DETERMINATION OF PALM BIODIESEL / PETROLEUM DIESEL BLEND RATIO THROUGH SPECTROSCOPIC METHOD

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ABSTRACT

Biodiesel, defined as the alkyl esters (usually methyl esters) of vegetable oils, is miscible with conventional petroleum diesel fuel at all blend levels. Blends of biodiesel with conventional petroleum diesel fuel represent a common utilization of biodiesel. The Malaysian Government has initiated the implementation of palm biodiesel since 2007 and the proposed blend is B5. Accordingly, there is interest and need for the development of methods for determining or verifying the blend level of biodiesel in petroleum diesel. To date, the most widely used and acceptable method for determination of biodiesel blend levels is using IR spectroscopy.

The present study investigated the determination of blend level of palm biodiesel in petroleum diesel fuel in accordance to European Standard EN 14078:2003. The method was established for the determination of fatty acid methyl esters (FAME) in middle distillates—Infrared spectroscopy method. Principal component analysis of the region 1670 cm^{-1} to 1820 cm^{-1} and maximum carbonyl (C=O) absorption peak at 1745 $cm^{-1} \pm 5$ cm^{-1} could distinguish blends of petroleum diesel fuel with palm biodiesel. The calibration model was built by following the parameters specified in EN 14078:2003. The peak height was correlated against the FAME concentration in g/L, and the calibration is reported. In the present study, the linearity over the selected range is very good, as evidenced by the R^2 value of 0.9999. By using the data from the calibration function, the blend level of palm biodiesel in petroleum diesel was determined easily.

Up to 0.2 % error occurs between the measured and an estimated value when used this method to determining the FAME contents in the palm biodiesel-petroleum diesel fuel blend.

The adulteration of biodiesel/petroleum diesel blends by palm cooking oil was also successful traced by using thin layer chromatography (TLC) method. Good separation between methyl ester and glycerol was traced using TLC silica gel plate and solvent system chloroform : hexane (1:1 *v*/*v*). The amount of acylglycerols adulteration as low as 0.05% can be detected. The detection of adulterant such as acylglycerols in palm biodiesel and petroleum diesel fuel blends *via* TLC method is a useful and rapid method. It is highly recommended for enforcement exercise during implementation of palm biodiesel blend as there is a high possibility that acylglycerols may be used as an adulterant due to the fact it is cheaper than FAME and it cannot be differentiated from FAME due to the presence of carbonyl functional group.

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ABBREVIATIONS

%	per cent
A.R.	analytical reagent
ASTM	American Society of Testing and Material
BSI	British Standard Institution
cm	centimetre
CPO	crude palm oil
EN	European Standard
EU	European Union
FAME	fatty acid methyl ester
FFA	free fatty acid
FID	flame ionization detection
FT	Fourier transform
FT-IR	Fourier transform-infrared
FT-Raman	Fourier transform-raman
g	gram
GC	gas chromatography
HPLC	high performance liquid chromatography
IR	infrared
kg	kilogram

L	litre
mL	millilitre
mm	millimetre
MPOB	Malaysian Palm Oil Board
NaCl	sodium chloride
^{o}C	degree Celsius
PAHs	polycyclic aromatic hydrocarbons
RBD	refined bleached deodorized
R_f	retention factor
TLC	thin layer chromatography
v	volume

CHAPTER ONE

LITERATURE REVIEW

1.1 Biodiesel

The scarcity of conventional fossil fuels, growing emissions of combustion generated pollutions and their increasing costs will make renewable sources. Experts suggest that current oil and gas reserves would suffice to last only a few more decades. To meet the rising energy demand and replace reducing petroleum reserves, biodiesel fuel is in the forefront of alternative technologies. Accordingly, the viable alternative for compression ignition engines is biodiesel.

1.1.1 Definition of Biodiesel

Biodiesel refers to a diesel equivalent, processed fuel derived from biological sources. Biodiesel is the name for a variety of ester based oxygenated fuels from renewable biological sources. It can be made from processed organic oils and fats.

Chemically, biodiesel is defined as the monoalkyl ester of long chain fatty acids derived from renewable biolipids. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to

yield methyl or ethyl ester and glyceride (Demirbas, 2002). Fatty acid methyl esters or biodiesels are produced from natural oils and fats. Generally, methanol is preferred for transesterification because it is less expensive than ethanol (Graboski and McCormick, 1998).

In general terms, biodiesel may be defined as a domestic, renewable fuel for diesel engines derives from natural oil like soybean oil that meets the specifications of ASTM D6751. In technical terms, biodiesel is a diesel engine fuel comprised of monoalkyl esters of long chain fatty acids derives from vegetable oils or animal fats, designated B 100 and meeting the requirements of ASTM D6751. Biodiesel in application as an extender for combustion in diesel possesses a number of promising characteristics, including reduction of exhaust emission (Dunn, 2001). Chemically, biodiesel is referred to as the monoalkyl esters, especially methylester, of long chain fatty acids derived from renewable lipid sources via a transesterification process.

Biodiesel is a mixture of methyl esters of long chain fatty acid like lauric, palmitic, stearic, oleic and *etc*. Typical examples are rapeseed oil, canola oil, soybean oil, sunflower oil, palm oil and their derivatives from vegetable sources. Beef and sheep tallow and poultry oil from animal sources and cooking oil essentially the same. Oil or fat reacts with methanol or ethanol in the presence of a sodium hydroxide or potassium hydroxide catalyst to form biodiesel, methyl esters and glycerine.

1.1.2 Sources of Biodiesel

The source for biodiesel production is usually chosen according to the availability in each country. In Brazil, biodiesel production has been adjusted to the available crop in each region. In the north, palm kernel and soybean are the most used oil sources while in the northeast, castor bean, palm oil, palm kernel, babassu, soybean and cotton seed are more popular. In the central west, soybean, cotton seed, castor bean and sunflower seed are more preferred while in the southeast, soybean, castor bean, cotton seed and sunflower seed are more suitable (Pinto *et al*., 2005).

The widespread use of soybeans in the USA for food products has led to the emergence of soybean biodiesel as the primary source for biodiesel in that country. In Malaysia and Indonesia, palm oil is used as a significant biodiesel source. In Europe, rapeseed is the most common base oil used in biodiesel production. In India and Southeast Asia, the jatropha tree is used as a significant fuel source.

1.2 Palm Biodiesel (Palm Fatty Acid Methyl Esters)

1.2.1 Production of Palm Cooking Oil (Refined, Bleached and Deodorised Palm Olein

Palm oil is a very common cooking ingredient in Southeast Asia and the tropical belt of Africa. Its increasing use in the commercial food industry in other parts of the world is buoyed by its cheaper pricing and the high oxidative stability of the refined product (Che Man *et al.,* 1999, Matthäus, 2007). In general, the raw material of producer of cooking oil is CPO (crude palm oil) or hash palm oil.

Production process of cooking oil with CPO as raw material basically pass through two phase that is process of refinery and fractionation which both representing the one unit of process. Refinery or process of purification is the process addressed to eliminate the physical or chemical elements, which is not desired to exist in CPO, so that oil become to be free from the aroma, low FFA (free fatty acid), normal color and other residue. Although that, the concentration of different types of fatty acids present in CPO found elsewhere (Tan and Flingoh, 1981). The fractionation is dissociation process between two existing fractions in cooking oil. In course of the fractionation process happened by the dissociation of stearin and olein.

As processing CPO become the cooking oil marginally divided into two step, that is purification phase (refinery) and dissociation phase (fractionation). Purification phase consisted of the omission of gum (degumming), bleaching and aroma omission (deodorization). Dissociation phase consisted of the crystal process (crystallization) and fraction dissociation.

1.2.2 Palm Oil as Raw Material for Biodiesel

Rapeseed and soybean oil are the most-used feed stocks for biodiesel production in the European Union and the United States, respectively. However, the use of palm oil based biodiesel is increasing due to strong production growth in tropical countries like Malaysia, Indonesia, Thailand, Nigeria and Colombia (Johnston and Holloway, 2008). Palm oil is a promising feedstock for biodiesel production because of its low cost and high productivity per unit of planted area.

Palm oil biodiesel is an environmentally friendly and renewable energy source that is produced from palm trees. The palm oil that is harvested and produced from palm trees is referred to as crude palm oil. The crude palm oil is then shipped to be refined by a palm oil refinery. The output is then referred to as refined palm oil which is then suitable to be used as a biodiesel fuel, or blended with petroleum diesel.

Palm oil biodiesel, also known as palm oil methyl ester, differs from other types of biodiesel in its grade of molecule unsaturation. Palm oil biodiesel is more saturated, which means it has a lower number of double carbon bonds in its molecules. For diesel engine applications, the degree of biodiesel molecule unsaturation represents a compromise. Saturated fuels such as palm oil biodiesel have high-ignition quality. However, they also harden at higher temperatures, making them difficult to use in cold weather. Since biodiesel is derived from renewable sources, its production and use are being promoted worldwide as a way to reduce oil dependency and decrease greenhouse gas emissions.

1.3 Production Technology of Biodiesel

The problems with substituting vegetable oil for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character. These characteristics of vegetable oil can be changed by transesterification reaction that can lead to the products commonly known as biodiesel or methyl esters of oil and fats (Van Gerpen and Knothe, 2005).

1.3.1 Transesterification

Transesterification, also called alcoholysis (Fangrui and Hanna, 1999) is the reaction of a triglycerides that the main component of vegetable oils or animal fats with an alcohol mainly methanol to form esters and glycerol as shown in Figure 1.1, which has been widely used to reduce the viscosity of vegetable oils (triglycerides). In transesterification, triglycerides in vegetable oil react with alcohol to form a mixture of glycerol and fatty acid alkyl esters, called biodiesel.

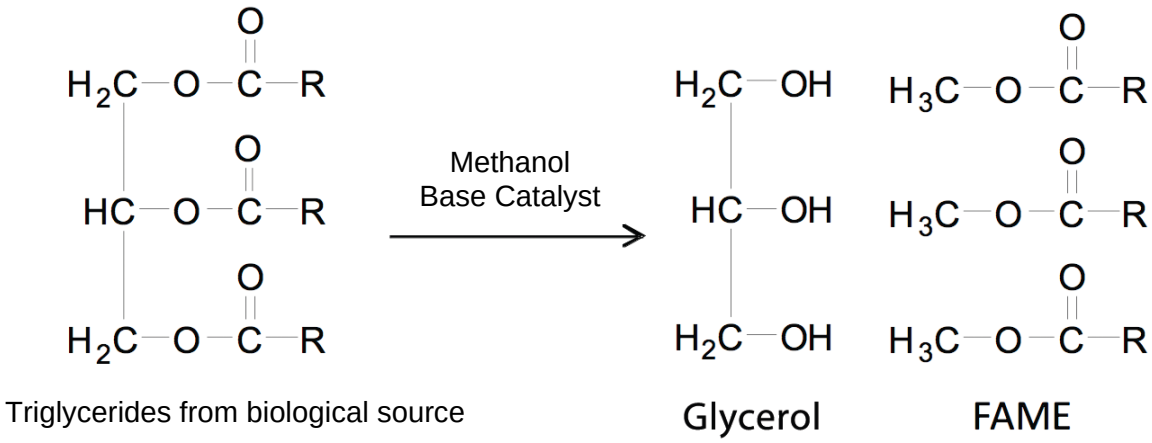


Figure 1.1: The Transesterification of Triglyceride with Alcohol

Biodiesel produced from vegetable oils can be used as an alternative to diesel fuels because its characteristics are similar to those of petroleum based diesel fuels. For example, they have a viscosity close to that of petroleum based diesel fuel, their volumetric heating values are a little lower, but they have high cetane and flash points (Fukuda *et al*., 2001). Many types of alcohols such as methanol and ethanol can be used in the transesterification. If methanol is used, the resulting biodiesel is fatty acid methyl ester (FAME), which has proper viscosity, boiling point and high cetane number.

Transesterification can be catalyzed by both acidic and basic catalysts. An acidic catalyst (e.g. sulphuric acid, hydrogen chloride, boron trifluoride, etc.) slowly catalyzes the transesterification of triglyceride. Alkaline metal hydroxides (e.g. metal alkoxide, alkaline hydroxide etc.) are preferred as the basic catalysts and giving faster reactions. All steps in the transesterification process are reversible but the equilibrium can be shifted with excess alcohol so that transesterification process practically to completion.

With the current trend towards the environmental friendly biofuel, coupled with financial incentives, producers are encourage to build new plants and improve the existing production plants to produce high quality methyl esters of biodiesel grade (Boocock *et al*., 1998).

1.3.2 Advantages of Palm Biodiesel

The production of biodiesel or more commonly fatty acid methyl esters (FAME) to be the most promising alternative for petroleum diesel fuels (Ma and Hanna, 1999; Stavarache *et al*., 2005) has attracted significant attention lately due to the increasing demand for a cleaner, safer and renewable energy. When biodiesel displaces petroleum diesel fuel, it reduces global warming gas emissions such as carbon dioxide. Biodiesel has no aromatics, almost no sulfur, and contains 11% oxygen by weight. These characteristics of biodiesel reduce the emissions of carbon monoxide, hydrocarbon, and particulate matter in the exhaust gas compared to petroleum based diesel fuel (Peterson and Hustrulid, 1998).

Graboski *et al.* (1998) and Tomasevic *et al.* (2003) also reported the same fact that biodiesel has higher cetane number than diesel fuel, and contains no aromatics, almost no sulfur and 10-12% oxygen by weight. Biodiesel-fueled engines produce less CO, HC and particulate emissions than petroleum diesel-fueled engines. It also improves the lubricity, which results in longer engine component life (Boehman, 2005, Gerpen, 2005, Kinast, 2001). The flash point of biodiesel is higher than that of diesel fuel. Although the flash point does not directly affect the combustion, it makes biodiesel safer regarding the storage and transport (Encinar *et al.,* 2005, Owen and Coley, 1995).

However, there are some drawbacks of biodiesel. Biodiesel has higher cost than diesel fuel mainly due to the cost of virgin vegetable oils (Felizardo, 2006). The cold flow properties of biodiesel are poor and these properties may cause problems in the start of engine and limits the use of biodiesel in cold climates (Knothe, 2005, Kinast, 2001). Another drawback of biodiesel is tendency to oxidize with air especially at high temperatures (Monyem *et al.,* 2000).

Tyson (2001) and Altıparmak *et al.* (2007) stated that the heating value for biodiesel is approximately 8% lower than that of diesel fuel. When diesel engine is fueled with biodiesel, there is an increase in NOx emissions compared to petroleum diesel-fueled engines due to the combustion and some fuel properties (Canakci and Gerpen, 2003). But, in the some studies from Dorado *et al.* (2003) and Kalam and Masjuki (2002) a reduction can be seen in NOx emissions.

1.4 Properties of biodiesel versus Petroleum diesel

The sizes of the molecules in biodiesel and petroleum diesel are about the same, but they differ in chemical structure. Biodiesel molecules consist almost entirely of chemicals called fatty acid methyl esters (FAME), which contain unsaturated “olefin” components. Low-sulfur petroleum diesel, on the other hand, consists of about 95 percent saturated hydrocarbons and 5 percent aromatic compounds.

The differences in chemical composition and structure between petroleum diesel and biodiesel result in several notable variations in the physical properties of the two fuels. The seven most significant differences are as follows. Biodiesel has higher lubricity that is more slippery than petroleum diesel. This is a good thing, as it can be expected to reduce engine wear. Biodiesel contains practically no sulfur. This is also a good thing, as it can be expected to result in reduced pollution from engines using biodiesel.

Biodiesel has higher oxygen content usually 10 to 12 percent than petroleum diesel. This should result in lower pollution emissions. But, relative to petroleum diesel, it causes slightly reduced peak engine power (~4 percent). Biodiesel tends to thicken and gel up at low temperatures more readily than petroleum diesel. Biodiesel is more likely to oxidize that is react with oxygen to form a semisolid gel-like mass. This is a concern, especially for extended fuel storage and when using engines that are only operated occasionally such as standby power generators. A good method for storage is to use a dry, semi-sealed, cool and light-tight container.

Biodiesel is more chemically active as a solvent than petroleum diesel. As a result, it can be more aggressive to some materials that are normally considered safe for diesel fuel. Biodiesel is much less toxic than petroleum diesel. This can be a real benefit for spill cleanups. The quality of petroleum diesel fuel tends to be more uniform and reliable, especially when compared to small-scale production of biodiesel where quality control may or may not have been good.

Petroleum diesel can vary in quality from plant to plant or from region to region, but the variations are typically much smaller. Poor-quality biodiesel fuel can lead to many problems in engine performance, and care should be taken to ensure that fuel is of good quality. Biodiesel that conforms to ASTM standard D6751 should be of a consistent and high quality.

1.5 Overview of Biodiesel Industry

1.5.1 Malaysia National Biodiesel Policy

It is known that fossil fuels are limited and will finish in the near future. The aim of replacing biodiesel for fossil fuels used at the moment should not lead to higher consumption of diesel by the thought of availability and renewability of this kind of fuel. Malaysia government has announced the introduction of the National Biofuel Policy on August 10, 2005. This policy is interchangeably known as the National Biodiesel Policy and is formulated after extensive consultation with all stakeholders and as a result of research findings by MPOB since 1982.

It takes into account the development, feasible use, sustainable supply and the spin-off effects of biodiesel in short, medium and long terms to underscore Malaysia's contribution to the global renewable fuel objective. The National Biofuel Policy envisions the use of environmentally friendly, sustainable and viable sources of energy to reduce the dependency on depleting fossil fuels. Besides, it is also expected to enhance prosperity and well being of all the stakeholders in the agriculture and commodity based industries through stable and remunerative prices (Mamat, 2009). The implementation of the national policy will be spearheaded by the Ministry of Plantation Industries and Commodities of Malaysia.

The Malaysian policy of biofuel is also in line with that in European Union (EU) which generally follows the following objectives: (1) competitiveness of the EU economy, (2) security of energy supply, and (3) environmental protection. All renewable energy policies in EU should be measured by the contributions they make to these goals (Bozbas, 2008). By following these objectives and by mandating the use of biodiesel, it is expected that Malaysia will be able to improve energy supply security and reduce greenhouse gas emissions while at the same time, enjoying a boost in rural incomes and employments (Yatim, 2009).

The National Biofuel Policy spurs the Malaysian biofuel industry. The policy report is expected to call for the production of biodiesel for use in the transport and industrial sectors to begin in October 2006 with a wider-scale use by 2007. It also promotes the production of biodiesel for export purposes by October 2006. There is also short term objective to make the sale B5 mandatory by end of 2008, with legislation currently being considered (Mamat, 2009). However, it has been delayed due to soaring oil price in 2008 (Hoh, 2008). The implementation only starts in 2009 with few identified sectors to be progressively extended to other sectors in the following years.

1.5.2 Biodiesel Industry in Malaysia

Recent increases in petroleum diesel fuels price, the high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread use of petroleum diesel fuels make it increasingly necessary to develop the renewable energy sources and lesser environmental impact than the traditional ones. This has encouraged recent interest of the scientists to find alternative sources for petroleum diesel fuel. The substitution fuel must be technically feasible, economically competitive, environmentally acceptable and readily available (Meher *et al*., 2006).

One of the most interesting alternatives of the renewable fuels is the vegetable oil fuel for diesel engine. Considerable efforts have been made to develop vegetable oil derivates that approximate the properties and performance of the hydrocarbon based diesel fuels. The most detrimental properties of these vegetable oils are their high viscosity, low volatility, poor atomization and auto-oxidation.

Palm oil is the second most traded vegetable oil crop in the world after soy oil. Malaysia is currently the world's second top producer of palm oil after Indonesia. However, palm oil is now starting to be used as an ingredient in biodiesel fuels. The development of biodiesel fuels in Malaysia has been identified as a new source of growth for the plantation commodities industry. The concentration is on biodiesel fuels from palm oil, because of the large domestic production of this feedstock.

A common use of biodiesel is in blends with conventional mineral petroleum diesel fuel. Malaysia was introduced a type of biodiesel which is a mixture of 95% petroleum diesel and 5% palm oil methyl ester and the Departments of Standards

Malaysia has accredited this as Malaysia's first biodiesel blend known as Envo diesel (B5) in February 2007 (Mamat, 2009b). The accreditation notes a new progress in the field of research and development of the Malaysia's biodiesel. The standard has been coded under section Petroleum and Gas (MS 2007:2007 P) with the name of B5 Palm Biofuel Blend Speciation (Malaysia Biodiesel Standard, 2007).

Because raw fatty oil can be present in blends either due to incomplete conversion to ester during reaction or due to illegal addition of this cheaper raw material, it is necessary to instil confidence in users that biodiesel blends are strictly according to quality standards and regulations. Thus it is important to develop reliable analytical methods to determine biodiesel in petroleum diesel fuel blends, considering the presence of raw vegetable oil.

1.5.3 Biodiesel Blends

Blends of biodiesel and petroleum diesel are products most commonly distributed for use in the retail diesel fuel marketplace. The volume percentages of biodiesel and petroleum diesel blends are denoted as B*X*, where *X* represents the volume percentage of biodiesel in the blend. Therefore, a B100 denotes 100% biodiesel while B2 is a blend of 2 volume percent of biodiesel and 98 volume percent of petroleum diesel (Pinto *et al.*, 2005). Blends of biodiesel with conventional petroleum diesel fuel represent a common utilization of biodiesel.

In the U.S., biodiesel is most commonly utilized as a 20 *v*/*v* % blend in petroleum diesel, which is commonly referred to as B20 and is recognized as an alternative diesel fuel. In France, biodiesel is utilized at a lower level blend in petroleum

diesel (5 *v*/*v* %), while recent energy initiatives in the U.S. have mandated the use of biodiesel as low as 2 *v*/*v* % in petroleum diesel. In the Malaysia, our Government has initiated the implementation of palm biofuel since 2007 and the proposed blend is B5. Therefore, the determination of blend levels is one important issue to the quality control of palm biodiesel due to the increase of palm biodiesel–diesel blends commercialization (Knothe, 2006).

1.5.3.1 Benefit of Biodiesel Blends

The biodiesel percentage in a biodiesel-petroleum diesel mixture determines many important characteristics of the blended fuel. Using biodiesel/petroleum diesel blends having higher biodiesel levels than recommended may compromise engine performance. Lower blend levels may reduce expected benefits such as fuel lubricity and lower tail pipe emissions of unburned hydrocarbons, carbon monoxide, particulate matter, nitrogen oxides, sulfates, polycyclic aromatic hydrocarbons (PAHs), and nitrated PAHs.

In addition, biodiesel cloud and pour points are usually higher than those of diesel fuel. The cloud point is the temperature at which the fuel becomes hazy or cloudy due to wax crystal formation. The pour point is the lowest temperature at which oil will flow. As a result, as the percentage of biodiesel increases that is higher blend level, the fuel blend becomes unsuitable or difficult to use in cold weather conditions. Further, engine injection timing can be adjusted based on the blend level in order to improve the engine emission and performance.

Actual biodiesel content in fuel sold at gas stations may be significantly different from the stated blend level. There are several reasons why the actual blend level may differ from the stated level. For instance, if biodiesel is blended at a temperature less than 10 °F above its cloud point, it does not mix well with diesel. This may cause a rich mixture in one portion of a tank versus a lean mixture in another portion (National Biodiesel Board, 2005).

1.5.4 Fuel Adulteration

Adulteration of fuel has a major influence on engine start-up control, engine heating, acceleration and fuel consumption, and it also increases the emission of particulate material, hydrocarbons and exhaustion gases (Kalligeros *et al.,* 2003). In addition to the problems related to engine performance and emission of atmospheric pollutants (Pereira *et al.,* 2006).

In India and Greece, the adulteration of petroleum by products has been a serious problem, particularly of diesel oil. Groups of researchers are developing new analytical techniques to detect these frauds which make use of adulterants such as kerosene and cyclohexane, among others (Patra and Mishra, 2002, Kalligeros *et al.,* 2003, Taksande and Hariharan, 2006). In Brazil, adulteration of gasoline has been extensively covered by the media, and the addition of a larger amount of anhydrous ethanol exceeding the specifications of Brazilian legislation is one of the most common practices (Oliveira *et al.,* 2004). However, the addition of light solvents as naphtha and rubber solvent is also observed (Pereira *et al.,* 2006).

Diesel oil is easily adulterated by adding non-transesterified vegetable oil, as edible vegetable oil, or even residual oils. The characterization of fuels is of fundamental importance in order to carry out an effective quality control, and the development of analytical methodologies to control the quality of biodiesel, detect adulterations and quantify the amount of biodiesel in blends with diesel oil has been the focus of increasing interest.

Infrared spectroscopy (IR) (Oliveira *et al.,* 2007, Aliske *et al.,* 2006, Pimentel *et al.,* 2006) and high performance liquid chromatography (HPLC) (Foglia *et al.,* 2005) stand out among the techniques used for this type of analysis. Aliske *et al.* (2006) developed a methodology, using infrared spectrometry, whereby the width and height of the peak corresponding to the carbonyl group of esters are used to quantify biodiesel mixed with diesel in the 0–100% (*v*/*v*) band. For the peak area as well as for the peak height methods, approximately 90% of the data are observed within 5% deviation from the fitted function. FTIR and FT-Raman, associated to multivariate calibration, were used to detect the adulteration of B2 and B5 samples with non-transesterified vegetable oil in the 0–5% (*w*/*w*) range (Oliveira *et al.,* 2007).

1.6 Technique for the Determination of Biodiesel Blends Ratio

Accordingly, there is interest and need for the development of methods for determining or verifying the blend level of biodiesel in petroleum diesel. Different methods have been used for determining or verifying the concentration of biodiesel in the petroleum diesel blend. However, low cost and fast analytical methods are desirable.

1.6.1 Spectroscopic

1.6.1.1 Infrared Spectroscopy

To date, the most widely used and acceptable method for determining biodiesel blends level is infrared (IR) spectroscopy that allows the reliable, direct and fast determination of several properties, without sample pre-treatment (Maria *et al.,* 2006). For direct determination of blend levels of biodiesel with petroleum-based diesel fuel by IR spectroscopy, the peak of the carbonyl moiety at approximately 1740 cm^{-1} was used (Birova *et al.,* 2002). Principal component analysis of the region 1700-1800 cm^{-1} could distinguish blends of petroleum diesel with biodiesel or untransesterified vegetable oil. This is the basis of the European Standard EN 14078 for the determination of fatty acid methyl esters (FAME) in middle distillates—Infrared spectroscopy method (BSI, 2003).

The petroleum and petrochemical industries use IR spectroscopy method to determine the physical and chemical properties of fuels and industrial streams (Guachardi *et al.,* 1998, Faber *et al.,* 1998) and also have been reported to monitor quality of biodiesel and petrodiesel blends (Knothe, 2001, 2000, 1999, Birova *et al.,* 2002). In similar work, Aliske *et al.* (2007), developed a FT-IR method to the determination of biodiesel and diesel mixtures. The method covers the full ranges of mixture (0-100%) and it employs the carbonyl peak present only in biodiesel spectrum for the quantification. This methodology stands for a simple way to perform quality control and monitoring of biodiesel–diesel blends. It is worth to notice that the method was developed using ethyl biodiesel from soybean oil and diesel blends.

Recently, Guarieiro *et al.* (2008) also described a FT-IR method to determine biodiesel content in diesel blends through area measurement of the peak at 1754cm^{-1}. The method is fast, low-cost and it allows the determination of biodiesel content upper than 0.1%. Zagonel *et al*. (2004) observed the overlapped peaks of soybean oil and its corresponding ester in MID spectra. Both of authors used multivariate calibration of the peaks in the region 1800 cm^{-1} to 1700 cm^{-1}, corresponding to the vibration of carbonyl groups to distinguish soybean oil from its ester.

Sadeghi *et al*. (1994), Siekmann *et al.* (1982) reported that the mid-IR carbonyl absorption has been used for determining biodiesel contamination in lubricating oil. Knothe (2001) in the reported state that the carbonyl peaks in the mid-IR range have the drawback that they are virtually identical for vegetable oils and their methyl esters as both contain the carbonyl functionality in ester form.

1.6.1.2 Nuclear Magnetic Resonance (NMR)

^{1}H NMR has been used extensively to analyze biodiesel the vegetable oil feeds, reaction intermediates, and final products of the biodiesel transesterification process. Gelbard *et al.* (1995) described the first work on the utilization of nuclear magnetic resonance, particularly ^{1}H NMR, for monitoring the yield of transesterification reaction. The peaks of methylene group adjacent to ester moiety in triacylglycerols and the methoxy group in the esters were used to follow the reaction progress.

After that, a ^{1}H NMR methodology to monitor the soybean oil ethanolysis as well as to quantify the content of fatty ethyl esters in mixtures of biodiesel and oil was developed (Neto *et al.,* 2004). The region of 4.05-4.40 ppm (ester ethoxy and glycerol

methylene hydrogens) was chosen for the quantification of the reaction. In the other studied, Morgenstern *et al.* (2006) developed a ^{1}H NMR method to monitor the transesterification reaction of soybean oil. Through NMR analysis, they were able to establish the average degree of fatty acid unsaturation and methyl esters in biodiesel.

Knothe (2001) stated that the Nuclear Magnetic Resonance (NMR) can be used to determine relative amounts of biodiesel and diesel in blends. Note that the ^{1}H NMR spectrum of conventional diesel fuel exhibits a multitude of peaks at 7-8 ppm that arise from the aromatic compounds present in that fuel. Those peaks were not taken into account in biodiesel blend level determinations.

For blend level determination by ^{1}H NMR spectroscopy, the peak of the methyl ester protons in the region of 3.6-3.7 ppm was selected as one standard peak area, and the second standard peak area was the cluster of peaks between 0.8 and 3.0 ppm, which arises from the methylene and terminal methyl protons of the hydrocarbon moieties in conventional diesel fuel and biodiesel, and the peaks at 5.3-5.4 ppm arising from the protons attached to the olefinic carbons in biodiesel. The integration value of the methyl ester protons should be set to 3 in all spectra regardless of blend levels.

However, the NMR method depends on the biodiesel fatty acid profile, which varies based on the biodiesel feedstock. In addition, using NMR to detect the blend level is prohibitively expensive based on the price of instrumentation and the costs of the maintenance. Additionally, NMR cannot readily be implemented at point-of-sale locations.

1.6.2 Chromatographic

Chromatography involves passing a mixture dissolved in a mobile phase through a stationary phase, which separates the analyte to be measured from other molecules in the mixture based on differential partitioning between the mobile and stationary phases. In the chromatography analysis mainly gas chromatography, have been applied to analyze methyl esters in the biodiesel (Knothe, 2006). The most important parameters of biodiesel (fatty mono-alkyl esters, fatty acids, glycerol and their acyl derivatives) are commonly analyzed by gas chromatography (GC) and high-performance liquid chromatography (HPLC). In fact, GC has been the most used technique due to its high accuracy for the quantification of minor components.

However, baseline drift, overlapping signals, and aging of standards and samples can destructively affect the GC accuracy. Moreover, GC analyses frequently require sample derivatization, mainly to afford trimethylsilyl derivatives of the hydroxyl groups. Although this procedure improves chromatographic separation, it also increases the analysis time. Flame ionization detection (FID) is the most widespread detector used in GC, but the utilization of mass spectrometer has increased. The latter eliminates any ambiguities about the identification of the eluting materials, but their quantification could be affected.

Freedman *et al.* (1986) developed the first GC methodology to monitor fatty acids, tri-, di-, and monoglycerides in the transesterification reaction of soybean oil. In this method, before performing the analyses, mono- and diglycerides have to be silylated with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). Such procedure affords the trimethylsilyl derivatives, allowing a better separation and tailing reduction. In this first GC work, authors used a short fused silica capillary column (1.8m; 100%

dimethylpolysiloxane), and tridecanoin as internal standard. The complete separation of acylglycerols and fatty esters was obtained in a run time of 12 minute.

HPLC analysis is less employed in biodiesel characterization, but the analysis time is shorter than GC and sample derivatization is not needed. Moreover, this technique can be applied to biodiesel from different feedstock and it is more appropriate for blend analysis than GC. Several detectors for HPLC biodiesel analysis are described, among them evaporative light scattering detection (ELSD) is quite suitable.

The first HPLC method for monitoring transesterification was developed by Trathnigg and Mittelbach (1990). They describe a HPLC methodology with density detection (DD), which allows the determination of the overall content of tri-, di-, and monoglycerides in biodiesel samples from methanolysis mixtures as well as the methyl esters detection. The analyses were performed through coupling a cyano-modified silica with two-gel permeation chromatography (GPC)-columns, and using an isocratic eluent (chloroform/ethanol 0.6%).

However, for determining the blend level of biodiesel in diesel, chromatography seems to be less suitable due to the complexity of diesel composition (Knothe, 2001). Currently, the most widely used technique is medium FT-IR spectroscopy, which is also the base of the European standard reference method (Foglia *et al.,* 2005).

1.7 Objective of the Present Study

The increasing demand for energy because of increases in petroleum diesel fuels price and environmental awareness has prompted a considerable amount of research effort to produce alternative fuels from renewable resources that are environmentally acceptable. So, the production of biodiesel from renewable lipid sources has gained international attention.

Because of raw fatty oil can be present in blends either due to incomplete conversion to ester during reaction or due to illegal addition of this cheaper raw material, it is necessary to in still confidence in users that biodiesel blends are strictly according to quality standards and regulations. Therefore, the determination of blend levels is one important issue to the quality control of palm biodiesel due to the increase of palm biodiesel-petroleum diesel fuel blends commercialization.

In respect of that, the objective of this study is to investigate the reliability of EN 14078, the standard method establish by European Standard for the determination of fatty acid methyl esters (FAME) in middle distillates—Infrared spectroscopy method. Other objective is to examine the consistency of infrared spectroscopy to determine the adulteration in palm biodiesel blends and study other significance methods to detect adulteration in palm biodiesel blends.

CHAPTER TWO

DETERMINATION OF PALM BIODIESEL BLEND RATIO

2.1 Introduction

In Malaysia, the government has initiated the implementation of palm biofuel since 2007 and the proposed blend is B5 (National Biofuel Policy, 2007). Therefore, the determination of blend levels is one important issue to the quality control of biodiesel due to the increase of biodiesel–petroleum diesel fuel blends commercialization. The European Committee for Standardization established a test method for the determination of FAME content in petroleum diesel fuel by mid infrared spectrometry in 2003 and published as EN 14078. The suitable test method has been verified to be applicable for samples containing fatty acid methyl ester (FAME).

For direct determination of blend levels of FAME with petroleum diesel fuel, the peak of the carbonyl moiety at approximately 1745 cm^{-1} ± 5 cm^{-1}. Principal component analysis of the region 1670 cm^{-1} to 1820 cm^{-1} could distinguish blends of petroleum diesel fuel from FAME. This is the basis of European Standard EN 14078 for the determination of fatty acid methyl esters (FAME) in middle distillates—Infrared spectroscopy method (BSI, 2003).

EN 14078 is only reliable for quantitative results obtained from samples not containing any significant amount of other interfering components, especially ester and other carbonyl compounds which possess adsorption bands in the spectral region used for quantification of FAME. If such interfering components are present, this test method is expected to produce higher value (BSI, 2003).

2.2 Experimental Procedure

2.2.1 Reagents and Materials

Fatty acid methyl ester (FAME) was obtained from Malaysian Palm Oil Board (MPOB), Bandar Baru Bangi. The sample was produced through transesterification of RBD Palm Oil with methanol. Petroleum diesel fuel and palm cooking oil was purchased from Petronas Station in Bangsar and Giant Hypermarket, respectively. Chloroform A.R. and cyclohexane A.R. was purchased from Fisher Scientific (M) Sdn. Bhd.

2.2.2 Apparatus/Instrumentation

A Perkin-Elmer Spectrum RX1 spectrometer was employed to obtain the FTIR spectra in the mid spectra range from 4000 cm^{-1} to 400 cm^{-1}. All spectra were recorded using an average of 16 scans, a spectral resolution of 4 cm^{-1} and interval of 2 cm^{-1}. The sealed cell used is made of NaCl with path length of 0.10 mm.

2.2.3 Procedure

2.2.3.1 Preparation of Calibration Solution

A set of five calibration solutions of FAME in petroleum diesel blends was prepared accurately. FAME was weighed accurately into appropriate volumetric flasks and filled to the mark with petroleum diesel (Table 2.1). The nominal FAME concentration for the calibration solutions were selected in such a way that the absorbance at about 1745 cm^{-1} ± 5 cm^{-1} is in the range from 0.1 to 1.1 absorbance unit. The selected five calibration solutions for this study are B1, B2, B3, B4 and B5.

Table 2.1: Preparation of Calibration Solutions in 50 mL Volumetric Flask

B*X*	Volume (mL)	
	FAME	**Petroleum Diesel**
B1	0.50	49.50
B2	1.00	49.00
B3	1.50	48.50
B4	2.00	48.00
B5	2.50	47.50

Note: B*X* = *X* represents the volume percentage of biodiesel (FAME) in the blend

2.2.3.2 Infrared Spectrometric Measurement of Calibration Solutions

Calibration solution was filled into a cleaned NaCl cell made with path length of 0.10 mm and the mid infrared spectrum was recorded in range from 4000 cm^{-1} to 400 cm^{-1} with a linear absorption in the absorbance range from 0.1 to 1.1 absorbance units. The background of spectra was obtained using a clean empty sealed cell.

The spectra were collected from 16 scans together at a slow mirror speed. Software baseline corrected was done to bring the baseline to zero at 4000 cm^{-1}. The absorbance unit at the maximum peak of carbonyl band at about 1745 cm^{-1} ± 5 cm^{-1} was measured using a baseline from 1670 cm^{-1} to 1820 cm^{-1}.

After each measurement, the sealed cell was cleaned thoroughly by repeated rinse with chloroform and petroleum diesel. The cell was considered as sufficiently clean when the recorded infrared spectrum of the sealed cell filled with petroleum diesel exactly matches with the reference petroleum diesel spectrum. The cell was dried thoroughly before each measurement because the presence of residual petroleum diesel fuel in the cell will affect the concentration of the next palm biodiesel sample.

2.2.3.3 Calibration Function

In accordance to EN 14078, a linear calibration function was computed by plotting the calibration graph using the absorbance measurement for the FAME calibration solutions. The absorbance, *A*, was used as the dependent and the concentration, *q*, as the independent variable. The calibration function for a calculated standard cell path length of 1 cm is as follows:

$$A/L = a * q + b$$

where:

A is the measured absorbance in units of absorbance
L is the actually used cell path length in cm
q is the concentration of FAME in g/L
a is the slope of regression line
b is the y intercept of the regression line

The calibration procedure was repeated when the correlation coefficient (R^2) for the regression line is below 0.99.

2.2.3.4 Preparation and Spectroscopic Measurement of Test Samples of Palm Biodiesel and Petroleum Diesel Fuel Blends

Test samples of palm biodiesel and petroleum diesel fuel blends were prepared by adding petroleum diesel fuel at room temperature with appropriate blend ratio. The prepared test samples were analysed using mid infrared spectrometer. The procedure for spectroscopic measurement is similar to procedure describe in Section 2.2.3.2. If the absorbance measured on this prepared sample does not fall in the absorbance range of the calibration, the test sample will be diluted accordingly using petroleum diesel fuel (Table 2.2).

Table 2.2: Preparation of Diluted Samples in 50 mL Volumetric Flask

B*X*	**Dilution factor**	**Volume (mL)**	
		Palm Biodiesel Blends (B*X*)	**Petroleum Diesel**
4	1	50	0
5	1	50	0
10	10	5	45
30	10	5	45
50	10	5	45

Note: B*X* = *X* represents the volume percentage of biodiesel (FAME) in the blend

2.2.3.5 Calculation

As specified in EN 14078, FAME contents (*Q*), in the unknown sample was calculated using the given formula:

$$Q = \frac{X}{a}\left[\frac{A}{L} - b\right]\frac{100}{d}$$

where:

Q is the FAME content in % *(v/v)*
X is the dilution factor (i.e. *X* = 10 for a dilution of 1:10)
a is the slope of regression line
b is the y intercept of the regression line
A is the absorbance measured in IR spectrum
L is the cell path length in cm
d is the density of FAME (d = 880.0 kg/m^3) at 20 ^{o}C in kg/m^3

2.3 Result and Discussion

2.3.1 Mid Infrared Spectra for Qualitative Analysis

2.3.1.1 Spectra of Palm Biodiesel, Refined Bleached Deodorized Palm Olein and Petroleum Diesel Fuel

After performing mid infrared absorption measurements, many unmatched peaks between palm biodiesel (FAME) and petroleum diesel fuels on the results of mid infrared spectra were found. Figure 2.1 shows spectra for both FAME and petroleum diesel fuels over the 4000 cm^{-1} to 400 cm^{-1} measured range. Mid infrared spectra of the palm methyl ester (FAME) and RBD palm olein were compared with petroleum diesel fuel, as shown in Figure 2.1. From the spectra, there is no absorption peak from petroleum diesel fuel in the regions of 3700 cm^{-1} to 3000 cm^{-1}, 1900 cm^{-1} to 1500 cm^{-1}

and 1300 cm^{-1} to 800 cm^{-1}, while FAME and RBD palm olein absorb well in those regions.

Stretching vibration carbonyl bands, around 1745 cm^{-1} ± 5 cm^{-1}, for the RBD palm olein are overlapped with their methyl ester. Zagonel *et al*. (2004) also observed overlapped peaks of soybean oil and its corresponding ester in mid spectra. Authors used multivariate calibration of the peaks in the region 1800 cm^{-1} to 1700 cm^{-1}, which correspond to the vibration of carbonyl groups to distinguish soybean oil from its ester. Knothe (2001) reported that the carbonyl peaks in the mid infrared range have the drawback that they are virtually identical for vegetable oils and their methyl esters as both contain the carbonyl functionality in ester form. Sadeghi *et al.* (1994) and Siekmann *et al.* (1982) reported that the mid infrared carbonyl absorption also have been used to determining biodiesel contamination in lubricating oil.

Peaks in the region 1300 cm^{-1} to 800 cm^{-1} are also indicate overlapping bands between palm cooking oil and their methyl ester. Peaks in the region 1000 cm^{-1} to 900 cm^{-1} may be assigned to symmetric angular deformation out of plane of the C–H bonds of olefins. Peaks around 1200 cm^{-1} may be assigned to the axial deformation of CC(= O) –O bonds of the ester, while peaks around 1183 cm^{-1} may be assigned to asymmetric axial deformation of O–C–C bonds (Silverstein *et al*., 2004).

The region between 1300 cm^{-1} to 900 cm^{-1} is known as the fingerprint region of complex spectra that include many coupled vibration bands. These overlapped peaks indicate that univariate calibration models may cause significant prediction error to quantify ester concentration when raw oil is present. Those models are also inadequate for identifying the presence of raw oil in a spoiled blend either because of incomplete conversion during transesterification reaction or an adulteration in the FAME. Knothe

(2006) admitted that some contaminants come up from the transesterification reaction and the author suggested to monitoring the biodiesel production to recognize and correct problems at an early stage.

The parameters, which are used to define the quality of biodiesel, can be divided in two groups. One of them is also used for mineral diesel, and the second describes the composition and purity of fatty esters (Mittelbach, 1996). Knothe (2000) and Mittelbach (1996) on the other studied proposed that the amount of glycerol and glycerides is a major factor in determining fuel quality. Mittelbach (1996) reported that the carbon residue is the most important indicator for the quality of biodiesel since it corresponds strictly to the content of glycerides, free fatty acids, soaps, remaining catalysts, and other impurities. However, Mahajan *et al.* (2006) state that one of the most important features of biodiesel is the acid number, which represents almost exclusively the fatty acid content. In addition, the factors such as composition of feedstock (oil or fat), production process (reaction and purification steps), storage and handling also can influence biodiesel fuel quality.

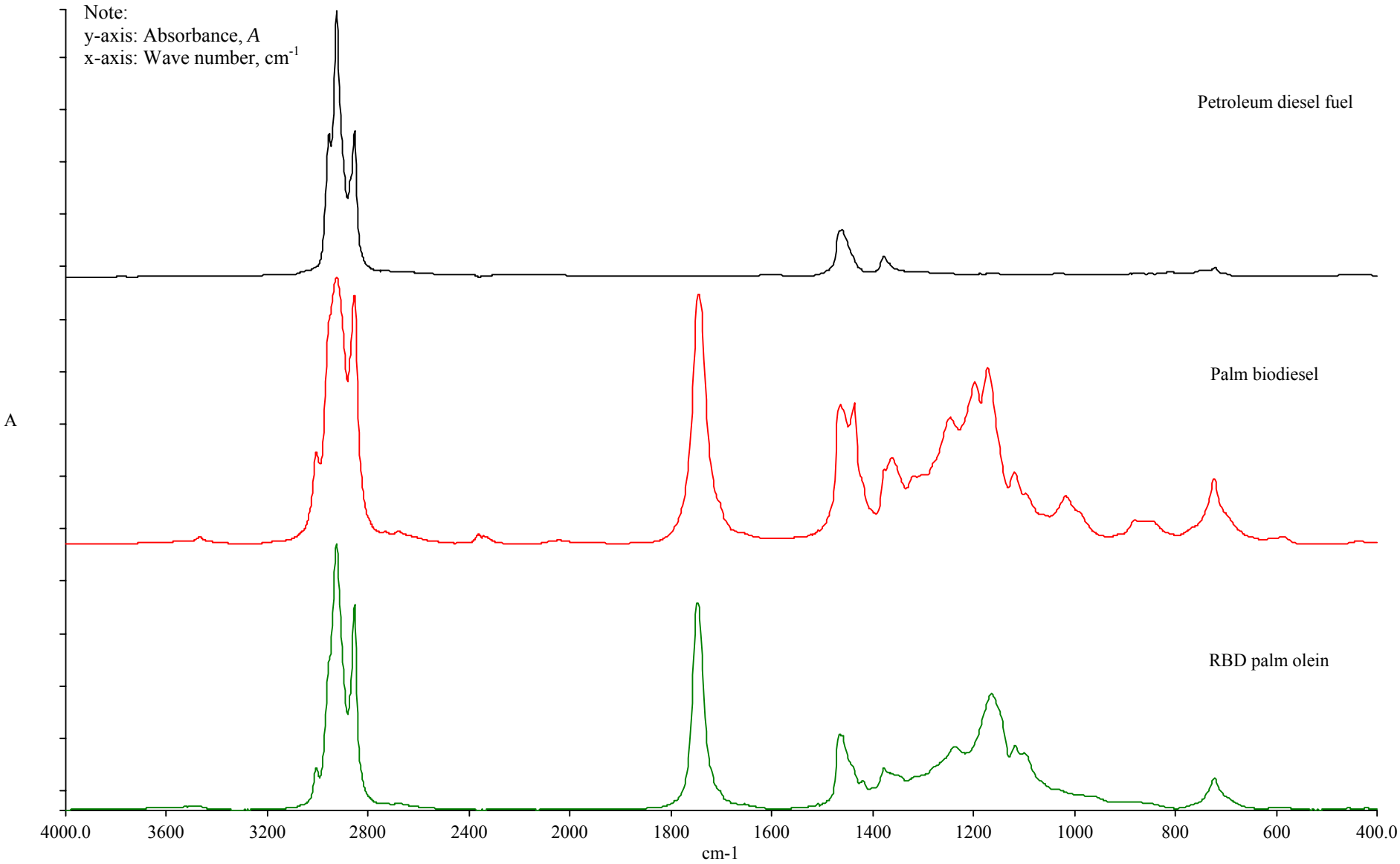
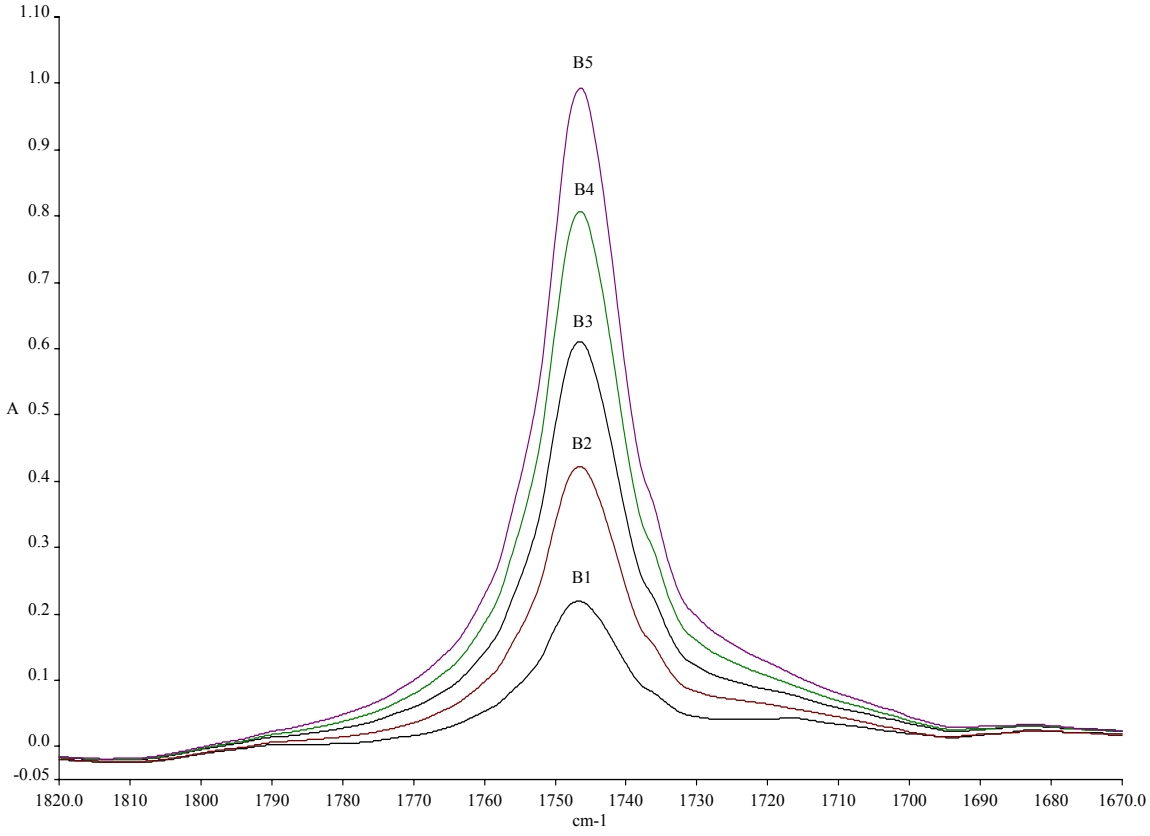


Figure 2.1: Mid IR Spectra from 4000 cm^{-1} to 400 cm^{-1}: Fatty Acid Methyl Ester (FAME), RBD Palm Olein and Petroleum Diesel Fuel

2.3.1.2 Spectra of Palm Biodiesel and Petroleum Diesel Fuel Blends

Palm biodiesel and petroleum diesel fuel blends prepared were subjected to infrared measurement. Figure 2.2 shows an evolution of the carbonyl peak with blending percentile. It is important to notice that the peak is observable even at very low blending percentiles. The carbonyl peak evolution quantification was performed over the range from 1670 cm^{-1} to 1820 cm^{-1}. A uniform increase in absorbance was apparent when the concentration of blending increases.



Note: y-axis: Absorbance, *A*
x-axis: Wave number, cm^{-1}
B1 = 1% FAME in petroleum diesel
B2 = 2% FAME in petroleum diesel
B3 = 3% FAME in petroleum diesel
B4 = 4% FAME in petroleum diesel
B5 = 5% FAME in petroleum diesel

Figure 2.2: Carbonyl Peak (C=O) Evolution with Increasing Blending Percentile

2.3.2 Infrared Spectroscopy for Quantitative Measurement

An infrared spectroscopy technique for determining the percentage of biodiesel in a blend was demonstrated on FAME-petroleum diesel fuel blend samples. The technique was highly linear and can be used for quantitative determination of the percentage blend ratio of FAME in a petroleum diesel fuel sample. Foglia *et al*. (2005) stated that the most suitable technique determining the blend level of biodiesel in diesel was mid infrared spectroscopy technique base of the European standard reference method (EN 14078).

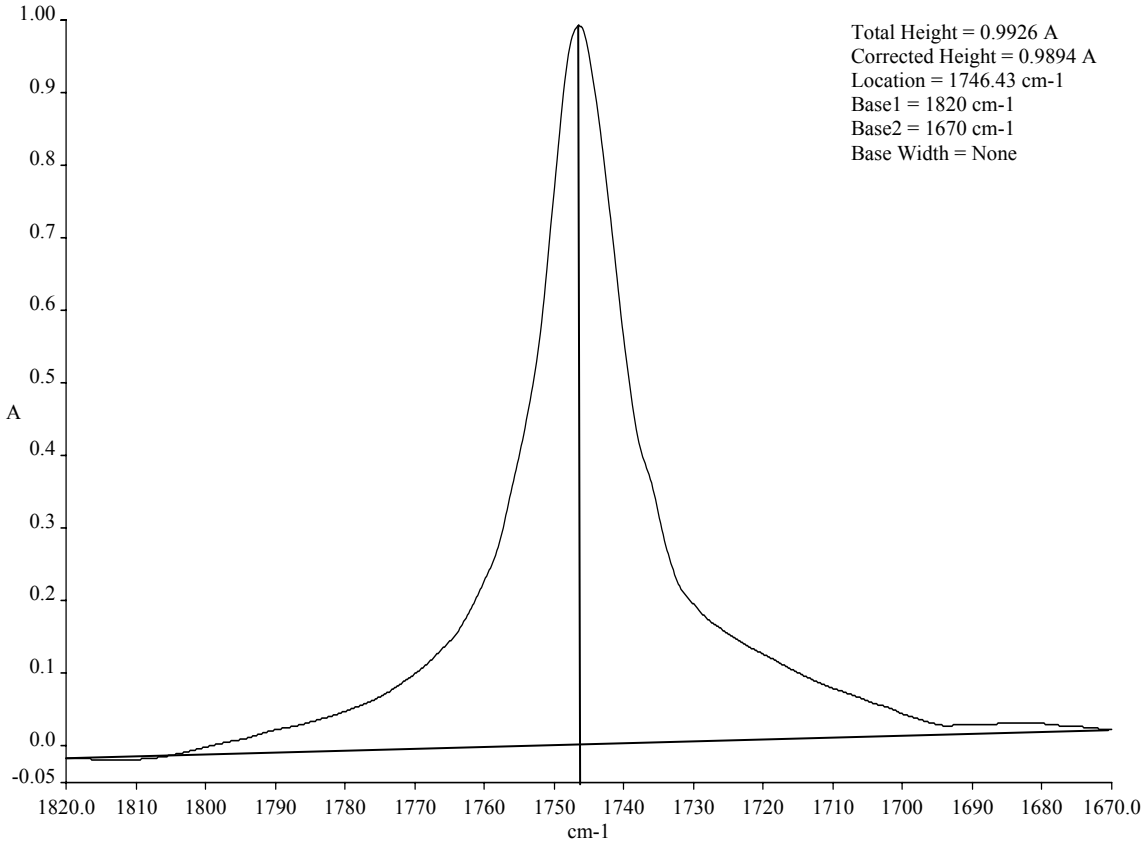
Infrared spectroscopy are most suitable technique due to the reliable data, direct and fast determination of several properties, without any sample pre-treatment (Maria *et al.,* 2006). Guarieiro *et al.* (2008) also described an infrared spectroscopy method to determine biodiesel content in diesel blends through area measurement of the peak at 1754cm^{-1}. The author stated that the method is fast, low-cost and it allows the determination of biodiesel content upper than 0.1%.

2.3.3 Calibration of Palm Biodiesel Blends

The methyl ester component, biodiesel, can be measured independently from petroleum diesel at the carbonyl band at 1745 cm^{-1} ± 5 cm^{-1} without interference from fuel additives, as specified in the European Standard EN 14078. The peak was used to determine the percentage of FAME in the blending petroleum diesel fuel.

In the present study, five series of blends were produced using the FAME in a petroleum diesel fuel (B1, B2, B3, B4 and B5). Figure 2.5 showed the linear calibration function was produced using blends with varying percentages of FAME in petroleum diesel fuel by plotting the calibration graph using the absorbance measurement for the five series of FAME calibration solution. The absorbance, *A*, was used as the dependent and the concentration, *q*, as the independent variable.

The Table 2.3 shows the absorbance measurements for B1, B2, B3, B4 and B5 blends in petroleum diesel fuel used as calibration solutions for plotting the linear calibration function. The absorbance of blends was determined by the peak maximum at about 1745 cm^{-1} ± 5 cm^{-1} by using a baseline from 1670 cm^{-1} to 1820 cm^{-1} (Figure 2.3)**.**



Note: y-axis: Absorbance, *A*
x-axis: Wave number, cm^{-1}

Figure 2.3: Typical Spectrum for FAME in Petroleum Diesel Fuel (B5, cell path 0.10 mm)

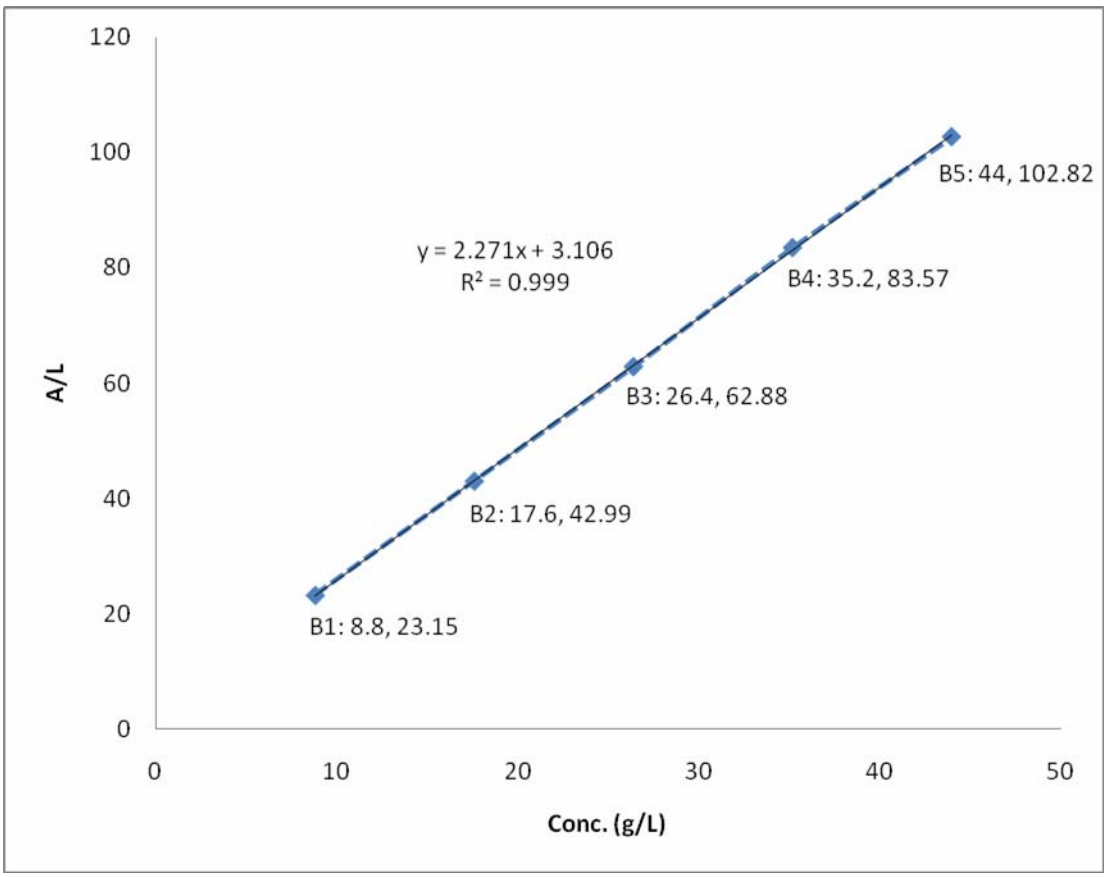
Table 2.3: Absorbance Measurements of B1, B2, B3, B4 and B5 using NaCl Sealed Cell

B*X*	Concentration, *q* (g/L)	Absorbance, *A*	*A*/*L*
B1	8.8	0.2315	23.15
B2	17.6	0.4299	42.99
B3	26.4	0.6288	62.88
B4	35.2	0.8357	83.57
B5	44	1.0282	102.82

Note: B*X* = *X* represents the volume percentage of biodiesel (FAME) in the blend
Density, *d* = 880.0 kg/m^3 at 20 ^{O}C in kg/m^3
Path length, *L* = 0.01 cm

By using the absorbance over path length of cell value, the calibration graph was successfully plotted. The absorbance over path length, *A*/*L*, was used as the dependent (y-axis) and the concentration, *q*, as the independent variable (x-axis). The Figure 2.4 below show the calibration curve of FAME blends as measured by infrared spectroscopy.

A calibration curve was produced using blends with varying percentages of FAME in diesel fuel (B1, B2, B3, B4 and B5). A simple linear regression yielded a correlation of 0.9999 shows in Figure 2.4. The robustness of the technique will allow for quantitative determination of unknown blending of biodiesel (FAME) in petroleum diesel fuel (Alleman and McCormick, 2006). During plotting of the calibration function, the calibration procedure was repeated when the correlation coefficient (R^2) for the regression line is below the 0.99.



Note : y-axis: absorbance over path length of cell, *A/L*
x-axis: concentration of FAME (g/L)

Figure 2.4: Calibration Curve of FAME and Petroleum Diesel Blends as Measured by Infrared Spectroscopy

According to the European standard method EN 14078, FAME contents will calculated by using the data information from the plotted calibration function that is:

$$y = 2.2718x + 3.106$$

This equation is equal to the equation given in 2.2.3.3. From the equation, the slope, *a*, of the regression line is 2.2718 and the *y*-intercept, *b*, of the regression line is 3.106.

Infrared spectroscopy measurement was conducted on known concentration of biodiesel-petroleum diesel fuel blends to study the accuracy and precision of the proposed method. Table 2.4 shows the absorbance of the five test sample prepared in

Section 2.2.3.4. The test samples were diluted until the measured absorbance fall in the absorbance range between 0.1 and 1.1 absorbance units.

The absorbance for any chemical components is proportional to its concentration in a solution. When the component is diluted, its absorbance at each wavelength decreases proportionately. The spectrum shape remains the same after dilution, but the amplitude is attenuated.

Table 2.4: Absorbance Measurements of Diluted Samples of Biodiesel-Petroleum Diesel Fuel Blends

B*X*	Dilution factor,*X*	Absorbance, *A*
4	1	0.8305
5	1	1.0299
10	10	0.2319
30	10	0.6301
50	10	1.0301

Note: B*X* = *X* represents the volume percentage of biodiesel (FAME) in the blend

By using the equation that given in 2.2.3.5 and all information from the calibration function, the FAME contents in biodiesel blends was successfully calculated. According to EN 14078, the FAME contents in the each sample, *Q*, in % (*v*/*v*), should round off to the nearest 0.1. The percentage of error for each blend has also calculated to declare the accurate percentage of FAME blends in each sample to reassure the precision and accuracy of this method. Table 2.5 presents the FAME contents in each sample and the percentages of error.

Table 2.5: FAME Blend Ratio as Determined Using EN 14078 Values and the Percentage of Error

B*X*	FAME contents, *Q*, % (*v*/*v*)	Percentage of error,%
4	4.0	0
5	5.0	0
10	10.0	0
30	30.0	0
50	49.9	0.2

Note: B*X* = *X* represents the volume percentage of biodiesel (FAME) in the blend
Density, *d* = 880.0 kg/m^3 at 20 ^{O}C in kg/m^3
Path length, *L* = 0.01 cm
Slope, *a* = 2.2718 cm^{-1}
y-intercept, *b* = 3.1060 cm^{-1}

Table 2.4 shows up to 0.2 % error occurs when used this method to determining the FAME contents in the palm biodiesel-petroleum diesel fuel blend. This proved that by using the mid infrared spectroscopy, the blending ratio was accurate and easily to determined. Ertan and Mustafa (2008) investigated the determination of blend ratio of biodiesel– diesel fuel blends using density and viscosities. But this method will give the maximum absolute error between the measured and an estimated value is about 0.42% for biodiesel–fuel blends.

The present study has demonstrated that the mid infrared spectroscopy method (EN 14078) can be used to determine the FAME contents in palm biodiesel blends. Infrared spectroscopy method is easy to conduct and will perform the result in only at short period of time. Other advantages using infrared spectroscopy is non-destructive analytical technique which allows reliable, direct and fast determination of several properties, without sample pre-treatment (Maria *et. al*., 2006).

CHAPTER THREE

DETERMINATION OF ADULTERATION IN PALM BIODIESEL BLENDS

3.1 Introduction

The addition of adulterants is called adulteration. Adulterants are chemical substances which should not be contained within other substances (eg. food, beverages, fuels or pesticides) for legal or other reasons. Adulterants may be intentionally added to substances to reduce manufacturing costs, or for some deceptive or malicious purpose. Adulterants may also be accidentally or unknowingly introduced into substances.

The presence of adulterate in fuel gives major negative effect towards engine start-up control, engine heating, acceleration and fuel consumption, and it also increases the emission of particulate material, hydrocarbons and exhaustion gases (Kalligeros *et al.,* 2003). In relation to the problems associated to engine performance and emission of atmospheric pollutants (Pereira *et al.,* 2006), groups of researchers are developing new analytical techniques to detect these frauds which make use of adulterants such as kerosene and cyclohexane, among others (Patra & Mishra, 2002, Kalligeros *et al.,* 2003, Taksande & Hariharan, 2006).

In the Malaysian biodiesel industry, petroleum diesel fuel it is easily adulterated by adding non-transesterified vegetable oil, as edible vegetable oil, or even residual oils. It is happened because of high price of palm biodiesel compared to the raw oil. Subsequently, it is necessary to instil confidence in users that biodiesel blends are strictly according to quality standards and regulations. Thus it is important to develop reliable analytical methods to determine biodiesel in petroleum diesel fuel blends, considering the presence of raw vegetable oil.

Thin layer chromatography (TLC) on silica gel methodology was developed by Cvengros *et al.* (2002), to trace the acylglycerols in blend samples for the qualitative analysis. Generally, TLC is used for informative evaluation of conversion of acylglycerols to methyl esters during transesterification of vegetable oils. The TLC is based on comparison of the acylglycerols and methyl ester. Because of the good separation, TLC was used to trace the acylglycerols adulterant in biodiesel blends.

For the quantitative analysis, Knothe (2001, 2000, and 1999) monitored the quality of biodiesel and petroleum diesel blends using mid infrared spectroscopy method. Although, the presence of carbonyl functional group in palm methyl ester and palm cooking oil cause the limitation to mid infrared spectroscopy to detect palm cooking oil adulteration in the blends sample.

3.2 Experimental Procedure

3.2.1 Reagent and Material

Chloroform A.R. and n-hexane 95% A.R. was purchased from Fisher Scientific (M) Sdn. Bhd. and Starform Enterprise, respectively. Fatty acid methyl ester (FAME) from palm oil was obtained from Malaysian Palm Oil Board (MPOB), Bandar Baru Bangi. Petroleum diesel fuel and palm cooking oil was purchased from Petronas Station in Bangsar and Giant Hypermarket, respectively. The thin layer chromatography plates pre-coated with silica gel 60 F_{254} with 0.25 thicknesses was purchased from Merck Sdn. Bhd.

3.2.2 Apparatus/Instrumentation

A Perkin-Elmer Spectrum RX1 spectrometer was employed to obtain the FTIR spectra in the mid spectra range from 4000 cm^{-1} to 400 cm^{-1}. All spectra were recorded using an average of 16 scans, a spectral resolution of 4 cm^{-1} and interval of 2 cm^{-1}.

3.2.3 Procedure

3.2.3.1 Preparation of Adulterated Palm Biodiesel

Five samples of adulterated palm biodiesel blends were prepared by adding 1% of palm cooking oil as acylglycerols in to each sample palm biodiesel blends and the resultant blends were stirred vigorously (Table 3.1). Palm biodiesel blends (B1, B2, B3, B4 and B5) were prepared as described in Section 2.2.3.1.1. In order to prepare 1% adulterated

blends, the 0.5 mL palm cooking oil was added in 50 mL volumetric flask and known palm biodiesel fuel blends was filled until the calibration mark.

Table 3.1: Preparation of Adulterated Palm Biodiesel Blends in 50 mL Volumetric Flask

Sample	B*X*	Volume (mL)	
		Palm Cooking Oil	**Palm Biodiesel Blends (B*X*)**
A1.1	B1	0.5	49.50
A1.2	B2	0.5	49.50
A1.3	B3	0.5	49.50
A1.4	B4	0.5	49.50
A1.5	B5	0.5	49.50

Note: B*X* = *X* represents the volume percentage of biodiesel (FAME) in the blend
A1.1 = 1% palm cooking oil in B1
A1.2 = 1% palm cooking oil in B2
A1.3 = 1% palm cooking oil in B3
A1.4 = 1% palm cooking oil in B4
A1.5 = 1% palm cooking oil in B5

3.2.3.2 Preparation of Palm Cooking Oil/Petroleum Diesel Fuel Blends for Sensitivity of Thin Layer Chromatography (TLC) Study

In order to study the sensitivity of thin layer chromatography (TLC), blend samples of palm cooking oil and petroleum diesel fuel were prepared (Table 3.2).

Table 3.2: Preparation of Palm Cooking Oil and Petroleum Diesel Fuel Blends in 100 mL Volumetric Flask

Sample	Volume (mL)	
	Palm Cooking Oil	**Petroleum Diesel Fuel**
P1	1.00	99.00
P2	0.70	99.30
P3	0.50	99.50
P4	0.30	99.70

P5	0.10	99.90
P6	0.07	99.93
P7	0.05	99.95

Note: B*X* = *X* represents the volume percentage of biodiesel (FAME) in the blend
P1 = 1% palm cooking oil in petroleum diesel fuel
P2 = 0.7% palm cooking oil in petroleum diesel fuel
P3 = 0.5% palm cooking oil in petroleum diesel fuel
P4 = 0.3% palm cooking oil in petroleum diesel fuel
P5 = 0.1% palm cooking oil in petroleum diesel fuel
P6 = 0.07% palm cooking oil in petroleum diesel fuel
P7 = 0.05% palm cooking oil in petroleum diesel fuel

3.2.3.3 Spectrometric Measurement of Adulterated Palm Biodiesel

The spectrometric measurement for adulterated samples is similar to that conducted for calibration solutions as describe in Section 2.2.3.2. The palm biodiesel (FAME) contents in adulterated sample were calculated using the given formula as specified in the standard method EN 14078 as described in Section 2.2.3.5.

3.2.3.4 Analysis of Adulterated Palm Biodiesel Blends by Thin Layer Chromatography (TLC)

Qualitative analysis of adulterated palm biodiesel blends in petroleum diesel fuel was performed on 5 cm x 10 cm TLC silica gel 60 F_{254} with 0.25 thicknesses. The solvent system used was hexane-chloroform (1:1 *v*/*v*). The solvent tank was allowed to be fully saturated with solvent vapour before the chromatogram was developed. The biodiesel sample was spotted using the capillary tube on 1 cm from the lower of plate. The plate was developed in the saturated chromatographic tank until the solvent front was 1 cm from the top of plate at room temperature.

The visualization technique using iodine vapour as the staining agent was used to reveal the presence of the separated compounds on the TLC silica gel plates. Then, the separation of compounds was spotted on the TLC silica gel plates. The spots on the chromatograms were then marked on the TLC silica gel plate respectively. The retention factor, R_f was calculated by dividing the distance travelled by the analyte by the distance travelled by the solvent.

$$R_f = \frac{distance\ traveled\ by\ the\ compound}{distance\ traveled\ by\ the\ solvent}$$

3.3 Result and Discussion

3.3.1 Mid Infrared Spectra of Adulterated Palm Biodiesel/Petroleum Diesel Blends

The carbonyl absorption peaks in the mid infrared range are virtually identical for palm cooking oils and their methyl esters as both contain the ester carbonyl functionality appear at 1745 cm^{-1} ± 5 cm^{-1} (Figures 3.1 and 3.2). The overlapping absorption of palm methyl ester and palm cooking oil peak making them impossible to be distinguished between one and another whether petroleum diesel fuel was blended with palm biodiesel (FAME) or palm cooking oil.

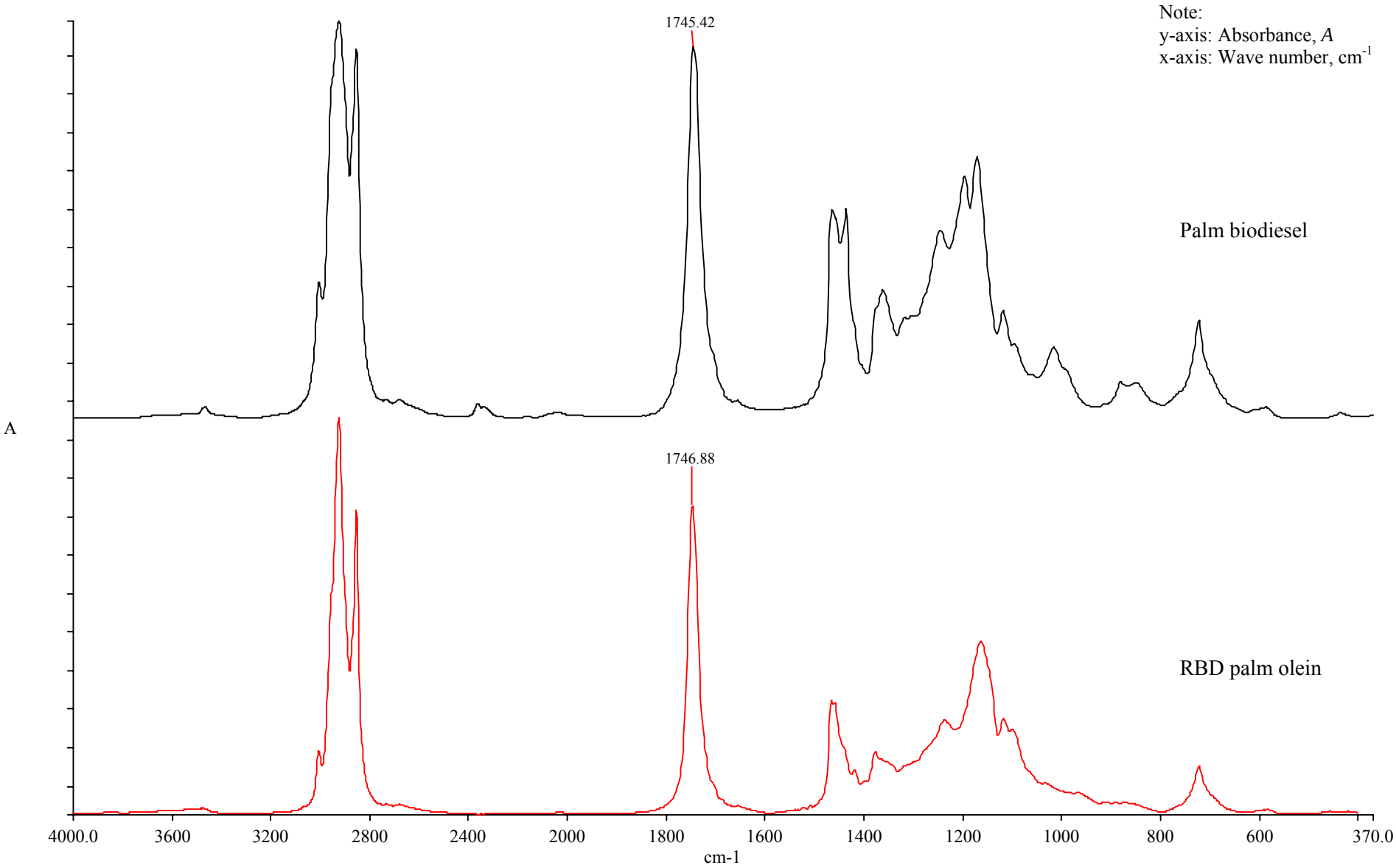


Figure 3.1: Mid IR Spectra from 4000 cm^{-1} to 400 cm^{-1}: Palm Methyl Ester and RBD Palm Olein

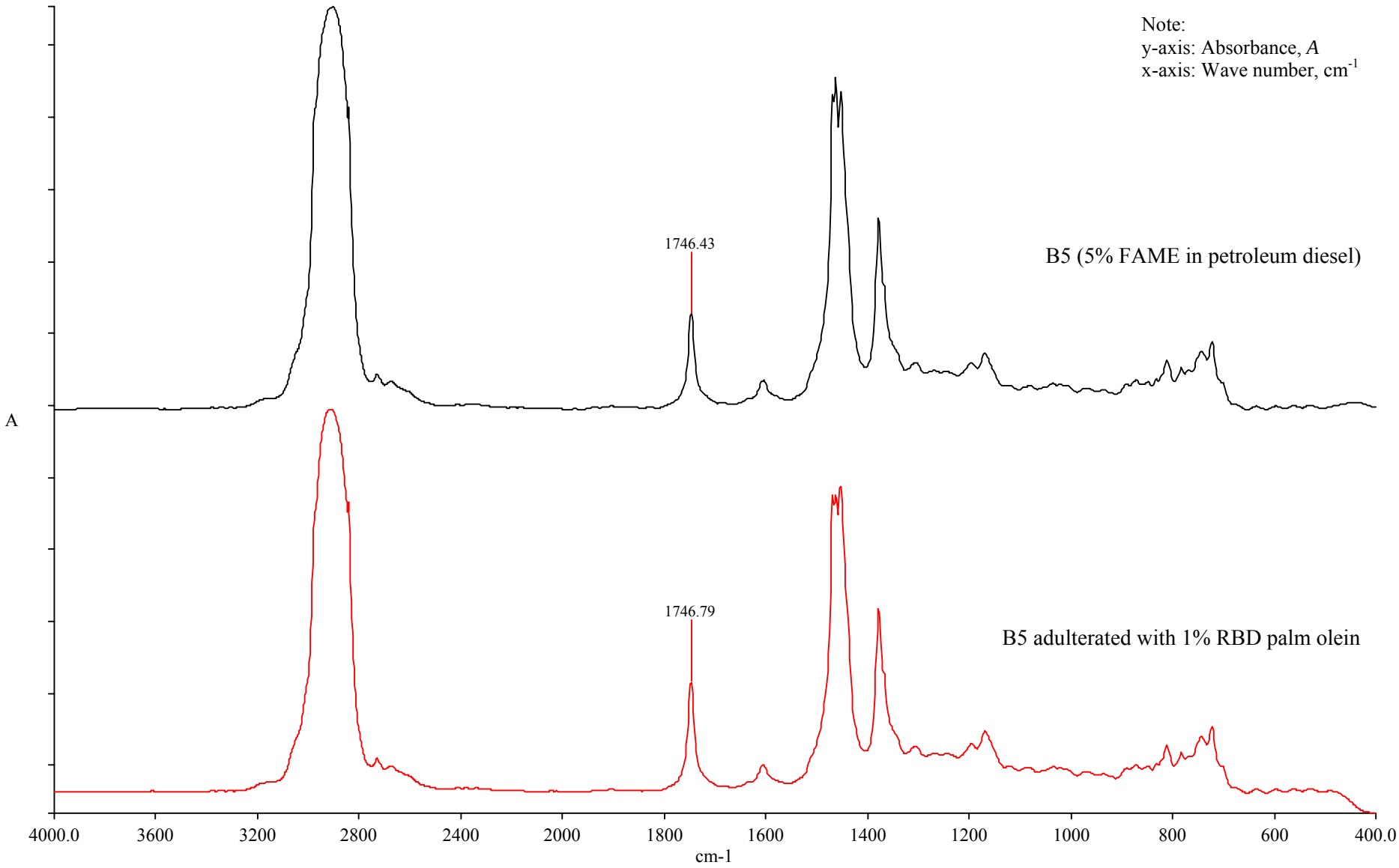


Figure 3.2: Mid IR Spectra for B5 and B5 Adulterated with 1% RBD Palm Olein

3.3.2 Palm Biodiesel (FAME) Content Measurement for Adulterated Palm Biodiesel/Petroleum Diesel Blends

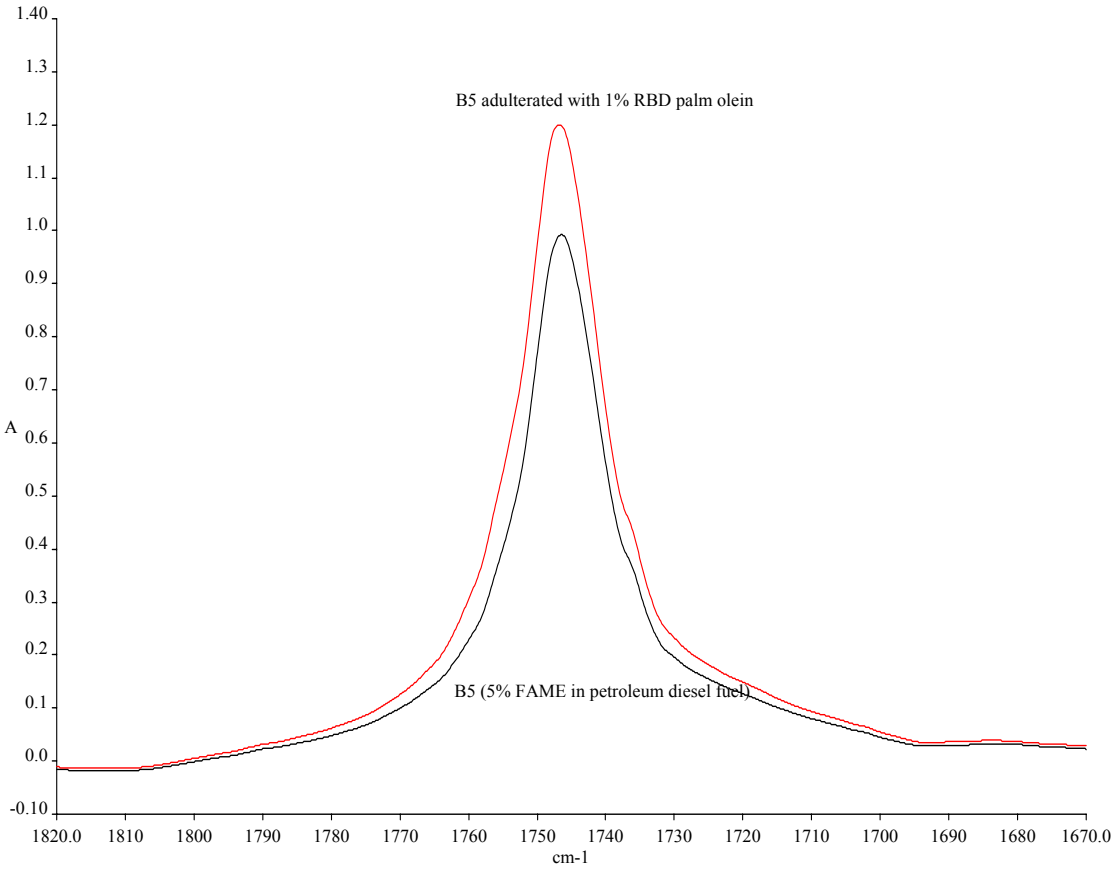
The palm biodiesel (FAME) contents in adulterated samples were calculated by using the given formula in 2.2.3.3. All other parameters required in the formula were obtained from the calibration function in 2.3.3. Table 3.3 shows the calculated palm biodiesel (FAME) contents for each adulterated sample. The present study shows that addition of 1% palm cooking oil to each B1, B2, B3, B4 and B5 will increase the actual concentration about 1% in each sample respectively (Figure 3.3).

Obviously, palm cooking oil could be used by irresponsible companies as an adulterant into their biodiesel blends to get a higher blending ratio. This situation may happen due to lower price of vegetable oil compared to biodiesel.

Table 3.3: Calculated Palm Biodiesel (FAME) Content of Adulterated Sample using EN 14078

Sample	Absorbance, *A*	FAME content, *Q*, % (*v*/*v*)	Actual FAME content, %
A1.1	0.4517	2.1	1.0
A1.2	0.6735	3.2	2.0
A1.3	0.8321	4.0	3.0
A1.4	1.0095	4.9	4.0
A1.5	1.1923	5.8	5.0

Note: A1.1 = 1% palm cooking oil in B1
A1.2 = 1% palm cooking oil in B2
A1.3 = 1% palm cooking oil in B3
A1.4 = 1% palm cooking oil in B4
A1.5 = 1% palm cooking oil in B5
B*X* = *X* represents the volume percentage of palm biodiesel (FAME) in the blend
Density, *d* = 880.0 kg/m^3 at 20 ^{O}C in kg/m^3
Path length, *L* = 0.01 cm
Slope, *a* = 2.2718 cm^{-1}
y-intercept, *b* = 3.1060 cm^{-1}



Note: y-axis: Absorbance, *A*
x-axis: Wave number, cm^{-1}

Figure 3.3: Increasing of Carbonyl Peak (C=O) with 1% Addition of RBD Palm Olein in B5

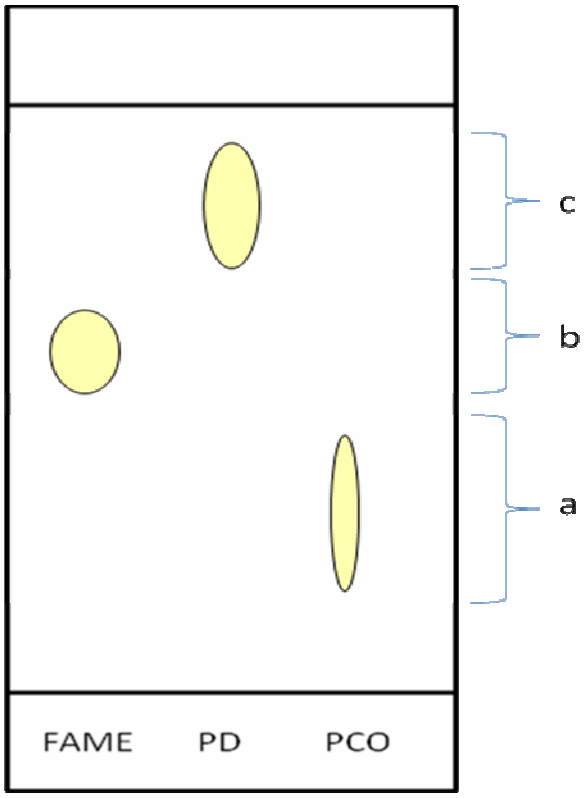
Although, EN14078 has been proven to be a reliable method to determine blend ratio, the only drawback is it cannot detect adulterant such as palm cooking oil. Therefore, other suitable analytical method must be established to trace amount of adulterants in commercialization biodiesel industry.

3.3.3 Analysis of Adulterated Palm Biodiesel (FAME) by Thin Layer Chromatography (TLC)

The adulteration monitoring is an important issue to biodiesel quality control since some contaminants arise during the reaction or due to illegal addition of the cheaper raw material. Subsequently, thin layer chromatography (TLC) on silica gel methodology was developed to trace the presence of acylglycerols during transesterification reaction of vegetable oil (Cvengros *et al*., 2002). Karan *et al*. (2008) reported a method based on TLC that can be effectively used to determine the presence of unconverted acylglycerols in biodiesel by using hexane-chloroform (1:1 *v*/*v*) and hexane-diethyl ether-acetic acid (7:3:1 *v*/*v*) solvents system.

Basically, TLC was used for monitoring the progress of the transesterification reactions. The completion of the reaction was judged by disappearance of the acylglycerols and the formation of methyl esters in the TLC silica gel plate. By following this judgement, the adulteration of biodiesel blends (methyl ester) by palm cooking oil (acylglycerols) also can be determine with the same method. In this method, the all spots on the TLC silica gel was marked and compared with the standard. The formation of acylglycerols spot referred to the adulterated of biodiesel blends.

In the present study, palm biodiesel blends were analysed using solvent system hexane-chloroform (1:1 *v*/*v*). Figure 3.4 shows that the palm methyl ester, acylglycerols and petroleum diesel fuel will give the spot at different retention factor, R_f value. The Table 3.4 shows the R_f value for each spot traced at the TLC silica gel plate with solvent system hexane-chloroform (1:1 *v*/*v*). Consequently, the adulteration of palm biodiesel/petroleum diesel fuel blends will be traced by using TLC method as discussed before.



Note: FAME = Fatty acid methyl ester
PCO = Palm cooking oil
PD = Petroleum diesel
a = Acylglycerols
b = Methyl ester
c = Hydrocarbons
Solvent system = Hexane : Chloroform (50:50 *v*/*v*)

Figure 3.4: The TLC Silica Gel Plate for Palm Methyl Ester, Palm Cooking Oil and Petroleum Diesel Fuel

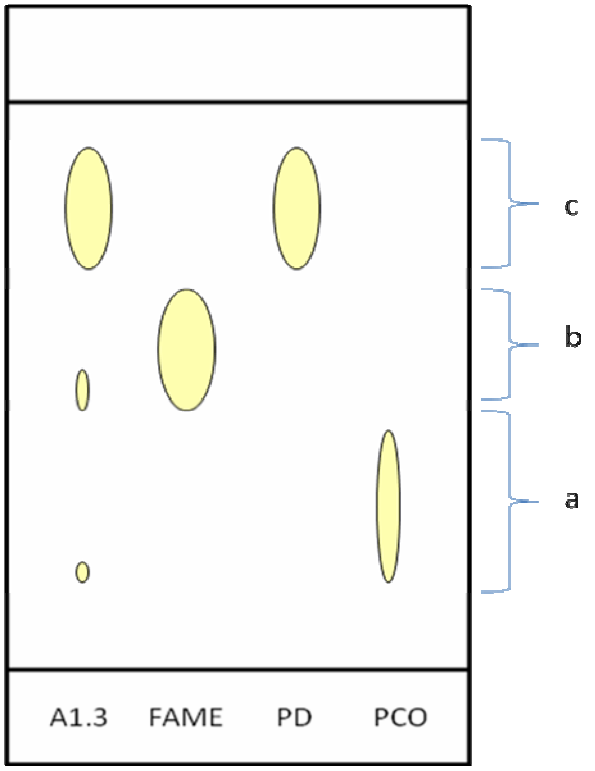
Table 3.4: Retention Factor,R_f Value of Palm Methyl Ester, Palm Cooking Oil and Petroleum Diesel Fuel

Sample	Retention factor, R_f		
	Spot a	**Spot b**	**Spot c**
FAME	-	0.53	-
PCO	0.36	-	-
PD	-	-	0.78

Note: FAME = Fatty acid methyl ester
PCO = Palm cooking oil
PD = Petroleum diesel
a = Acylglycerols
b = Methyl ester
c = Hydrocarbons

According to the Cvengros *et al*. (2002) studies, the adulteration of palm biodiesel/petroleum diesel fuel blends can be mark out by using TLC method. The samples of adulterated palm biodiesel blends were spotted on the TLC plates using the capillary tube. After several time, adulterated sample was give three different spots corresponding to methyl ester, acylglycerols and hydrocarbon. The spots on the chromatograms were then marked from the TLC plate respectively and compared with the standard used as reference. The standard used is original palm cooking oil, palm methyl ester and petroleum diesel fuel.

The Figure 3.5 shows the separation of spot for adulterated samples and Table 3.5 shows their retention factor, R_f for each spot. From the Figure 3.5, its can concluded that the sample of palm biodiesel/petroleum diesel fuel was adulterated by palm cooking oil based on the traced of acylglycerols spot. However, acylglycerols also can be traced in biodiesel sample because of their incompleted conversion to methyl ester during transesterification process.



Note: FAME = Fatty acid methyl ester a = Acylglycerols
PCO = Palm cooking oil b = Methyl ester
PD = Petroleum diesel c = Hydrocarbons
A1.3 = 1% palm cooking oil in B3 (3% FAME in PD)
Solvent system = Hexane : Chloroform (50:50 *v*/*v*)

Figure 3.5: The TLC Silica Gel Plate for Adulterated Biodiesel Blends, Palm Methyl Ester, Palm Cooking Oil and Petroleum Diesel Fuel

Table 3.5: Retention Factor, R_f Value of Adulterated Sample, Palm Methyl Ester, Palm Cooking Oil and Petroleum Diesel Fuel

Sample	Retention factor, R_f		
	Spot a	Spot b	Spot c
A1.3	0.11	0.38	0.78
FAME	-	0.53	-
PCO	0.36	-	-
PD	-	-	0.78

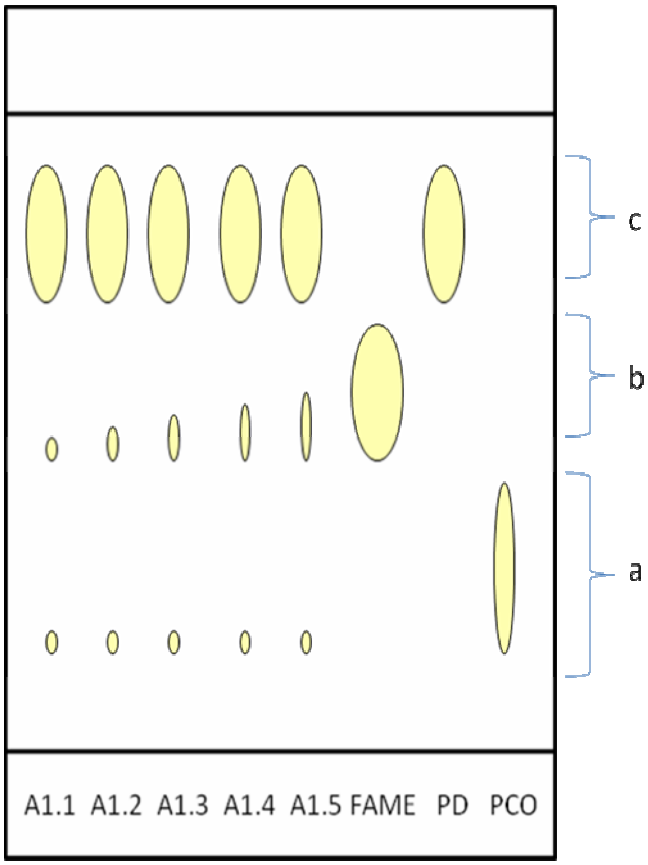
Note: FAME = Fatty acid methyl ester a = Acylglycerols
PCO = Palm cooking oil b = Methyl ester
PD = Petroleum diesel c = Hydrocarbons
A1.3 = 1% palm cooking oil in B3 (3% FAME in PD)

3.3.4 Qualitative Analysis by Using Thin Layer Chromatography (TLC)

The thin layer chromatography (TLC) method also done to adulterated palm biodiesel/petroleum diesel (B1, B2, B3, B4 and B5) and the spot marked was compared with the standard. Standard is the reference sample of methyl ester, acylglycerols and hydrocarbon. The standard used as reference are palm methyl ester, palm cooking oil and petroleum diesel fuel. The Figure 3.6 and Table 3.6 show the TLC plate and retention factor, R_f value of this study, respectively.

From the Figure 3.6, we can see the different size of spot because of the different quantity added in each blending. The high amount of FAME will give big spot compared to the little amount of FAME only give the small spot. However, the exact amount of acylglycerols cannot be determined accurately. This finding is agreeable to that of Pinto *et.al*. (2005).

According to the Pinto *et al*. (2005), although the TLC analysis is only a fast and effective qualitative method, it does not allow the exact determination of the degree of adulteration or conversion process during transesterification process.



Note: FAME = Fatty acid methyl ester
PCO = Palm cooking oil
PD = Petroleum diesel
A1.1 = 1% palm cooking oil in B1 (1% FAME in PD)
A1.2 = 1% palm cooking oil in B2 (2% FAME in PD)
A1.3 = 1% palm cooking oil in B3 (3% FAME in PD)
A1.4 = 1% palm cooking oil in B4 (4% FAME in PD)
A1.5 = 1% palm cooking oil in B5 (5% FAME in PD)
Solvent system = Hexane : Chloroform (50:50 *v*/*v*)
a = Acylglycerols
b = Methyl ester
c = Hydrocarbons

Figure 3.6: The TLC Silica Gel Plate for Adulterated Biodiesel Blends Samples, Palm Methyl Ester, Palm Cooking Oil and Petroleum Diesel Fuel

Table 3.6: Retention Factor, R_f Value of Adulterated Samples, Palm Methyl Ester, Palm Cooking Oil and Petroleum Diesel Fuel

Sample	Retention factor, R_f		
	Spot a	Spot b	Spot c
A1.1	0.11	0.37	0.78
A1.2	0.11	0.37	0.78
A1.3	0.11	0.38	0.78
A1.4	0.11	0.39	0.78
A1.5	0.11	0.41	0.78
FAME	-	0.53	-
PCO	0.36	-	-
PD	-	-	0.78

Note: FAME = Fatty acid methyl ester a = Acylglycerols
PCO = Palm cooking oil b = Methyl ester
PD = Petroleum diesel c = Hydrocarbons
A1.1 = 1% palm cooking oil in B1 (1% FAME in PD)
A1.2 = 1% palm cooking oil in B2 (2% FAME in PD)
A1.3 = 1% palm cooking oil in B3 (3% FAME in PD)
A1.4 = 1% palm cooking oil in B4 (4% FAME in PD)
A1.5 = 1% palm cooking oil in B5 (5% FAME in PD)

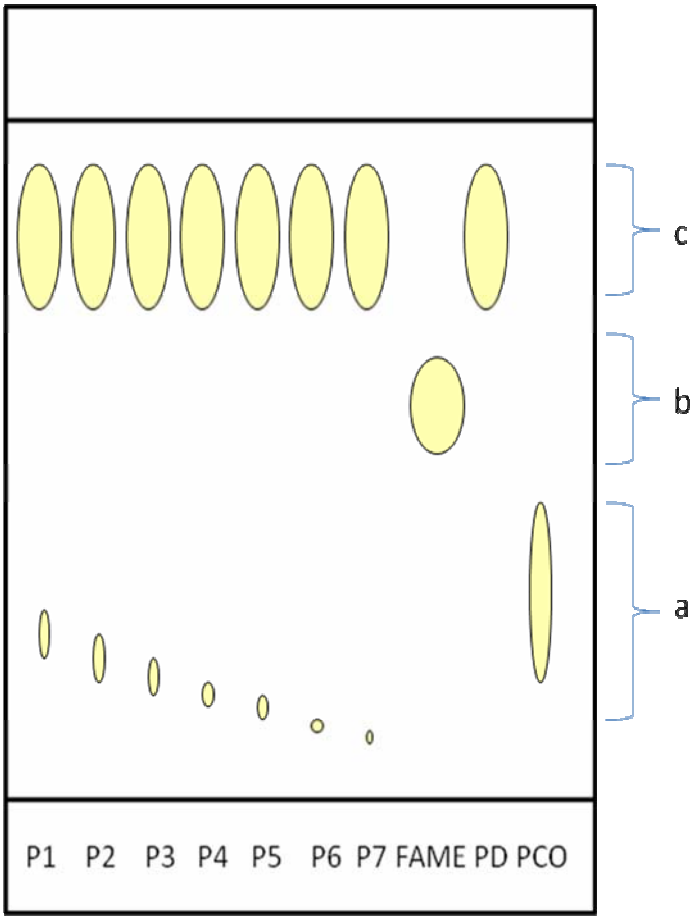
3.3.5 Sensitivity of Thin Layer Chromatography (TLC) to Trace the Adulteration in Palm Biodiesel Blends

Sensitivity is the measures of the proportion of actual positives which are correctly identified. Under this section, the sensitivity of thin layer chromatography (TLC) to trace a minimum amount of adulteration of palm biodiesel/petroleum diesel blends by palm cooking oil was studied. The sample was continuously prepared by decreasing the amount of palm cooking oil added into the petroleum diesel fuel.

For this study, palm cooking oil blended with petroleum diesel fuel samples sufficed for the study of sensitivity of TLC, regardless of FAME content. It is because;

the main objective of sensitivity study is to find out the limitation of TLC in tracing the presence of adulterant which is palm cooking oil in this case.

The Figure 3.7 shows the spotted of separation from the each sample and Table 3.7 shows their retention factor, R_f.



Note: FAME = Fatty acid methyl ester
PCO = Palm cooking oil
PD = Petroleum diesel
P1 = 1% palm cooking oil in PD
P2 = 0.7% palm cooking oil in PD
P3 = 0.5% palm cooking oil in PD
P4 = 0.3% palm cooking oil in PD
P5 = 0.1% palm cooking oil in PD
P6 = 0.07% palm cooking oil in PD
P7 = 0.05% palm cooking oil in PD
Solvent system = Hexane : Chloroform (50:50 *v*/*v*)

a = Acylglycerols
b = Methyl ester
c = Hydrocarbons

Figure 3.7: Sensitivity of TLC to Trace Adulteration

Table 3.7: Retention Factor, R_f Value of Sensitivity Study

Sample	Retention factor, R_f		
	Spot a	**Spot b**	**Spot c**
P1	0.22	-	0.78
P2	0.21	-	0.78
P3	0.20	-	0.78
P4	0.18	-	0.78
P5	0.13	-	0.78
P6	0.11	-	0.78
P7	0.09	-	0.78
FAME	-	0.53	-
PCO	0.36	-	-
PD	-	-	0.78

Note: FAME = Fatty acid methyl ester
PCO = Palm cooking oil
PD = Petroleum diesel
P1 = 1% palm cooking oil in PD
P2 = 0.7% palm cooking oil in PD
P3 = 0.5% palm cooking oil in PD
P4 = 0.3% palm cooking oil in PD
P5 = 0.1% palm cooking oil in PD
P6 = 0.07% palm cooking oil in PD
P7 = 0.05% palm cooking oil in PD
a = Acylglycerols
b = Methyl ester
c = Hydrocarbons

As exhibited in Figure 3.7, TLC used in the present study is able to trace adulteration from as low as 0.05 % acylglycerols in the palm biodiesel/petroleum diesel fuel blends sample. However, other quantitative analytical method should be established to determine the exact amount of adulteration.

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APPENDIX 1
European Standard EN 14078:2003

BRITISH STANDARD

BS EN
14078:2003

Liquid petroleum products — Determination of fatty acid methyl esters (FAME) in middle distillates — Infrared spectroscopy method

The European Standard EN 14078:2003 has the status of a British Standard

ICS 75.160.20

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14078:2003

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The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

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- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
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NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 14078

December 2003

ICS 75.160.20

English version

Liquid petroleum products - Determination of fatty acid methyl esters (FAME) in middle distillates - Infrared spectroscopy method

Produits pétroliers liquides - Détermination de la teneur en esters méthyliques d'acides gras (EMAG) des distillats moyens - Méthode par spectrométrie infrarouge

Flüssige Mineralölprodukte - Bestimmung von Fettsäure-Methylester (FAME) in Mitteldestillaten - Infrarotspektrometrisches Verfahren

This European Standard was approved by CEN on 7 November 2003.

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Ref. No. EN 14078:2003 E

Contents

Foreword

This document EN 14078:2003 has been prepared by CEN/TC 19, "Petroleum products, lubricants and related products", the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2004, and conflicting national standards shall be withdrawn at the latest by June 2004.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard : Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a test method for the determination of Fatty Acid Methyl Ester (FAME)content in diesel fuel or domestic heating fuel by mid infrared spectrometry in the range from about 1,7 % *(V/V)* to 22,7 % *(V/V)*. Other FAME contents can also be analyzed in principle, however, no precision data for results outside the specified range are available at this time.

The test method has been verified to be applicable to samples which contain FAME conforming to the European specifications EN 14214 or EN 14213. Reliable quantitative results are obtained only when the samples do not contain significant amounts of other interfering components, especially esters, which possess absorption bands in the spectral region used for quantification of FAME. When such interfering components are present, this test method is expected to produce higher values

NOTE 1 When interfering components are suspected to be present, it is recommended for cases of doubt or dispute to record the full infrared spectrum and to compare it to spectra of samples with well known FAME contents.

NOTE 2 For the purposes of this European Standard, the term "% *(V/V)*" is used to represent the volume fraction of a material.

NOTE 3 For conversion of g/l to % *(V/V)*, a fixed density of FAME of 880,0 kg/m^3 is adopted.

Warning – The use of this standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Normative references

This European Standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed thereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references, the latest edition of the publication referred to applies (including amendments).

EN 14213, *Heating fuels - Fatty acid methyl esters (FAME) - Requirements and test methods.*

EN 14214, *Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods.*

EN ISO 3170, *Petroleum liquids – Manual sampling (ISO 3170:1988, including Amendment 1:1998).*

EN ISO 3171, *Petroleum liquids – Automatic pipeline sampling (ISO 3171:1988).*

3 Principle

The mid infrared absorption spectrum of a test portion of a sample which has been diluted as appropriate with cyclohexane, is recorded. The absorbance at the peak maximum of the typical absorption band for esters at about 1 745 cm^{-1} ± 5 cm^{-1} is measured. The FAME content is then calculated with a calibration function produced from standard solutions with a known FAME content.

4 Reagents and materials

4.1 FAME for calibration

FAME as specified in EN 14214 or EN 14213

4.2 Cyclohexane, > 99,5 % *(V/V)*

5 Apparatus

5.1 Infrared spectrometer, dispersive or interferometric type, capable of operating in the wave number range from 400 cm^{-1} to 4 000 cm^{-1}, with a linear absorption in the absorbance range from 0,1 to 1,1 absorbance units, and having a minimum resolution of 4 cm^{-1}

5.2 Cell, made of KBr, or NaCl, or CaF_2, with accurately known path length

EXAMPLE A solution with a FAME concentration of 3 g/l (0,34 % (*V/V*)) should give an absorbance of about 0,4 at the maximum peak at about 1 745 cm^{-1} when a cell with a path length of 0,5 mm is used.

6 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171 and/or in accordance with the requirements of national standards or regulations for the sampling of the product under test.

7 Procedure

7.1 General

Because of the viscosity of FAME solutions, cleaning the cells used for measurement is of great importance. Cells shall be cleaned thoroughly by repeated rinsing with cyclohexane. The cells are considered as sufficiently clean when the recorded IR spectrum of the cell filled with cyclohexane exactly matches the reference cyclohexane spectrum.

7.2 Calibration

7.2.1 Preparation of calibration solutions

A set of at least five calibration solutions with precisely known concentrations of FAME (4.1) in cyclohexane (4.2) shall be prepared by weighing FAME into appropriate graduated flasks and filling to the mark with cyclohexane. The nominal FAME concentrations for the set of five calibration solutions shall be selected in such a way that the absorbance at the maximum peak at about 1 745 cm^{-1} is in the range from 0,1 to 1,1 absorbance units

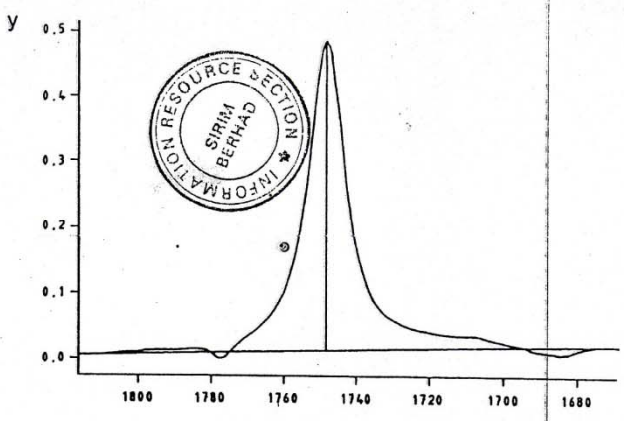
EXAMPLE For a cell with a nominal path length of 0,5 mm (see also 5.2), the calibration solutions are 1 g/l, 2 g/l, 4 g/l, 6 g/l and 10 g/l.

It is important to use identical cells both for calibration and measurement.

7.2.2 Spectrometric measurement

This procedure is identical for the calibration solutions and for the samples under test. The test portion or the calibration solution is filled into the cell and the IR spectrum is recorded against a spectrum of cyclohexane (4.2). The absorbance at the peak maximum at about 1 745 m^{-1} is then measured, using a baseline from 1 670 cm^{-1} to 1 820 cm^{-1} (see Figure 1).

NOTE Great care should be exercised to accurately perform the measurement against cyclohexane. The IR absorption bands from cyclohexane should either be directly optically compensated (double beam instruments), or subtracted by calculation (single beam instruments).



Key

y Absorbance

Figure 1 — Typical spectrum for FAME in diesel fuel diluted in cyclohexane (cell path 0,5 mm, concentration: 44 g/l after a 1:10 dilution (*V/V*))

7.2.3 Calibration function

Using the absorbance measurements for the set of FAME calibration solutions (see also 7.2.1), a calibration function is calculated by linear regression or by plotting, using the absorbance, *A*, as the dependent, and the concentration, *q*, as the independent variable. This gives the calibration function for a calculated standard cell path length of 1 cm as follows:

$$A/L = a * q + b \quad (1)$$

where:

- *A* is the measured absorbance in units of absorbance;
- *L* is the actually used cell path length in cm;
- *q* is the concentration of FAME in g/l;
- *a* is the slope of the regression line;
- *b* is the *y* intercept of the regression line.

NOTE It is strongly recommended to repeat the calibration procedure when the correlation coefficient (R^2) for the regression line is below 0,99.

7.3 Quantitative analysis

7.3.1 Preparation of samples

Samples containing FAME in a middle distillate are analysed after appropriate dilution in cyclohexane. If the absorbance measured on this test solution does not fall in the absorbance range of the calibration, a new sample with a more suitable dilution shall be prepared. For FAME contents below about 100 g/l (11,4 % *(V/V)*), a dilution ratio of at least 1:10 *(V/V)* shall be used. For FAME contents above 100 g/l (11,4 % *(V/V)*) and below about 200 g/l (22,7 % *(V/V)*), a dilution ratio of at least 1:20 *(V/V)* shall be used.

NOTE 1 For FAME contents above 200 g/l (22,7 % *(V/V)*), adequate dilution ratios should be used in order to bring the absorption in the specified absorbance range of the calibration.

NOTE 2 The given dilution ratios are based on a nominal path length of the cell of 0,5 mm

7.3.2 Spectrometric measurement

The spectrometric measurement is performed on the test solution according to 7.2.2. It is important to ensure that the same cells are used both for measurement and calibration.

Due to the great importance of cleaning the cells, it is recommended to record the IR spectrum of the cell filled with cyclohexane between each sample, to check its cleanliness (see also 7.1).

8 Calculation

Calculate the FAME content, Q, in the sample using:

$$Q = \frac{X}{a}\left[\frac{A}{L} - b\right]\frac{100}{d} \qquad (2)$$

where:

- Q is the FAME content in % *(V/V)*;
- X is the dilution factor (i.e. X = 10 for a dilution of 1:10);
- a is the slope of the regression line;
- b is the y intercept of the regression line;
- A is the absorbance measured according to 7.3.2;
- L is the path length of the cell in cm;
- d is the density of FAME (d = 880,0 kg/m^3) at 20 °C in kg/m^3.

9 Expression of results

Report the FAME content in the sample, Q, in % *(V/V)*, rounded off to the nearest 0,1.

10 Precision

10.1 Repeatability

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed 0,3 % *(V/V)* in absolute value in only one case in twenty.

10.2 Reproducibility

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, for concentrations lower or equal to 11,4 % *(V/V)*, exceed 0,9 % *(V/V)* in absolute value in only one case in twenty. For concentrations higher than 11,4 % *(V/V)* and below 22,7 % *(V/V)*, it would exceed 1,4 % *(V/V)* in absolute value in only one case in twenty.

11 Test report

The test report shall contain at least the following information:

a) a reference to this European Standard;

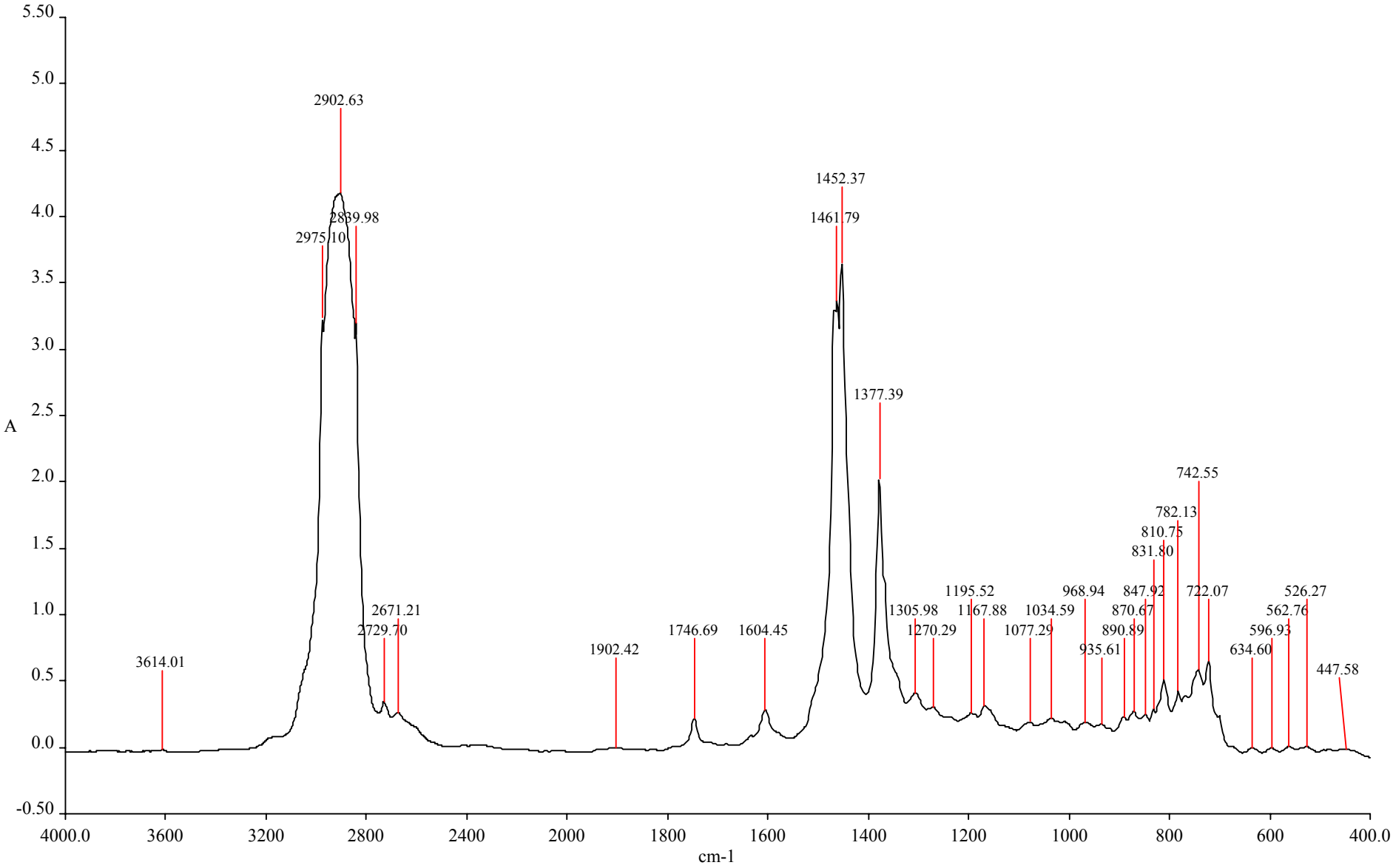
b) the type and complete identification of the product tested;

c) the result of the test (see clause 9);

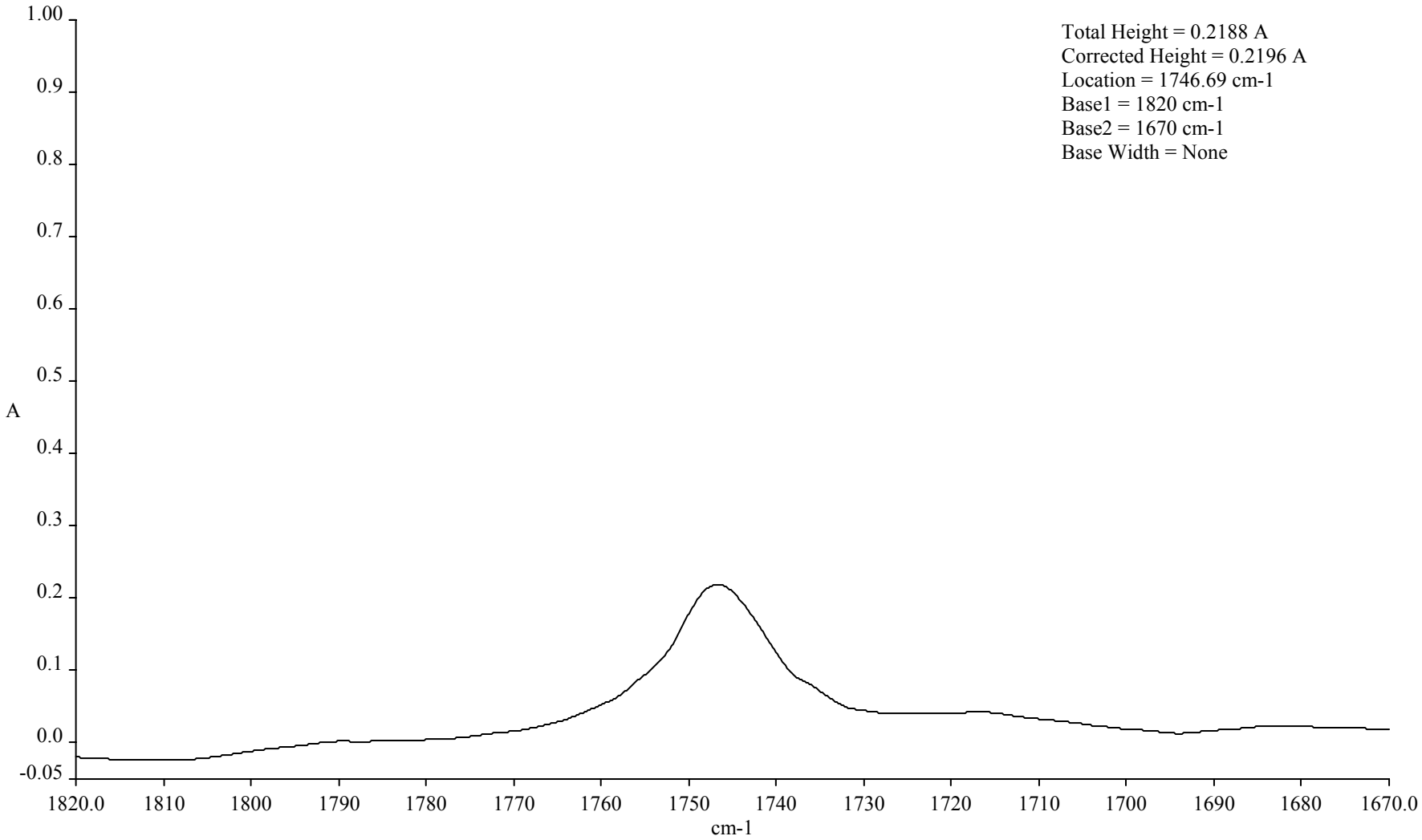
d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

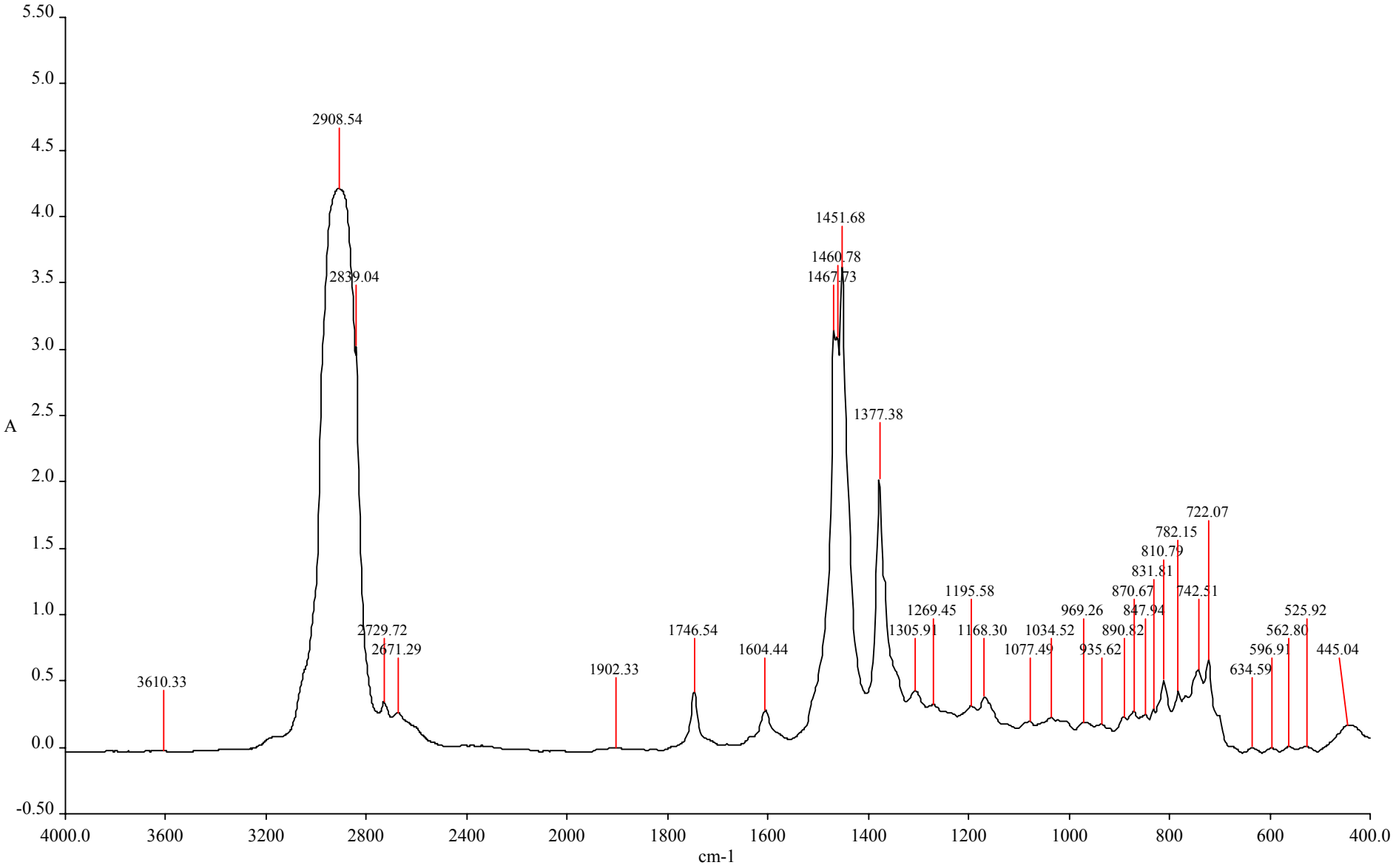
APPENDIX 2



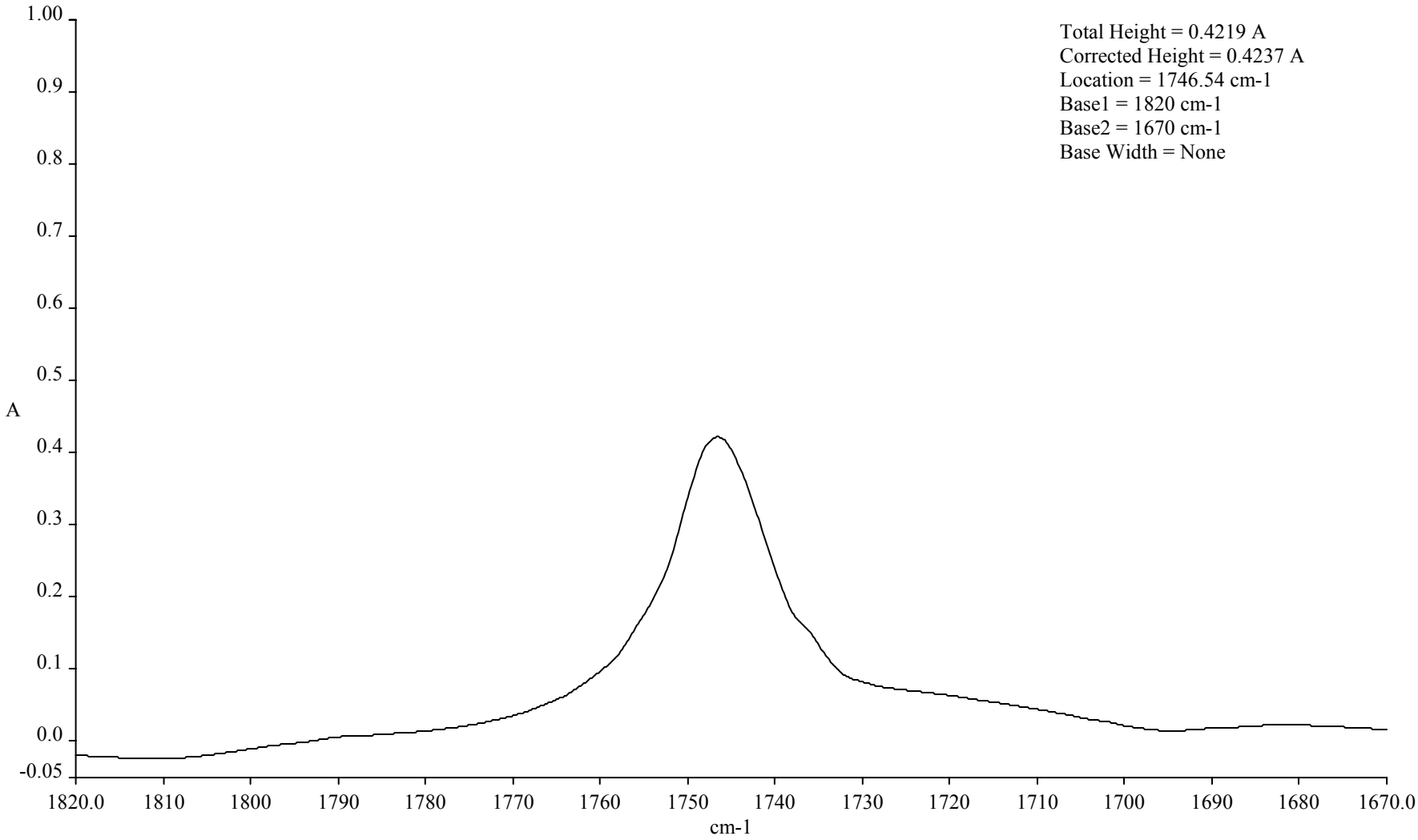
Mid IR Spectra from 4000 cm^{-1} to 400 cm^{-1}: B1 (1% FAME in petroleum diesel) ; cell path length 0.10 mm



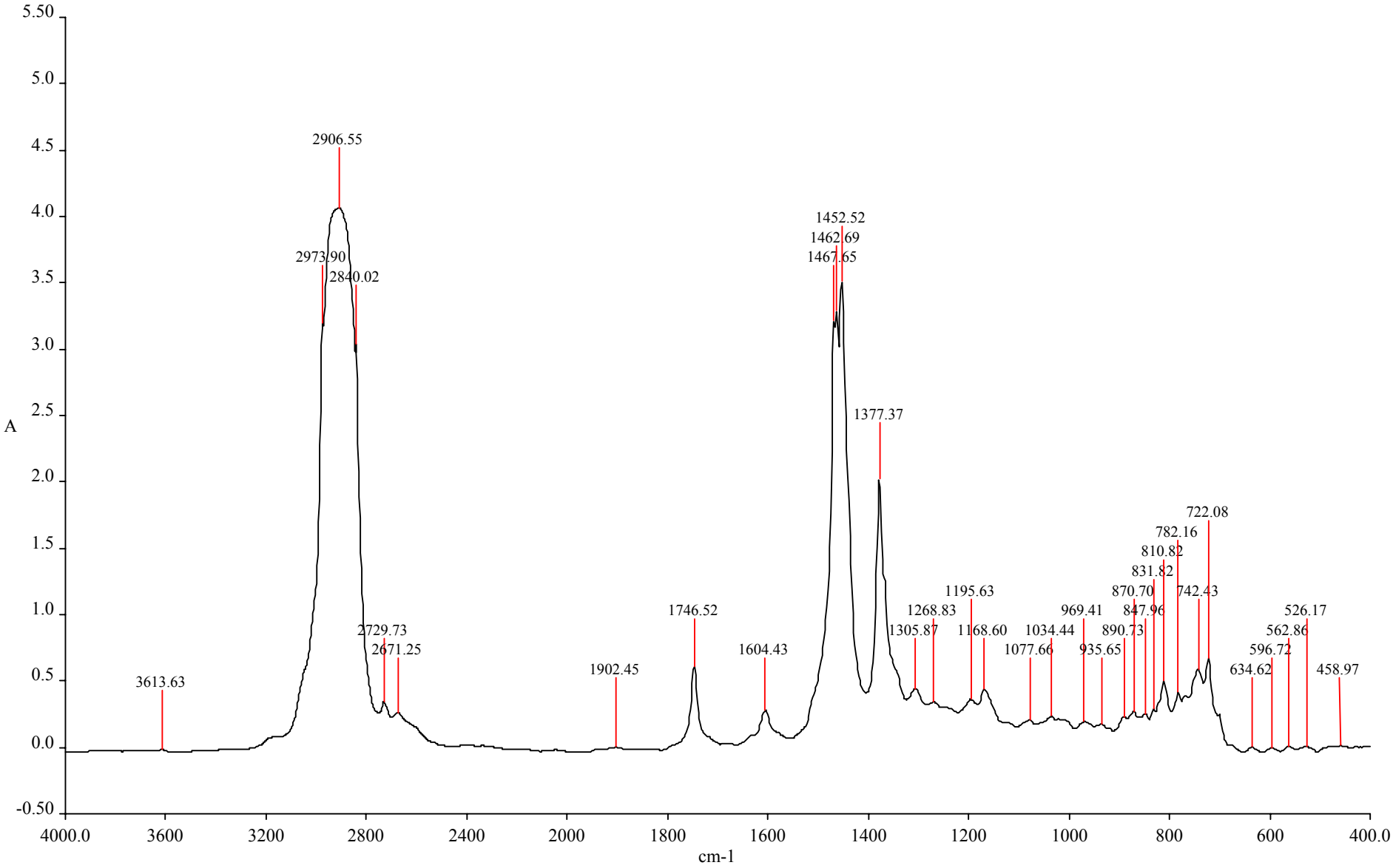
Mid IR Spectra from 1820 cm^{-1} to 1670 cm^{-1}: B1 (1% FAME in petroleum diesel) ; cell path length 0.10 mm



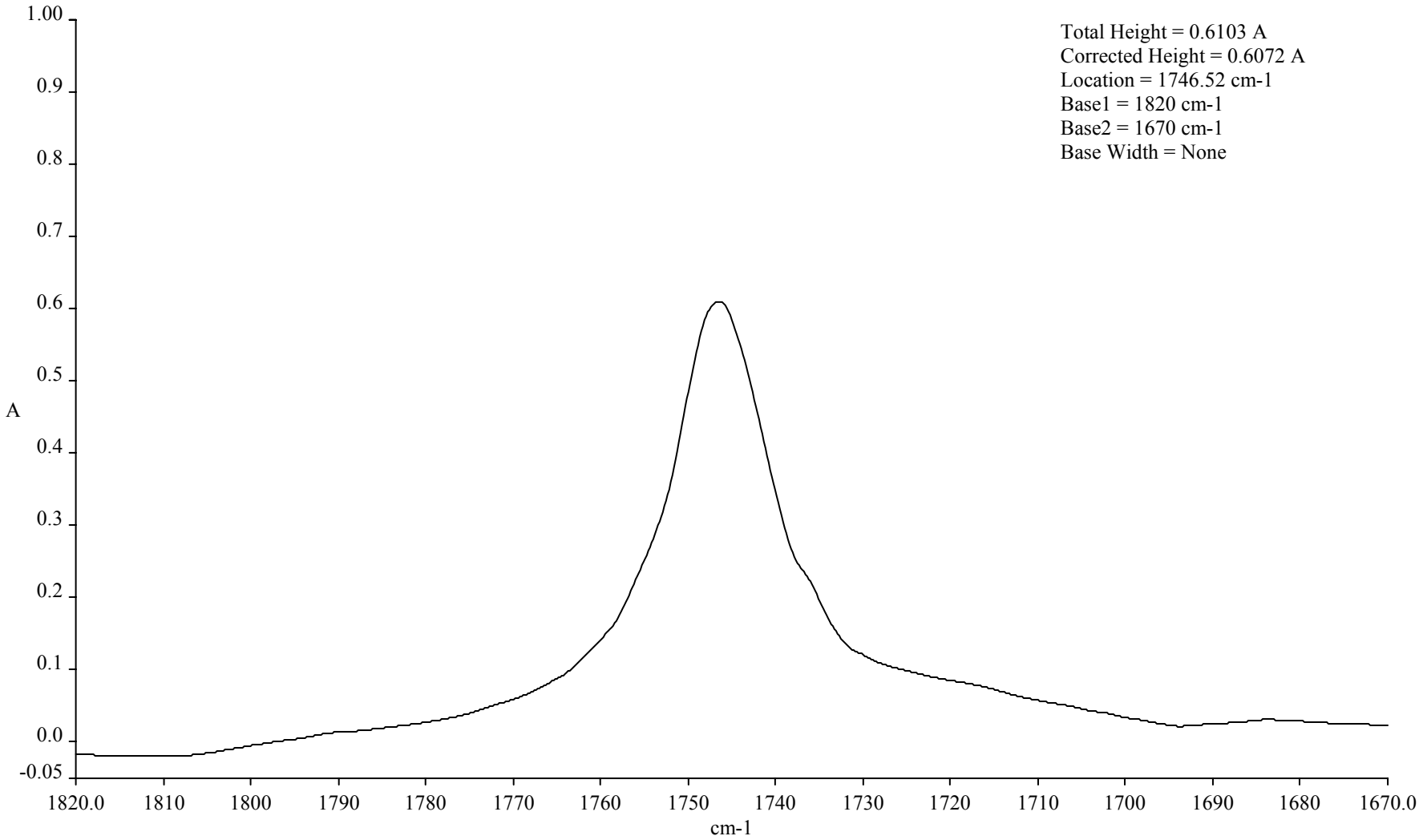
Mid IR Spectra from 4000 cm^{-1} to 400 cm^{-1}: B2 (2% FAME in petroleum diesel) ; cell path length 0.10 mm



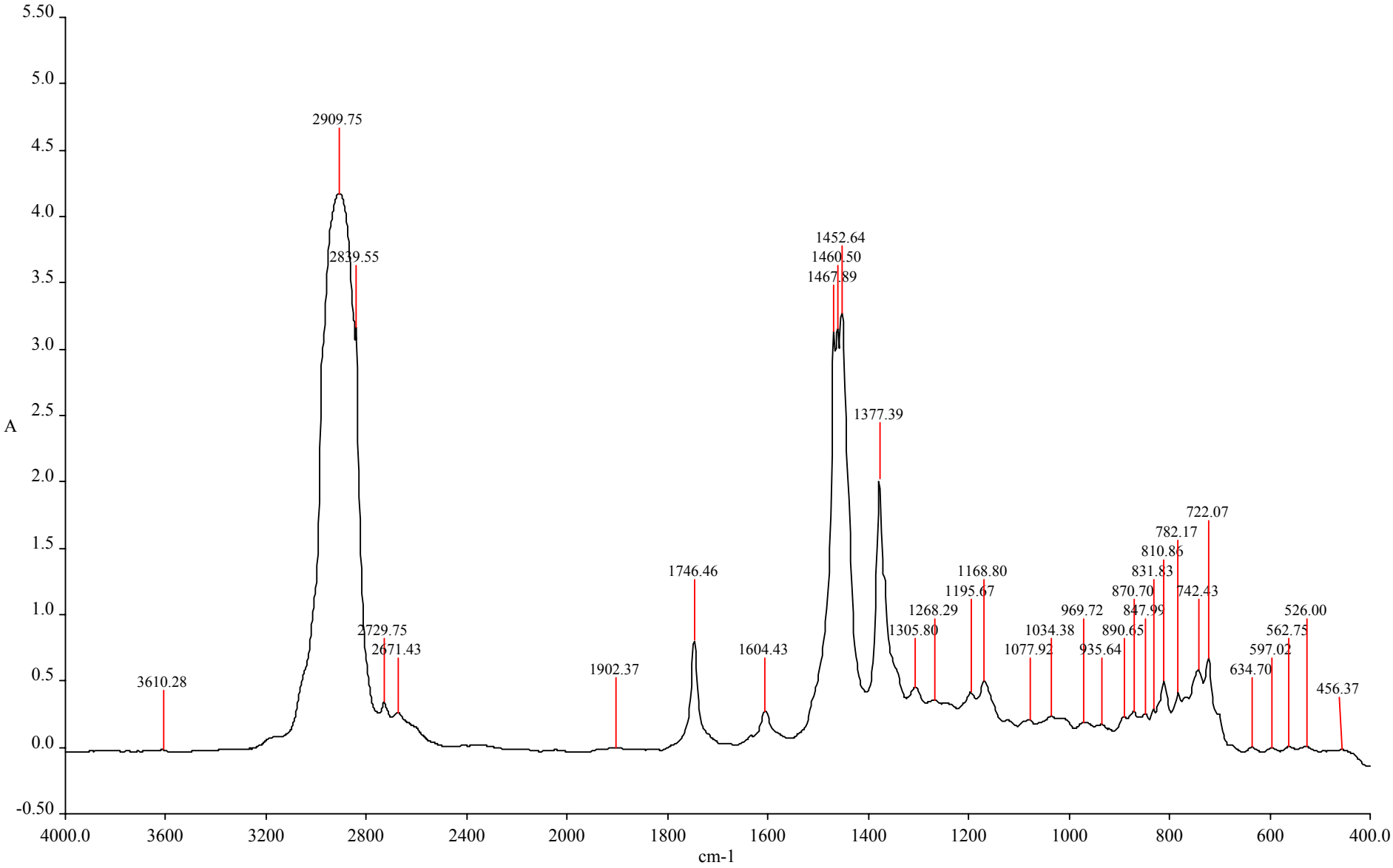
Mid IR Spectra from 1820 cm^{-1} to 1670 cm^{-1}: B2 (2% FAME in petroleum diesel) ; cell path length 0.10 mm



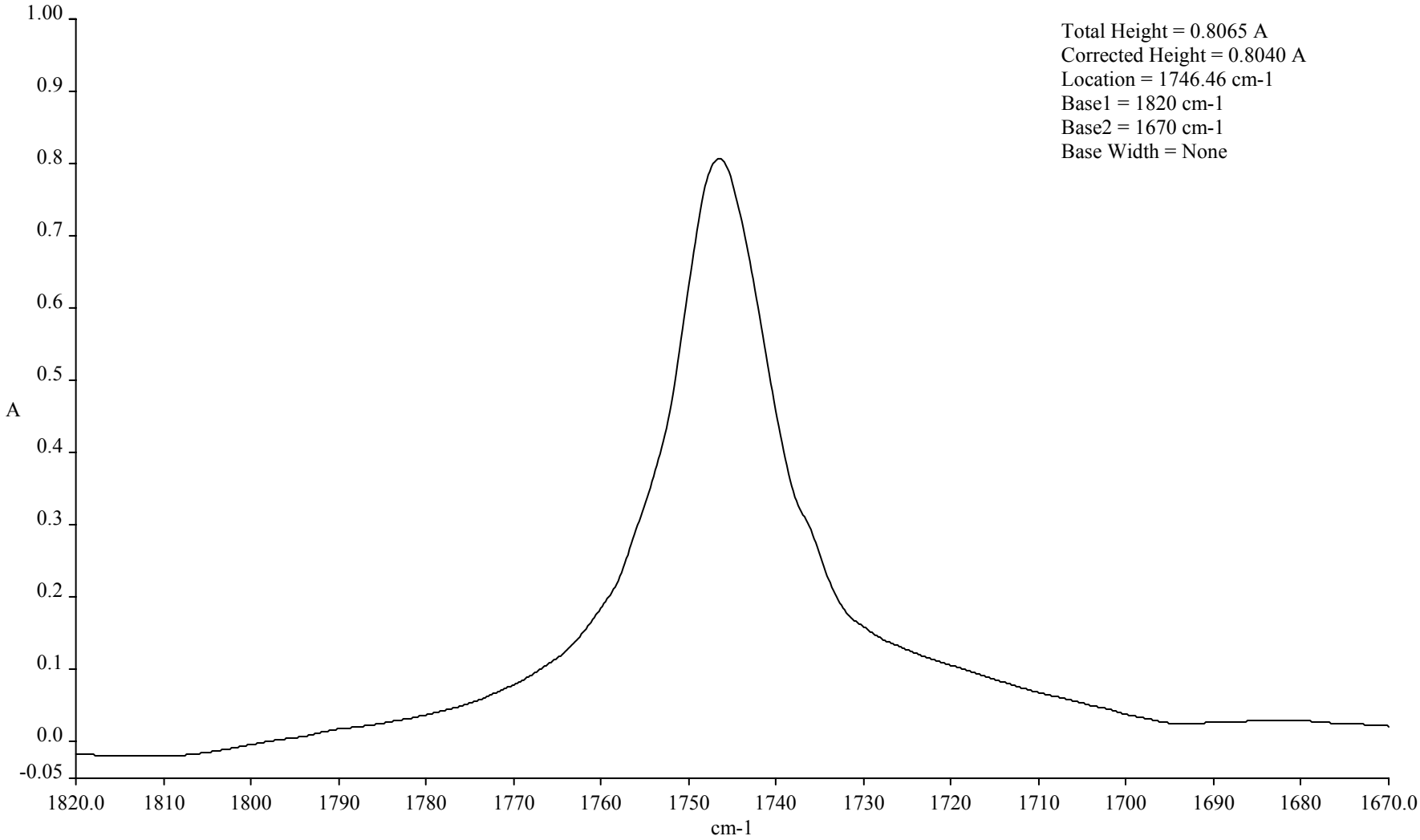
Mid IR Spectra from 4000 cm^{-1} to 400 cm^{-1}: B3 (3% FAME in petroleum diesel) ; cell path length 0.10 mm



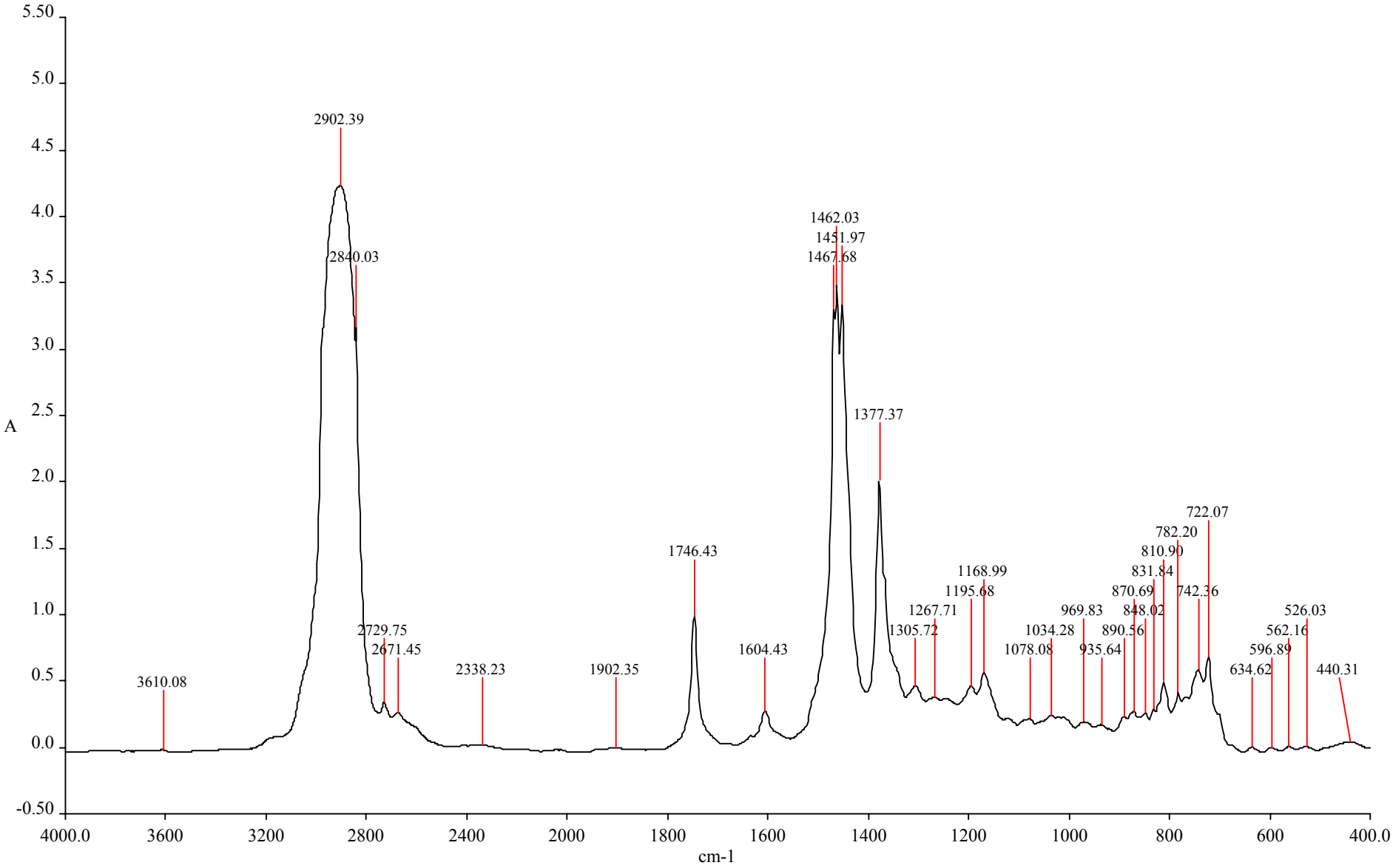
Mid IR Spectra from 1820 cm^{-1} to 1670 cm^{-1}: B3 (3% FAME in petroleum diesel) ; cell path length 0.10 mm



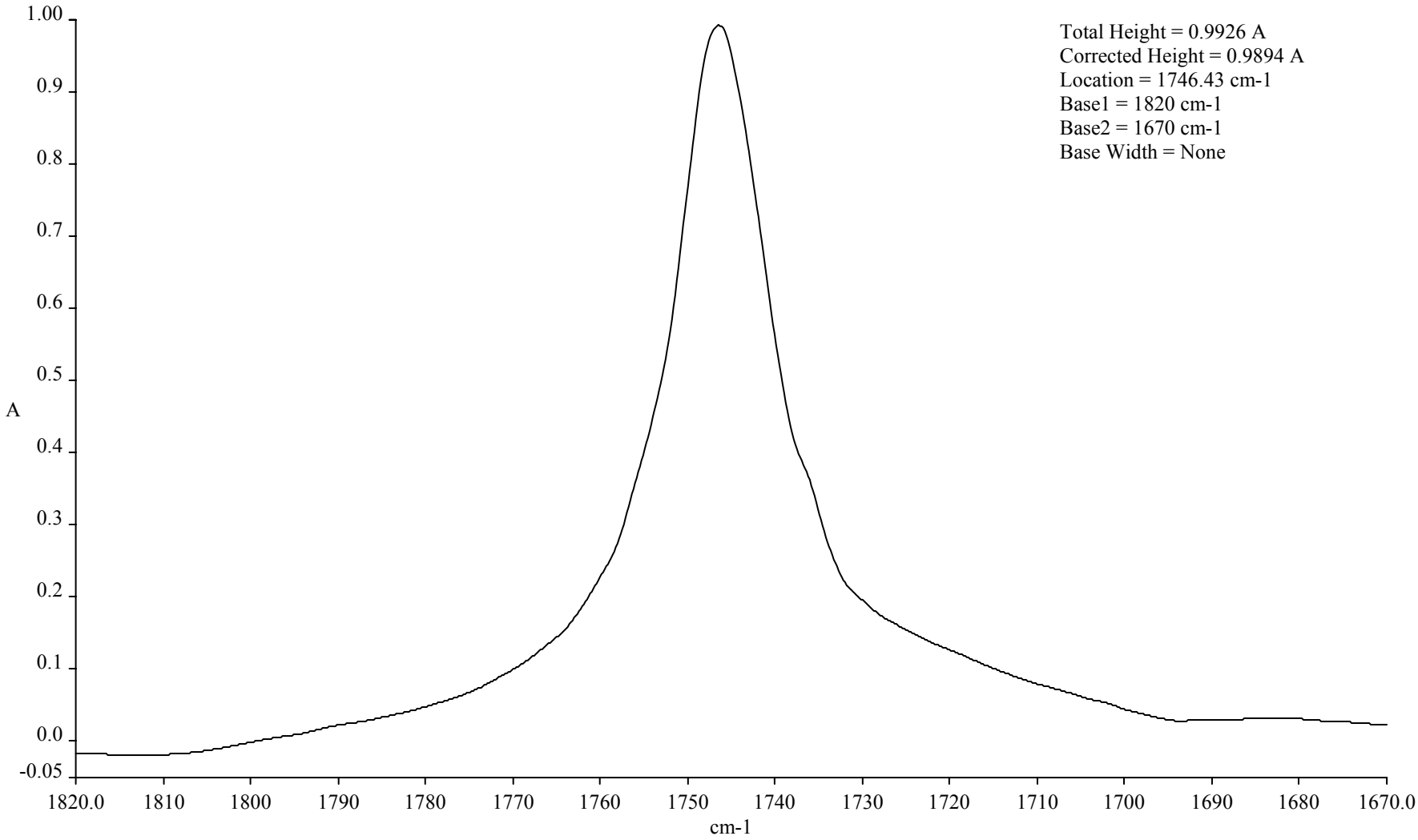
Mid IR Spectra from 4000 cm^{-1} to 400 cm^{-1}: B4 (4% FAME in petroleum diesel) ; cell path length 0.10 mm



Mid IR Spectra from 1820 cm^{-1} to 1670 cm^{-1}: B4 (4% FAME in petroleum diesel) ; cell path length 0.10 mm



Mid IR Spectra from 4000 cm^{-1} to 400 cm^{-1}: B5 (5% FAME in petroleum diesel) ; cell path length 0.10 mm



Mid IR Spectra from 1820 cm^{-1} to 1670 cm^{-1}: B5 (5% FAME in petroleum diesel) ; cell path length 0.10 mm