and c) solvent analyzed with PLS at 3000-2850 cm^{-1}, 1750-1375 cm^{-1} and 730-650 cm^{-1}

As can be followed from Figure 3.7, the R^2 values of biodiesel, mineral oil and solvent were found to be higher than 0.97 but, less than 0.999. Besides, the R^2 value of solvent was found to be higher than the other two components but, some of the data deviates from linearity. This indicates that R^2 value alone is not satisfactory parameter for the evaluation of data. Therefore, RMSEC and RMSEP values should be included as tabulated in Table 3.2.

Table 3.2 Statistical parameters of model developed with PLS-FTIR/ATR for biodiesel, mineral oil and solvent at 3000-2850 cm^{-1}, 1750-1375 cm^{-1} and 730-650 cm^{-1}

Working Spectral Region	**3000-2850 cm^{-}1, 1750-1375 cm^{-1}and 730-650 cm^{-}1**		
Optimum PC Number 4	**Biodiesel (w/w %)**	**Mineral Oil (w/w %)**	**Solvent (w/w %)**
R^2	0.9773	0.9868	0.9803
RMSEC	3.34	3.11	1.86
RMSEP	1.92	1.82	2.02

According to the data presented in Table 3.2, for biodiesel and mineral oil components the RMSEC values were found to be high but not close to RMSEP values. This can be concluded as the region chosen does not represent the variability as desired. Therefore, another region was chosen for further analysis.

Since the wavelength ranges of 1750-1730 cm^{-1}, 1550-1000 cm^{-1} and 800-650 cm^{-1} reflect spectral variation, these regions used in new PLS modelling for quantitative analysis of blends. Ten principal components were found to be optimum for simultaneous determination of biodiesel, mineral oil and solvent. In this context, for the evaluation of the model, the plots of the calibration and validation data sets are given in Figure 3.8.

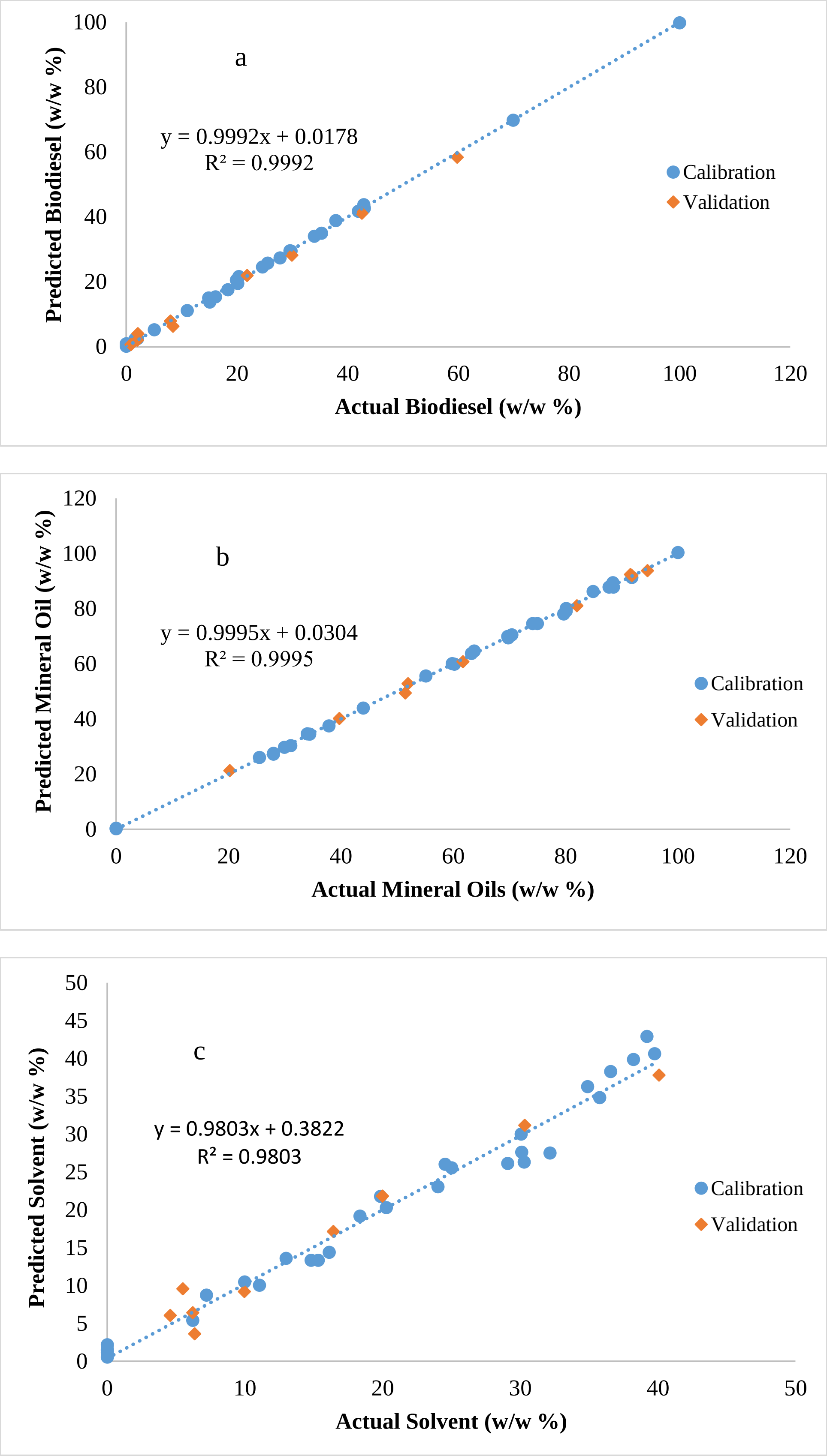

Figure 3.8 a) Actual versus predicted plot of a) biodiesel, b) mineral oil and c) solvent analyzed with PLS

In order to predict biodiesel, mineral oil and solvent content in blends, PLS model has given best results as shown in Figure 3.7. The regression coefficient, which gives the relationship between the actual values and the predicted values, is quite high and coefficient of biodiesel, mineral oil and solvent were found as 0.9992, 0.9995, and 0.9992, respectively. Table 3.3 shows RMSEC of the model, R^2, RMSEP for independent validation data set and optimum number of principal component (PC) for the PLS modelling.

Table 3.3 Statistical parameter of model developed with PLS-FTIR/ATR for biodiesel, mineral oil and solvent.

Working Spectral Region	**1750-1730 cm^{-}1, 1550-1000 cm^{-1}and 800-650 cm^{-}1**		
Optimum PC Number 10	**Biodiesel (w/w %)**	**Mineral Oil (w/w %)**	**Solvent (w/w %)**
R^2	0.9992	0.9925	0.9992
RMSEC	0.64	0.64	0.38
RMSEP	1.29	1.04	1.83

As can be followed from Table 3.3, the PLS model developed is applicable for the determine biodiesel, mineral oil and solvent content in blends. Plot of actual biodiesel, mineral oil and solvent values versus their PLS predicted concentration values support these results. The normal residual plot given in Figure 3.9 reveals that residuals values of biodiesel, mineral oil and solvent are within the error limits at 95% confidence level and no outlier observed. These results clearly display the adequacy of the model.

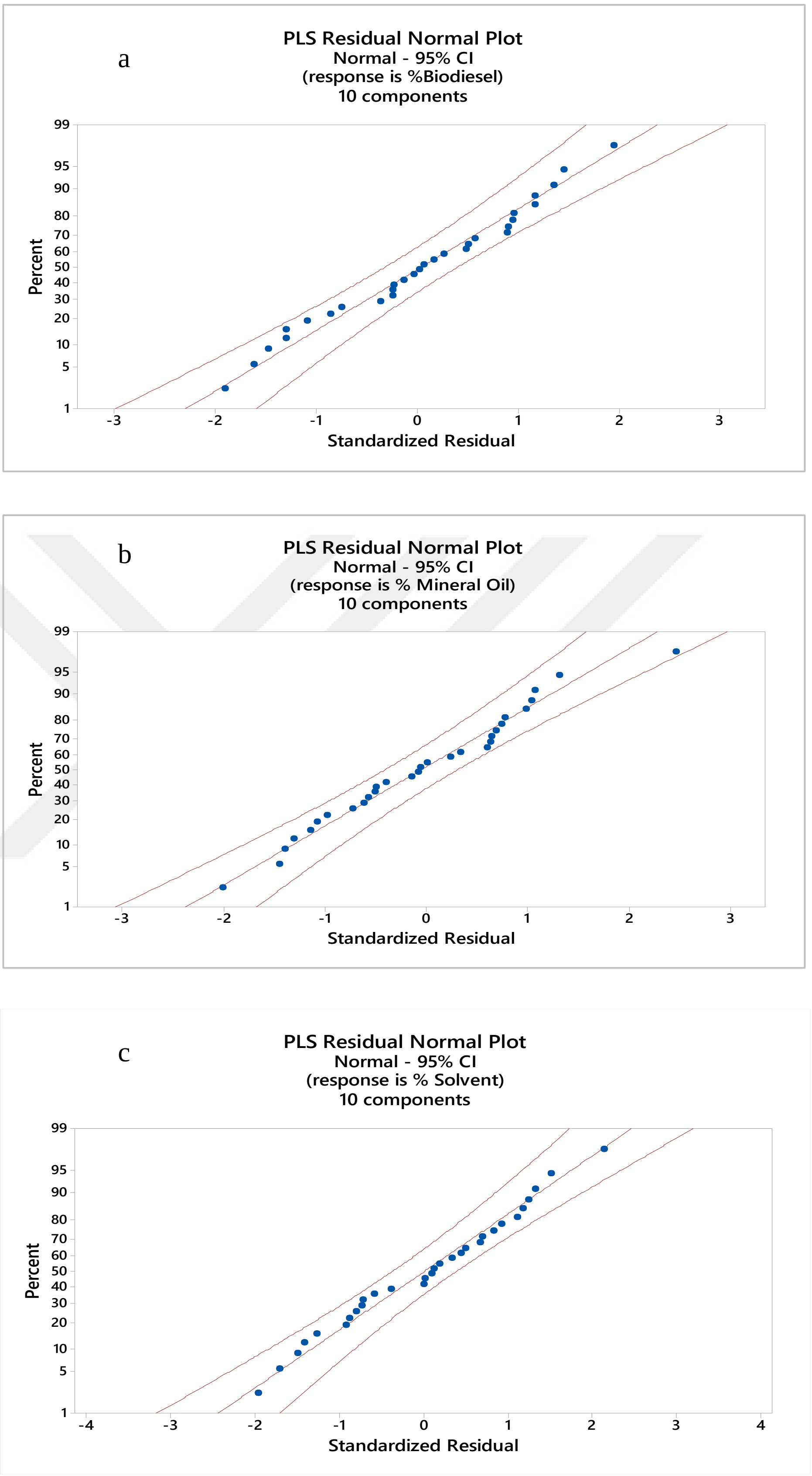

Figure 3.9 a) PLS Residual Normal Plot of a) Biodiesel, b) Mineral Oil and c) Solvent

Finally, ternary blends of biodiesel, mineral oil and white spirit were analyzed with FTIR-ATR. The spectra of their pure forms are shown in Figure 3.9

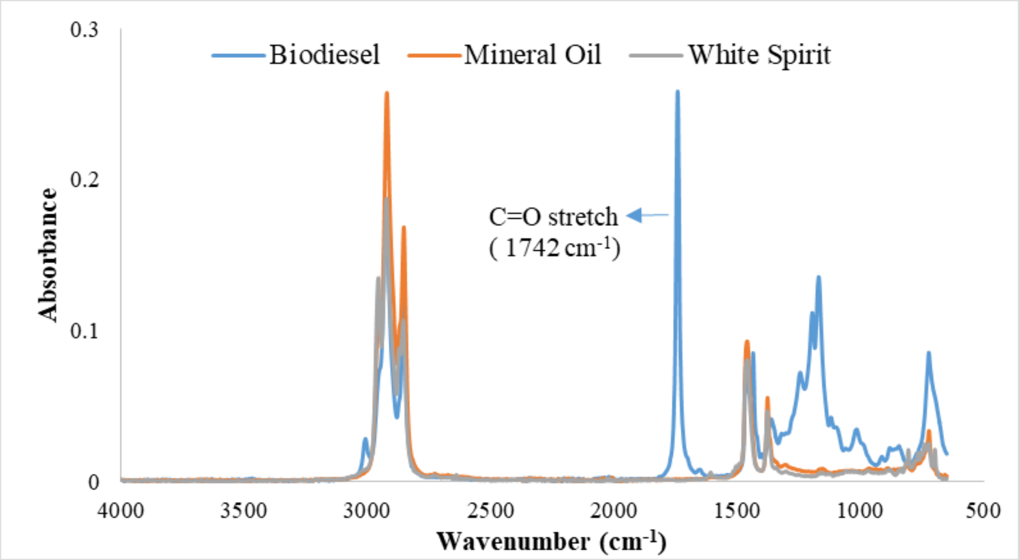

Figure 3.10 FTIR-ATR spectrum of pure form of biodiesel, mineral oil and white spirit.

As can be seen in Figure 3.10, each spectrum of biodiesel, mineral oil and white spirit have displayed high absorbance values around of 3000 and 2700 cm^{-1} wavenumber and only biodiesel have absorbance peak around of 1741 cm^{-1}. There are absorption peaks resulting from the biodiesel in the region of 1350-790 cm^{-1}. Figure 3.11 displays the IR spectra of all the ternary mixtures at different variations recorded around 1330-900 cm^{-1} and 780-650 cm^{-1} wavenumber range.

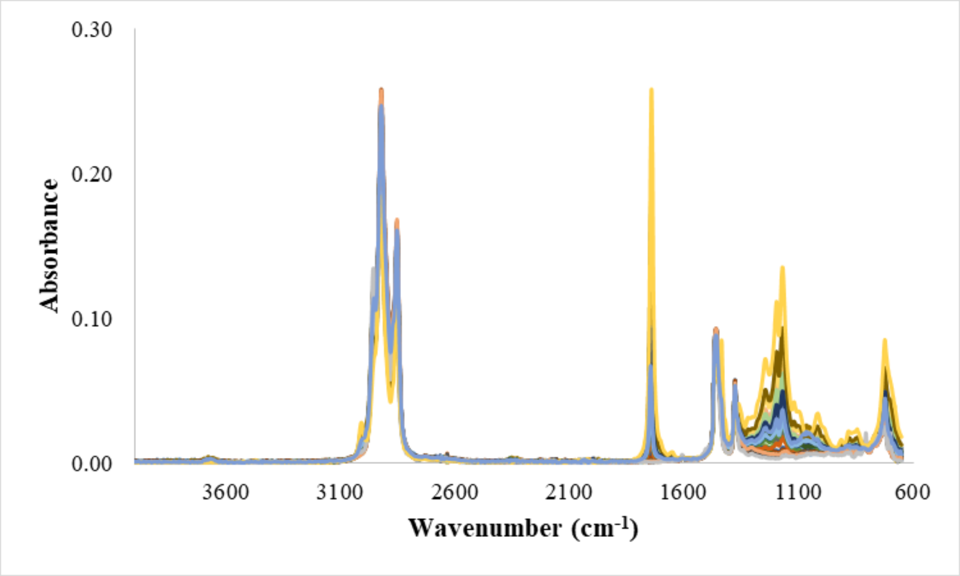

Figure 3.11 FTIR ATR spectrums of all blends of biodiesel, mineral oil and white spirit.

In addition, there are no absorption bands between 2600 and 2100 cm^{-1}. Besides, peaks in 3100-2600 cm^{-1}, 1600-1330 cm^{-1} and 1500-1330 cm^{-1} indicate overlapping bands indicating that univariate calibration techniques are insufficient.

The regions of 1750-1730, 1550-1000 and 730-630 cm^{-1} wavenumbers were chosen to the simultaneous determination of biodiesel, mineral oil and white spirit in ternary blends. After recording the spectra of 39 samples as prepared for the PLS calibration model, the validation at these regions was made with FTIR-ATR and the results were loaded into the Minitab program.

The number of principal component which are explained variations in the data set is obtained seven important variables. When the graphs in Figure 3.12 are examined, the variance which can be explained by the model with fewer new variables, are 99.89%, 99.87% and 99.77% for biodiesel, mineral oil and white spirit, respectively.

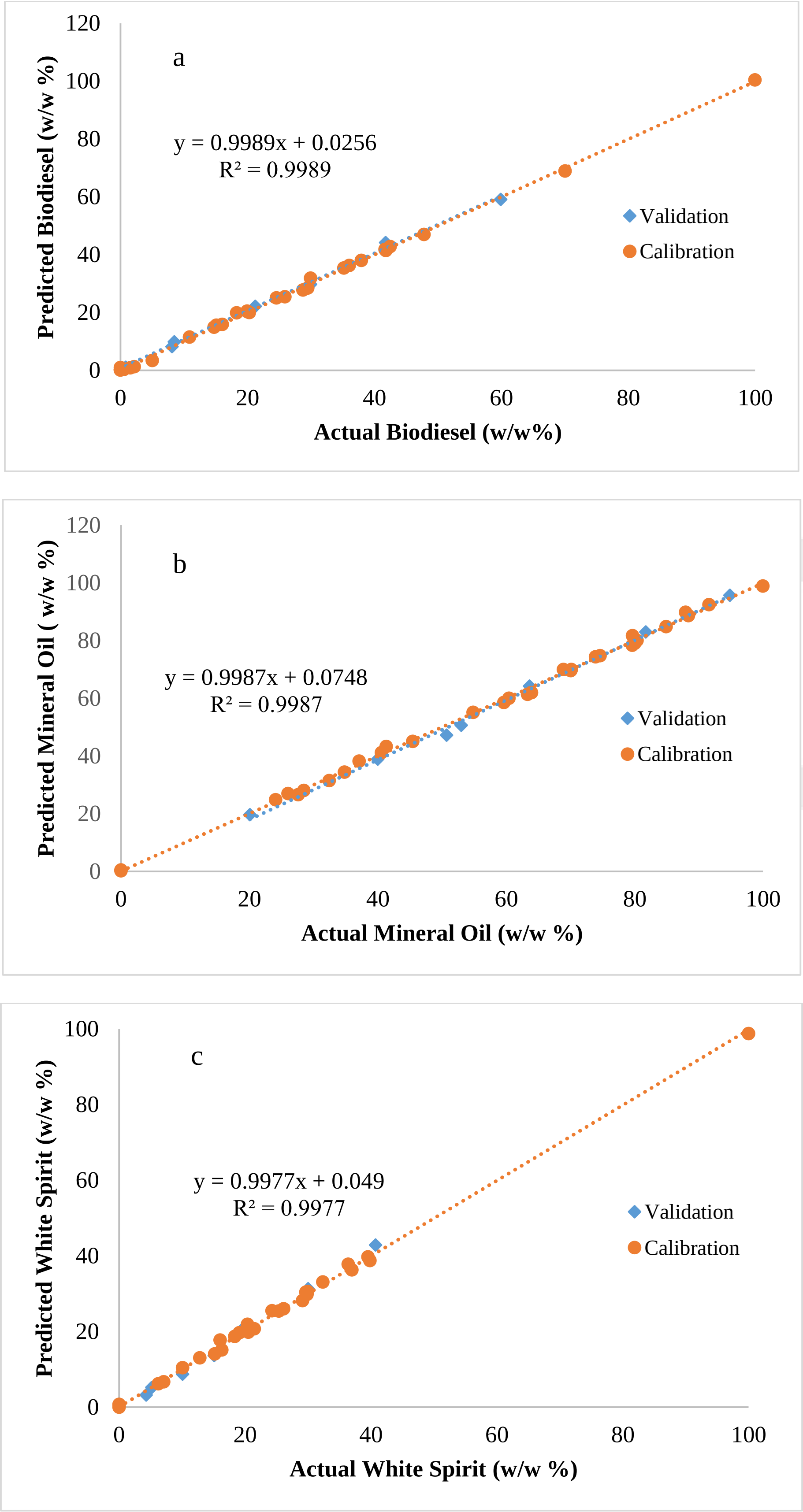

Figure 3.12 a) Actual versus predicted plot of a) biodiesel, b) mineral oil and c) white spirit analyzed with PLS

The parameters of model performance are given in Table 3.4 where RMSEC of each component in blends were found between 0.774 (w/w %) and 1.084 (w/w %), RMSEP were found between %1.280 and 1.825.

Table 3.4 Statistical parameter of model developed with PLS-FTIR/ATR for biodiesel, mineral oil and White Spirit.

Working Spectral Region	**1750-1730 cm^{-}1, 1550-1000 cm^{-1}and 800-650 cm^{-}1**		
Optimum PC Number 7	**Biodiesel (w/w)**	**Mineral Oil (w/w)**	**White Spirit (w/w)**
R^2	0.9989	0.9977	0.9987
RMSEC	0.77	1.05	0.92
RMSEP	1.28	1.04	1.83

It should be noted that the R^2 values close to unity is not always an indication of the suitability of the model. Besides, in determining the adequacy of the model, the residuals must be examined. Hence, according to the Figure 3.13, standard residual values of biodiesel, mineral oil and white spirit are within the error limits at 95% confidence level and no outlier observed. These results prove that the model is well fitted.

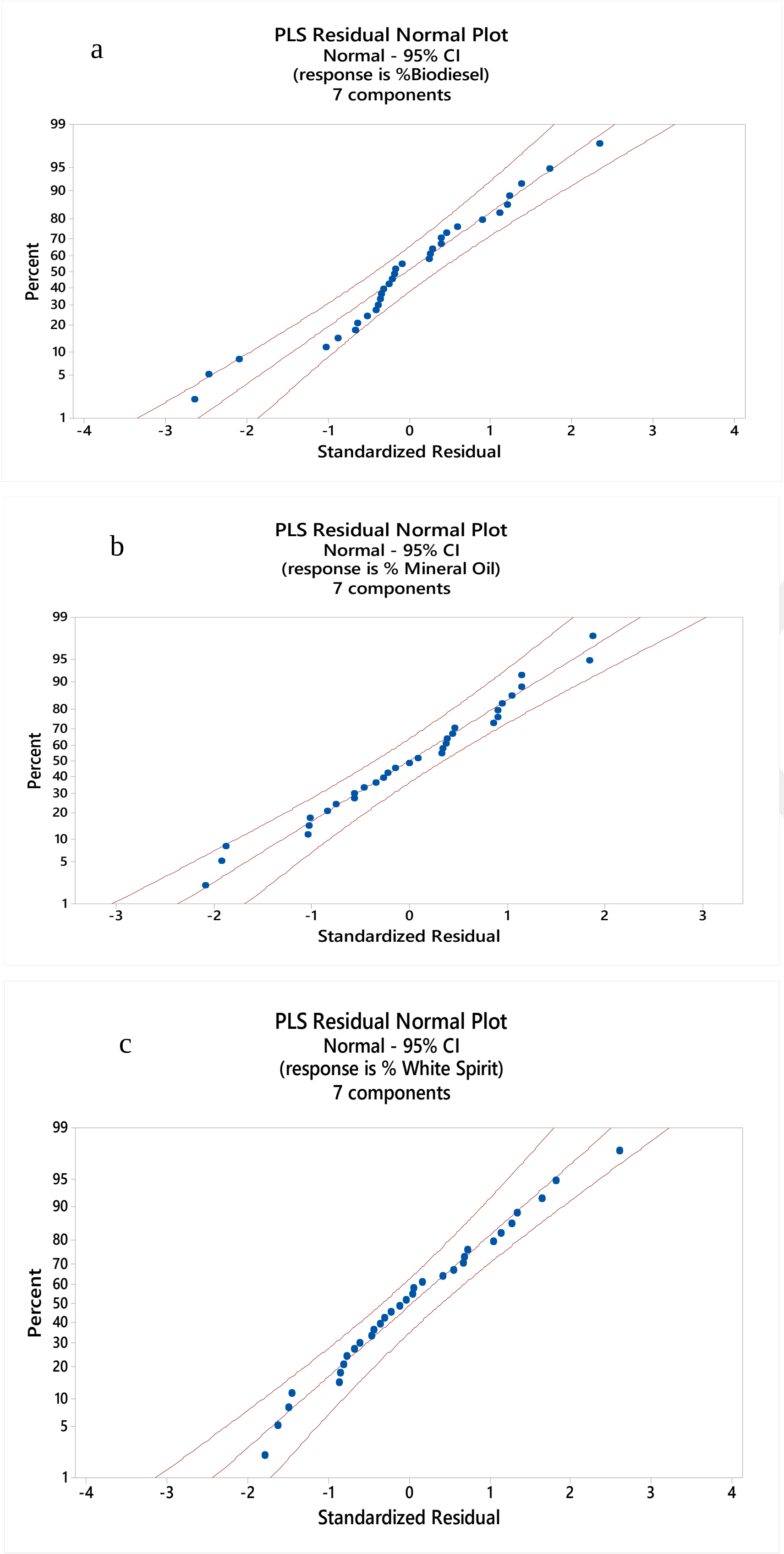

Figure 3.13 a) PLS Residual Normal Plot of biodiesel, b) mineral oil and c) white spirit

4. CONCLUSION

This work presents the combination of mid-infrared spectroscopy and chemometric technique used for rapid analyzing to detect diesel, biodiesel, mineral oil and solvent in binary or ternary blends. The PLS multivariate calibration model associated with FTIR-ATR spectral data was successfully applied for detection of biodiesel in diesel samples in the range from % 0 to % 10 (v/v) at which 2% of biodiesel to diesel blend has been encouraged by government (EPDK). Hence, the developed method would allow to laboratories, particularly refinery one, for the determination of biodiesel blended in gasoil (diesel) with highly accurate and precise measurement at the 95 % CI level. This also conveys to the laboratories a good opportunity in terms of quickness, readiness of sample to analysis, less chemical consumption requirements and cost-effect per analysis compared to the traditional method like GC-FID. In addition, this coupled technique is well suited to analyzing to ternary blends of biodiesel, mineral oil, solvent and white spirit with a small error in an acceptable confidence level.

The main advantage of using PLS is reducing to dimension of the data matrix and it take care most important variables explained maximum variance. Computational methods enable cost and saving time. Therefore, Combining FTIR-ATR with chemometrics can be used fuel adulteration with a good prediction level.

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