Characterization of Crude oil sample from a local South African Refinery

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Abstract

Characterization of crude oil and petroleum products comprises of numerous analytical techniques which are complex, time consuming and do not address the major hydrocarbon classes present. SARA analysis have been shown to produce rapid analysis for classifying crude oil and petroleum products in terms of saturates, aromatics, resins and asphaltenes hydrocarbon composition, and an in-depth understanding of asphaltenes structural characteristics, but have not been well investigated in South African refineries. The aims of this study were to use an in-house developed HPLC method and a combination of analytical techniques to determine the estimates of four major hydrocarbon classes in crude oil, lubricant oil, petrol and diesel samples obtained from local refineries, and further investigate the structural characteristics of asphaltenes. The four major classes were successfully identified and determined in the samples studied and from SARA composition of crude oil the colloidal instability index and crystallite parameters were obtained. The crude oil investigated was found to be composed of 38% of saturates, 28% of aromatics, 21% of resins and 11% of asphaltenes. From this composition the colloidal instability index of crude oil sample is estimated to value of 1.02 which suggests a good stability for refining. The composition of petroleum products samples of lubricant oil, petrol and diesel successfully identified saturates and aromatics hydrocarbon classes with a large presence of aromatics. These results provide an understanding of major hydrocarbon classes present in crude oil and petroleum products in the South African fuel specifications.

Acknowledgements

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Nomenclature

Aliphatic Carbon	C_{al}
Aliphatic Hydrogen	H_{al}
Alpha Carbon	$C\alpha$
Alpha Hydrogen	H_{α}
Angstrom	*Å*
Area under graphene peak	$A_{(graphene)}$
Area under γ-Peak	$A_{(\gamma)}$
Aromatic Carbon	C_{ar}
Aromatic Hydrogen	H_{ar}
Aromaticity Factor of Carbon	$F_{CA}=(f_a)$
Aromaticity Factor of Hydrogen	F_{HA}
Bragg angle	θ
Colloidal Instability Index	*CII*
Density	ρ
Full width at half maximum	$B_{1/2}$
Inter-chain layer distance	d_{γ}
Inter-planar Spacing	d_m
Methyl Carbon	C_{Methyl}
Methyl Hydrogen	H_{Methyl}
Methylene Carbon	C_{Me}
Methylene Hydrogen	H_{Me}
Naphthenic Carbon	C_{Naph}
Naphthenic Hydrogen	H_{Naph}
Normal	n-
Octane Number 93 Rating	‘93
Octane Number 95 Rating	‘95
Parts Per Million	*ppm*
Wavelength	λ

List of abbreviations

^{13}C-NMR	Carbon Nuclear Magnetic Resonance
^{1}H-NMR	Hydrogen Nuclear Magnetic Resonance
Amt	Amount
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
HPLC	High Performance Liquid Chromatography
LRP	Lead Replacement Petrol
mAU	milli-Absorbance Unit
Min	Minute(s)
nRIU	nano Refractive Index Unit
PAH	Polycyclic Aromatic Hydrocarbon
RID	Refractive Index Detector
SAPIA	South African Petroleum Industry Association
SARA	Saturates Aromatics Resins Asphaltenes
ULP	Un-Leaded Petrol
VWD	Variable Wavelength Detector
XRD	X-Ray Diffraction
wt%	Weight Percentage

1. INTRODUCTION

The analysis of petroleum and petroleum products is necessary to determine the properties that can assist in resolving process problems as well as properties that indicate the function and performance of the product in service (Speight, 2002). Fuel properties are determined experimentally in the laboratory on fluid samples taken from the process under study; however an extensive experimental program can be complex, expensive and time consuming and undermine the motivation for analyzing each feedstock in a daily refinery operation. It is necessary to analyse crude oils in terms of their SARA composition in order to address and mitigate process problems such as asphaltene precipitation that can clog wells, pipelines, surface facilities and subsurface formations in the upstream operations, while in the downstream refining of heavy crude oils can lead to coking, fouling and catalyst deactivation. These problems are undesirable because they reduce productivity, limit fluid flow and are costly, hence laboratory analysis can assist to remediate such problems.

The composition of petroleum can vary depending on many factors, like location and age of the field. Petroleum oil mainly consists of hydrocarbons and additional small amounts of nitrogen, oxygen, sulphur and metals (Speight, 1999). Petroleum Products according to (Speight, 2002) are any petroleum-based products that can be obtained by refining and comprise of refinery gas, liquefied petroleum gas (LPG), naphtha, gasoline, aviation fuel, marine fuel, kerosene, diesel fuel, distillate fuel oil, residual fuel oil, gas oil, lubricants, white oil, grease, wax, asphalt as well as coke. Four main classes of hydrocarbons present in crude oils can identified and measured: saturates (alkanes and cyclo-paraffins), aromatics (mono, di and polyaromatic), resins and asphaltenes (Speight, 2001).

This study discusses parameters such as aromaticity, asphaltene precipitation, colloidal stability index, crystallite parameters and SARA composition. Samples are obtained from petroleum oil, petrol, diesel fuel and engine oil produced from any local refineries. According to (Likhatsky, 2010) the asphaltenes stability of crude oils can be evaluated using colloidal stability index based on the composition of crude oil and this can be used to mitigate crude oil fouling (Sinnathambi, 2012). Aromaticity factors calculated are able to predict SARA concentration based on developed correlation equations developed by (Sanchez-Minero *et al*, 2012) using NMR data. Structural characteristics of asphaltene are from crystallite parameters such as aromaticity and interplanar spacing. The petroleum products are investigated for composition content with in-house developed HPLC method and these products include ULP 95 petrol, LRP 95 petrol, 50ppm diesel and lubricant engine oil samples.

The chemical constituents of petroleum are determined by techniques available to separate and analyse the various compounds that are found in petroleum (Behrenbruch, 2007). The spectrometric techniques used in this study are useful for analyzing petroleum crude samples by separating the sample into the major hydrocarbon classes. By using high performance liquid chromatography (HPLC), crude oil separated into components according to their polarity.

1.1. RESEARCH STATEMENT

The determination of SARA composition of crude oil and petroleum products by the use of analytical techniques is necessary to provide an in-depth understanding of asphaltene precipitation in crude oil and estimates of four major hydrocarbon groups.

1.2. RESEARCH OBJECTIVES

The analysis involves a number of analytical instruments used not only in determining the group type composition of crude oil, petrol and diesel samples, but also in determining physical properties such as colloidal instability index, aromaticity factors of hydrogen and carbon in crude oil, and structural characteristics of asphaltenes. The objectives of this research are to:

- To determine the composition of crude oil in terms of hydrocarbon group type of saturates, aromatics, resins and asphaltenes using HPLC and NMR.
- To characterize the asphaltenes samples by XRD.
- To determine the saturates and aromatics hydrocarbons in petrol, diesel, lubricant samples
- To find the API and colloidal instability index of crude oil.

1.3. RESEARCH SCOPE AND LIMITATIONS

There is a vast majority of test methods on petroleum products that is available that cannot all be covered on this topic. Laboratory tests and analysis that are relevant to the research is covered in this report. The limitations involved in this research project include:

- Comparison of different types of crude oil cannot be achieved as only one sample of crude oil is obtained.
- The HPLC equipment available restricts the determination of resins fraction because the method requires two amino columns connected in series and a column switching valve.
- Hexane solvent as a single parameter for asphaltenes precipitation is only used to produce asphaltenes, hence parameters such as temperature, pressure and different solvents are kept constant.

2. LITERATURE REVIEW

2.1. CRUDE OIL PROPERTIES

Elemental analysis of petroleum shows that the major constituents are carbon and hydrogen with smaller amounts of sulphur, nitrogen, oxygen and trace elements such as vanadium, nickel, iron and copper. Sulphur is the most abundant non hydrocarbon and often considered the most important by refiners. However nitrogen and trace metal can be poisonous on the refining catalyst (Speight, 2002). Crude oils form a continuum of hydrocarbon species from gas to the heaviest components made up of asphaltenes, given the complexity of the mixtures, it is difficult to analyze crude oils completely, and hence techniques of fractionation are used in the characterization of petroleum as well as techniques of elemental analysis applied to the fractions obtained. When it comes to the heaviest of petroleum fraction such as asphaltenes, modern analytical methods are not able to isolate and characterize completely (Wauquier, 1994). The physical properties such as API gravity are considerably influenced by high-boiling constituents, in which the heteroatoms (Sulphur, nitrogen and metals) concentrate, therefore these lead to determining the percentage of asphaltenes and resins (Fahim, 2012).

The determination of various compounds present in crude oils can be used for classification, such as boiling point fractionation which is widely used for classification based on the temperature range at which types of compounds are removed and the boiling point range is directly related to the size and complexity of crude oil components (Klein, 2005). Depending on the boiling point range of the sample, fractionated products fall into three major categories: light distillates, middle distillates, and heavy distillates. All gasoline range materials and naphtha are considered light distillates, the middle distillate are diesel, jet fuel and kerosene range samples. The ideal chromatographic method for the determination of individual compounds, boiling point distribution, and the method should fulfill the following the requirements that it should be (i) reproducible, (ii) rapid, (iii) adequate for quality control, (iv) quantitative and (v) applicable to the whole sample without requiring prefractionation (Barman, 2000). Different classes of hydrocarbon in petroleum oil are shown in figure 2.1:

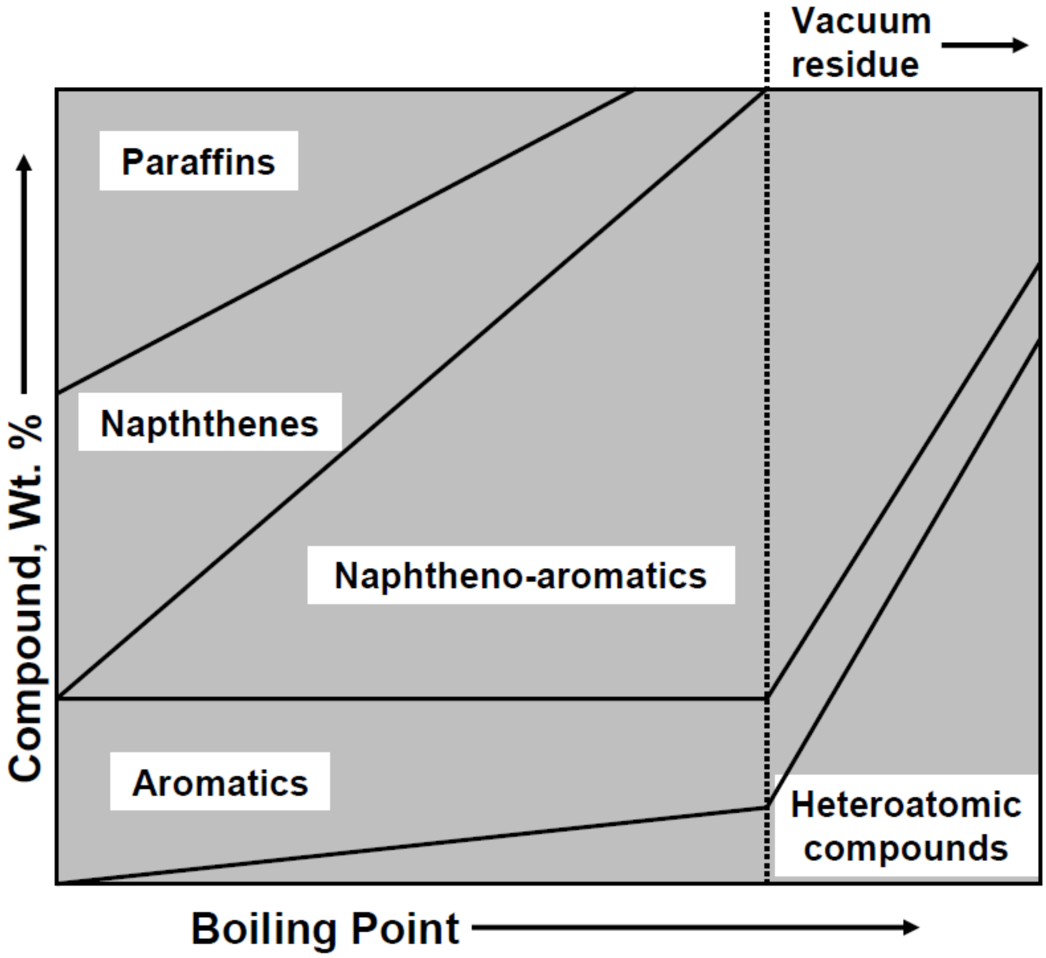
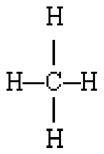
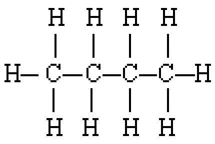
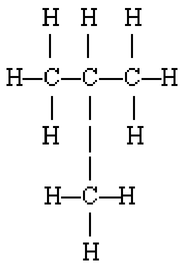


Figure 2.1: Distribution of compounds throughout crude oil (Speight, 2001)

2.1.1. *Chemical Composition*

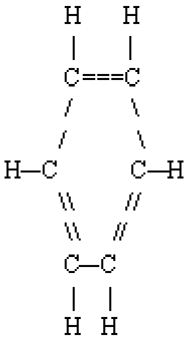
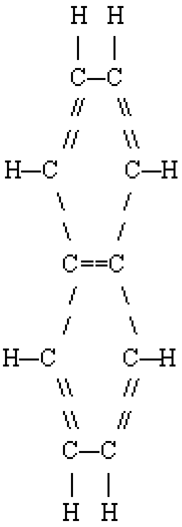
The elemental composition of crude oil is normally made up of high carbon content in the range 83-87%, the hydrogen content tend to fall in the range 10-14%, and varying small amounts of nitrogen, oxygen, sulphur and metals such as nickel and vanadium (Speight, 1999). According to (Mathpro, 2011) the chemical properties of hydrocarbons depends on nature of chemical bonds between species and the different classes of hydrocarbons are formed from carbon atoms bonded with carbon, hydrogen and heteroatoms in single, double and triple bonds. Generally hydrocarbons in crude oil are grouped as paraffins, olefins, naphthenes, aromatics and hetero-atomic compounds as shown in figure 2.1. Paraffins are also known as alkanes with a general molecular formula of C_nH_{2n+2} and occur as straight or branched chains of carbon atoms. This group of compounds are saturated hydrocarbons with branched chain paraffins possessing higher octane number than the normal paraffins (Speight, 1980). Examples of straight chain molecule (Butane) and branched chain paraffin molecule isobutane are illustrated in Table 2.1 .

Table 2.1: Examples of Paraffin molecules

Methane (CH_4)	Butane (C_4H_{10})	Isobutane (C_4H_{10})
		

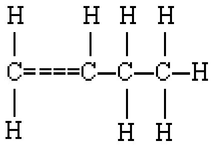
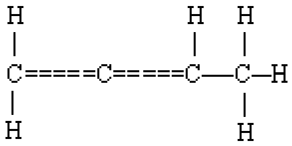
Aromatic compounds are characterized by at least single benzene ring as part of their molecular structure and the aromatics class of compounds are unsaturated cyclic compounds which tend to react readily because of presence of chemical double bonds. Typical examples of aromatic compounds include Benzene and Naphthalene as shown on the following table:

Table 2.2: Typical examples of aromatic compounds

Benzene (C_6H_6)	Naphthalene ($C_{10}H_8$)
	

Olefins are usually not present in crude oil and are produced in refining operations that mainly focus on gasoline production (Mathpro, 2011). Olefins are usually formed by thermal and catalytic cracking processes and can be further classified as alkenes, dienes and alkynes. Alkenes (mono-olefins) possess only one carbon-carbon double bond in the chain and have a general chemical formula C_nH_{2n}, dienes (di-olefins) possess two carbon-carbon double bonds and have a general chemical formula of C_nH_{2n-2}, and alkynes have a triple carbon-carbon bond and a similar general chemical formula as dienes. Olefins class of compounds are unsaturated hydrocarbons and more reactive than paraffins and naphthenes (Speight, 1980). Below are typical olefins compounds:

Table 2.3: Typical Examples of Olefins compounds

1-Butene (C_4H_8)	1,2-Butadiene (C_4H_6)	Acetylene (C_2H_2)
		H—C==C—H

Compounds containing oxygen, nitrogen and sulphur are termed hetero-compounds, these compounds appear throughout the whole boiling range of the crude oil, but they tend to concentrate in the heavier fractions. Sulphur may be present in crude oil as hydrogen sulphide (H_2S) and other compounds such as mercaptans, sulphides, disulphides. Oxygen compounds in crude oil are typically alcohols, phenols, acids, esters, ethers and hydrides and many of them are acidic. Typical nitrogen compounds found in crude oil are pyridine and quinolone that are basic, and pyrole, indole and carbazole that are non-basic (Borgund, 2007) as shown in the figure 2.2:

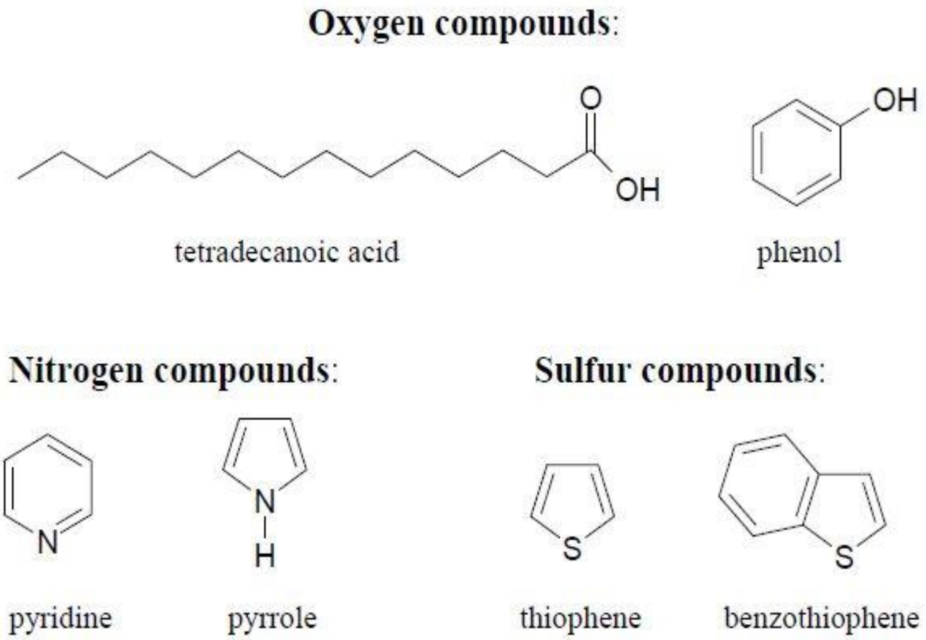


Figure 2.2: Examples of hetero-compounds containing oxygen, nitrogen and sulphur compounds. (Borgund, 2007)

Vanadium, nickel, iron and copper are normally found in petroleum as naturally occurring elements associated to the formation process and although present only in small amounts, they are very important to the petroleum refining. Their determination is of considerable importance, since they have deleterious effects on refinery operation: they may corrode refinery equipment, poison and foul catalysts and cause undesirable reactions in refinery operation (Brandao, 2007). Vanadium is usually the most abundant trace metal in petroleum samples, it might be found in concentrations levels up to 1500 $mgkg^{-1}$, although some crudes contain less than 0.1 $mgkg^{-1}$. Vanadium occurs predominantly as the vanadyl ion (VO^{2+}) in the form of organometallic complexes with porphyrins as examples shown in the below figure:

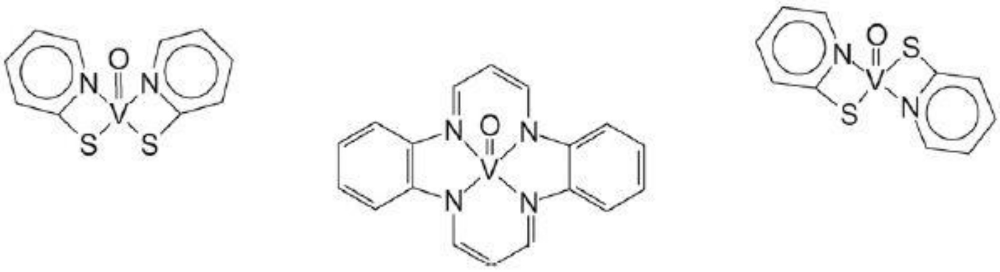


Figure 2.3: Chemical structures of typical vanadyl complexes in crude oil (Amorim, 2007)

Inorganic salts such as sodium chloride, magnesium chloride and calsium chloride in suspension or dissolved in water are present in crude oil and are usually removed by a process of desalination before processing with the aim to prevent catalyst poisoning, salt corrosion and fouling. Carbon dioxide and naphthenic acids may also be present in crude oil. (Speight, 1980)

2.1.2. *Physical Properties*

One of the most important physical characteristics of petroleum crude is its density expressed in terms of API gravity given by the following relationship; $API = 141.5/SG - 131.5$, where SG is the specific gravity of crude oil or petroleum products usually obtained by the use of hydrometer guided by ASTM D287-92 procedure (Albahri, 2011). In addition the boiling point distribution and kinetic viscosity are important properties of crude oil; the former indicates how much gasoline and other transportation fuels can be made from petroleum with conversion and the latter permits the assessment of its undesirable residual material that causes resistance to flow. Knowledge of these parameters allows for evaluating selling price, production rates and pipeline oil quality control (Filgueiras *et al*, 2013). The physical properties such as API gravity are considerably influenced by high-boiling constituents, in which the heteroatoms (Sulphur, nitrogen and metals) concentrate, therefore these lead to determining the percentage of asphaltenes and resins (Fahim, 2012). The different boiling ranges of petroleum products are displayed in figure 2.4:

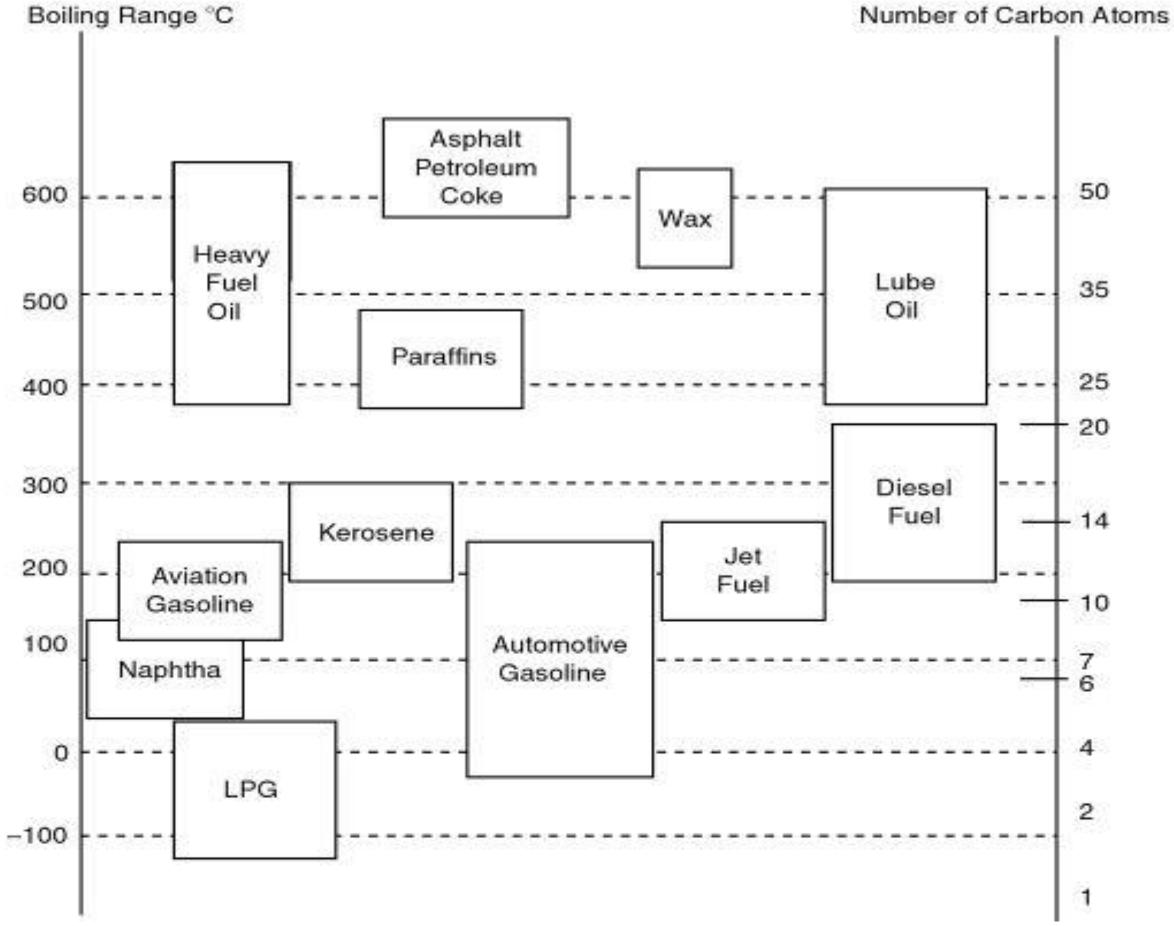


Figure 2.4: Petroleum products with carbon numbers and boiling ranges (Fahim, 2010)

2.2. PETROL FUEL PROPERTIES

It is important to note that the properties of petrol fuel are depended on one another. For example, properties such as volatility, composition, density and distillation parameters are all inter-related in such a way that when one property is changed then the other properties are changed as well (Sapia, 2008). Typically a grade of petrol is made from six to ten blend stocks which are produced by refinery or purchased (Mathpro, 2011). The most common petrol blend stocks and properties are shown in Table 2.4:

Table 2.4: Typical volume share and properties of Gasoline fuel (Mathpro, 2011)

Source	**Blendstock**	**Typical Share (vol%)**	**Typical Properties**						
			Octane		**S**	**RVP**	**Aromatics**	**Benzene**	**Olefins**
			RON	**MON**	**(ppm)**	**(psi)**	**(vol%)**	**(vol%)**	**(vol%)**
Crude distillation	Straight Run Naphtha	5.0-10	71	70	~120	12	_	_	_
Upgrading units	Isomerate	0-10	82	80	1	13	_	_	_
	Alkylate	5.0-10	94	92	<10	3	_	_	_
	Reformate	20-30	97	88	<4	5	60	5	
Conversion Units	FCC Naphtha	30-35	92	80	500-1500	5	25	1	30
	Coker Naphtha	0-5	88	80	~500	19	0.5	0.5	50
	Hydrocraked Naphtha	5.0-15	78	76	<4	11	2	2	
Purchases	Natural Gas Liquids	0-5	73	71	~150	13	3	1	1
	MTBE	0-15	118	102	<5	8	_	_	_
	Ethanol	0-10	123	103	<5	18	_	_	_

The olefin content found in petrol depends on the refinery configurations and feedstock, petrol fuel that is catalytically cracked tends to be higher in olefins. While olefins are good octane component, they are thermally unstable and this can lead to gum formation in the engine intake systems. (Sapia, 2008)

2.3. DIESEL FUEL PROPERTIES

Diesel grade is usually made from a blend of three to five blend stocks produced from a refinery and in some instances depending on regulation blended with biodiesel. Refineries normally produce one or two diesel grades and their properties are commonly identified by the sulphur content primarily, cetane number, density and other physical properties (Mathpro, 2011). Table 2.5 shows the most common diesel blend stocks. Most of the blend stock for diesel contains aromatics as reflected on this table, but the PAHs in particular are of great concern which contribute particulate emission as well as sulphur content which is directly related to particulate matter (Sapia, 2008).

Table 2.5: Typical volume shares and properties of diesel fuel (Mathpro, 2011)

Source	**Blendstock**	**Typical Share (vol%)**	**Typical Properties**			
			Sulphur (ppm)	**Cetane Number**	**Aromatics (vol%)**	**Specific Gravity**
Crude Distillation	Str. Run Kerosene	25-33	~3000	45	19	0.82
	Str. Run Distillate	31-35	~7000	53	21	0.85
Conversion Units	FCC Light Cycle Oil	15-21	~12500	22	80	0.93
	Coker Distillate	8.0-10	~32000	33	40	0.89
	Hydrocracked Distillate	7.0-15	~100	45	20	0.86

2.4. SARA ANALYSIS

There are four major classes of hydrocarbons found in crude oils, which include saturates, aromatics, resins and asphaltenes. The SARA analysis determines the content of each class hydrocarbons (Sinnathambi *et al*, 2012). Using this method crude oil is separated into components according to their polarizability and polarity. There are three main ways to separate crude oils by chromatography into saturate, aromatics, resins and asphaltenes fractions: A clay-gel adsorption chromatography method which manually samples a high volume of crude oil and large quantities of solvents, this is based on the ASTM D2007 standard method of procedure. Secondly high performance liquid chromatography methods are faster, more reproducible and more readily automated than the first chromatography method. In both methods it is very important to note that the asphaltenes fraction is removed before proceeding with the chromatography since the asphaltenes are either irreversibly adsorbed or precipitated in the saturate elution step. The third and fastest method uses thin layer chromatography (TLC) with quartz rods with sintered silica particles, this method uses very small amounts of samples and does not require asphaltenes to be removed before chromatographic analysis (Fan, 2002). Below is the general scheme of SARA analysis using liquid chromatographic separation:

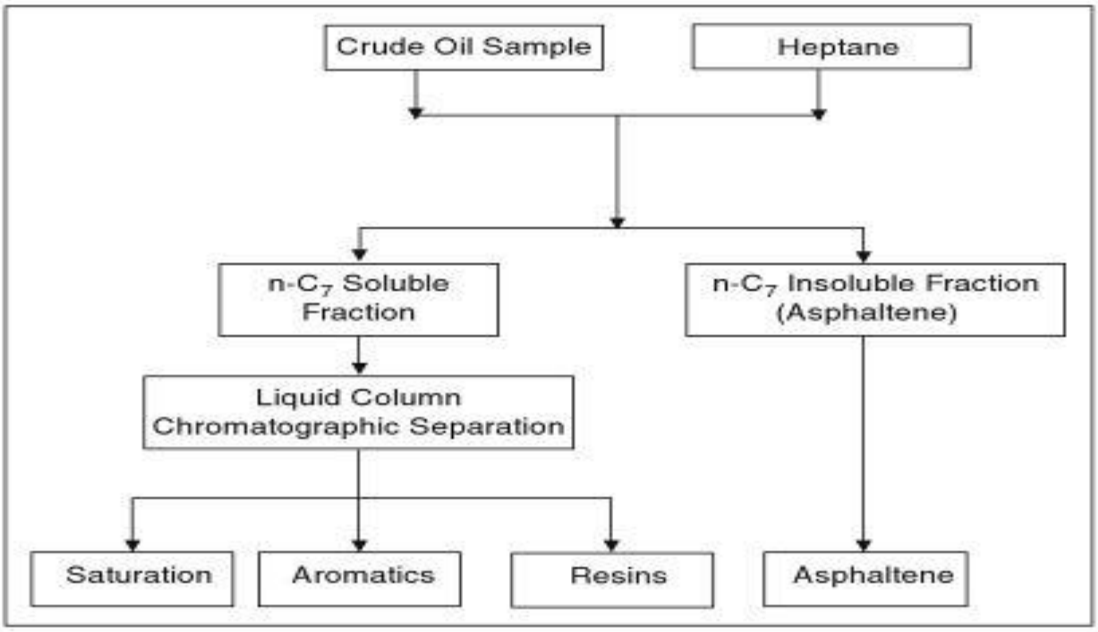


Figure 2.5: Schematic diagram for SARA fractions (Fahim, 2010)

SARA composition of crude oil can be calculated using developed correlations with aromaticity factors for a wide range of API gravity (10 – 33^0). The study on "*Predicting SARA composition of crude oil by means of NMR"* used NMR results to obtain the concentration of aromatic hydrogen (*H_{ar}*) and aromatic carbon (*C_{ar}*), and then the aromaticity factors of carbon (F_{CA}) and hydrogen (H_{ar}) were calculated and correlated to SARA analysis through the following equations:

$$F_{HA} = {}^{H_{ar}}\!/_{(H_{ar} + H_{al})} \tag{1}$$

$$F_{CA} = {}^{C_{ar}}\!/_{(C_{ar} + C_{al})} \tag{2}$$

Concentrations as a function of F_{HA}:

$$\%\,Aromatics(F_{HA}) = -4090.3F_{HA}^2 + 31F_{HA} + 32.9 \tag{3}$$

$$\%\,Resins(F_{HA}) = 414.6F_{HA} + 4.9 \tag{4}$$

$$\%\,Asphaltenes(F_{HA}) = 561.6F_{HA} - 10.5 \tag{5}$$

Concentrations as a function of F_{CA}:

$$\%\,Aromatics(F_{CA}) = -748.5F_{CA}^2 + 198.3F_{CA} + 16.8 \tag{6}$$

$$\%\,Resins(F_{CA}) = 113.9F_{CA} + 2.38 \tag{7}$$

$$\%\,Asphaltenes(F_{CA}) = 301.2F_{CA}^2 + 32F_{CA} - 2.8 \tag{8}$$

Saturates concentration is determined by difference:

$$\%\,Saturates = 100 - \%Aromatics - \%Resins - \%Asphaltenes \tag{9}$$

It is important to note that the above correlation (3) to (8) are particularly suitable for API gravity in the range of 10 – 33^0, Hence they cannot be generalised for crude oil samples that falls out of this range (Sanchez-Minero *et al*, 2013). In the oil industry, colloidal in-stability index (CII) is related to the SARA composition of crude oils and can be used to evaluate fouling tendency and asphaltenes stability (Likhatsky, 2010). According to (Sinnathambi, 2012) the higher CII values greater than 2 are undesirable since it suggests that the crude oil is a heavy fouler. The relationship between CII and SARA composition is given by the following equation:

$$CII = \frac{(\% Saturates + \% Asphaltenes)}{(\% Aromatics + \% Resins)} \tag{10}$$

The saturate hydrocarbon class is made of non-polar, straight and branched chain alkanes and cycloalkane (Naphthenes). They are the lightest fraction of crude oil and wax is also a sub class of saturates because it is made of straight long chain alkanes typically ranging from C_{20} to C_{30} (Aske, 2002). The aromatic fraction contains the groups with aliphatic side chain and these groups ranges from mono to poly-aromatic depending on the number of benzene ring present (Aske, 2002).

Resins are polar molecules having aromatics characteristics and contain heteroatoms (N, O, S, occasionally Ni & V) and their molecular weight ranges from 500 to 1000 (Wauquier, 1994). According to (Fahim, 2010) the resin molecules surround the asphaltenes clusters and suspend them in liquid oil, hence the content of resins in crude oils is higher than that of the asphaltenes since each asphaltenes is surrounded by a number of resin molecules. Resin fraction is soluble in light alkanes such as pentane and heptane but is insoluble in liquid propane (Aske, 2002).

The chemical composition of asphaltenes is complex and varies considerably on the type of crude oils (Siddiqui, 2001). The molecular composition of asphaltenes is described by two proposed models; Archipelago model, and Island model, the Archipelago model suggests asphaltenes are made of several aromatic components that are bridged together by aliphatic chains (Strausz, 1992), whereas (Dickie & Yen, 1967) suggested that asphaltenes comprise of one fused poly aromatic hydrocarbon with attached aliphatic chains. The asphaltene fraction contains the largest percentage of heteroatoms, highest polarity and highest in terms of molecular weight. Asphaltenes are normally soluble in aromatic organic solvents such as toluene an insoluble in normal alkanes such as n-pentane (Akbarzadeh *et al*, 2007). Asphaltenes are black to dark brown friable solids in colour depending on the nature of crude oil and have a density ranging from 1.1 to 1.2 g/mL and an atomic ratio ranging from 1.0 to 1.2 (Goual, 2013).

2.5. ASPHALTENE PRECIPITATION

The process of precipitation of asphaltenes is a complex phenomenon which involves the interaction of asphaltenes and resins since resins have a strong association with asphaltenes in terms of their solubility in crude oil (Buenrostro-Gonzalez *et al*, 2004). Asphaltene precipitation is promoted by pressure, temperature and composition variations (Goual, 2013). However the effect of composition and pressure on precipitation is mostly reported to have a stronger effect than the effect of temperature. Both pressure and temperature are the main contributors of formation of asphaltene phase during the oil production process and this behaviour can be described by thermodynamic models in order to forecast or predict the onset points of precipitation (Buenrostro-Gonzalez *et al*, 2004).

Precipitation by composition changes is usually achieved by addition of paraffinic solvents to the sample of crude oils. The interaction among asphaltenes and resins molecules is affected by the solvent used as a medium, hence the amount of asphaltenes precipitated from any crude oil sample varies according to the nature of solvent and dilution ratio used (Mansoori *et al,* 2007). Figure 2.6 show the comparison of asphaltene precipitated using different dilution ratios and n-alkanes:

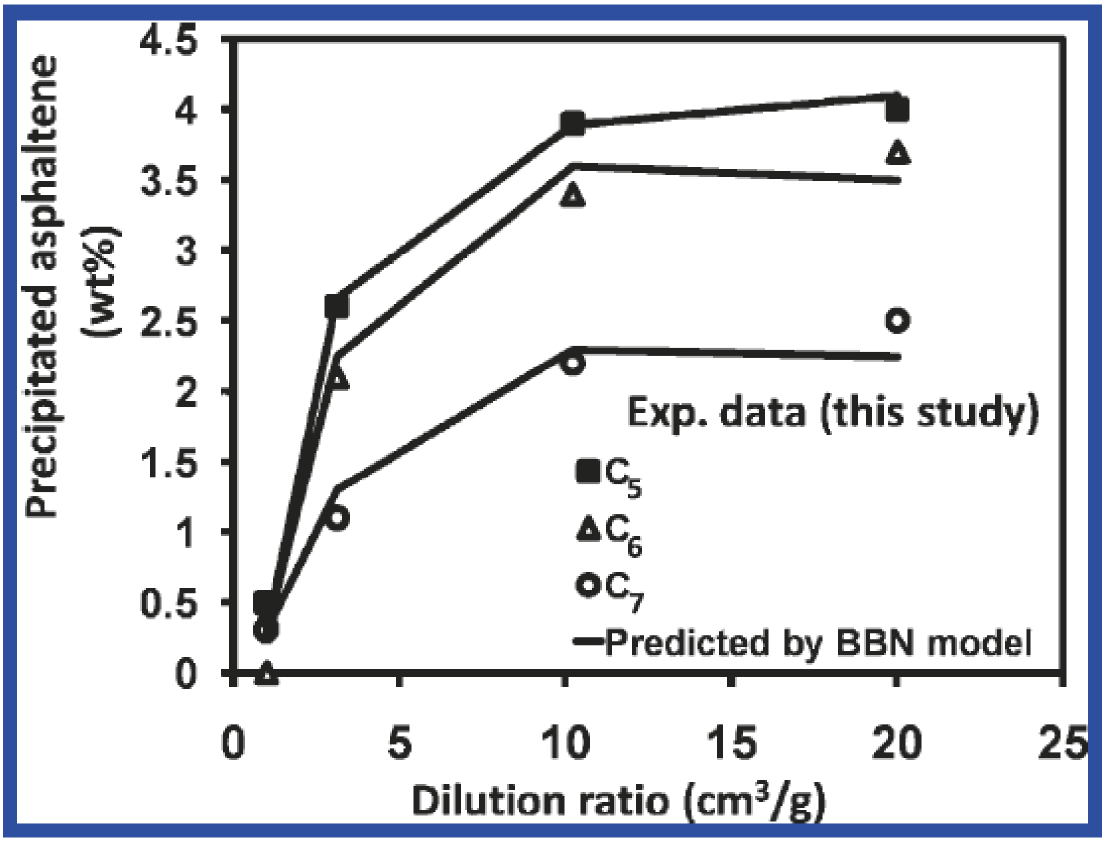


Figure 2.6: Example of Asphaltene precipitation using three different solvents (Amin, 2010)

2.6. ASPHALTENE MOLECULAR STRUCTURE

The structural characteristics of asphaltenes are very significant in determining yields from residual fraction of crude oil (Siddiqui *et al*, 1996). Asphaltenes are believed to be suspended as micro colloid in the crude oil, consisting of particle of about 3nm (Sheu and Mullins, 1996). X-Ray diffraction and NMR are two established techniques for the determining the structural and crystallite characteristics of asphaltene molecules.

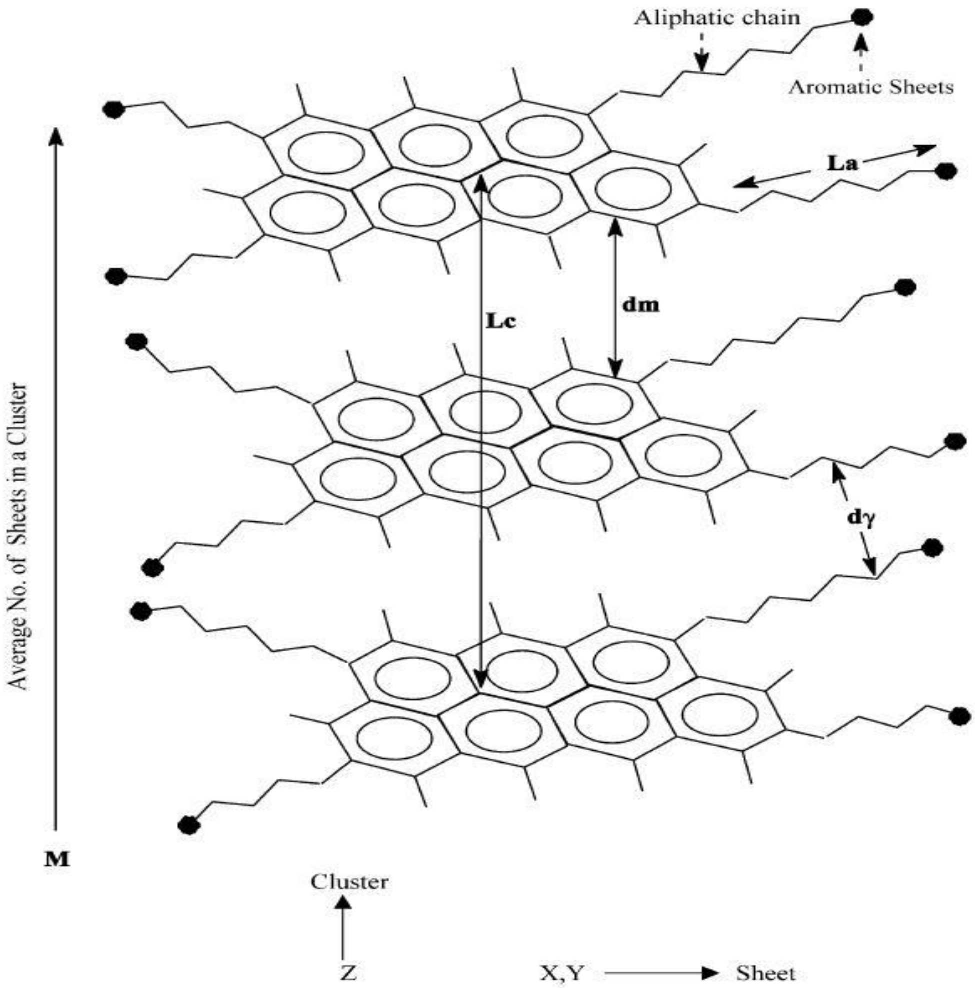


Figure 2.7: Cross-section of asphaltene model and group types that give rise to XRD peaks (Yen, 1961)

The crystallite parameters shown by figure 2.7 are discussed by both Shirokoff *et al* (1997) and Siddiqui *et al* (2002) by the following relation; the layer distance between aromatic sheets is calculated by the Bragg relation:

$$d_m = {}^{\lambda}/_{(2\sin\theta)} \qquad (11)$$

And the interchain layer distance is given by the following equation:

$$d_\gamma = {}^{5\lambda}/_{(8\sin\theta)} \qquad (12)$$

The method used by Siddiqui *et al* (2002) to obtain to estimate of Aromaticity f_a is determined from the calculated areas A of the resolved peaks of γ and graphene bands using the formula:

$$f_a = {C_A}/{C} = {C_A}/{(C_A + C_S)} = {C_{(Graphene)}}/{\left(C_{(Graphene)} + C_{(\gamma)}\right)} \tag{13}$$

Where C_S, C_A and C are the number of saturated aromatic and total carbon atoms per structural unit respectively.

3. EXPERIMENTAL METHODS AND MATERIALS

3.1. ASPHALTENE PRECIPITATION METHODOLOGY

The aim of this analysis is to separate crude oil into asphaltene and maltenes fractions. Maltenes are composed of the remaining saturates, aromatics and resins fractions, Initially the treatment of crude oil with n-hexane provides the separation of asphaltenes. Crude oil is added to n-hexane in a solvent ratio (cm^3 of n-hexane per $5cm^3$ of crude oil) of 10, 15, 30, 40 and 50 into separate 250ml volumetric flasks. The mixture is continuously stirred for 4 hours at room temperature and atmospheric pressure. Then the solution is then left to stand overnight prior to filtering. Filtering is achieved under vacuum with filter membrane of pore size 0.25 microns and normal hexane is used to wash any presence of wax by further washing with hexane. The asphaltenes precipitated are dried overnight in an oven at 60^0C to remove any volatile material present. So finally the maltenes sample of each is collected by from the filtrate and the samples are run in HPLC unit while the sample asphaltenes is further subjected to X-ray diffraction to characterize its structure. Figure 3.1 shows a summary of asphaltene precipitation method:

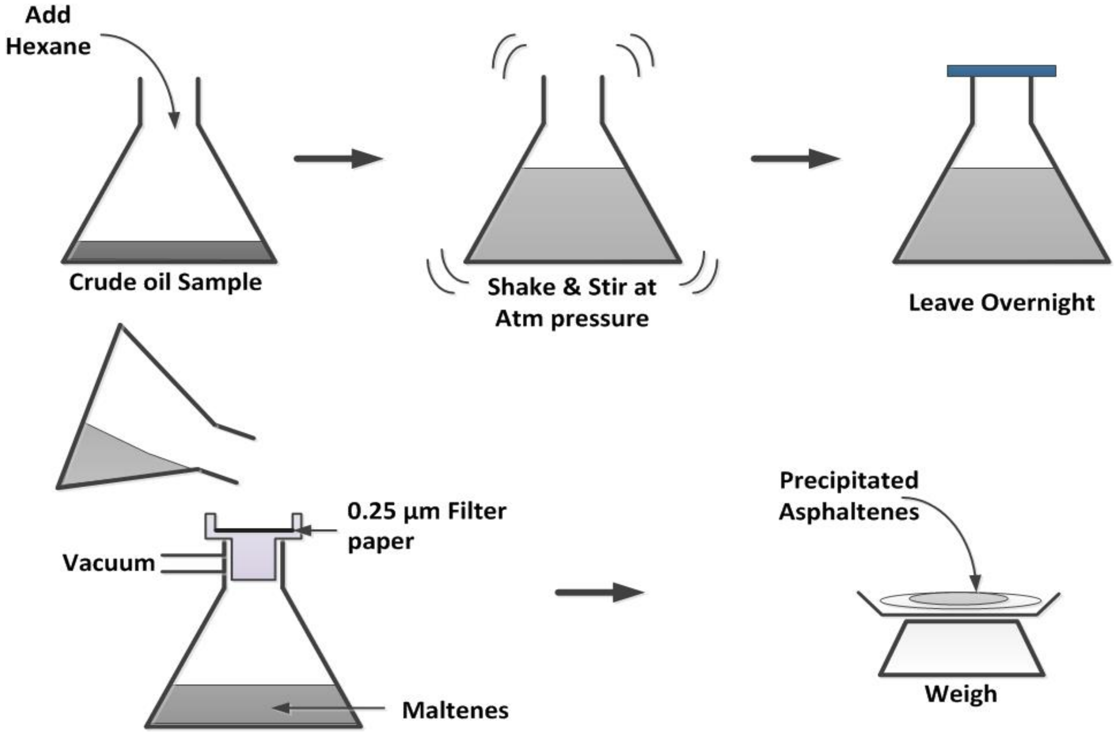


Figure 3.1: Summary of Asphaltene precipitation (Wu, 2004)

3.2. X-RAY DIFFRACTION METHODOLOGY

The asphaltene examined in this study are samples collected from the asphaltene precipitation experiment. The asphaltene samples produced are shown in figure B13. The sample were first grounded into fine powder particles, then XRD measurements were performed on the prepared samples with an automated diffractometer using cobalt radiation at a wavelength of 1.78897 Ǻ. The analysis is aided by computer software to perform a peak profile analysis. The profile fitting used a Lorentzian mix-mathematical model to obtain the area under γ and graphene peak, and also determine the peak positions.

3.3. NMR ANALYSES METHODOLOGY

600µl crude oil sample is dissolved in 100µl deuterochloroform solvent and tetramethylsilane is used as a chemical shift standard in both ^{1}H-NMR and ^{13}C-NMR analysis performed on Bruker 500MHz spectrometer. The quantitative ^{13}C spectrum is obtained by using a decoupling pulse delay sequence, with no relaxation agent and a 20 second pulse delay. Two spectra are obtained for the sample of crude oil, and the integration for ^{1}H spectra is expected to show peaks in the range 0 – 4 ppm and 6 – 9 ppm for aromatic hydrogen, While the ^{13}C spectra, it is expected that the aliphatic carbon in the range 0 – 70 ppm and aromatic carbon in the range 100 – 170 ppm chemical shifts.

3.4. HPLC ANALYSIS METHODOLOGY

The HPLC chromatographic separation system utilized comprise of pump system, auto-sampler injection system, ultra-violet (UV) detector and refractive index (RI) detector. The column used is a 4.6x250mm amino (NH_2) analytical column. The HPLC unit will be calibrated under various condition to optimize solvent usage by comparison of separation of components at different flow rates ranging from 0.5 to 1.5 ml min^{-1}, then the optimum peak resolution together with the least amount of solvent is the target operating conditions. The aromatic and polar resins are measured with UV detector at 254nm and the response of the saturate peak is obtained from the RI detector. The figure below shows key units in the HPLC equipment:

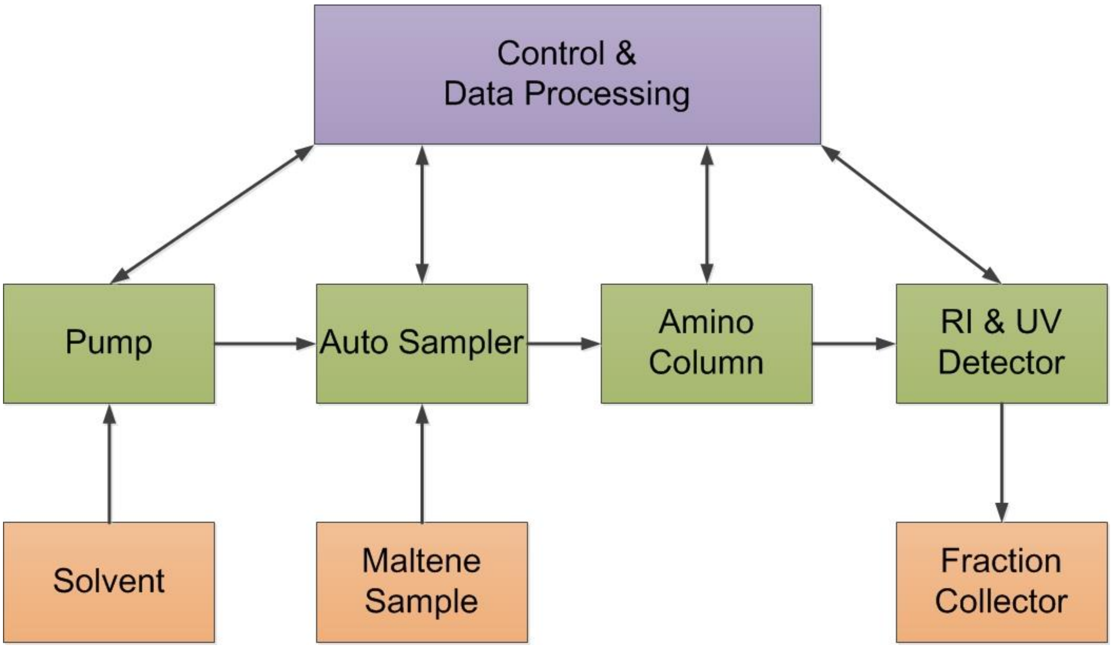


Figure 3.2: HPLC process diagram

A chemical standard or mixtures of 40 gl^{-1} of each of n-decane, n-tridecane, n-pentadecane, n-octadecane (saturates), benzene, toluene, 1.3 diisopropylbenzene (mono-aromatics), 1-methylnaphthalene (di-aromatic), Phenanthrene (tri-aromatic) and carbazole (polar compound) dissolved in hexane for representatives of each compound group of saturates, aromatics and polar. Hence the retention times and response factor of each compound group is determined. The response factor is obtained by dividing the peak area (expressed as units) by sample concentration in w/v%. The PH of the solvents and standard should not be below PH 2 or PH 7.5 using PH indicators, the maximum operating temperature is 60^0C.

10 grams of maltenes is dissolved in 100ml n-hexane and 1.5ml samples are transferred to the sample vials. The column is pre-wetted with 300ml hexane and 5µL sample solution is injected onto the HPLC column and eluted using hexane at an optimum flow rate found. Elution of the column will yield a saturate peak on the RI detector, hence using the RI detector the total saturates and total aromatic is obtained by back flushing with polar solvent dichloromethane after the saturate peak to give a peak constituting of both aromatics and polar compounds. The aromatic peak will show on the UV detector at 254nm and when the tri-aromatic peak comes down to baseline the polar peak will show after back flushing with dichloromethane.

3.5. API DETERMINATION METHODOLOGY

The estimated API for the crude oil sample collected is carried out by measuring the mass of the specific volume (10ml) of crude oil sample at different temperatures of 10, 20 and 30^0C since density is affected by temperature in such a way that density of liquids tends decreases as temperature increases, then the density calculated at each temperature is averaged to calculate the API using equation API = 141.5/SG – 131.5. The results are reported in Table B8.

4. EXPERIMENTAL RESULTS AND DISCUSSION

This Section summarizes the main findings of this research project, and finding for each particular experiment is discussed for each individual section ending with a conclusion and recommendation. The first experiment involved asphaltene precipitation of crude oil and the products formed in this experiment are used in structural characterization using XRD and HPLC analysis for asphaltene and maltene samples respectively. NMR is used on crude oil to predict the SARA composition of crude oil samples using developed equations as discussed in part 2.5 of literature review, Then finally the HPLC analysis on crude oil, petrol, diesel and engine oil lubricant samples are discussed. The following figure shows the order of results obtained:

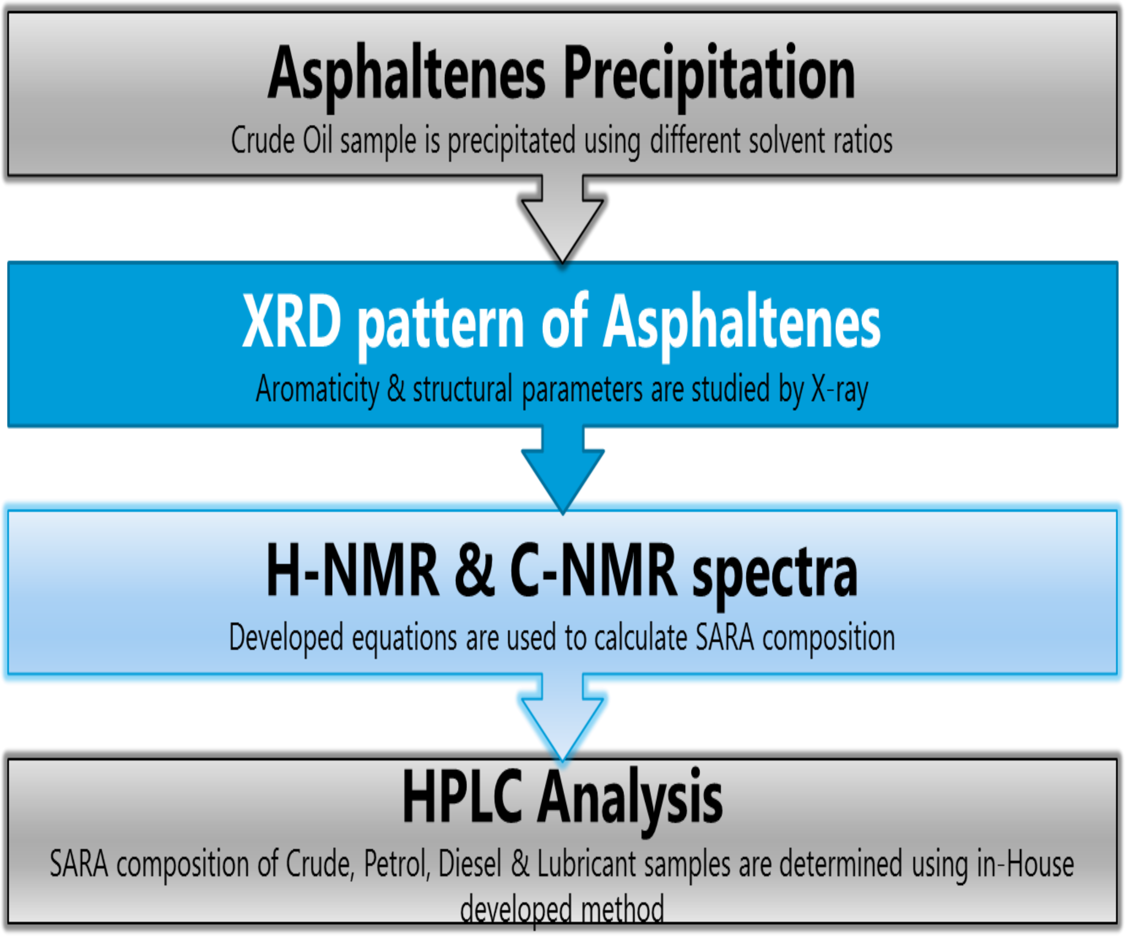


Figure 4.1: Summary of experimental results

4.1. ASPHALTENE PRECIPITATION DISCUSSION

The total amount of asphaltenes precipitated from the crude oil sample using normal hexane with five different dilution ratios was determined and the results are reported in Table 4.1 and figure 4.2 below. The values obtained were compared with those previous done by (Amin, 2010) shown on figure 2.6.

Table 4.1: Experimental data of asphaltene precipitation (Appendix B)

Dilution Ratio*	**Asphaltene Precipitated %wt**
10	2.098%
15	2.528%
30	2.914%
40	2.889%
50	2.841%

*Solvent ratio: ml of n-Hexane per 5ml of crude oil

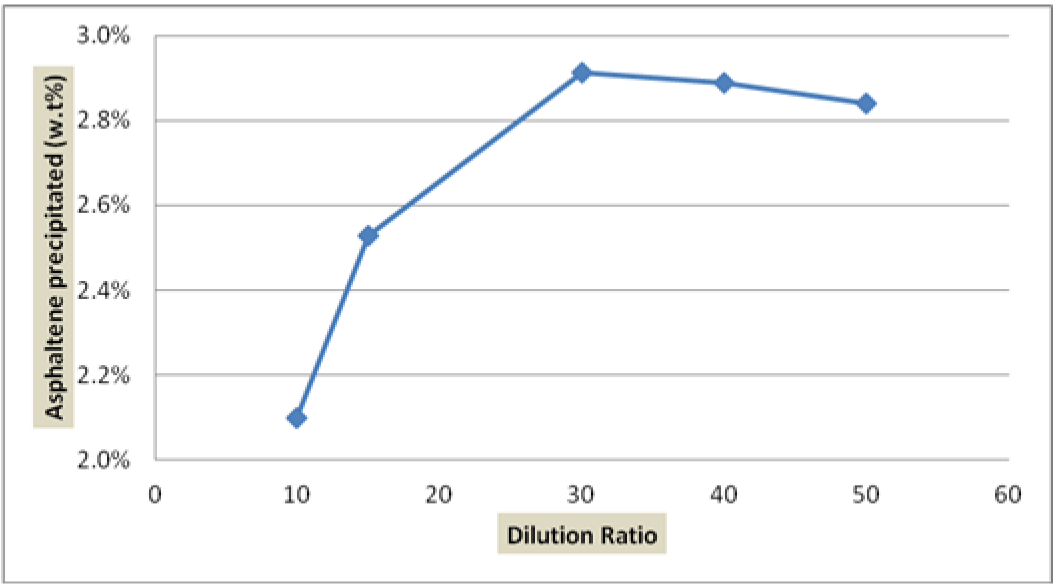


Figure 4.2: Fraction precipitated from crude oil

From the results obtained it is notable that the amount of precipitation increases as the dilution ratio increases until the optimum point of 30 where the precipitation decreases by small amounts. However the values obtained are subject to error that may have occured during the experiments since there were no repeatition of runs done. It is also important to note that parameter such as pressure, temperature and different alkane solvents were not investigated due to the complexity of the experiment. Hence the solvent used in this experiment at atmospheric pressure and ambient temperature, does not necessarily precipitate all the asphaltene present in the sample, but the extent to which the precipitation occurs will be compared with the NMR results.

4.2. STRUCTURAL CHARACTERIZATION OF ASPHALTENE

The XRD pattern of asphaltenes sample shows a general trend obtained by similar analysis done on four asphaltenes samples from different crude oils. Table 4.2 shows the calculated crystallite parameters of asphaltene sample and the x-ray pattern clearly shows the γ and graphene peak as shown on figure 4.3.

Table 4.2: Crystallite parameters of asphaltene (Appendix B)

Parameter	**Symbol**	**Calculated Values**
Wavelength(Co)	λ	1.78897
γ Peak bragg angle	θ	6.03
Graphene angle	θ	10.49
Aromacity	f_a	0.906141681
Area under peak	A(graphene)	13865.78
Area under γ peak	$A(\gamma)$	1436.22
Interplanar spacing	d_m	4.913027455
Interplanar spacing(γ)	$d\gamma$	6.141284319

The results tabulated are obtained by calculating the parameter that includes; the layer distance between aromatic sheets and it found to be 4.9 Ǻ using equation 11, the interchain layer distance is found to be 6.14 Ǻ using equation 12. The doublet of the γ and graphene layer stacking peaks has determined at about 12.06^{o} and 20.98^{o} at 2θ scale respectively. The peak profiles were fitted using a Lorenzian mix mathematical model to obtain the area under γ and graphene peak, then the Aromaticity factor f_a was determined using equation 13 and found to be 0.90 which suggests that the asphaltene molecules comprises mostly of aromatic sheets.

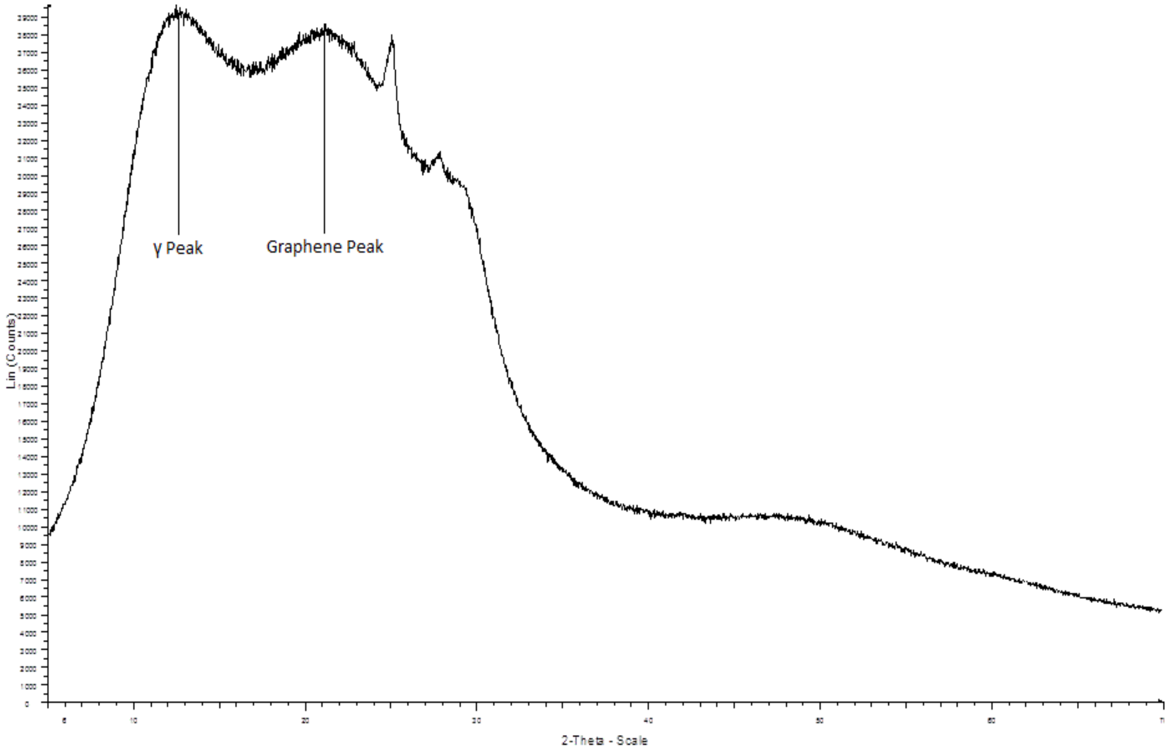


Figure 4.3: XRD pattern of asphaltene precipitate (Appendix B)

The results obtained are compared to those found by Shirokoff *et al* (1997) on Figure 4.4 and Table 4.3. It can be observed that the values found from this report are slightly higher than those found on the publications, the differences in values could arise from the sample preparation carried out to make sure that the asphaltene samples are grounded to 50-200μm, in this form many grains are suggested by Shirokoff *et al.* to come into orientation and the quality of the diffraction is improved. In conclusion the x-ray diffraction study on the asphaltenes produced in the first experiment supports the concept and model that the asphaltenes are made of fused aromatic sheet bearing aliphatic chains. Below are the results that are used in comparison:

Table 4.3: X-Ray diffraction pattern of four Saudi crude asphaltene (Shirokoff *et al*, 1997)

Aromaticity and crystallite parameters	**Asphaltene**			
	Arab Heavy	**Arab Medium**	**Arab Light**	**Arab Berri**
f_a	0.19	0.16	0.19	0.2
d_m, Å	3.6	3.6	3.6	3.6
d_γ, Å	4.4	4.5	4.4	4.4
L_c, Å	12.3	11.9	13	13
L_a, Å	24.7	23.1	24	22.7
M	8	7.5	7.8	7.4

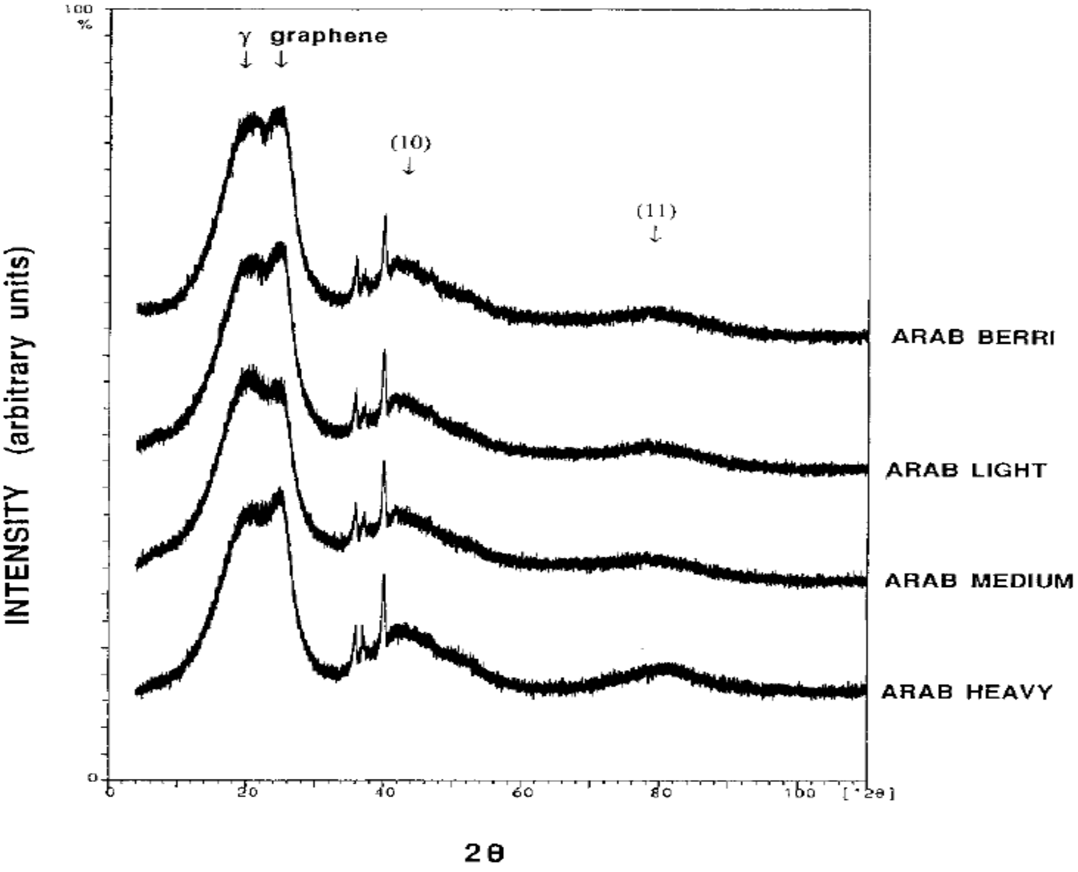


Figure 4.4: X-ray diffraction pattern of four Saudi crude asphaltene (Shirokoff *et al*, 1997)

4.3. NMR SPECTRA OF CRUDE OIL SAMPLES

The crude oil used in this study has an API gravity estimated to be 30.03^0 from the results in Table B7 and enables one to determine the SARA composition using the similar work approach carried out by (Sanchez-Minero *et al*, 2013). The developed correlation equations are used to estimate the SARA composition from both the ^{1}H-NMR and ^{13}C-NMR data. Both NMR spectra of crude oils are integrated to obtain the concentration of aromatic and aliphatic hydrogen and carbon as shown in the Figure 4.5 and 4.6:

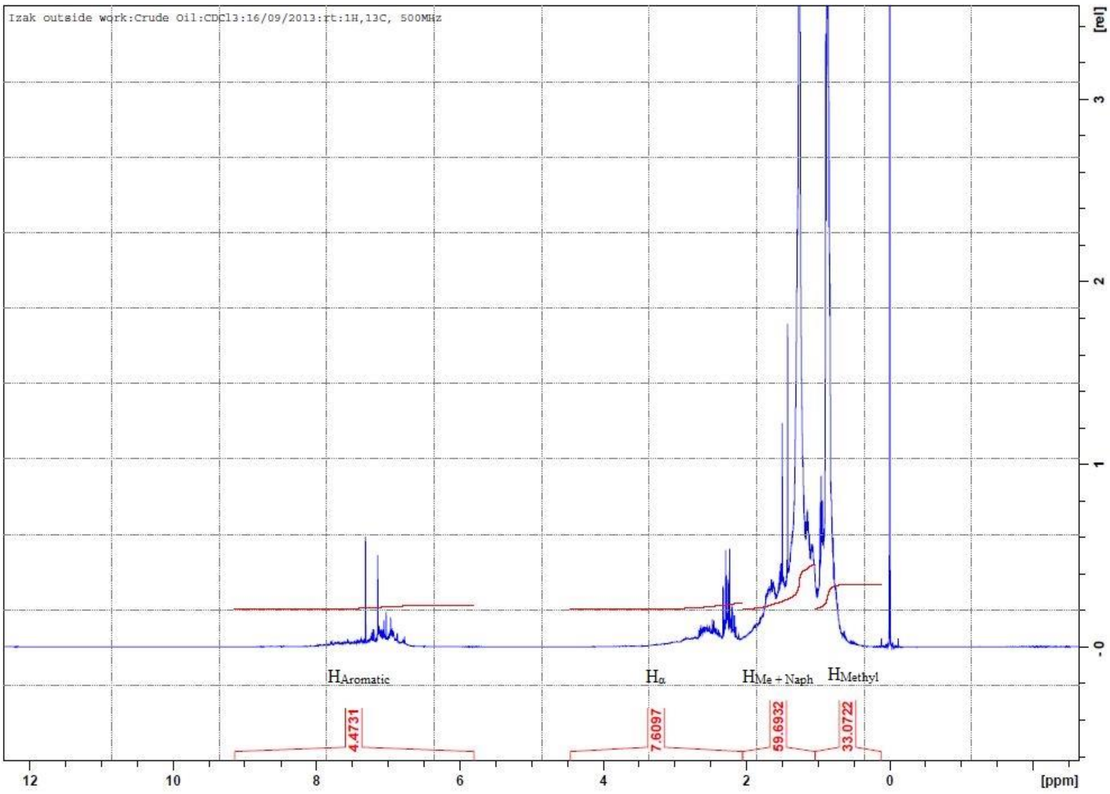


Figure 4.5: H-NMR spectrum of crude oil sample (Appendix B)

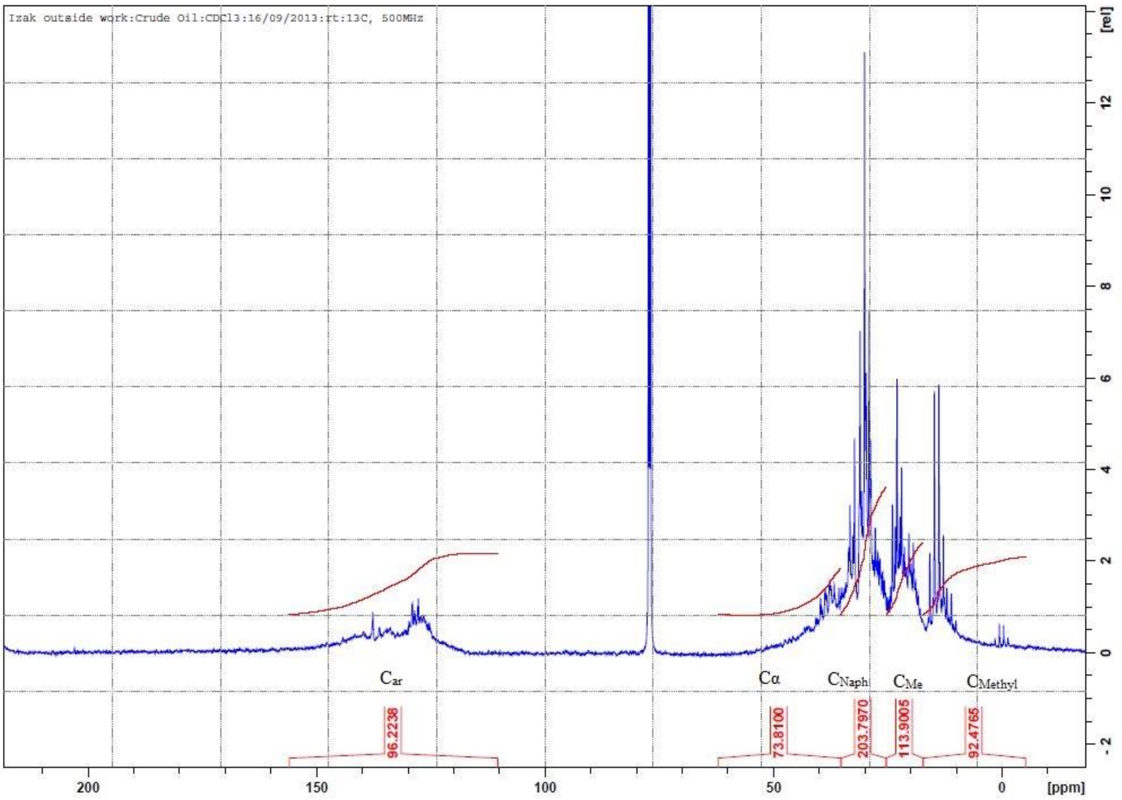


Figure 4.6: C-NMR spectrum of crude oil sample (Appendix B)

The results of the SARA composition is summarised and reported in Table 4.4. The values reported for the aromaticity factors are obtained using equations 1 and 2 then the SARA composition is calculated using equations 3 to 9 from both the NMR data to get values that are slightly closer to each other. However this according to (Sanchez-Minero *et al*, 2013) is mainly due to the better prediction using aromaticity F_{HA} compared with F_{CA}. Their respective SARA composition values are averaged as shown in the Table B6 in Appendix B. From the SARA composition obtained the CII value is calculated from equation 10 to obtain a value of 1.03, which according to (Sinnathambi *et al*, 2013) the CII value less than two suggest crude oil has less extent to fouling than when the value is greater than two. Below is a table that summarises the results found, however a more detailed results are found in Table B6.

Table 4.4: Sara Composition of Crude oil sample (Appendix B)

Parameters	**Estimated Values**
Saturates %	38.37
Aromatics %	28.09
Resins %	21.73
Asphaltenes %	11.81
CII	1.03

It is important to note that from both the NMR spectra shown on figure 4.5 and 4.6, depicts that the aromatic hydrogen H_{ar} region are represented by peaks located on chemical shifts between 6 – 9 ppm on the ^{1}H-NMR spectrum and while the aromatic carbon C_{ar} is represented by peaks located on chemical shifts 110 – 160 ppm. The distribution of the aliphatic hydrogen and carbon can be further grouped according to structural types that make up the aliphatic class as shown by the sub-integration on the NMR spectra. So the aliphatic fraction consists of α-hydrogens (H_α), Naphthenic hydrogen (H_{Naph}), methylene hydrogen (H_{Me}) and methyl hydrogen (H_{Methyl}).

4.4. HPLC ANALYSIS ON PETROLEUM CRUDE AND PRODUCTS

Two major hydrocarbon class of saturates and aromatic compounds were identified as present to the samples used in this study. The chromatogram of Maltene sample obtained from Asphaltene precipitation experiment is similar to those chromatograms of petrol, diesel and lubricant oil samples in such a way that all of the saturate peaks are detected by RID and corresponds to the first peak due to the non-polar saturate fraction that is eluted first as displayed in Figures B5 – B9, However the aromatic peaks were not well defined mostly in crude oil sample than as observed with petroleum products, but this is an expected trend as shown in Figure B1:

The standards prepared for three different concentrations of 40, 8 and 1 g/l were used to calibrate the HPLC as shown on Table B1. The calibration was obtained by using linear regression of these three concentrations of saturate and aromatic standards. The saturate standards comprised of equal amounts of equal amounts of n-tridecane, n-pentadecane, n-decane, n-octadecane, n-tetradecane, n-hexadecane, n-heptadecane.

While the aromatics standards were further subdivided into mono-, di- and tri-aromatics prepared from equal amount of 1, 3-Diisopropylbenzene, 1-Methylnaphthalene and respectively. A good agreement was observed for the linear fit as indicated in Figures B2-B4.

For all the samples analysed in this study, higher amounts of saturates and aromatics were found using the HPLC method. While these two major hydrocarbon were detected using RID and VWD, it is important to note that petroleum products that includes petrol, diesel and lubricant oil are blended fuels from refinery feed stocks that contains olefins and additives to meet the desired specifications. Hence unidentified peaks of such components may be present on the chromatograms. For instance the presence of benzene in petrol fuel at maximum 5% v/v as indicated by specification on Table A1 may be possibly regarded as one of the unidentified peaks in the aromatic region which were not calibrated for.

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

An understanding of the composition of major hydrocarbon groups found in petroleum crude oil and products was provided and highly depended on the experimental procedures used in this study. Hydrocarbon group type analysis on samples of crude oil, petrol fuel, diesel and lubricant oil was achieved by a combination of experiments and analytical instrumentation that involved ^{13}C-NMR, ^{1}H-NMR, XRD and HPLC. The results obtained were able to identify and quantify the major hydrocarbon classes of compounds found in the studied samples. The asphaltene precipitation experiment achieved the separation of dark black solid asphaltene and maltene samples that were subsequently used in XRD and HPLC analysis respectively. The amount of asphaltene precipitated was found to be over a quarter of the content present as determined by both ^{13}C-NMR and ^{1}H-NMR.

The XRD analysis provided insight into the chemical structure of Asphaltene obtained; the high value of the aromaticity factor obtained suggested that the compound is mostly aromatic as expected from literature and previous studies. The use of correlations as a function of aromaticity factors calculated from NMR data enabled for the determination SARA composition for crude oil and consequently a colloidal instability index which takes into account the composition of crude oil. The HPLC analysis on all samples investigated, was able to identify and quantify the hydrocarbon class of saturates and specific aromatic compounds without identifying the asphaltene and resin fraction. In conclusion the set of techniques and instrumentation used in this study demonstrated to be useful in obtaining group type composition of the petroleum crude and products samples but are not desirable for daily refinery operations as they are time consuming and expensive. It is also important to note that measurements of SARA composition is mostly depended on the methodology of analysis and results from different methods may not be the same. The overall results provide a good basis for determining the major hydrocarbon classes present in crude oil and petroleum products, investigating asphalt precipitation, calculating colloidal instability index and testing for aromatics fuel specifications.

5.2. RECOMMENDATION

The results obtained in this study can be further enhanced and investigated by comparing different samples of crude oils and petroleum products. Methods used in asphaltene precipitation, obtaining density of crude oil, calculating colloidal instability index, sample preparation for XRD and HPLC analysis can be further improved to obtain a higher degree of certainty by; repeatability of runs for Asphaltene precipitation and taking into consideration the effect of temperature, pressure and solvent changes, the API of crude oil can be accurately obtained by using a ASTM D287 standard procedure using a Hydrometer, appropriate values of CII can be calculated based on SARA composition and polarity of components.

Asphaltene samples can be finely grounded about 50-200µm and checked on a scanning electron microscope prior to XRD as it is shown by previous work that in this form, many grains are well oriented and the quality of diffraction pattern is improved. Lastly the HPLC analysis methodology can be improved by calibrating with standards of olefins, benzene and toluene in order to identify these components which are of greater importance to analyse.

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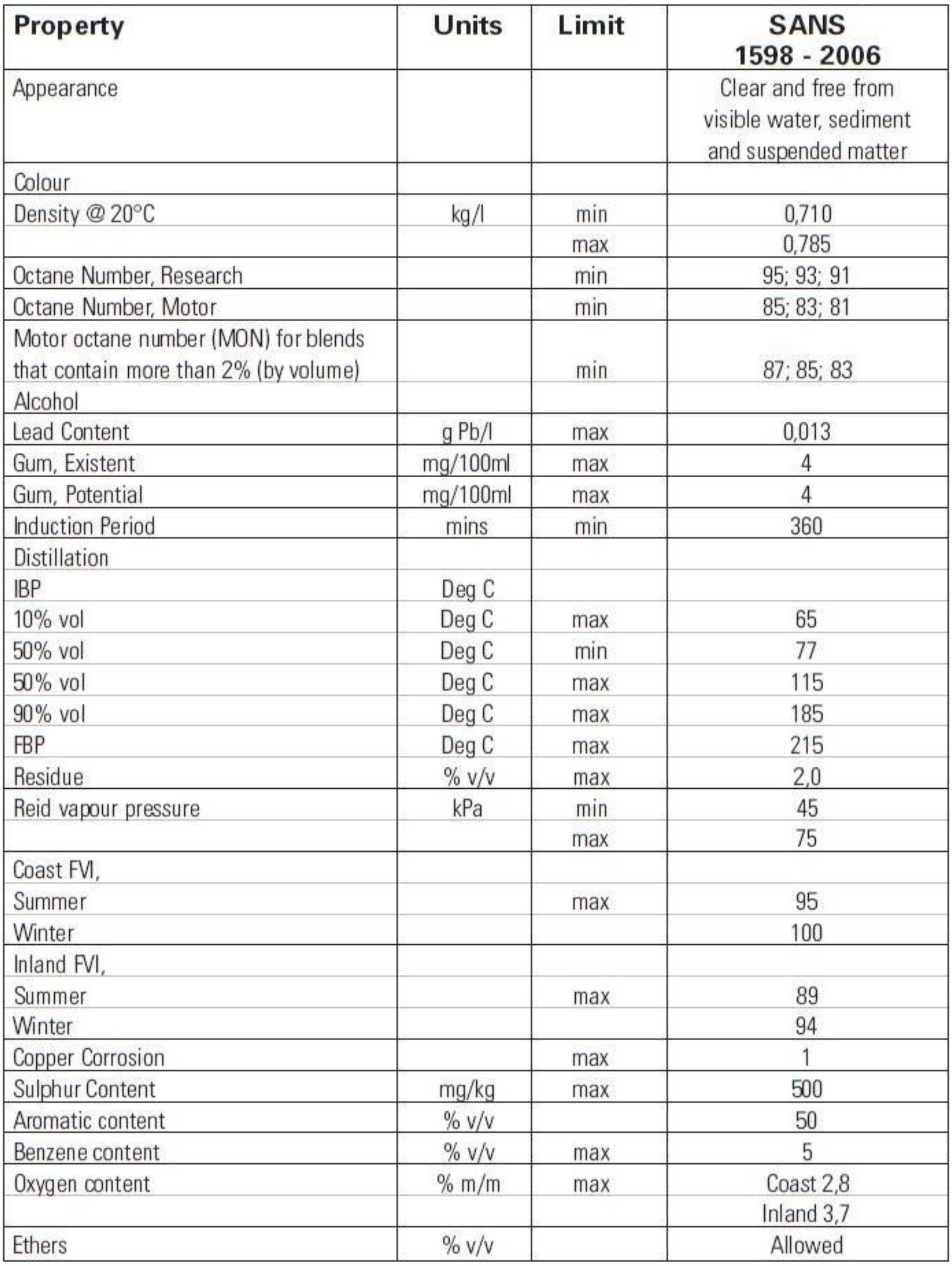
7. APPENDIX

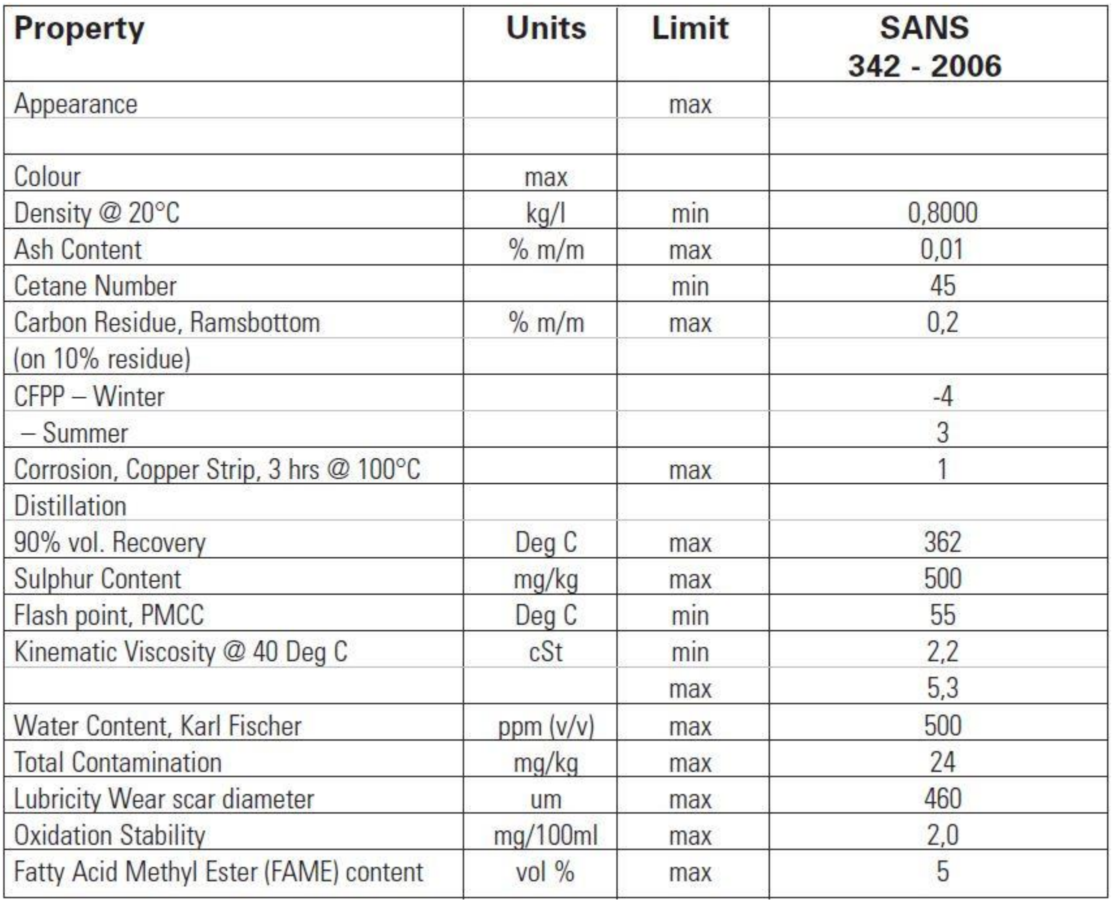
7.1. APPENDIX A: SOUTH AFRICAN FUEL SPECIFICATIONS

Table A1: South African Unleaded Petrol Specifications (SAPIA, 2008)



Property	Units	Limit	SANS 1598 - 2006
Appearance			Clear and free from visible water, sediment and suspended matter
Colour			
Density @ 20°C	kg/l	min	0,710
		max	0,785
Octane Number, Research		min	95; 93; 91
Octane Number, Motor		min	85; 83; 81
Motor octane number (MON) for blends that contain more than 2% (by volume) Alcohol		min	87; 85; 83
Lead Content	g Pb/l	max	0,013
Gum, Existent	mg/100ml	max	4
Gum, Potential	mg/100ml	max	4
Induction Period	mins	min	360
Distillation			
IBP	Deg C		
10% vol	Deg C	max	65
50% vol	Deg C	min	77
50% vol	Deg C	max	115
90% vol	Deg C	max	185
FBP	Deg C	max	215
Residue	% v/v	max	2,0
Reid vapour pressure	kPa	min	45
		max	75
Coast FVI,			
Summer		max	95
Winter			100
Inland FVI,			
Summer		max	89
Winter			94
Copper Corrosion		max	1
Sulphur Content	mg/kg	max	500
Aromatic content	% v/v		50
Benzene content	% v/v	max	5
Oxygen content	% m/m	max	Coast 2,8
			Inland 3,7
Ethers	% v/v		Allowed

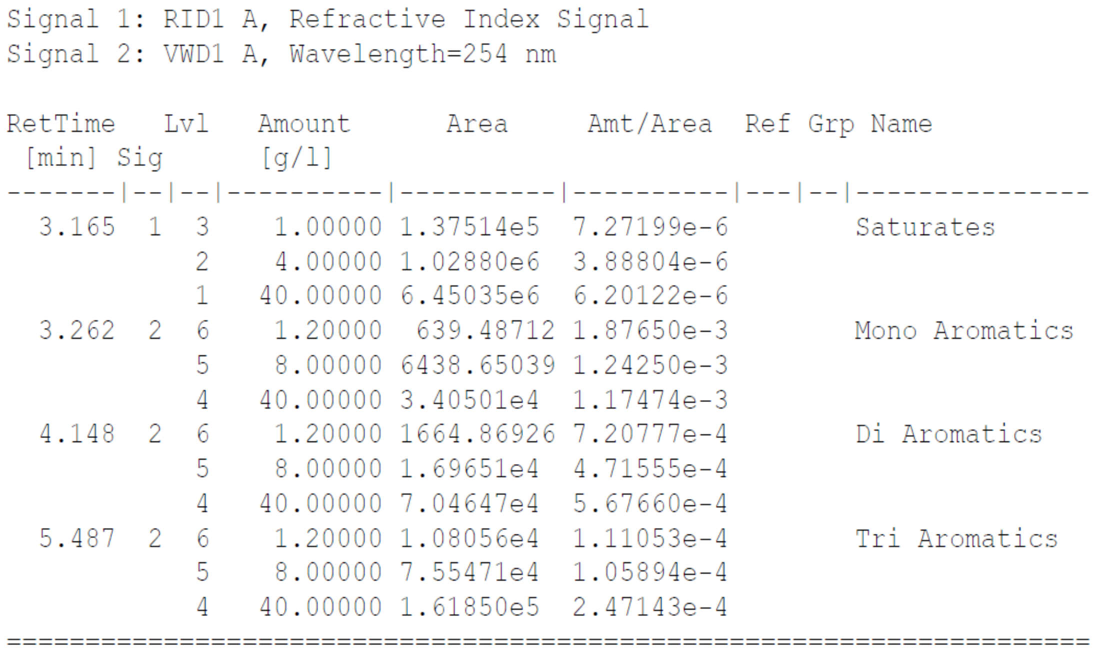
Table A2: South African Automotive Diesel Fuel Specifications (SAPIA, 2008)



Property	Units	Limit	SANS 342 - 2006
Appearance		max	
Colour	max		
Density @ 20°C	kg/l	min	0,8000
Ash Content	% m/m	max	0,01
Cetane Number		min	45
Carbon Residue, Ramsbottom	% m/m	max	0,2
(on 10% residue)			
CFPP – Winter			-4
– Summer			3
Corrosion, Copper Strip, 3 hrs @ 100°C		max	1
Distillation			
90% vol. Recovery	Deg C	max	362
Sulphur Content	mg/kg	max	500
Flash point, PMCC	Deg C	min	55
Kinematic Viscosity @ 40 Deg C	cSt	min	2,2
		max	5,3
Water Content, Karl Fischer	ppm (v/v)	max	500
Total Contamination	mg/kg	max	24
Lubricity Wear scar diameter	um	max	460
Oxidation Stability	mg/100ml	max	2,0
Fatty Acid Methyl Ester (FAME) content	vol %	max	5

7.2. APPENDIX B: EXPERIMENTAL RESULTS

Table B1: Calibration of standards used in HPLC



```
Signal 1: RID1 A, Refractive Index Signal
Signal 2: VWD1 A, Wavelength=254 nm

RetTime   Lvl   Amount      Area      Amt/Area  Ref Grp Name
 [min] Sig      [g/l]
-------|--|--|----------|----------|----------|---|--|---------------
  3.165  1  3    1.00000 1.37514e5  7.27199e-6       Saturates
            2    4.00000 1.02880e6  3.88804e-6
            1   40.00000 6.45035e6  6.20122e-6
  3.262  2  6    1.20000  639.48712 1.87650e-3       Mono Aromatics
            5    8.00000 6438.65039 1.24250e-3
            4   40.00000 3.40501e4  1.17474e-3
  4.148  2  6    1.20000 1664.86926 7.20777e-4       Di Aromatics
            5    8.00000 1.69651e4  4.71555e-4
            4   40.00000 7.04647e4  5.67660e-4
  5.487  2  6    1.20000 1.08056e4  1.11053e-4       Tri Aromatics
            5    8.00000 7.55471e4  1.05894e-4
            4   40.00000 1.61850e5  2.47143e-4
=====================================================================
```

Saturates Standard = equal amount of n-tridecane, n-pentadecane, n-decane, n-octadecane, n-tetradecane, n-hexadecane, n-heptadecane.

Mono-Aromatic Standard = 1, 3-Diisopropylbenzene.

Di-aromatic standard = 1-Methylnaphthalene.

Tri-aromatic standard = Phenanthrene.

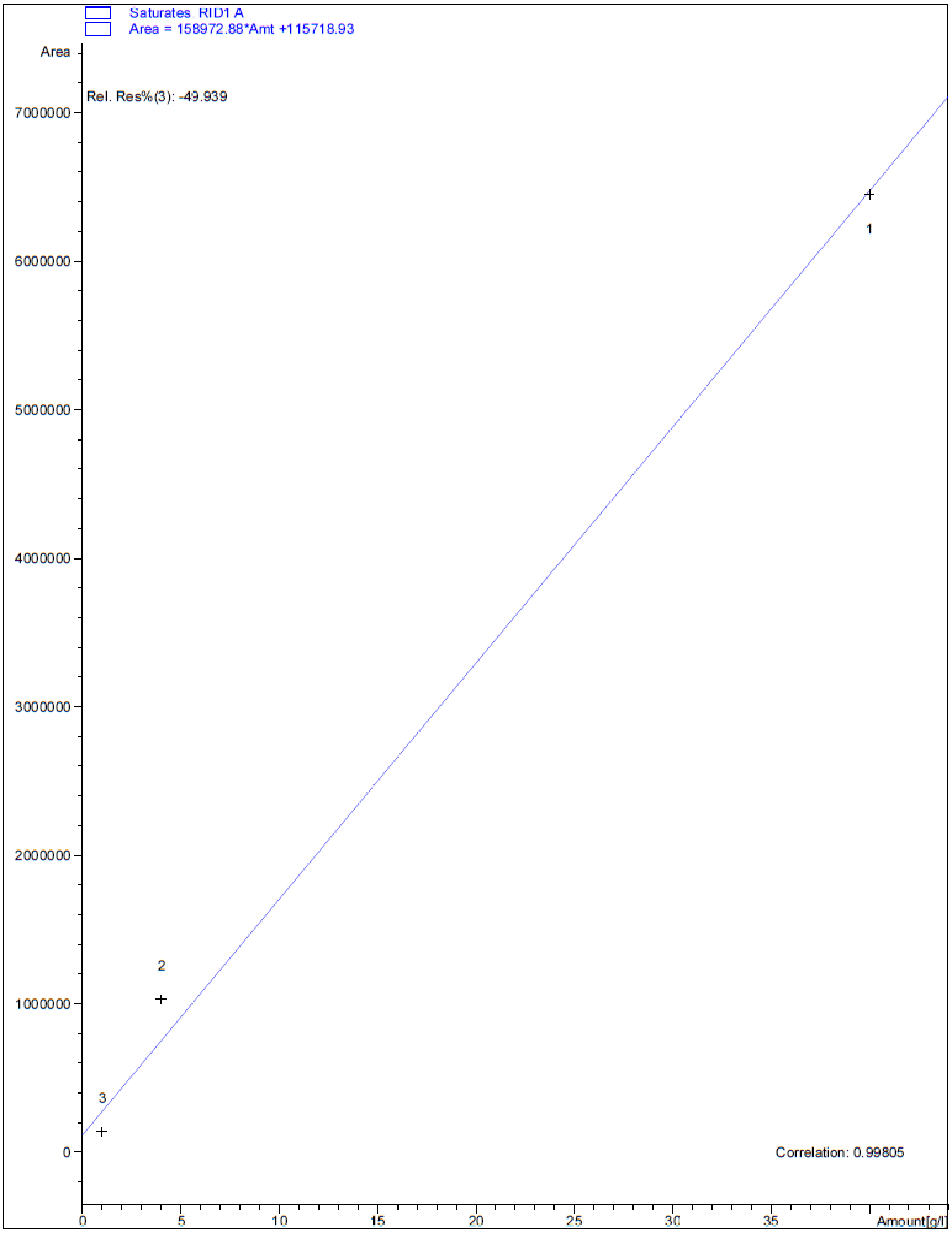


Figure B1: Calibration curve of Saturates standards

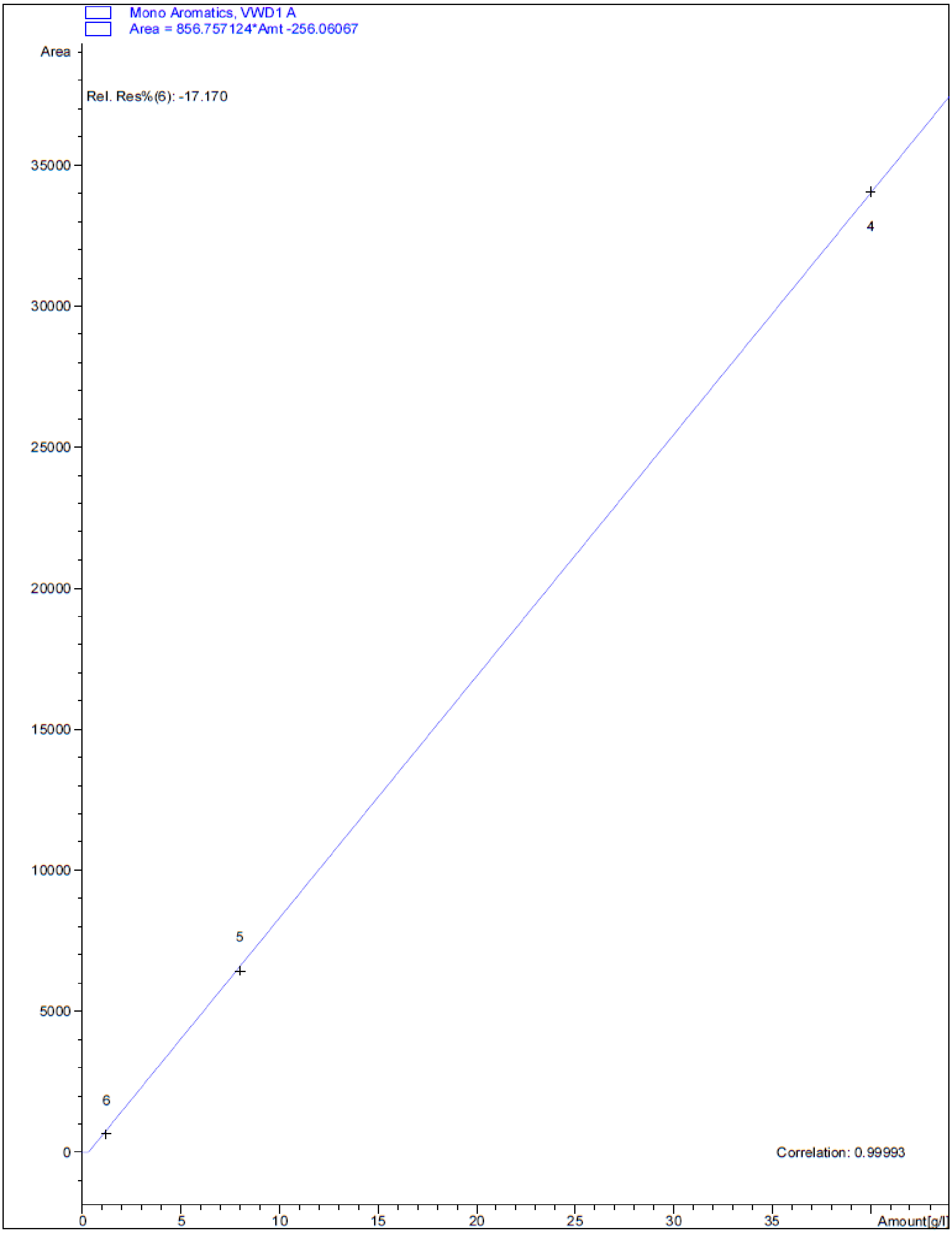


Figure B2: Calibration curve of mono-aromatic standard

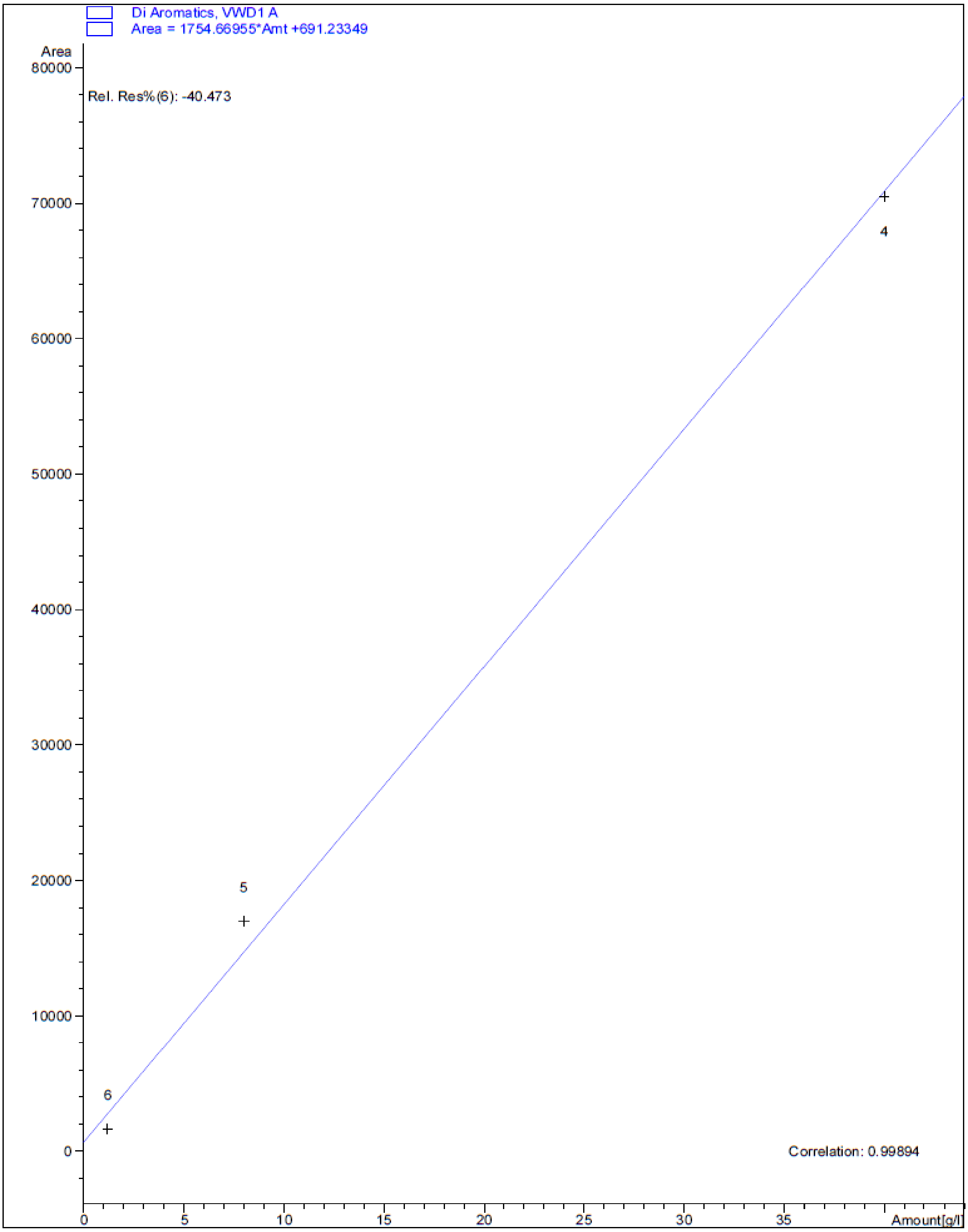


Figure B3: Calibration curve of Di-aromatic standard

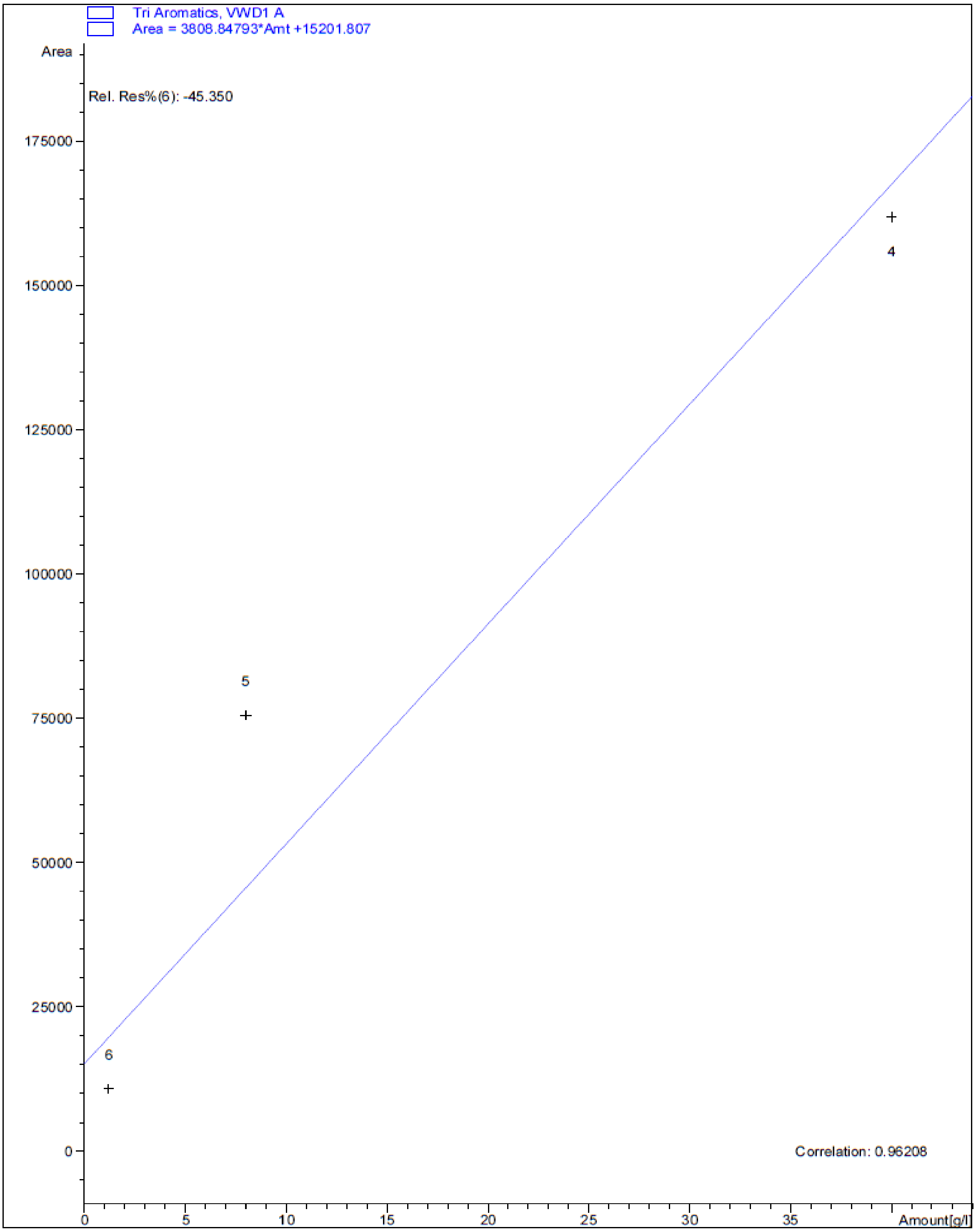


Figure B4: Calibration curve of Tri-aromatic standard

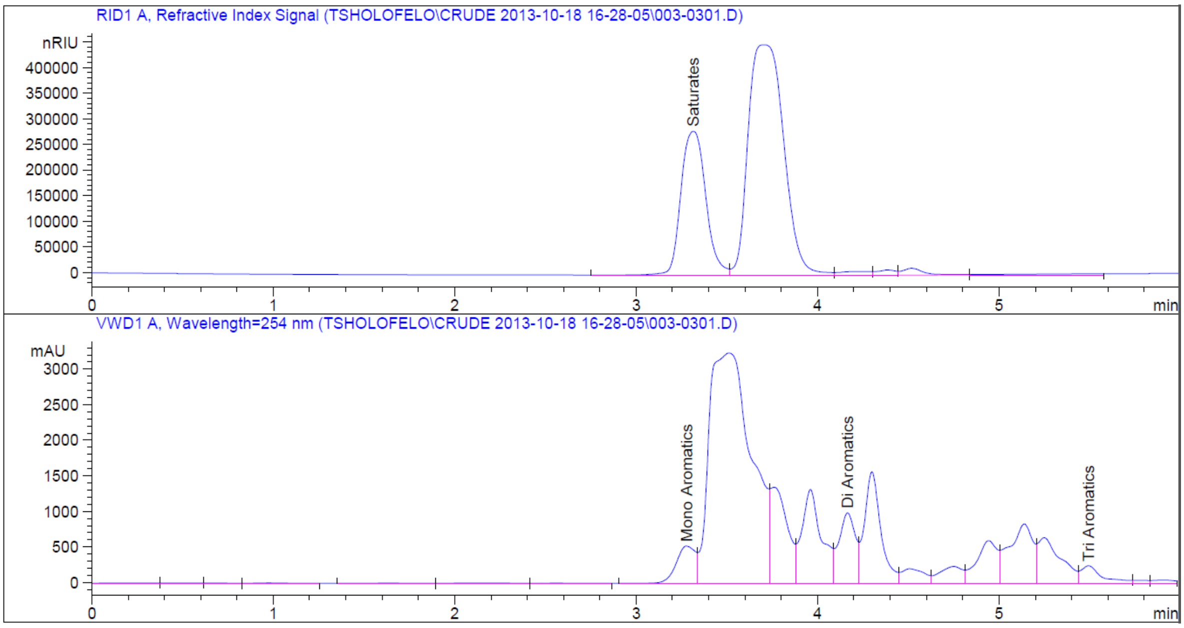


Figure B5: Lubricant engine oil HPLC chromatograph

Table B2: Lubricant engine oil HPLC results

```
Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [g/l]
-------|------|----------|----------|----------|--|------------------
  3.314 VV     2.66779e6  6.01753e-6   16.05348     Saturates

Totals :                               16.05348



Signal 2: VWD1 A, Wavelength=254 nm

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          mAU    *s                [g/l]
-------|------|----------|----------|----------|--|------------------
  3.279 BV     3756.15015 1.24676e-3    4.68302     Mono Aromatics
  4.165 VV     6210.58984 5.06478e-4    3.14552     Di Aromatics
  5.493 VV     2000.66724    0.00000    0.00000     Tri Aromatics
```

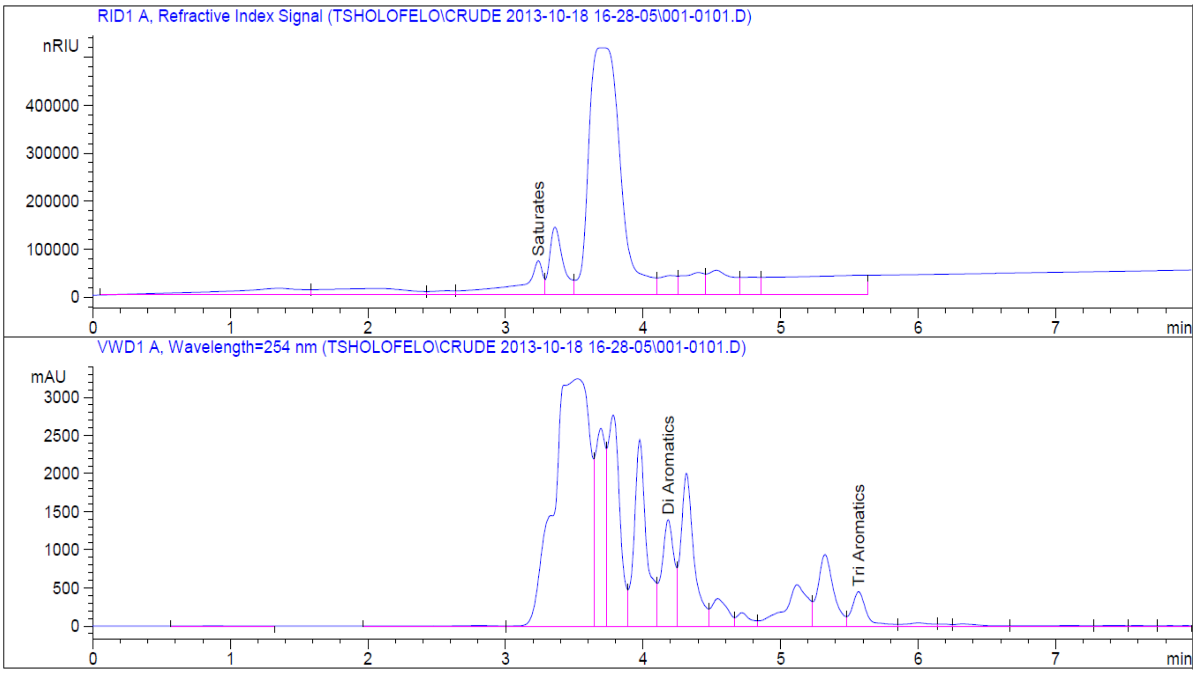


Figure B6: '95 ULP fuel HPLC chromatograph

Table B3: '95 ULP fuel results

```
Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [g/l]
-------|------|----------|----------|----------|--|------------------
  3.238 VV     8.17081e5  5.39951e-6    4.41184     Saturates

Totals :                                4.41184


Signal 2: VWD1 A, Wavelength=254 nm

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          mAU    *s                [g/l]
-------|------|----------|----------|----------|--|------------------
  3.262            -          -           -         Mono Aromatics
  4.183 VV     8509.06055 5.23611e-4    4.45544     Di Aromatics
  5.567 VV     3294.86890    0.00000    0.00000     Tri Aromatics

Totals :                                4.45544
```

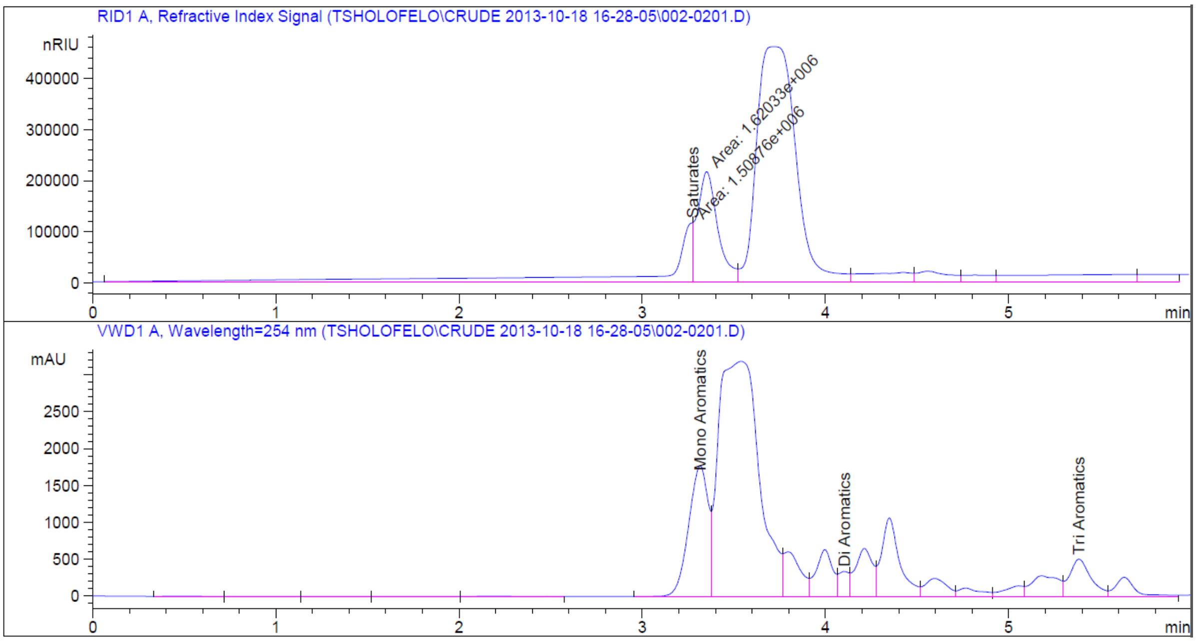


Figure B7: ’95 LRP fuel HPLC chromatograph

Table B4: ’95 LRP fuel results

```
Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp    Name
 [min]          [nRIU*s]                 [g/l]
-------|------|----------|----------|----------|--|------------------
   3.276 MF      1.50876e6  5.80792e-6    8.76274     Saturates

Totals :                                  8.76274


Signal 2: VWD1 A, Wavelength=254 nm

RetTime  Type     Area      Amt/Area     Amount    Grp    Name
 [min]          mAU    *s                [g/l]
-------|------|----------|----------|----------|--|------------------
   3.316 BV      1.29091e4  1.19034e-3   15.36622     Mono Aromatics
   4.103 VV      1310.60937 2.69331e-4 3.52987e-1     Di Aromatics
   5.384 VV      4055.01294    0.00000    0.00000     Tri Aromatics
```

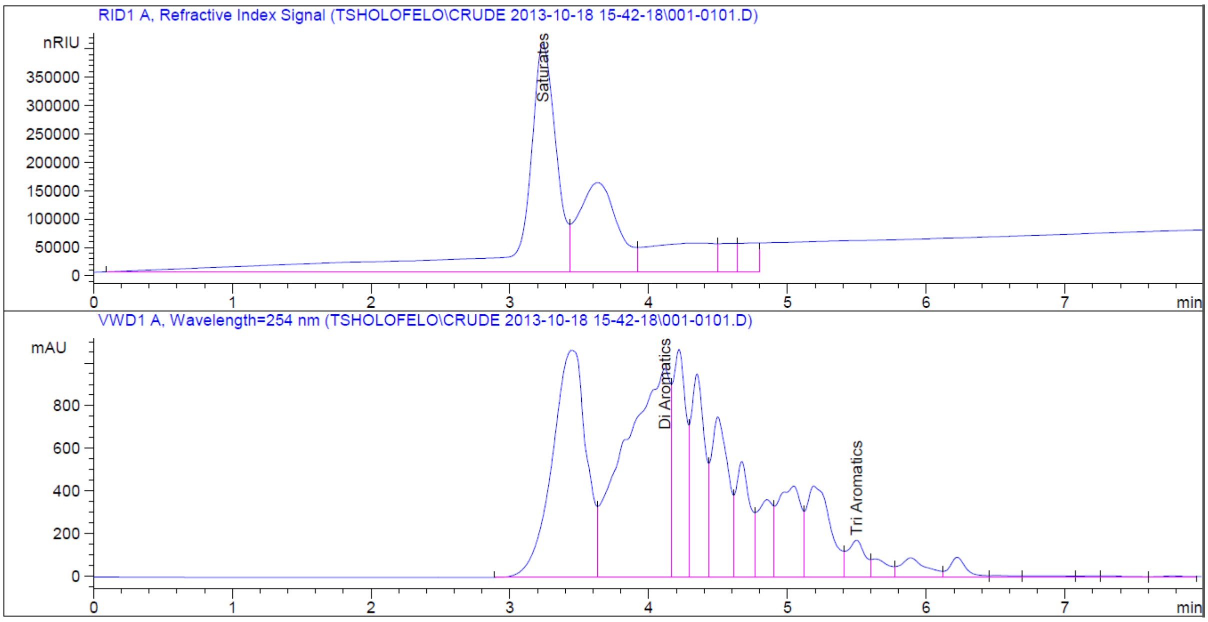


Figure B8: Diesel 50 ppm fuel HPLC chromatograph

Table B5: Diesel 50ppm fuel results

```
Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
  [min]         [nRIU*s]                 [g/l]
-------|------|----------|----------|----------|--|------------------
   3.238 BV     7.42918e6  6.19240e-6   46.00444     Saturates

Totals :                                46.00444


Signal 2: VWD1 A, Wavelength=254 nm

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
  [min]         mAU   *s                 [g/l]
-------|------|----------|----------|----------|--|------------------
   3.262             -          -           -        Mono Aromatics
   4.115 VV     2.20299e4  5.52026e-4   12.16106     Di Aromatics
   5.497 VV     1512.60315    0.00000    0.00000     Tri Aromatics

Totals :                                12.16106
```

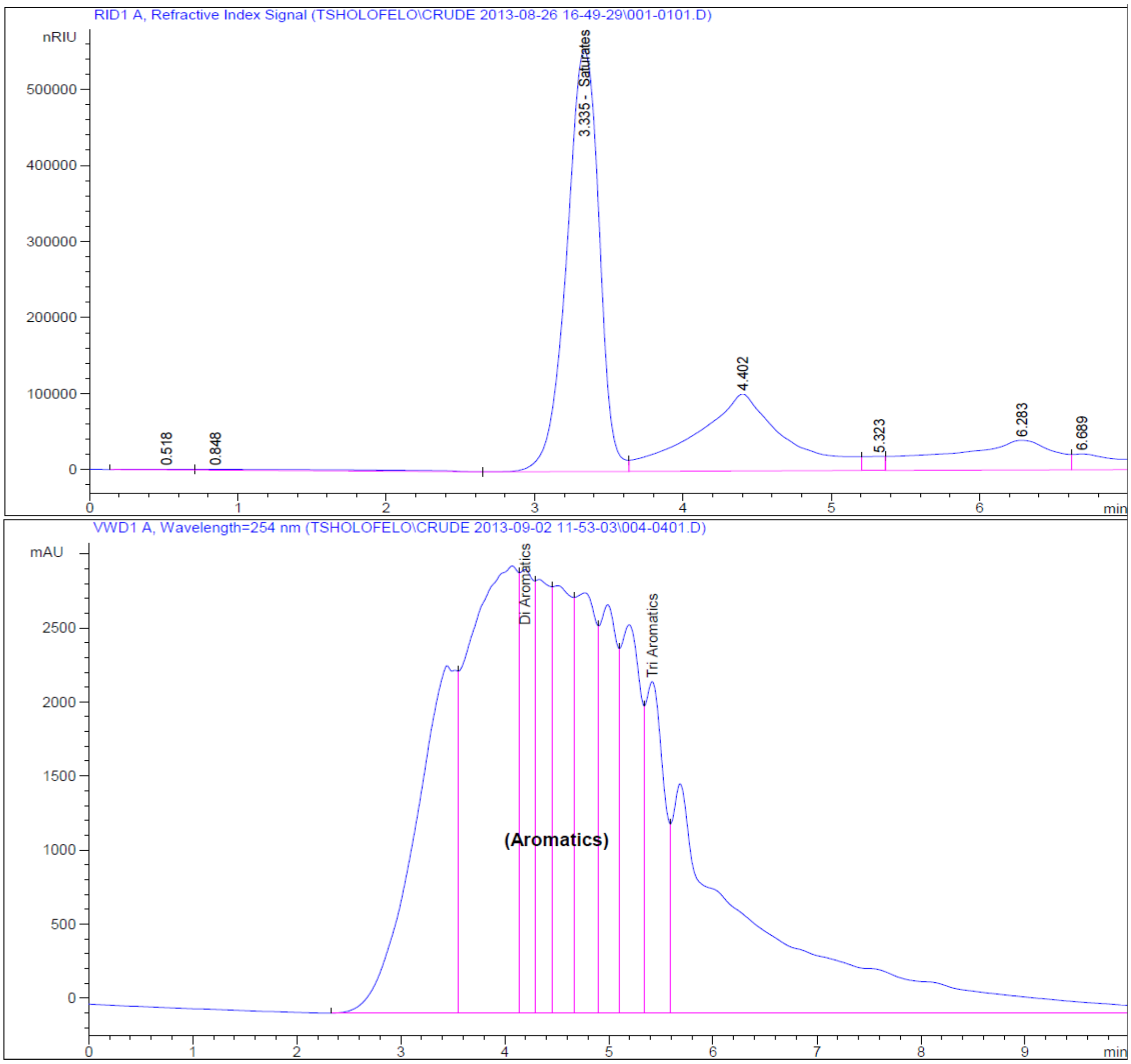
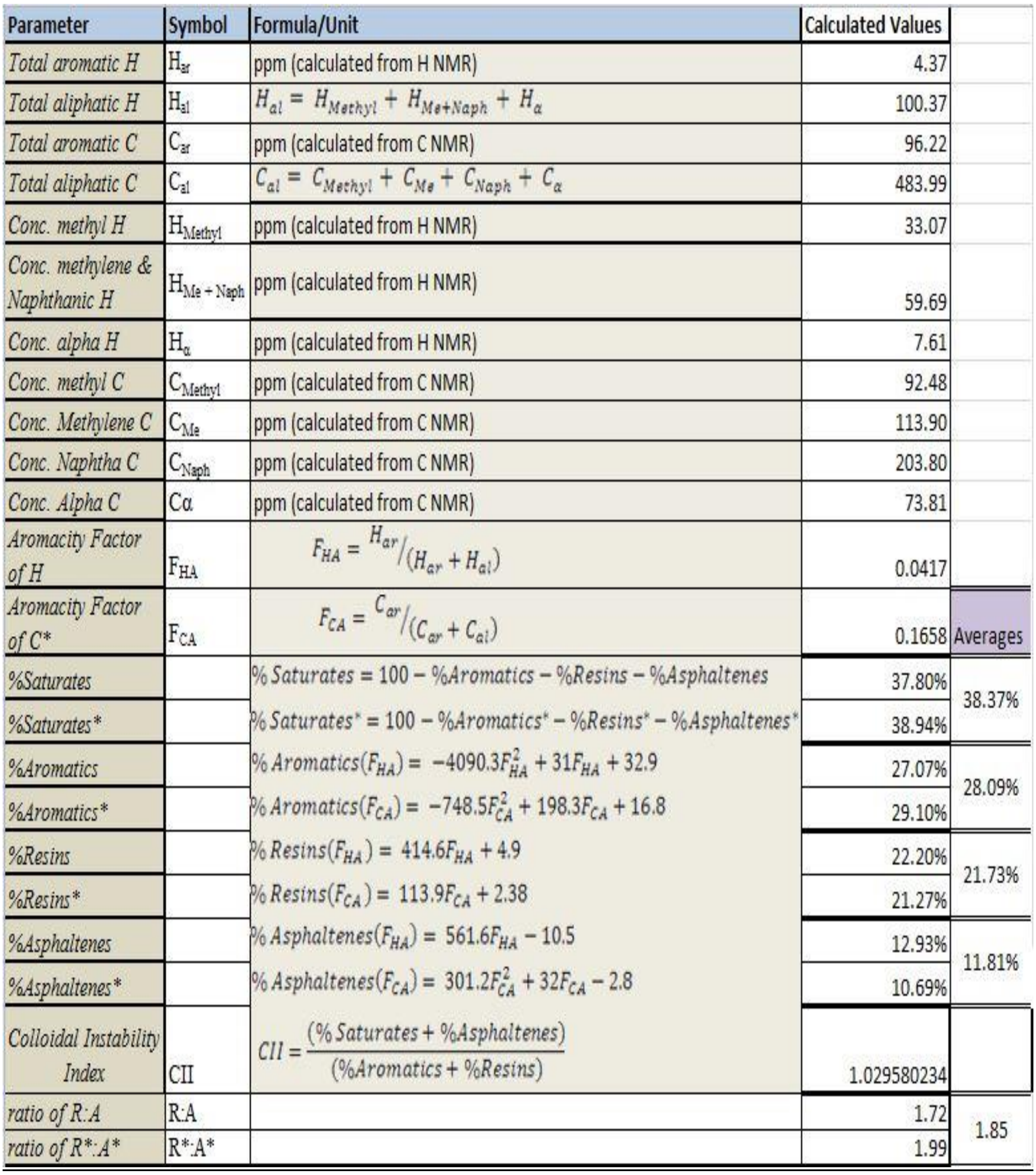


Figure B9: Crude oil sample HPLC chromatograph

Table B6: Sara composition calculations using NMR data



Parameter	Symbol	Formula/Unit	Calculated Values	
Total aromatic H	H_{ar}	ppm (calculated from H NMR)	4.37	
Total aliphatic H	H_{al}	$H_{al} = H_{Methyl} + H_{Me+Naph} + H_{\alpha}$	100.37	
Total aromatic C	C_{ar}	ppm (calculated from C NMR)	96.22	
Total aliphatic C	C_{al}	$C_{al} = C_{Methyl} + C_{Me} + C_{Naph} + C_{\alpha}$	483.99	
Conc. methyl H	H_{Methyl}	ppm (calculated from H NMR)	33.07	
Conc. methylene & Naphthanic H	$H_{Me+Naph}$	ppm (calculated from H NMR)	59.69	
Conc. alpha H	H_{α}	ppm (calculated from H NMR)	7.61	
Conc. methyl C	C_{Methyl}	ppm (calculated from C NMR)	92.48	
Conc. Methylene C	C_{Me}	ppm (calculated from C NMR)	113.90	
Conc. Naphtha C	C_{Naph}	ppm (calculated from C NMR)	203.80	
Conc. Alpha C	$C\alpha$	ppm (calculated from C NMR)	73.81	
Aromacity Factor of H	F_{HA}	$F_{HA} = H_{ar}/(H_{ar} + H_{al})$	0.0417	
*Aromacity Factor of C**	F_{CA}	$F_{CA} = C_{ar}/(C_{ar} + C_{al})$	0.1658	Averages
%Saturates		$\% Saturates = 100 - \%Aromatics - \%Resins - \%Asphaltenes$	37.80%	38.37%
*%Saturates**		$\% Saturates^* = 100 - \%Aromatics^* - \%Resins^* - \%Asphaltenes^*$	38.94%	
%Aromatics		$\% Aromatics(F_{HA}) = -4090.3F_{HA}^2 + 31F_{HA} + 32.9$	27.07%	28.09%
*%Aromatics**		$\% Aromatics(F_{CA}) = -748.5F_{CA}^2 + 198.3F_{CA} + 16.8$	29.10%	
%Resins		$\% Resins(F_{HA}) = 414.6F_{HA} + 4.9$	22.20%	21.73%
*%Resins**		$\% Resins(F_{CA}) = 113.9F_{CA} + 2.38$	21.27%	
%Asphaltenes		$\% Asphaltenes(F_{HA}) = 561.6F_{HA} - 10.5$	12.93%	11.81%
*%Asphaltenes**		$\% Asphaltenes(F_{CA}) = 301.2F_{CA}^2 + 32F_{CA} - 2.8$	10.69%	
Colloidal Instability Index	CII	$CII = \frac{(\% Saturates + \%Asphaltenes)}{(\%Aromatics + \%Resins)}$	1.029580234	
ratio of R:A	R:A		1.72	1.85
ratio of R:A**	R*:A*		1.99	

*Calculations based on ^{13}C-NMR data

Table B7: Asphaltene precipitation experimental data

Sample	Vol. of crude oil (ml)	Cal. Mass of Crude oil(g)	Vol. of n-Hexane added(ml)	Vol. of oil to solvent ratio	Mass of filter paper	Mass of precipitate & Filter paper	Mass of precipitate (g)	Mass of Maltene	Weight(Mass) % asphalt	Weight(Mass)% Maltene
A	15.00	13.14	150.00	1 to 10	0.096	0.366	0.270	12.870	2.098%	97.902%
B	10.00	8.76	150.00	1 to 15	0.096	0.312	0.216	8.544	2.528%	97.472%
C	5.00	4.38	150.00	1 to 30	0.094	0.218	0.124	4.256	2.914%	97.086%
D	5.00	4.38	250.00	1 to 50	0.095	0.216	0.121	4.259	2.841%	97.159%
E	5.00	4.38	200.00	1 to 40	0.094	0.217	0.123	4.257	2.889%	97.111%
Average	8		180		0.095	0.2658	0.1708		2.65%	0.973460146
STD Dev	4.472135955		44.72135955		0.001	0.06949964	0.068627254			0.003474315

Table B8: Estimation of density of crude oil results

Crude oil sample	**Mass of Cylinder**	**Mass of cylinder + sample**	**Mass of sample**	**Volume**	**Density of Sample (g/ml)**	**Temp Deg**
1	39.881	48.698	8.8170	10.00	0.8817	10
2	39.889	48.691	8.8020	10.00	0.8802	15
3	39.881	48.680	8.7990	10.00	0.8799	20
4	39.890	48.680	8.7900	10.00	0.879	25
5	39.892	48.672	8.7800	10.00	0.878	30
Average	39.8866	48.6842	8.7976	10	0.87976	20
STD Dev	0.0052249	0.010256705	0.01383112	0	0.00138311	7.9056942

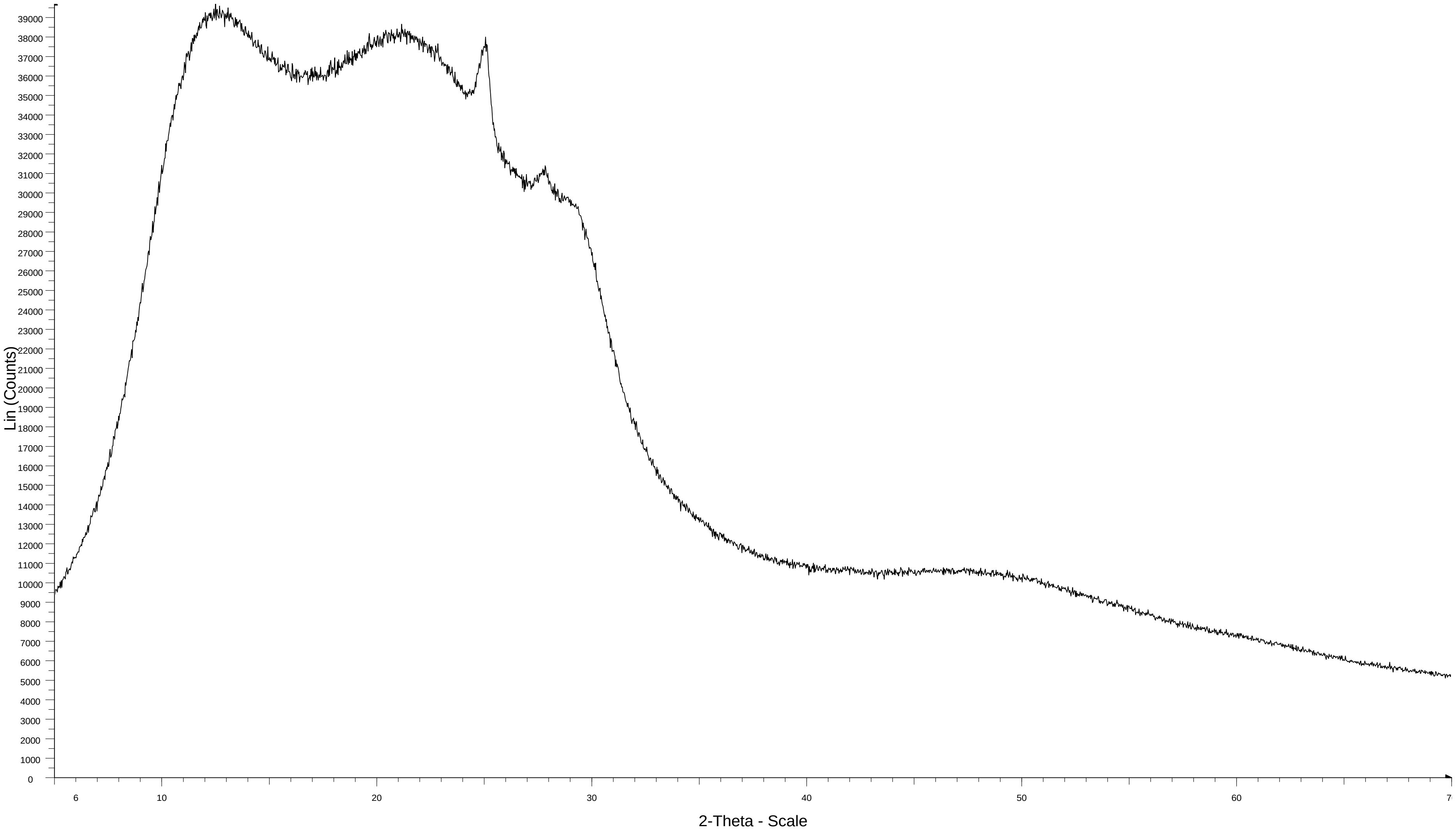


Figure B10: X-Ray pattern of asphaltene precipitate

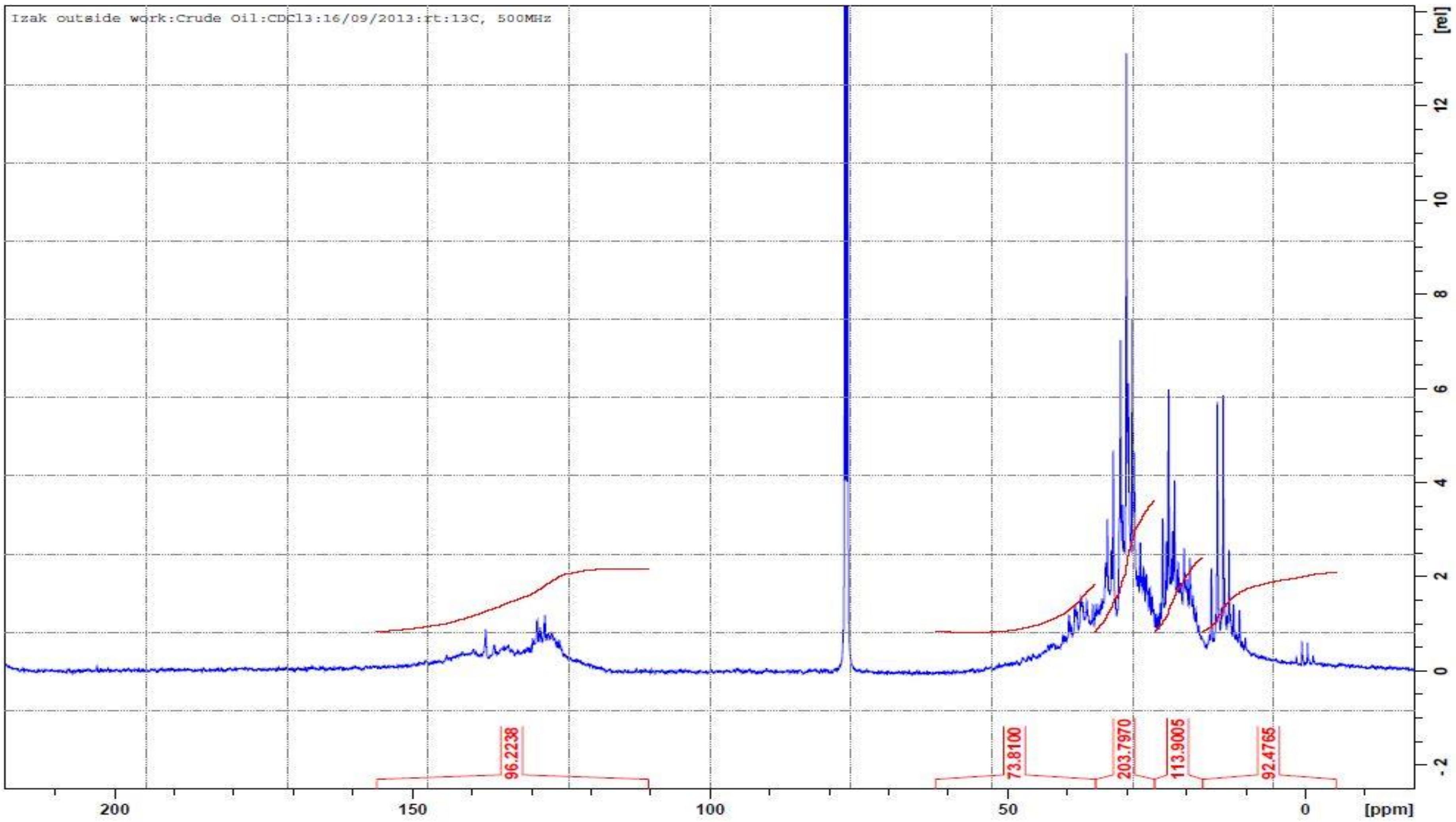


Figure B11: 13C-NMR spectrum of crude oil sample

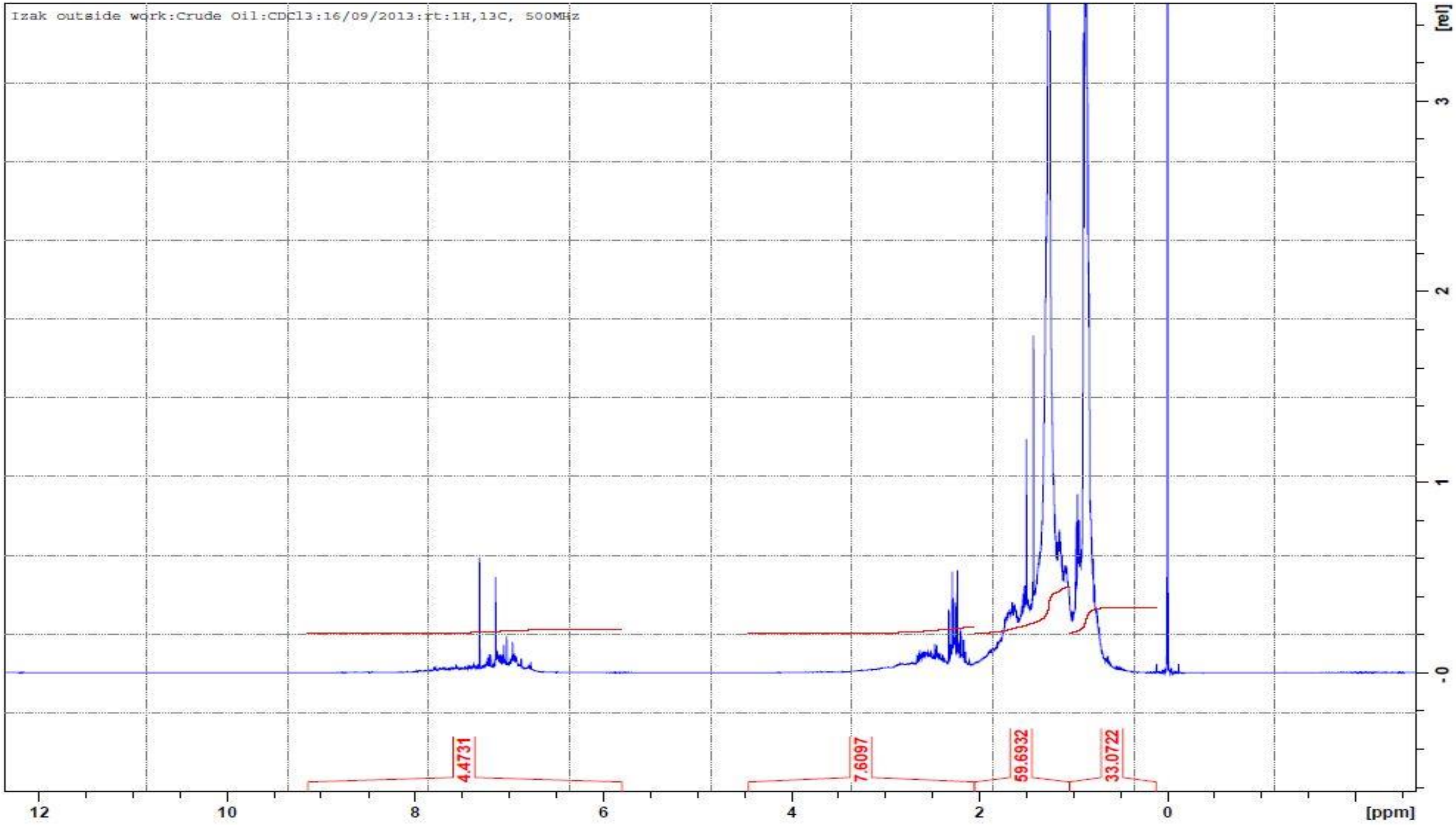


Figure B12: 1H-NMR spectrum of crude oil sample

7.3. APPENDIX C: PICTURE SAMPLE OF ASPHALTENES PRECIPITATE

Figure B13: Asphaltene precipitate sample