CARBOXYLIC ACID COMPOSITION AND ACIDITY IN CRUDE OILS AND BITUMENS

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DECLARATION

I hereby certify that the work described in this thesis is my own, except where otherwise acknowledged, and has not been submitted previously for a degree at this, or and other university.

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ABSTRACT

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As the world's demand for crude oil increases and the amount of conventional reserves decline, the proportion of high acidity oils being produced is increasing, but this acidity can cause corrosion problems during production and refining. Total Acid Number (TAN) values are often used to predict whether a crude oil may cause corrosion problems and thus affect the value of the oil, although the relationship between TAN and the organic acid composition of oils is not fully understood. This thesis investigate the types of acidic compounds that contribute to acidity in crude oils and the geochemical factors that influence the compositions and concentrations of these compound classes in a suite of oils and bitumens from a variety of different locations, including the North Sea, Venezuela, Canada and California.

This work in this thesis includes the development of a modified ASTM D664 titrimetric assay method for measuring acid numbers on small samples of heavy crude oil, core extracts and also isolated maltene and asphaltene fractions. The TAN values in the crude oils and their fractions analysed ranges from 0.04 to 21.24 (mg KOH/g). The results show that in general, the maltene fraction contributes most to the acidity in crude oils, however in some samples a large proportion of the oil TAN is contributed by the asphaltenes, even though they are quantitatively a small percentage of the oil. The geological reasons for the occurrence of oils with these highly acidic asphaltenes are not currently known.

The analysis of isolated carboxylic acid fractions from ten oils of different origins, including those from different source depositional environments, levels of biodegradation and thermal maturity, using a gas chromatographic method, showed that the concentrations of total carboxylic acids corresponded well with TAN and biodegradation, indicating that these acidic compounds may be a major control on the acidity in crude oils and that the concentration of these were in turn controlled by the extent of biodegradation.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) was used to characterise a set of North Sea crude oils with TAN values ranging from 0.11 to 7.58 (mg KOH/g oil). This showed that the O_2 compound class (assumed to be mainly carboxylic acid "COOH" species) appeared as the dominant compound class under the analytical conditions used, with a strong correlation (r^2 = 0.989) of the O_2/N ratio with the TAN values of the oils, indicating that these compounds may control the TAN in these samples. This observation also applied to their maltene and asphaltene fractions. The dominant acid species in the high acidity North Sea oils, maltenes and asphaltenes were three and four ringed naphthenic acids. As the TAN of the oils increased, the double bond equivalent (DBE) distributions shifted to higher values indicating that their molecular structures became more highly aromatic.

Fourier Transform Infrared (FTIR) spectroscopy potentially offers a much more rapid analysis of acids in oils compared to the ASTM D664 method. This study included the development of a rapid method for the determination of TAN by FTIR spectroscopy of conventional and heavy crude oils using single bounce attenuated total reflectance (ATR) and multi bounce horizontal HATR accessories. Using multivariate data analysis software, a multivariate model that correlates infrared spectra with the TAN value was developed using carbonyl (C=O) absorption bands ranging from 1770 to 1650 cm^{-1}. It was found that the correlation of FTIR measured TAN versus ASTM D664 measurements, obtained by multi bounce HATR (r^2 = 0.943) were better than correlations produced by single bounce ATR (r^2 = 0.812). Based on these findings, the measurement of oil acidity and TAN using FTIR is simpler and faster and also allows the analysis of small sample sizes and avoids other problematic issues such as the fouling of electrodes that can be experienced using the ASTM D664 standard method.

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CHAPTER 1

INTRODUCTION

Chapter 1. Introduction

1.1   General Introduction

The issue of acidity in crude oil is always linked to a huge industrial risk as it causes significant corrosion problems in storage and refining equipment (Barrow et al., 2003; Laredo et al., 2004b; Fafet et al., 2008). However, because of the large increase in the world's demand for crude oil, heavy, acidic oils are being increasingly produced (Barrow et al., 2009) and have thus become a topic of interest among researchers in order to get a greater understanding of the sources of their negative behavior.

One of the acidic compound classes believed to be a major cause of acidity in crude oils are the so-called naphthenic acids, and a number of previous studies have shown that naphthenic acid concentration in oils is associated with their acidity (Meredith et al., 2000; Zhang et al., 2006; Fafet et al., 2008). Naphthenic acids are defined as carboxylic acids that include one or more saturated ring structures, with the general formula $C_nH_{2n+z}O_2$, where n refers to the number of carbon atom, while z refers to hydrogen deficiency (Barrow et al., 2003; Borgund et al., 2007a; Han et al., 2009).

As the presence of this compound class in crude oils continues to be a concerning issue in the oil production and refinery industries, it is necessary to better understand the chemistry and variability of naphthenic acid distributions in oils. However, understanding the controls on naphthenic acid compound compositions in crude oils is difficult due to the lack of knowledge of this variability in their molecular structures in individual petroleum from different sources.

For many years, a parameter called Total Acid Number (TAN), which is obtained by non-aqueous potentiometric titration, is used to measure the acidity in oils (Barrow et al., 2003; Lutnaes et al., 2006; Borgund et al., 2007a). Recently however, the use of the TAN value, which is defined as the number of milligrams of potassium hydroxide (KOH) needed to neutralise the acidity in one gram of crude oil, as an indicator to measure oil acid content, has been questioned (Barrow et al., 2003; Lutnaes et al., 2006). Arguments have also arisen regarding the usage of TAN values in petroleum analysis since TAN can be a poor indicator to measure the corrosiveness of crude oils. For example, Laredo et al. (2004b) reported that some oil samples with high corrosion

behavior have lower TAN values than those with low corrosion behaviour. An explanation for this is that the corrosiveness depends on the specific acids rather than the total acids in the crude oil (Tomczyk and Winans, 2001; Laredo et al., 2004a). In estimating the molecular weight distributions of naphthenic acids in crude oil, the use of TAN values also relies on the assumption that only one group of (monoprotic) acids is involved. However, work by for example (Barrow et al., 2009) has revealed the presence of others acidic compound with empirical formulae $C_nH_{2n+z} O_2$, where x is from 2 to 5 in their samples, which means that the acids are not all monoprotic. These findings might explain why TAN values are not as reliable an indicator of acid content as first believed. In other cases i.e. (Meredith et al., 2000) TAN values appeared to have a strong correlation with concentration of carboxylic acids and degree of biodegradation, though this correlation was not as strong for oils with lower TAN values (<1.0 mg/KOH/g) or oils with high sulphur contents.

As TAN values alone are not able to characterise the acid content in crude oils sufficiently, numerous other analytical tools have been used. The characterisation of naphthenic acids in crude oil has been previously studied using various methods such as gas chromatography (GC) and gas chromatography-mass spectrometry i.e. Fafet et al. (2008), Fourier Transform Infra-Red spectroscopy i.e. (Tomczyk and Winans, 2001; Barrow et al., 2003) and recently, Fourier Transform Ion Cyclotron Resonance mass i.e. (Borgund et al., 2007a; Barrow et al., 2009). Although various studies on naphthenic acids have been carried out, the effects of geological origin and other geochemical factors on the types and composition of acidic compound in crude oils are not known in detail.

This project use standard geochemical laboratory analytical techniques such as gas and liquid chromatography and acid-base titrations, as well as recent advances in analytical technologies including gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), Fourier Transform Infra-Red spectroscopy (FTIR) and the powerful technique of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) for characterising petroleum acids in oils.

These analyses are aimed at providing a better understanding of the types of acidic compounds that contribute to acidity in crude oils and the geochemical factors that influence the compositions and concentrations of these compound classes in oils. Thus, prediction of the occurrence of acidic oils can be improved, hence, reducing exploration

risk. Also, improving understanding of the compound classes responsible for acidity can allow better treatment strategies to be devised for processing those types of oils.

In view of the limited amount of reported work that identifies the range of acid species and their origins, that are responsible for acidity in crude oils, this project aims to i) investigate the types of acidic compounds that contribute to acidity in crude oils, ii) investigate the geochemical factors that influence the composition and concentration of these compound classes in oils and iii) to characterise the variations in petroleum acids found in crude oils by analysing biodegraded and non-degraded oil samples from a variety of locations throughout the world.

1.2   Crude Oil Composition

Petroleum is one of the most complex mixtures generated by nature (Hemmingsen et al., 2006; Klein et al., 2006a) due to compositional complexity that depends on a number of factors including their origin and age (Teräväinen et al., 2007). In general, crude oil predominantly consists of ~ 90% of hydrocarbon compound (i.e. naphthenes, parraffins, aromatics) and other ~10% consists of polar compounds such as nitrogen (N), oxygen (O), sulphur (S) and trace metal containing compounds (Teräväinen et al., 2007). According to Tissot and Welte (1978) the gross composition of crude oil can be defined by the relative amounts of saturates, aromatics, resins and asphaltene (SARA) fractions. The saturates generally consist of naphthenes and paraffins, while the aromatics, resins and asphaltenes appear to form a continuum of polynuclear aromatic species of increasing molar mass, polarity and heteroatom content (Alboudwarej et al., 2002).

1.2.1   Hydrocarbons

The total hydrocarbon fractions of crude oils consist of saturated and aromatic fractions where saturated hydrocarbon generally comprise normal and branched alkanes (paraffins) and cycloalkanes (naphthenes), while aromatic hydrocarbons include pure aromatics, cycloalkanoaromatics and cyclic sulphur compounds (Tissot and Welte, 1978). In the saturated hydrocarbon fractions, the paraffins are saturated compounds with general formula of C_nH_{2n+2}. They can be either straight chain (i.e. methane, ethane, hexane, etc) or branched chain compounds. Naphthenic hydrocarbons are also saturated compounds with the general formula of C_nH_{2n}. These compound are the most abundant (~25% to 75%) class of hydrocarbons in most crude oils (Simanzhenkov and Idem, 2003).

Aromatic hydrocarbons have at least one benzene ring, which can be fused together with others (i.e. naphthalene and phenanthrene) and also can be more complex structures with alkyl chains, and other naphthenic rings. It has been reported that the amount of aromatics in different crude oils varies from 15-50% (Simanzhenkov and Idem, 2003).

1.2.2   Polar compounds

Polar compounds in crude oil generally consist of one or more heteroatoms of nitrogen, sulphur and oxygen (N, S, O) and metals i.e. vanadium (V), iron (Fe), Nickel (Ni) compounds (Mapolelo et al., 2011). It has been reported that over 20, 000 different polar organic compounds with different elemental composition of $C_cH_hN_nO_oS_s$ has been found in crude oils (Teräväinen et al., 2007). Generally, the amount of NSO compounds in crude oil has been suggested to be less than 10% (Hughey et al., 2004). However, despite this small percentage, their presence has great capacity to cause problems during oil production, refining and processing, for example corrosion, fouling or poisoning of catalysts, formation of emulsions and cokes (Teräväinen et al., 2007; Mapolelo et al., 2011). These have caused huge economic costs for the oil and gas industry. As well as these drawbacks, polar compound also have some significant positive uses in petroleum exploration, production and refining. (Hughey et al. (2002); 2007) reported that polar compound such as phenols, acids carbazoles and naphthenic acids have been used as indicators to determine the origin of deposited source organic matter, thermal maturity, migration and biodegradation, while organic sulphur compound provide another source of geochemical clues.

The amount of nitrogen in crude oils varies from about 0.1 to 0.9% (Speight, 2007). Crude oil contains neutral and basic nitrogen-containing compounds, where, neutrals include carbazoles, indoles and pyrroles, while the basic compounds include pyridine and quinolone derivatives (Teräväinen et al., 2007). Nitrogen compounds in crude oils are believed to be responsible for the poisoning of cracking catalysts, the formation of gum in fuel oils, fuel instability during storage, (Hughey et al., 2004; Teräväinen et al., 2007; Simon et al., 2010). It has been suggested that nitrogen compounds that present in crude oils are mainly cyclic compounds and Figure 1.1 show some examples of nitrogen compounds found in crude oils.
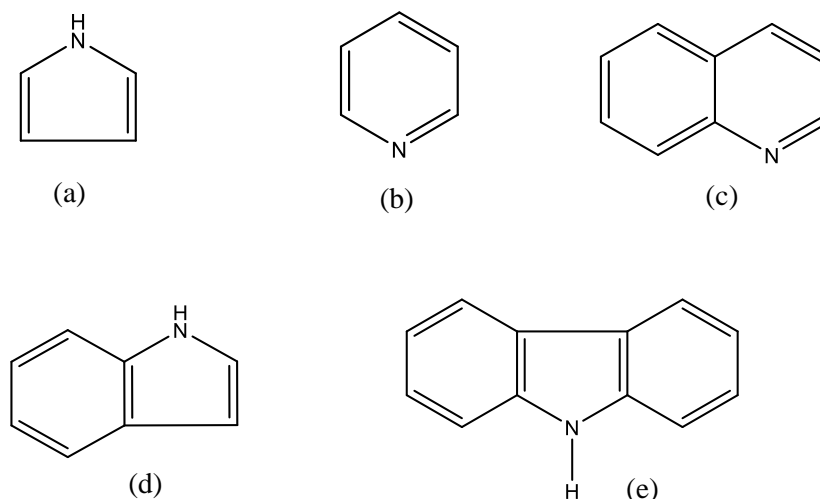
Figure 1.1 Example of nitrogen compounds in crude oils (a) pyrrole (b) pyridines (c) quinoline (d) indole (e) carbazoles (Tissot and Welte, 1978; Simanzhenkov and Idem, 2003; Speight, 2007)

The amount of total oxygen content may vary in crude oil crude oils with less than 2% w/w (Speight, 2007). Oxygen compounds may be present in crude oil as neutral and acidic compounds (Simanzhenkov and Idem, 2003) such as ethers, anhydrides, furans, ketones, esters, aldehydes and carboxylic acids (Tissot and Welte, 1978; Jada and Salou, 2002). The most important acidic oxygen containing compounds are the naphthenic acids. Naphthenic and naphthenoaromatic are the most abundant petroleum acid compounds followed by polyaromatic and heterocyclic types. The following Figure 1.2 shows some of oxygen-containing compounds present in crude oils.
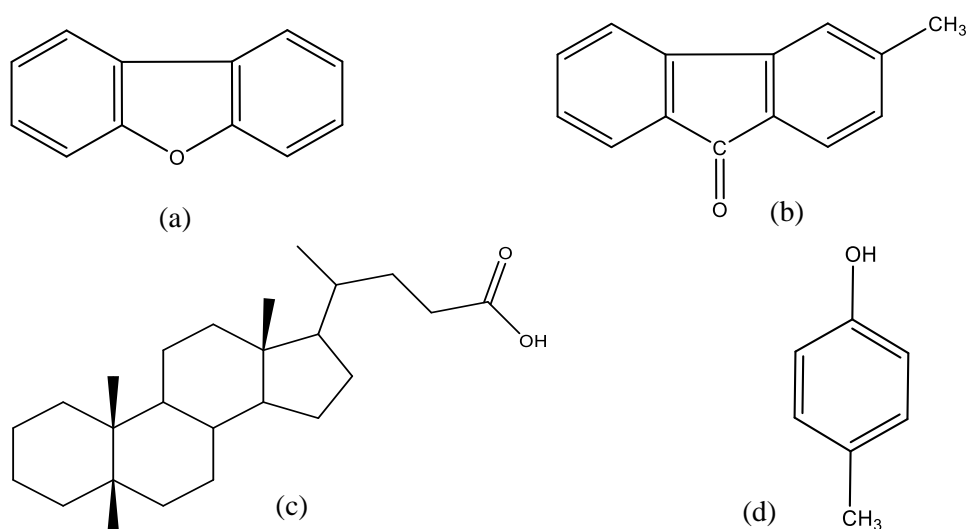
Figure 1.2 Examples of oxygen compounds in crude oils: (a) dibenzofuran (b) methylfluorenone (c) steroidal carboxylic acid (d) p- cresol (Tissot and Welte, 1978)

Sulphur has been reported to be the third most abundant atomic constituent of crude oils following carbon and hydrogen (Tissot and Welte, 1978). This compound often varies from 0.2 to 2.5 et % but can be as high as 6% in some crude oils (Laredo et al., 2004b) particularly due to the difference in geological environments (Speight, 2007). The major sulphur-containing compounds in crude oils are thiophenes and sulphides while a minor group consists of elemental sulphur, mercaptans and hydrogen sulphides (Teräväinen et al., 2007). Examples of some sulphur compounds present in crude oils are shown in Figure 1.3. Qian et al. (2001a) suggested that major sulphur-containing compounds in crude are normally incorporated in crude oil as five membered ring cyclic sulphides or thiophenes (i.e. dibenzothiophenes) and higher benzologues .
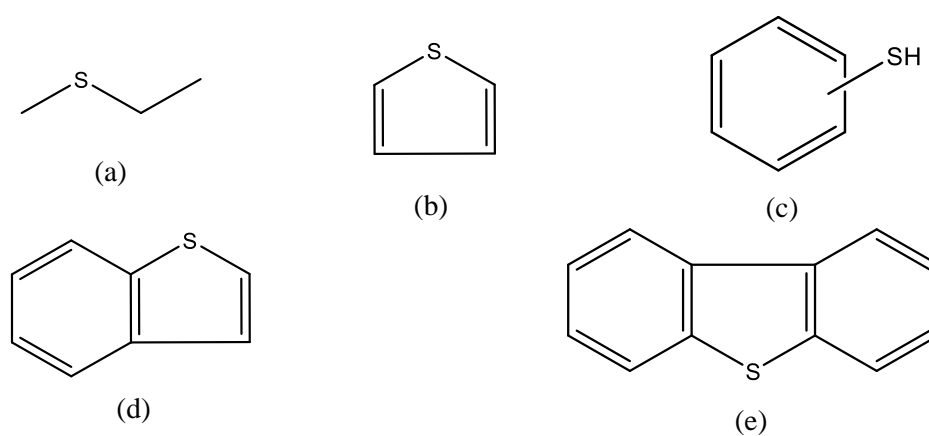
Figure 1.3 Example of sulphur compounds in crude oils (a) 2-thiabutane (b) thiophene (c) thiophenols (d) benzothiophene (e) dibenzothiophene (Tissot and Welte, 1978; Simanzhenkov and Idem, 2003; Speight, 2007)

Sulphur compounds are environmentally hazardous and together with nitrogen compounds may act as catalyst poisons (Teräväinen et al., 2007). Thus a high sulphur content in crude oil affects the refined products and increases the demand for more efficient downstream processes requiring an extensive desulphurisation process in refining of the crude oil fractions to ultimately reduce emissions from combustion engines (Al-Hajji et al., 2008).

1.2.3 **Asphaltenes and maltenes**

Asphaltenes are dark brown to black substances which are known as the most complex compounds in crude oils due to presence of various types of heteroatoms in their structure (Speight et al., 1984; Simanzhenkov and Idem, 2003; Kok et al., 2011). Asphaltenes are not a well-defined compound class as they are not chemically defined by structure or functional groups. The most widely used definition is that they are insoluble in the low molecular weight saturated hydrocarbons and are soluble in toluene (Wang and Buckley, 2003). Asphaltenes can be obtained as solids that precipitate from oils by the addition of an excess of low molecular weight *n*-alkane (i.e. pentane, hexane or heptane). The amount of asphaltenes in crude oils has been reported to vary from less than 1% to more than 20% (Jones et al., 1988; Klein et al., 2006a). Maltenes can be defined as the residual oil after asphaltenes have been removed from a crude oil (Groenzin and Mullins, 1999) or the heptane soluble fraction (Hughey et al., 2002).

Although the exact structure of asphaltenes is still unclear, in general, asphaltenes consist of fused polyaromatic rings, aliphatic chains and polar heteroatom-containing functional groups (Rogel, 2002; Silva et al., 2008). It has been suggested that asphaltenes are like micelle clusters dispersed in a hydrocarbon solvent where the clusters are considered to be composed of polyaromatic nuclei bearing chains of various lengths (Behar and Pelet, 1984).
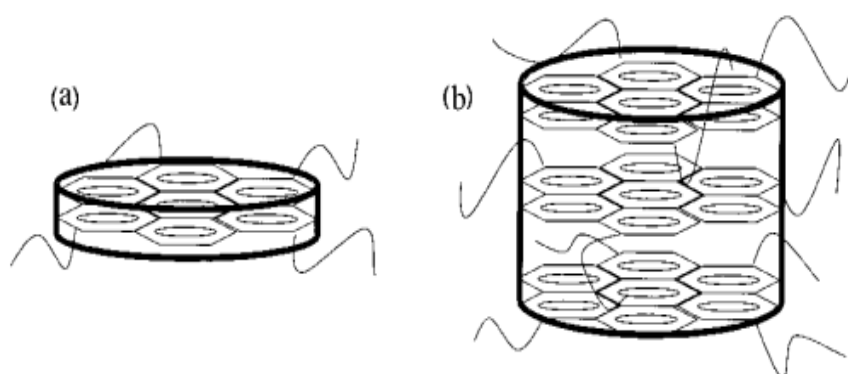
Figure 1.4. Schematic representation of an asphaltene molecule (a) and asphaltene aggregate from (Rogel, 2002).

The structures and compositions of oil asphaltenes depend on their origin and mode of formation, and they are inherently instable in the hydrocarbon bulk phase meaning that the interaction with other components of the oil phase is needed for stabilisation .Thus, if the bulk oil composition changes, the asphaltenes can become unstable in the oil which can lead to self-association, precipitation, flocculation and deposition in wells, pipelines and within refinery and production equipment resulting in pipeline plugging and failure of field equipment (Hughey et al., 2004; Barth et al., 2005). Asphaltenes may also be separated from their crude oils as a solid phase when pressure and temperature condition vary (Rogel et al., 2003).

1.3   Petroleum Acids

It has been known for many years that petroleum acids in crude oils include simple aliphatic acids, naphthenic acids (carboxylic acids containing one or more alicyclic rings), aromatic acids, phenols and sulfonic and other sulphur–containing acids (Lochte and Littmann (1955). McKay et al. (1975) reported that 28% of acid compound types in Wilmington crude oil were carboxylic acids, 28% phenols, 28% pyrroles (indoles and carbazoles) and 16% amides. Characterisation of oils from the San Joaquin valley by Tomczyk and Winans (2001) using high resolution mass spectrometry showed that approximately 40% of the acids were not plain carboxylic acids but also contained heteroatoms such as sulphur and nitrogen. A study by Qian et al. (2001a) using ultra high resolution mass spectrometry (FT-ICR MS) reported that the distribution of acids in crude oils consists of 1 to 6 naphthenic acid rings, 1 to 3 aromatic rings and O_2, O_3 ,O_4, O_2S, O_3S, O_4S species.

According to Babaian-Kibala et al. (1998), oils can vary in TAN from less than 0.1 to as high as 8. In the report of Li et al. (2010), their samples TAN measured up to 16.2. Oil is considered to be of high acidity if the TAN is higher than 0.5 oil and could potentially cause corrosion and refinery problems (Meredith et al., 2000). High TAN crude oil production has already increased to more than 10% of global oil supply (Anne et al., 2003 as cited in Dou et al. (2008) and this continues to increase as heavy oil production grows, providing future financial opportunities as well as technical challenges to the oil industry.

It is known that alongside temperature and fluid flow rate, oil TAN number is one of the factors that are associated with naphthenic acid corrosion and is thus commonly used in the oil industry to indicate the corrosive potential of crude oils and their fractions (Groysman et al., 2005). However, TAN measurement has been claimed to be only sufficient to provide a first indication whether the tested crude oil may be corrosive and does not provide information on its severity since it has been observed that some crude oils with a comparable TAN values show different corrosive behaviors while some low TAN crude oils cause higher corrosion behavior than their TAN might indicate (Laredo et al., 2004a).

Since TAN analysis only offers information on the total amount of acid species contained in crude oil, relying only on TAN measurement may not provide sufficient information to explain the full picture of acidity in crude oils. Previous work on oil TANs has given some understanding on the correlation of this measurement with their carboxylic acid contents.For example, Meredith et al. (2000) demonstrated a strong correlation (r^2= 0.91) existed between the TAN values and the amount of carboxylic acids in their crude oil samples from different sources of thermal maturities. This strong correlation was seen for TAN value more than 1.0 but was less strong for samples of less than 1.0. Also, some low TAN oils had values that did not correlate well with amount of carboxylic acids, suggesting that factors other than this carboxylic acid fraction concentration controls the acidity in those low TAN crude oils and that further study was needed to understand the reasons for that. The similar carboxylic acid concentration with TAN correlation observation was reported by Fafet et al. (2008) while this correlation remained unclear in other studies (Dou et al., 2008).

There has been some work investigating the role of sulphur in controlling crude oils TAN values Laredo et al. (2004a) and Meredith et al. (2000) reported that the total sulphur content of their crude oil samples showed limited correlation with their oil TAN values. Biodegradation has been found to be a primary control on the acidity of crude oils (Meredith et al., 2000). This observation was supported by (Li et al., 2010) who reported a clear correlation of increasing oil TAN with decreasing reservoir depth.

1.3 .1 Naphthenic acids

As cited in Lochte and Littmann (1955), it is thought that the first paper on naphthenic acids was by Hell and Medinger in 1874, although apart from some notable exceptions like the work on petroleum acids by Lochte and Littmann (1955), there was relatively little published on them until the last 15 years. Since then, there has been an increasing amount of research reported on naphthenic acids (i.e. (Hsu et al., 2000; Tomczyk and Winans, 2001; Rogers et al., 2002; Barrow et al., 2003; Fafet et al., 2008; Mapolelo et al., 2011; Rowland et al., 2011). Naphthenic acids are carboxylic acids that consist of one or more saturated ring structures and in general, they are non-volatile, chemically stable and act as surfactants (Clemente and Fedorak, 2005). It also has been generally reported that naphthenic acids are one of the main acidic compound classes that causes acidity in crude oils i.e. (Meredith et al., 2000; Zhang et al., 2006; Fafet et al., 2008).

Naphthenic acids are natural components present in crude oil at different concentrations depending on the origin of the oil (Clemente and Fedorak, 2005). Their presence in crude oils has been suggested to arise from acids from the source rock and acids synthesised or generated from crude oil biodegradation by microorganisms (Tissot and Welte, 1978; Meredith et al., 2000; Saab et al., 2005). Barth et al. (2004) stated that the origin of acids that were present in the biodegraded oil samples they analysed were product of microbial degradation. Moreover, carboxylic acids (including naphthenic acids) have also been observed to be produced in a series of laboratory crude oil biodegradation experiments by Watson et al. (2002).

Although naphthenic acids are characterised as carboxylic acids that include one or more saturated ring structures with general chemical formula of $C_nH_{2n+z}O_2$, they occur as an extremely complex variety of structures (Zhang et al., 2006). In this chemical formula, z is refers to hydrogen deficiency which is determined by the number of cyclic rings and double bonds (the double bond equivalent or DBE value) present in the molecule. The rings may be fused or attached by bridges (Clemente and Fedorak, 2005), while carboxylic acid groups are normally attached to a side chain of a cycloaliphatic ring (Groysman.2005). Hsu (2010) described how z-numbers can be used to represent hydrogen deficiency as well as the total number of double bond and cyclic rings from the chemical formula. It has been suggested that the most common structure of naphthenic acids is with five and six membered rings (Barrow et al., 2003; Teräväinen

et al., 2007) although fatty acids, monocyclic, polycyclic, aromatic and polyaromatic acids may also present at various levels subject to the source of crude oil (Meredith et al., 2000; Qian et al., 2008; Mapolelo et al., 2011). Naphthenic acid compounds are also known to be toxic to aquatic organisms (Headley et al., 2002; Clemente and Fedorak, 2005; Barrow et al., 2009).

Although challenging to gain, a better understanding of naphthenic acid compound compositions, molecular structures and variability of their distributions in crude oils will help to provide better solutions for minimising or overcoming the negative impact of petroleum acids in the oil industry.

Figure 1.5 Some possible acid structures with molecular formula $C_nH_{2n+z}O_2$. Z refers to hydrogen deficiency, DBE refers to double bond equivalent. Modified from (Qian et al., 2001a; Laredo et al., 2004b)

1.4   Processes affecting the concentration of petroleum acids

Petroleum acids in crude oils have been suggested to rise from different sources. (Mackenzie et al., 1983) suggested that they might come from the original acids of the source rock or biodegradation of the oil or even in-reservoir biosynthesis by the microorganisms that render the biodegradation. While microbial degradation of crude oil in the reservoir has been long associated with increased acidity of the oil phase (Behar and Albrecht, 1984; Meredith et al., 2000; Barth et al., 2004), it has also been reported that the concentration of acids in a number of crude oils samples decreased with increasing biodegradation (Behar and Albrecht, 1984) . It has been reported that oil migration processes severely affect the molecular distribution of carboxylic acids in crude oils (Jaffé and Gallardo, 1993), while the concentration of these acids in reservoired crude oils can be further affected by alteration processes such as removal by water washing, further biodegradation and also thermal alteration (Mackenzie et al., 1983).

Carboxylic acids are found to be generated under both aerobic and anaerobic conditions during the biodegradation of crude oils (Mackenzie et al., 1983; Jaffé and Gallardo, 1993; Meredith et al., 2000; Erstad et al., 2009). It has been suggested that either the neoformation of acids during biodegradation or preferential removal of non-acidic compounds have led to an increasing amount of acidic compounds in biodegraded oil (Behar and Albrecht, 1984). A report on biodegraded oil samples by Barth et al. (2004) showed that the concentration of total carboxylic acids in them increased with extent of biodegradation from approximately 300 mg/g oil to over 38,000 mg/g oil. In fact, this two order of magnitude increase appeared to be still increasing although biodegradation was stopped. Although, no direct correlation between the degree of biodegradation and the carboxylic acid concentration in oils had been reported up to that date, Meredith et al. (2000) showed that (except for undegraded samples) the degree of biodegradation correlated with the concentration of carboxylic acids in their samples.

Apart from acidity in biodegraded reservoirs, acidity of low maturity crude oils is also one of the concerns in oil industry (Fafet et al., 2008). It has been proposed that thermal degradation may be responsible for the fate of acids produced during biodegradation (Mackenzie et al., 1983). Meredith et al. (2000) stated that thermally immature oils may have high acidities but were unable to test that hypothesis due to the insufficient low

maturity oils in their sample set. Thermal alteration has been suggested to potentially reduce oil acidity in oils due to decarboxylation, dehydration and desulfuration of petroleum constituents (Tissot and Welte, 1978).

1.4.1   Biodegradation

Biodegradation can be defined as the alteration of organic matter or crude oil by microbial activities in reservoir, during migration or at the surface of seep locations (Peters and Moldowan, 1993). This alteration process can involve the degradation of hydrocarbons by both surface and subsurface microorganisms. It is thought that the biodegradation occurs widely and that most of the earth's oil reserves have been biodegraded (Head et al., 2003). Biodegradation is affected by many factors and also requires conditions that support microbial life. In order for petroleum degradation to occur, it requires factors such as **i)** a suitable subsurface temperature (less than 80°C), **ii)** oil-water contact **iii)** the availability of circulating groundwater containing sufficient nutrients, **iv)** the salinity of the formation water is less than 100-150 parts per thousand (ppt), **v)** the rock fabric must have sufficient porosity and permeability to allow the diffusion of nutrients and bacterial motility, **vi)** the petroleum also must be free from H_2S which poison the bacteria (Peters and Moldowan, 1993; Meredith et al., 2000).

Although biodegraded oils are commonly encountered in shallow reservoirs with temperatures < 80 °C, it has been found that oils in some low temperature reservoirs are not biodegraded. One of the possible reasons for this is a phenomenon called reservoir pasteurisation prior to hydrocarbon charging in (Wilhelms et al., 2001). Moreover, petroleum accumulation is usually comprised of mixture of oils due to interaction of biodegradation and charge mixing (Larter et al., 2012). Dou et al. (2008) reported that in the past, aerobic degradation of petroleum has long been thought to be a principal process in subsurface shallow reservoirs. However, anaerobic degradation process now has been confirmed to be dominant, (Head et al., 2003; Aitken et al., 2004). Studies of anaerobic oil biodegradation have been reported by several authors such as (Rueter et al., 1994; Aitken et al., 2004) and it has been shown that anaerobic degradation is much slower than that carried out by aerobes. However, in terms of geologic time, the different in rate may not be critical as it can occur over geological timescales (Peters and Moldowan, 1993).

Compared to unaltered equivalents, oils that have experienced microbial biodegradation generally have higher density and viscosity than non-biodegraded samples. This is because, microbial alteration of oils preferentially consumes hydrocarbons, or it might also be due to production of heavy components including acids, as products of microbial process or by degradation of dead biomass (Behar and Pelet, 1984; Tomczyk and Winans, 2001). This results in the remaining oil becoming enriched with nitrogen, sulphur, and oxygen compounds (polar resin and asphaltenes fractions). Therefore, biodegraded oils have lower API gravity, are more viscous and are richer in sulphur, resins, asphaltenes and metals (Peters et al., 2005).

The extent of crude oil biodegradation can be assessed based on the difference of the relative susceptibilities of various compound classes to biodegradation. Some compounds may be removed before others are affected. According to Rowland et al. (1986), the order of selective removal of hydrocarbons by bacterial appears according to the following ease of microbial attack of saturated hydrocarbons in crude oils: *n*-alkanes > alkylcyclohexanes > acyclic isoprenoid alkanes > C14 – C16 bicyclic alkanes > steranes > hopanes. For aromatic hydrocarbons, the sequence of ease of microbial attack are monoaromatics > diaromatics > triaromatics. There several reported schemes for assessing the level of biodegradation experienced by oils i.e. Peters and Moldowan (1993); Peters et al. (2005); Larter et al. (2012). The Peters and Moldowan (1993) biodegradation scale (PM scale) ranked oils in their extent of degradation from light to severe, as shown in Figure 3.1.
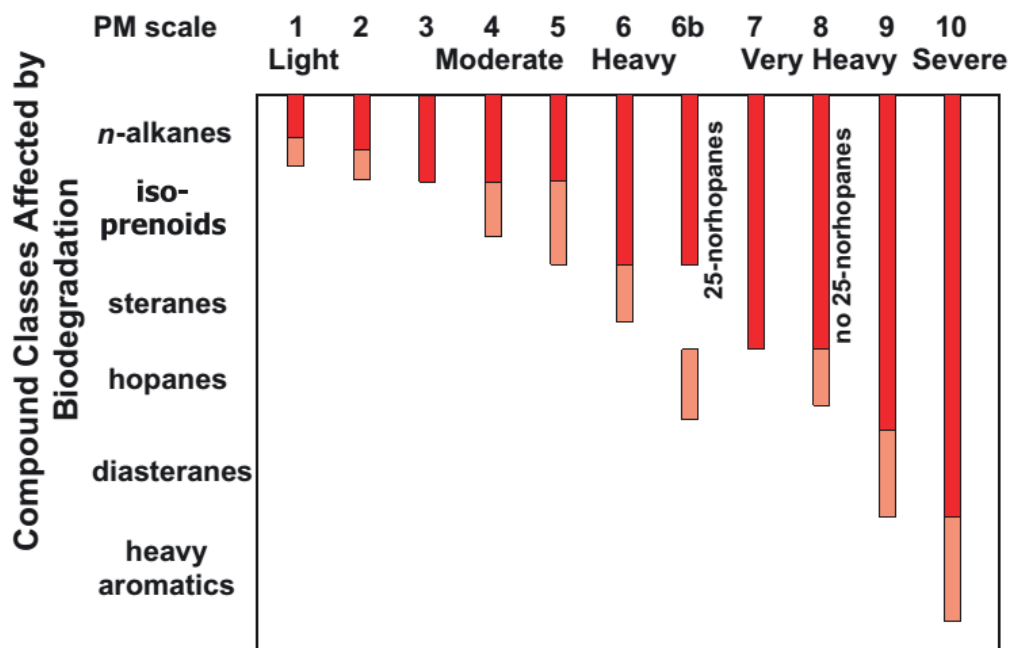
Figure. 1.6 Biodegradation scale of Peters and Moldowan (1993) adapted by Larter et al. (2012).The lightly shaded areas at the end of the bars reflect the extent of of alteration within a compound class.

However, it must also be noted that oil biodegradation is a complex process. Thus, it has been suggested that this biodegradation scale should be used cautiously as the complex biodegradation "quasi-stepwise" process cannot be described as a truly sequential alteration of compound classes. For instance, although hopanes are generally considered more resistant to biodegradation than steranes, it could be that significant alteration of the hopanes occurs before all steranes are destroyed in some oils exposed to heavy biodegradation (Peters and Moldowan, 1993).

1.4.2 *Thermal maturation*

Thermal maturity describes the extent of heat-driven reactions that convert sedimentary organic matter into petroleum. This process is generally associated with increasing burial which produces an increase in source rock and reservoir rock temperatures. As petroleum is a complex mixture of metastable products, crude oils change towards compositions of greater thermodynamic stability during maturation (Peters et al., 2005). For example, heavier components in crude oils will be cracked to lighter components as burial and temperature increases. (Tissot and Welte, 1978) classified organic matter according to its relationship to the so-called "oil window" **i)** *immature,* where organic matter has been affected by digenesis including biological, physical and chemical alteration without pronounced effect of temperature, **ii)** *mature* , where organic matter has been affected by catagenesis (thermal process covering the temperature range between diagenesis and metagenesis) or **iii)** *post mature*, where organic matter has been heated to such high temperature that is has been reduced to a hydrogen-poor residue capable of generating only small amounts of hydrocarbon gases.

Based on the variation of ratios attributed to molecular cracking and isomerisation, thermal maturity can be assessed and classified using maturity-dependent biomarker parameter such as terpanes, steranes, aromatic steroids, porphyrins and non-biomarker maturity parameter such as ratios involving *n*-alkanes, isoprenoid alkanes and aromatic hydrocarbons such as methyl phenanthrenes and methyl naphthalenes (Peters et al., 2005).

1.5 Petroleum acid analysis

In petroleum chemistry, various methods of analysis have been used to investigate acidic compounds in crude oils. Most of the acid characterisation studies on crude oils have been done with regards to the concerns of understanding the physical or technical properties of the oils such as corrosiveness, emulsion stability or wettability change of solid surfaces after adsorption (Borgund et al., 2007b). For quantitative analysis of naphthenic acids, gas chromatography (GC), high pressure liquid (HPLC) chromatography, Fourier Transform Infrared (FTIR) spectroscopy and mass spectrometry (MS) have previously been used. Conventional GC and GC-MS has been commonly applied on isolated acid fractions (usually derivatised to methyl esters) to quantify them and to investigate the stereochemistry of individual acidic components (Meredith et al., 2000; Jones et al., 2001; Clemente et al., 2003; Li et al., 2010). FTIR has been used to evaluate the functional group distributions in crude oils and in isolated oil fractions (Tomczyk and Winans, 2001; Li et al., 2010)

The analysis of polar species is much less well established than that of hydrocarbons since characterisation of acidic compounds in crude oils is more challenging. The challenges are due to factors such as this compound class is very polar and makes up a small fraction of the whole petroleum sample, thus requiring time consuming chromatographic isolation and derivatisation prior to analysis and that some components may be lost during the long isolation procedure. The isolated acid fractions are also highly complex and difficult to be resolve by traditional chromatographic or mass spectrometric techniques and their non-volatile nature may exclude many components from analysis by CG and ionization by traditional mass spectrometric ionization sources, especially those from severely biodegraded heavy oils (Hughey et al., 2002).

Mass spectrometry has revealed information on the range of acidic structure in petroleum crude oils (Qian et al., 2001a; Tomczyk and Winans, 2001). Recent developments of negative-ion electrospray Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) of the whole oils offers directly, extremely high resolution analyses of very complex mixtures of naphthenic acids to provide detailed overview of the distribution of acids in oils and oil fractions (Hughey et al., 2002; Hughey et al., 2004; Kim et al., 2005; Hemmingsen et al., 2006; Hughey et al., 2008; Barrow et al., 2009; Smith et al., 2009).

1.5.1 Total Acid Number (TAN)

Acidity in crude oil is commonly measured as the Total Acid Number (TAN), which is defined as the number of milligrams of potassium hydroxide (KOH) needed to neutralize the acidity in one gram of crude oil (Derungs, 1956, as cited in Meredith et al. (2000). TAN is routinely measured using a standard method based on titration with KOH using either a potentiometric (ASTM D664) or colorimetric method (ASTM D974) (Jones et al., 2001; Fafet et al., 2008).

1.5.2 Gas Chromatography Analysis (GC)

Gas chromatography has been well known as an analytical separation method for a long time i.e. (Grob and Barry, 2004) especially in petroleum acid analysis i.e. (Seifert et al., 1969; Behar and Albrecht, 1984; Meredith et al., 2000). However, due to the complexity of crude oils, it is often impossible to perform gas chromatography directly on whole crude oil to adequately resolve minor components without pre-separation into different fractions. One example of a pre-separation is a method developed by Jones et al. (2001) where carboxylic acid fractions were separated from their oil samples using non-aqueous ion-exchange solid phase extraction before analysis (as methyl esters) by GC. Investigation of crude oil acids using GC for quantitative analysis has been well reported for instance a study on correlations between carboxylic acids an degree of biodegradation five difference origins of crude oils by Behar and Albrecht (1984), study on extraction method development for analysis of aliphatic and naphthenic acids in light and heavy crude oil by (Jones et al., 2001) and a distribution study on formation of carboxylic acid fraction during 80 days of laboratory biodegradation experiment by Watson et al. (2002).

1.5.3. Fourier Transform Infrared (FTIR) spectroscopy analysis

Fourier Transform Infrared (FTIR) spectroscopy is a useful tool to characterise the organic and inorganic chemical composition of substances. This analysis can provide a fast overview on the average distribution of chemical bonds (functional groups) present in bulk petroleum samples. Based on the principle that each chemical bond and functional group that is exposed to infrared radiation absorbs at a different characteristic frequency, the presence and abundance of that chemical bond of a molecule can be determined. FTIR has been used for characterising either whole crude oils or various component of them i.e. isolated acid fractions, asphaltene fractions and interfacial materials (Tomczyk and Winans, 2001; Barth et al., 2004; Muller et al., 2009; Li et al., 2010). For example, Watson et al. (2002) used FTIR in order to investigate the changes in the carboxylic acid concentrations produced during an 80 day series of laboratory biodegradation of crude oil by measuring absorption bands due to a number of chemical bonds including, C=O (1706 cm^{-1}), O-H (3100-3700 cm^{-1}), C-H aliphatic (2924 cm^{-1}), C-H aromatic (3000-3100 cm^{-1}), CH$_3$ (1370-1390 cm^{-1}) and CH$_3$ + CH$_2$ (1430-1470 cm^{-1}).

FTIR analysis also has been used by Clemente and Fedorak (2005) for quantifying naphthenic acids present in their oil sand samples by measuring the absorbance of the monomeric and dimeric forms of the carboxylic groups at 1743 cm^{-1} and 1706 cm^{-1}, respectively. While both Silva et al. (2008) and Parisotto et al. (2010) developed a method for the determination of Total Acid Number (TAN) in petroleum, petroleum cuts, petroleum water in oil emulsions and residues of crude oil distillation, by mid infrared spectroscopy combined with multivariate analysis.

1.5.4 Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)

Recent developments of ultra-high resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) have resulted in one of the powerful techniques for direct analysis and characterisation of crude oils and petroleum fractions without any prior separation (Marshall, 2000; Hughey et al., 2002; Al-Hajji et al., 2008; Miyabayashi et al., 2009). This powerful technique measures the cyclotron frequency of ions in homogeneous magnetic field, resulting in ultra-high resolution and highly accurate mass measurement, with errors of less than 1 ppm. (Miyabayashi et al., 2009).

FT-ICR MS, usually coupled with Electrospray Ionization (ESI), has been used to determine the elemental compositions of compounds in petroleum samples (Hughey et al., 2002; Rodgers et al., 2002; Hemmingsen et al., 2006; Teräväinen et al., 2007). Positive mode Electrospray Ionisation (+ve) ESI preferentially ionises petroleum basic nitrogen compounds such as pyridine benzologs (Qian et al., 2001b), while negative mode Electrospray Ionization (-ve) ESI preferentially ionises strongly acidic groups (i.e. carboxylic acids including naphthenic acids), weakly acid compounds such as phenol and neutral nitrogen compounds such as pyrrole benzologs (Qian et al., 2001a; Hughey et al., 2002).

A number of studies have employed this technique for the detailed analysis of acid fractions in crude oils. For example, (Barrow et al., 2003; 2004, 2009) used FT-ICR MS to characterise complex mixtures of naphthenic acids in petroleum samples. While (Hemmingsen et al., 2006) studied the molecular compositions of different acidic fractions in North Sea acidic crude oil using FT-ICR MS and showed that 90% of acidic compounds in the oil samples were from carboxylic acids. FT-ICR MS also has been used to characterise petroleum acids related to microbial alteration of crude oil (Kim et al., 2005; Hughey et al., 2007; Liao et al., 2012), thermal maturity (Hughey et al., 2004) and geochemical origin (Hughey et al., 2002). Other than whole crude oils, the application of FT-ICR MS also been reported in characterisation on distillates fractions (Teräväinen et al., 2007), asphaltenes fraction (Klein et al., 2006b; 2006c), vacuum gas oil (Smith et al., 2009) and soil extracts (Hughey et al., 2008). Important information such as the acid molecular weight and elemental composition distributions obtained from these analysis may provide information useful in understanding and preventing corrosion and also may be used to fingerprint samples from different oil fields (Barrow et al., 2003).

1.6 Sample Sets

The samples in this study can be divided into two sets. Set 1 are an initial set of 43 mostly well characterised crude oils, Set 2 are 46 reservoir core extract samples from around the World. The following Tables (2.1-2.2) present the details of the samples together with their information on their origins and analyses performed on them (e.g, TAN, detailed hydrocarbon analyses, carboxylic acid analyses by GC and GC-MS, FT-ICR MS, FTIR).

1.6.1   Set 1: Crude oils

The sample set 1 consists of 43 crude oils representing a variety of biodegraded and non-degraded oil samples from different origins. i.e. 9 samples from the North Sea, 28 samples obtained from Canada, but comprising of various oils from around the world (and collectively called the Bumbleberry oil set), 2 samples from California, 1 sample from Congo, 1 sample from Venezuela and 2 samples from elsewhere in South America. (Table 1.1a-b)

1.6.2   Set 2: Core extracts

The sample set 2 consists of extracted oils from 46 core samples obtained from the University of Calgary, which had been given coded well names. These comprised of 6 samples from Saucy Saskatoon A (SSA), 10 samples from Saucy Saskatoon B (SSB), 5 samples from Saucy Saskatoon C (SSC) all from Canada, 16 samples from Gammel Ost (Chinese, Eocene, lacustrine) and 9 Canadian samples from Inniskillin. (Table 1.2a-b)

SAMPLES	LOCATION/ ORIGIN	ANALYSIS										
		TAN			Open column/hcs	Iatroscan	Carboxylic Acid separation	FT-ICR MS	FTIR			
		Oils	Asphaltene	Maltene					ARK (Oil)	ORBIT (Oil)	Asphaltene	Maltene
EN 149	North Sea	X	X	X	X	X	—	X	X	X	X	X
EN 151	North Sea	X	X	X	X	X	X	X	X	X	—	X
EN 154	West Shetland	X	X	X	X	X	—	X	X	X	X	X
EN 158	West Shetland	X	X	X	X	X	X3	—	X	X	X	X
EN 168	Italy	X	X	X	X	X	X	—	X	X	X	X
EN 169	Italy	X	X	X	X	X	—	—	X	X	X	X
EN 174	North Sea	X	X	X	X	X	X	X	X	X	X	X
H7	California	X	X	X	X	X	—	X	X	X	X	X
D13	California	X	X	X	X	X	—	X	X3	X	X	X
NSO-1	North Sea	X	Insufficient	X	X	X	X	—	X	X	X	—
Boscan	Venezuela	X	X	X	X	X	—	—	X	X	X	X
Heidrun	North Sea	X	Insufficient	—	—	X	X	—	X	X	—	X
Cold Lake	Canada	X	—	—	—	X	—	—	X	X	—	—
Lloydminster	Canada	X	—	—	—	X	—	—	X	X	—	—
Douk Daka	Congo	X	—	—	—	X	—	—	X	X	—	—
TRY	South America	X	—	—	—	X	—	—	X3	X3	—	—
SPY	South America	X	—	—	—	X	—	—	X	X3	—	—

Table 1.1(a) Details of analyses performed on crude oils **(Set 1)**

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SAMPLES (BB#)	LOCATION/ ORIGIN	ANALYSIS										
		TAN			Open column/ Hydrocarbon	Iatroscan	Carboxylic Acid separation	FT-ICR MS	FTIR			
		Oils	Asphaltene	Maltene					ARK(Oils)	ORBIT (Oils)	Asphaltene	Maltene
1		X	–	–	–	X	–	–	X	X	–	–
2		X	–	–	–	X	–	–	X	X	–	–
3		X	–	–	–	X	X	–	X	X	–	–
4		X	–	–	–	X	–	–	X	X3	–	–
5		X	–	–	–	X	–	–	–	X	–	–
6		X	–	–	–	X	–	–	X	X	–	–
7		X	–	–	–	X	–	–	–	X	–	–
8		X	–	–	–	X	X	–	X	X	–	–
9		X	–	–	–	X	–	–	X	X	–	–
10	Various worldwide oils supplied via University of Calgary, Canada	X	–	–	–	X	X	–	X	X	–	–
11		X	–	–	–	X	–	–	X	X	–	–
12		X	–	–	–	X	–	–	X	X	–	–
13		X	–	–	–	X	–	–	X	X	–	–
14		X	–	–	–	X	–	–	–	–	–	–
15		X	–	–	–	X	–	–	–	X	–	–
16		X	–	–	–	–	–	–	–	–	–	–
17		X	–	–	–	X	–	–	X	X	–	–
18		X	–	–	–	X	–	–	–	–	–	–
19		X	–	–	–	X	–	–	X	X	–	–
20		X	–	–	–	X	–	–	X	X	–	–
21		X	–	–	–	X	X	–	X	X	–	–
22		X	–	–	–	X	–	–	–	–	–	–
23		X	–	–	–	X	–	–	X	X	–	–
24		X	–	–	–	X	–	–	X	X	–	–
25		X	–	–	–	X	–	–	X	X	–	–
26		X	–	–	–	X	–	–	X	X	–	–

Table 1.1(b) Details of analyses performed on Bumbleberry oil samples (**Set 1**) cont.

SAMPLES (#)	LOCATION/ ORIGIN	ANALYSIS										
		TAN			Open column/ Hydrocarbon	Iatroscan	Carboxylic acid separation	FT-ICR MS	FTIR			
		Oils	Asphaltene	Maltene					ARK(Oil)	ORBIT (Oils)	Asphaltene	Maltene
1	SSA (Canada)	X	–	–	–	–	–	–	–	–	–	–
2		X	–	–	–	X	–	–	–	–	–	–
3		X	–	–	–	–	–	–	–	–	–	–
4		X	–	–	–	–	–	–	–	–	–	–
5		X	–	–	–	X	–	–	–	–	–	–
6		X	–	–	–	–	–	–	–	–	–	–
7	SSB (Canada)	X	–	–	–	X	–	–	–	–	–	–
8		X	–	–	–	X	–	–	–	–	–	–
9		X	–	–	–	X	–	–	–	–	–	–
10		X	–	–	–	X	–	–	–	–	–	–
11		X	–	–	–	–	–	–	–	–	–	–
12		X	–	–	–	X	–	–	–	–	–	–
13		X	–	–	–	X	–	–	–	–	–	–
14		X	–	–	–	X	–	–	–	–	–	–
15		X	–	–	–	–	–	–	–	–	–	–
16		X	–	–	–	X	–	–	–	–	–	–
17	SSC (Canada)	X	–	–	–	X	–	–	–	–	–	–
18		X	–	–	–	X	–	–	–	–	–	–
19		X	–	–	–	X	–	–	–	–	–	–
20		X	–	–	–	X	–	–	–	–	–	–
21		X	–	–	–	X	–	–	–	–	–	–

Table 1.2(a) Details of analyses performed on core extract samples. SSA-Saucy Saskatoon A, SSB-Saucy Saskatoon B, SSC-Saucy Saskatoon C, **(Set 2)**

SAMPLES (#)	LOCATION/ ORIGIN	ANALYSIS										
		TAN			Open column/hcs	Iatroscan	Carboxylic acid separation	FT-ICR MS	FTIR			
		Oils	Asphaltene	Maltene					ARK(Oil)	ORBIT (Oil)	Asphaltene	Maltene
22	GAMMEL OST (China)	X	–	–	–	X	–	–	–	–	–	–
23		X	–	–	–	X	–	–	–	–	–	–
24		X	–	–	–	X	–	–	–	–	–	–
25		X	–	–	–	X	–	–	–	–	–	–
26		X	–	–	–	–	–	–	–	–	–	–
27		X	–	–	–	–	–	–	–	–	–	–
28		X	–	–	–	–	–	–	–	–	–	–
29		X	–	–	–	X	–	–	–	–	–	–
30		X	–	–	–	–	–	–	–	–	–	–
31		X	–	–	–	X	–	–	–	–	–	–
32		X	–	–	–	–	–	–	–	–	–	–
33		X	–	–	–	–	–	–	–	–	–	–
34		X	–	–	–	–	–	–	–	–	–	–
35		X	–	–	–	X	–	–	–	–	–	–
36		X	–	–	–	–	–	–	–	–	–	–
37		–	–	–	–	–	–	–	–	–	–	–
38	INNISKILLIN (Canada)	X	–	–	–	X	–	–	–	–	–	–
39		X	–	–	–	X	–	–	–	–	–	–
40		X	–	–	–	X	–	–	–	–	–	–
41		X	–	–	–	X	–	–	–	–	–	–
42		X	–	–	–	X	–	–	–	–	–	–
43		X	–	–	–	X	–	–	–	–	–	–
44		X	–	–	–	–	–	–	–	–	–	–
45		X	–	–	–	–	–	–	–	–	–	–
46		X	–	–	–	–	–	–	–	–	–	–

Table 1.2(b) Details of analyses performed on core extract samples. **(Set 2)** Cont.

CHAPTER 2

METHODOLOGY

Chapter 2. Methodology

2.1 Materials

General solvents used in the analyses were reagent grade solvents, dichloromethane (DCM), light petroleum spirit, which was also called petroleum ether (b.p 40-60 °C), hexane, methanol, toluene obtained from LSL (UK) Ltd or VWR Ltd, which were re-distilled using all-glass 30 plate Oldershaw solvent stills. For asphaltene and maltene separation, the 30 ml Oak Ridge centrifuge tubes used were purchased from Thermo Scientific Nalgene.The hydrocarbon surrogate standards used were squalane and 1,1'-binaphthyl, while the internal standards were heptadecylcyclohexane and *p*-terphenyl, all purchase from Sigma-Aldrich Ltd The Iatroscan TLC-FID chromarods used were Type S-III (silica gel type) and were purchased from SES GmbH- Analyse Systeme, Germany.

The solvents used in TAN titrations were HPLC grade toluene and, iso-propyl alcohol purchased from Fisher Scientific, UK and potassium hydroxide 0.1 M in propan-2-ol from Yorlab Ltd. The spiking solution reagents used in this analysis were benzoic acid and stearic acid, purchased from Sigma-Aldrich Ltd.

In the carboxylic acid extractions, the reagents used included formic acid, diethyl ether, boron trifluoride-methanol solution (14%) purchased from Sigma-Aldrich and the 6 ml SAX-SPE glass columns as well as 6 ml silica columns were purchased from Biotage, Ltd.
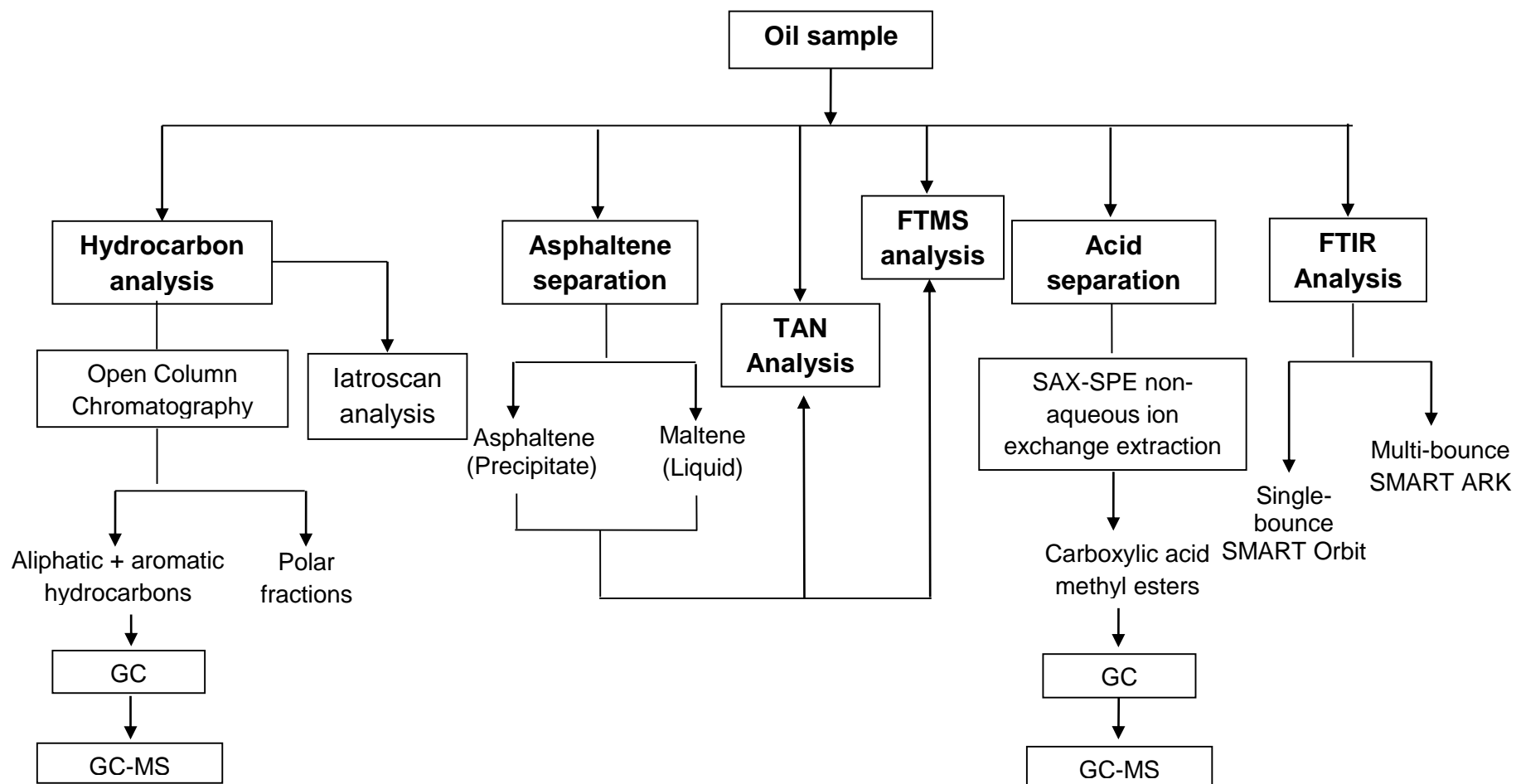
Figure 2.1 analytical schemes of oil analyses

2.2 Sample preparation

2.2.1 Sample Extraction

Solid samples (tar sand/ rock) were extracted using Soxhlet apparatus. Approximately 100 g aliquots of rock samples were crushed or ground into fine powder using a Tema disc mill. Weighed aliquots (~50 g) were transferred to a clean pre-extracted Whatman cellulose extraction thimble which was then loaded into the Soxhlet apparatus and subjected to 24 hours of extraction with an azeotropic mixture of 93:7 v/v of DCM/Methanol. A few anti-bumping granules and some (~3 g) activated copper turnings were added to the azeotropic solvent mixture before the extraction was started in order to maintain the boiling rate and to remove elemental sulphur from the extracts, respectively. The solvent extracts were finally concentrated using rotary evaporator followed by evaporation under nitrogen gas to a constant weight.

Figure 2.2 Tema disc mill

Figure 2.3 Soxhlet extraction apparatus

2.2.2 Asphaltene & Maltene Separation

The extraction of asphaltenes from crude oils was based on a method modified from (Speight et al., 1984). Asphaltenes were precipitate by adding 40 fold excess of n-hexane per 1 g (~1 ml) of oil in portions with application of sporadic swirling. For heavy oil samples, around 1-2 ml of toluene was added to the sample in order to dissolve the sample prior to mixing with n-hexane. The mixture was agitated for 2 h using an ultrasonic bath and then allowed to settle for 18 to 24 h to allow complete precipitation. The mixture was then centrifuged for 15 min at 3500 rpm, after which the hexane soluble (maltene) fraction was then decanted into a 500 ml round bottom flask (rbf).

The precipitated asphaltene was dissolved again in toluene (1 ml toluene per 100 mg asphaltene) and 40 ml of *n*-hexane was then added for each ml of toluene used. The asphaltene mixture was ultrasonicated and stirred for 30 min. and left to equilibrate for 3 h before centrifuging again for 15 min. at 3500 rpm. This precipitation step was repeated three times until colourless *n*-hexane was produced. For recovery of the asphaltenes and maltenes, the asphaltenes were left to dry in a weighed 100 ml rbf on dryng cabinet at 40 °C overnight, while the maltene fraction was obtained by solvent evaporation of the n-hexane using a rotary evaporator and then evaporation using a stream of dry nitrogen until constant weight was reached.

Further purification was applied to asphaltene fraction in order to remove co-precipitated resin and hydrocarbons (mainly waxes) as described in (Alboudwarej et al., 2002). The asphaltenes were transferred into a pre-extracted Whatman cellulose thimble and covered with a clean pre-extracted cotton wool. The thimble was then placed in Soxhlet apparatus subjected to 48 h extraction with *n*-hexane solvent at 30 °C. The purified asphaltene was finally left to dry and weighed until constant weight was achieved.

2.3 Hydrocarbon Analysis

2.3.1   Iatroscan TLC-FID

Gross compositions of crude oils, bitumen and core extract samples in terms of their saturated hydrocarbon, aromatic hydrocarbon, resin and asphaltene (SARA) fraction contents in were obtained using the Iatroscan SARA method described by Karlsen and Larter (1991). The Chromarod Type S-III (silica gel type) rods which was used for the thin layer chromatography (TLC) were first passed through the flame ionisation detector (FID) two to three times in order to remove any contamination and to obtain constant activity of the silica layer before sample application. Using a 5 µl syringe, 3 µl of the sample solution (10 mg dissolved in 1 ml DCM) was taken out and carefully spotted on a cleaned chromarod at approximately 2 cm from the bottom of the chromarod.
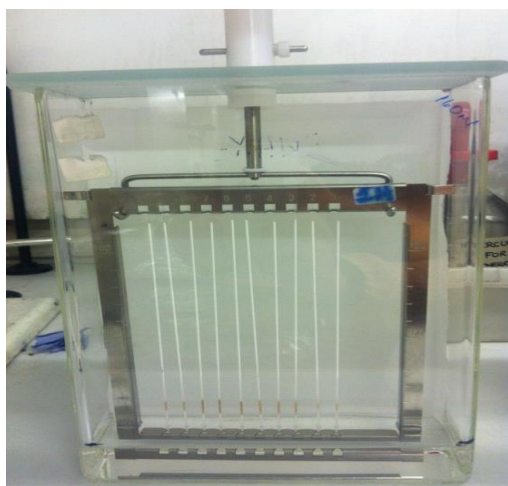
Figure 2.4 Sample spiked chromarods in a development tank

In order to assess repeatability each sample was analysed in triplicate. On two rods of each rack, standard oil (Norwegian Petroleum Directorate, NSO-1) was spotted, followed by 3 rods of the oil sample and finally the blank rods. The spotted chromarods underwent 3 development steps in different solvent tanks. Firstly, the rods were immersed in a tank containing *n*-hexane (150 ml) as mobile phase. The mobile phase was allowed to pass up the rod until it reached the mark of 100% rod length which is approximately (~29 min) and the rods were left to air dry for 3 minutes. Next, the samples were developed in a toluene solvent tank (60% rod length, ~11 min) followed by air drying for 6 minutes. The final step was in a DCM: Methanol (93:7) solvent mixture tank (30% rod length, ~3 min). The chromarods were then allowed to dry for 90 s in a 30 $^{\circ}$C oven before being analysed in a Iatroscan MK-5 TLC-FID analyser. The

results were recorded and processed using PC-based LabSystem ThermoAtlas data system.

2.3.2   Open Column Chromatography

Total hydrocarbon (THC) fractions containing both aliphatic and aromatic hydrocarbons, were separated from crude oils using an open column chromatography technique. A glass column (30 mm x 8 mm) was prepared by plugging the bottom of the column with pre-extracted cotton wool, followed by adding ¾ height layer of pre-extracted, dried and activated (110 °C overnight) silica gel (Merck 60) slurry and then 0.5 cm layer of activated alumina (Merck 90). An aliquot (approximately 100 mg) of an oil sample was first spiked with 150 µl of the surrogate standards (200 mg/100 ml of squalane and 45 mg/100 ml of 1,1-binapthyl) before being applied on to the top of prepared glass column. A THC fraction was eluted using 100 ml of a mixture of DCM:petroleum ether (20:80) followed by the elution of polar fraction with 100 ml of DCM:methanol (50:50). The THC fraction was further concentrated to 10 ml using a rotary evaporator.

Internal standards 2.5 µl of the internal standard solution (5 mg/5 ml of *p*-terphenyl and 5 mg/5 ml of *n*-heptadecylcyclohexane) were spiked into a 500 µl aliquot of the THC fraction and transferred to 2 ml Gas Chromatography (GC) vial. The sample aliquot was then analysed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) in order to determine their biomarker maturity values and to rank biodegradation degree according to the Peters and Moldowan (1993) scale.

2.3.3   Isolation of Aliphatic and Aromatic Hydrocarbon Fractions

Aliphatic and aromatic hydrocarbon fractions were separated from their total hydrocarbon fraction (THC) using the silver ion solid phase extraction (Ag-SPE) method adopted from Bennett and Larter (2000). A 3 ml silver nitrate-silica column was first conditioned with 2 ml hexane by pipetting the hexane onto the top of the cartridge followed by a gentle air flush to dry the column using 10 ml plastic syringe and adapter.

The THC sample (100 µl) was applied to the top of the column followed by a gentle positive pressure to allow sample to sorb to silica. The aliphatic fraction was eluted by washing the sample from the inside wall of the cartridge on to the silica with 0.25 ml

hexane using a Pasteur pipette. This step was further repeated three times (0.25 ml x 4 times) to ensure all the samples were washed on to the column and were collected in a clean 10 ml vial. A final air flush was applied to the column in order to remove all the solvent from silica. Aromatic hydrocarbon fractions were eluted with 4 ml DCM using Pasteur pipette followed by applying a gentle pressure to force the solvent through silica to a clean 10 ml vial. The fractions were then evaporated to 1 ml for aliphatic and 0.5 ml for aromatic hydrocarbon fraction under a gentle nitrogen stream. Finally, each fraction was transferred into a 2 ml GC vial for GC and GC-MS analysis.

2.4 Gas Chromatography (GC) / Gas Chromatography Mass Spectrometry (GC-MS)

2.4.1 *Gas Chromatography (GC)*

Gas chromatography analysis of the total hydrocarbon (THC), aliphatic hydrocarbon, aromatic hydrocarbon fractions and carboxylic acid methyl esters were performed on Hewlett Packard 5890 instrument equipped with a split/splitless injector and flame ionization detector (FID). A 1 µl aliquot of the sample dissolved in DCM was injected by a HP7673 autosampler. The separation was performed on a Hewlett Packard HP-5 phenylmethylsilicone coated fused silica capillary column (30 m x 0.25 mm i.d; and film thickness, 0.25 µm). The oven temperature was held at 50 °C for 2 minutes and was then programmed at 4 °C/min and up to 300 °C where it was held for 20 minutes. The carrier gas used was hydrogen. The data were processed using a PC-based, LabSystem Atlas data system.

2.4.2 *Gas Chromatography-Mass Spectrometry (GC-MS)*

Gas chromatography-mass spectrometry of total hydrocarbon (THC), aliphatic hydrocarbon, aromatic hydrocarbon fractions and carboxylic acid methyl esters were performed on a HP 6890-5973 GC-MS system in full scan or selected ion (SIM) mode (with ions m/z 177, 191, 217, 218, 91, 105, 142, 156, 184, 178 and 192). The chromatographic conditions used were for the GC analyses, except that helium was used

as the carrier gas. Data were acquired and processed using PC based Agilent ChemStation software.

2.5 Total Acid Number Development and Validation

2.5.1 Total Acid Number Method Development

The Total Acid Number (TAN) values for crude oils, bitumens, asphaltenes and maltenes samples were obtained separately according to the ASTM D664 standard method (or a modification of this method – see later). This is a standard test method for the determination of the acid number of petroleum products by potentiometric titration. The total acid number, according to ASTM D664 (2009), is the quantity of base, expressed as milligrams of potassium hydroxide (KOH) per gram of sample required to titrate sample in a specific solvent to a specified end point. Acid number is measured according to the following formula:

$$\textbf{TAN}\ (\text{mgKOH/g sample}): \frac{(A - B)\ \text{x}\ M\ \text{x}\ 56.1}{W}$$

Where,

A   : volume of alcoholic KOH solution used to titrate sample to end point, (ml)

B   : volume corresponding to A for blank titration, (ml)

M   : concentration of alcoholic KOH solution, (mol/ml)

W   : sample mass, (g)

Figure 2.5 The Metrohm 848 Titrino Plus titrator

The TAN measurement procedure was begun with the preparation of electrode system. The electrode used in this measurement was a Metrohm Solvotrode containing 0.4 mol/L tertraethylammonium bromide (TEABr) in ethylene glycol solution acting as the electrolyte. The electrolyte was refilled once a week to the designated level before performing any titration. The electrode was conditioned in distilled water for 5 min and was carefully wiped with wet tissue paper to remove any excess water.

For the preparation of the samples, approximately 1 g of crude oils and maltene samples were dissolved in 35 mL of a toluene:isopropanol:water, (500:495:5) solvent mixture. However for asphaltenes and for heavy oil and extract samples, approximately 100 mg aliquots of sample were used with a slightly different solvent ratio. In order to enhance the pre-dilution process of this low-solubility material, 10 mL of extra toluene was added to the samples which were then ultrasonicated for 10 minutes to ensure complete dissolution of the sample (i.e. asphaltenes) insolvent before the titration was performed. The mixture of asphaltene-solvent was then added to the 25 mL of a mixture of toluene:iso-propanol:water (500:495:5), and thus a new ratio of (643:353:4) solvent was achieved. The TAN titration for each sample was started with the determination of blank values. The blank sample used was the same mixture of solvent ratio i.e., 35 ml of toluene:iso-propanol:water, (500:495:5) and (643:353:4) for asphaltene. It was then followed by calibration using standard solutions of 0.1 M HCl which gave TAN values of 1, 5 and 10 respectively. Without further delay, the sample was then titrated using the automatic Metrohm 848 Tritrino Plus analyser until the graph reached the end point

(EP). Selected samples were repeated for three times to assess the repeatability of the method. Details of the procedure for the TAN analysis are given in the ASTM D664 method description.

2.5.2 Calibration

The calibration analysis was performed using standard solutions, where 0.1 M HCL (0.179 mL, 0.895 mL and 1.79 mL) was used to make up three different acid concentrations in the 35 mL of toluene:iso-propanol:water (500:495:5) solvent, used and which gave TAN values of 1, 5 and 10, respectively.

2.5.3 Spiking Method

Two spiking solutions of stearic acid ($C_{17}H_{35}COOH$) and benzoic acid (C_6H_5COOH) were also used to test and improve the method. These solutions were prepared separately by dissolving the acids in the organic solvent toluene:iso-pranol:water mixture (500:495:5) to a concentration of 0.02 M. Before the titration took place, 1 ml of the solution was spiked separately to three selected oil samples (~1 g). The full acid spiking method was previously described by (Fan and Buckley, 2007) in order to induce a clear endpoint.

Preparation of electrode system
•refill the electrolyte
•preconditioning electrode in organic solvent + deionised water (~10-15 min)
•calibration

Preparation of organic solvent
•mixture of toluene:IPA:water
•crude oils & maltenes = (500:495:5)
•asphaltenes & bitumen = (643:353:4)

Preparation of sample
•crude oils & maltenes = ~1 g
•asphaltenes = ~100 mg
•sonicate the sample + organic solvent (5-10 min) with heat 50-60 °C

Titration of sample
•perform a blank titration
•perform a titration for sample until reach a clear EP

Cleaning the electrode between titration
•clean with toluene wet paper
•clean with organic solvent wet paper
•immerse in deionised water (~5 min)

Figure 2.6 The workflow summary of TAN measurement

2.6 Carboxylic Acid Separation

2.6.1 *SAX-SPE nonaqueous ion-exchange method*

Carboxylic acid fraction separation of selected crude oils, oil fractions, core extracts and tar sand was achieved by using an amended acid separation procedure of non-aqueous ion-exchange method (Jones et al., 2001) developed for highly degraded oil and tar sand. An 6 ml SAX quaternary amine solid phase extraction (SPE) column

(International Sorbent Technology, UK) was initially conditioned using 10 ml of hexane and followed by 10 ml of hexane:DCM mixture (1:1) under gravity flow. The column was then dried with air flush using syringe and adapter.

The oil sample (100 mg for degraded oil and 200 mg for undegraded oil) was spiked with 10 µl of the recovery standard (1 mg/ml of 5β cholanic acid) before being applied to the top of the column. The interferents were removed by successive elution with 20 ml of a mixture of hexane: DCM (1:1) followed by 25 ml DCM. The acids fraction was eluted with 50 ml of 2% (by volume) formic acid in diethyl ether in round bottom flask. The acid extract was concentrated by rotary evaporation down to 1 ml and dried under gentle nitrogen stream until all the formic acid has completely evaporated. This fraction was then methylated using boron trifluoride-methanol (BF$_3$-methanol) for an hour in a 60 °C oven. After cooling to room temperature, the methylated acid fraction was washed by transferring to a 100 ml Quick-Fit test tube and then adding a total of 3 ml of petroleum ether and 10 ml of distilled water. The test tube was then shaken vigorously for 20 seconds and left to equilibrate for 10 minutes. This extraction step was repeated with 3 ml of petroleum ether for three times. The organic layer at the top that contained the methylated acids was pipetted to a clean 10 ml vial and was then evaporated down to dryness under nitrogen gas.

A 6 ml silica column was conditioned with 5 ml hexane followed by air flushing in order to dry the column. A total of 4ml of hexane was prepared to elute the sample. About 0.5 ml from corresponding hexane 4 ml) was used to dissolve the sample followed by sonication (~5 min) .After loading the dissolved sample onto the SPE column, these steps were repeated another two times and the remaining 2.5 ml of hexane was used to remove any residual n-alkanes in the column. The methylated acids were eluted with a mixture of hexane: DCM (3:7) solvent. Finally, the methylated acid fraction was evaporated under a gentle nitrogen gas stream to a smaller volume and transferred to a 2 ml glass vial with a 200 µl insert containing 5 µl of the internal standard solution (2 mgml^{-1} of methyl ester of 1-phenyl-1-cyclohexane carboxylic acid). Each of the samples was analysed in duplicate to assess the repeatability of the method. Blank samples were also analysed to assess any contamination. Finally, the methylated acid fractions were analysed by GC and GC-MS (refer to Sections 2.4.1 and 2.4.2).

2.7 Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS)

2.7.1 FT-ICR MS *Analysis*

An investigation of types of NSO heteroatomic species contained in selected samples i.e., oils, maltene and asphaltene fractions was performed using an FT-ICR mass spectrometer operated in negative ion electrospray ionisation mode. The analysis of samples was done by colleagues in Department of Geoscience, Faculty of Science, University of Calgary, Canada. Details on the experimental procedures, mass calibration and data analysis are describe elsewhere i.e Qian et al. (2001a); Muller et al. (2009); Mapolelo et al. (2011); Klein et al. (2006c). The data processing was done by using the Calgary group's own Ragnarök software.
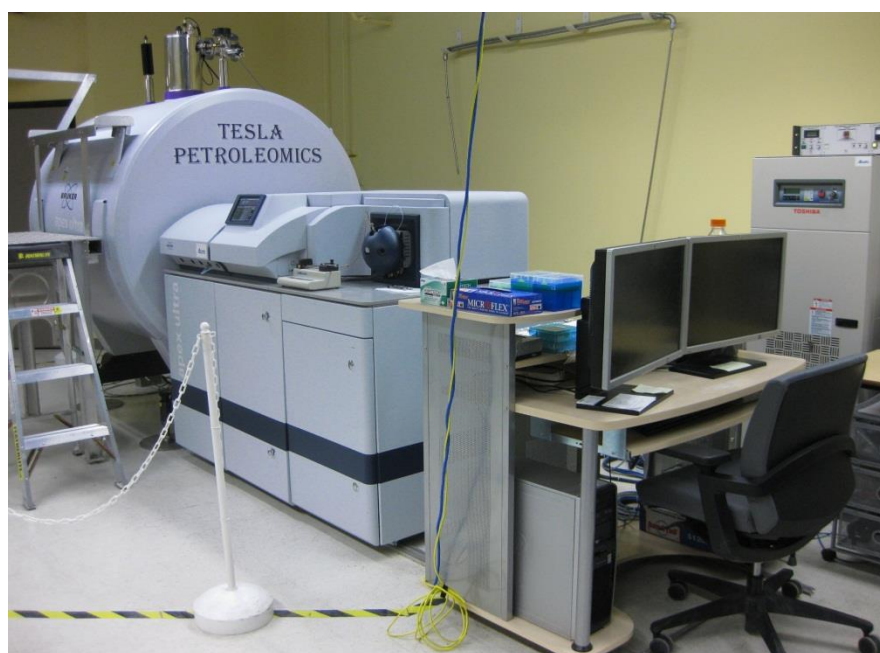
Figure 2.7 The Calgary 12T Bruker FT-ICR- MS instrument

2.8   Fourier Transform Infra-Red Spectroscopy (FTIR)

2.8.1   Single Bounce ATR- FTIR (SMART Orbit) and Multi Bounce ATR-FTIR (SMART ARK)

The FTIR analyses of selected crude oils, bitumen, core extracts samples together with their asphaltene and maltene fractions, were performed on ThermoNicolet 6700 FTIR spectrometer equipped with Smart Orbit (single bounce) and Smart ARK (multi bounce) attenuated total reflectance (ATR) accessories. Briefly, after the ATR crystal had been cleaned and background spectra has been collected, an oil sample was poured onto the crystal surface (no sample preparation involved) where a diamond ATR "Smart Orbit" and ZnSe crystal horizontal attenuated total reflection (HATR) trough plate "Smart ARK" was used (figure 2.8a-b). The average spectrum was acquired from 32 scans ranging over 525 to 4000 cm^{-1} wave numbers for Smart Orbit and from 600 to 4000 cm^{-1} for Smart ARK.

(a)   (b)

Figure 2.8 The Smart Orbit (single bounce) ATR accessory, **(b),** The Smart ARK (multi bounce) HATR accessory

For solid samples (asphaltenes), approximately 5-10 mg of sample was first dissolved in toluene (~100 ul) before being applied onto the top of the crystal and was left to dry for 15-20 min. The spectrum was recorded once the solvent has fully evaporated. Each sample was prepared and data collected three times in order to measure the reproducibility of the analyses. The spectra were collected in absorbance mode while, the data treatment and interpretation (i.e. spectra baseline correction, normalisation, main IR band identification) were determined using ThermoScientific OMNIC software.

CHAPTER 3

HYDROCARBON ANALYSES

Chapter 3: Hydrocarbon Analyses

3.1   Introduction

The distributions of biological markers such as isoprenoids, hopanes, steranes and aromatic steroids and geochemical markers that are not biomarkers such as *n*-alkanes and many aromatic hydrocarbons in crude oils can provide information on the origins of the organic matter in their source rocks, the environmental conditions during their deposition, burial (diagenesis) and thermal maturity (catagenesis), the degree of biodegradation, some aspect of source rock mineralogy (lithology) and the age (Peters et al., 2005). Examples of the structures of some of these types of compounds are shown in Figure 3.1. The steranes are an example of a class of biomarkers that can be used to provide information on a number of the processes mentioned above. In thermal maturity studies, it is seen that the 20R 5α(H),14α(H),17α(H) steranes usually dominate in immature bitumens because they represent the configurations inherited from the precursor sterols, while throughout the early part of the oil window the relative abundance of isosteranes increases. Thus the ratio 5α(H),14β(H),17β(H) to 5α(H),14α(H),17α(H) steranes can be used as a maturity parameter (Peters et al., 2005).

Hopane   Sterane

Biomarker compounds

Pristane   Phytane

Naphthalene   R: 1-Methyl or Ethyl   Phenanthrene
                           Naphthalene   R= 1-Methyl
                                                                                        Phenanthrene

Non-biomarker compounds
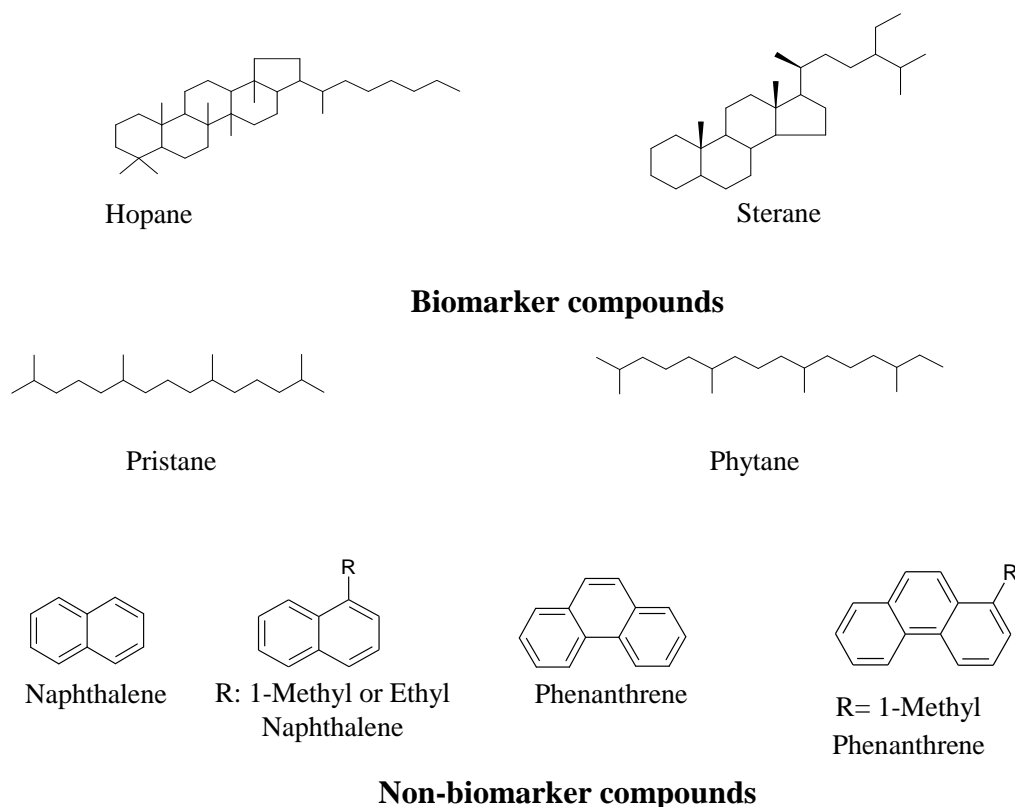
Figure 3.1 Figures showing some common hydrocarbon biomarker and non-biomarker compounds found in crude oil

Analysis of degree of biodegradation of crude oils can be performed by comparing the relative abundances of biomarker and non-biomarker components in them, as they are known to depleted in a "quasi stepwise" manner, due to the some compounds being more easily attacked by bacteria than others (Peters et al., 2005).

Biodegradation as described in previous chapter (Chapter 1) is secondary alteration of oils which is a process of microorganism altering the composition of light crude oil into a heavy crude oils. Table 3.1 shows the extent of destruction of compound class with their corresponding level of biodegradation classified by (Peters and Moldowan, 1993).

Extent of Destruction of Compound Class	Biodegradation Level	
No alteration	0	Undegraded
Lower homologs of *n*-paraffins depleted	1	Light
General depletion of *n*-paraffins	2	Light
Only traces of *n*-paraffins remain	3	Light
No *n*-paraffins, acyclic isoprenoids intact	4	Moderate
Acyclic isoprenoids absent	5	Moderate
Steranes partly degraded	6	Heavy
Sterane degraded, diasterane intact	7	Heavy
Hopanes partly degraded	8	Very heavy
Hopanes absent, diasteranes attacked	9	Very heavy
C26-C29 aromatic steroids attacked	10	Severe

Table 3.1 Biodegradation ranking of typical mature oil from Peters and Moldowan (1993)

The aims of this section of study are:

I.   To characterise gross composition of Saturates, Aromatic, Resin and Asphaltene (SARA) fractions in the crude oils, bitumen and core extract samples used in this study.

II. Assess the source depositional environment, thermal maturity and degree of biodegradation of the crude oil samples set using series of biological and non-biological markers (i.e. hopanes, steranes, aromatic steroids, isoprenoids, *n*-alkanes, aromatic hydrocarbons).

3.2 Results

3.2.1 *Gross composition Analysis (SARA)*

The distribution of saturates, aromatics, resins and asphaltenes (SARA) in the samples was measured using Iatroscan TLC-FID. The samples analysed comprised of over 60 crude oils (Set 1) and core extracts (Set 2) from various locations around the world, with various degrees of biodegradation and thermal maturity and the data is shown in Table 3.2 (a-b).
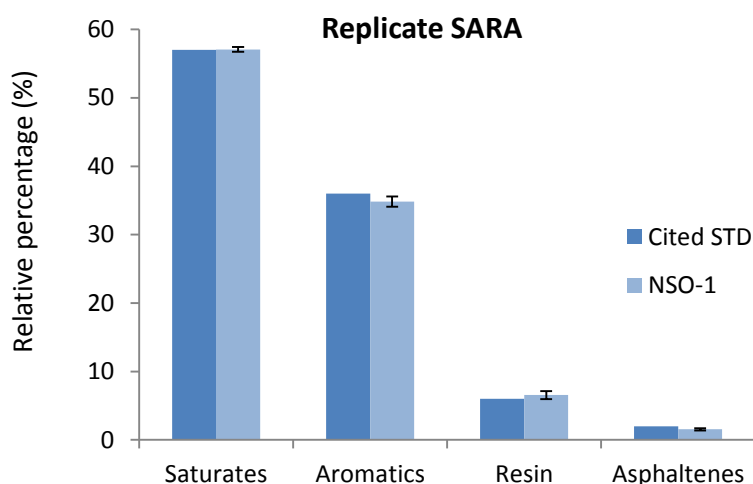
Figure 3.2 Comparison of cited (NIGOGA, 2000) SARA percentages of standard NSO-1 oil vs replicate analysis for NSO-1 in this study using Iatroscan TLC-FID technique

A replicate SARA analysis of the Norwegian Petroleum Directorate standard oil NSO-1 was performed in order to assess the accuracy and reproducibility of the Iatroscan TLC-FID analysis used in this work. As shown in Figure 3.2, the separation and quantification of complex mixture into saturates, aromatics, resins and asphaltenes fractions was accurate and had small standard errors (of 0.35, 0.77, 0.57 and 0.16, respectively).

Analysis of oils from Set 1 (Table 3.2a) using Iatroscan shows that the composition of total hydrocarbons (saturates and aromatics) of the oils is highly variable. The percentage of saturated hydrocarbons varies from about 14 to 70%, aromatic hydrocarbons from about 23 to 51%, resins from 5 to 30% and asphaltenes vary from approximately < 0.5 to 21%. Figure 3.3a shows the distribution of fractions in the crude oil samples from various origins (Set 1). Due to the samples wide variations in their properties and origins, the distribution of their compositions appear quite scattered. Oil samples from the same origin such as California and Italy however plot close to each other. This may indicate that these oils experience the similar physical and chemical properties or extents of alteration such as alteration by biodegradation, thermal maturity, reservoir mixing, etc.

Iatroscan analysis of core extracts from Set 2 (Table 3.2b) show that total hydrocarbons (saturated and aromatics) are the most abundant species (> 50%) in the total fractions. The saturated hydrocarbons in this set however shows a generally lower percentage than those in the oils and ranges from 10% to 33%, but were more highly enriched in aromatic fractions (ranging about 31 to 58%). The remaining fractions vary from 17 to 29% for asphaltenes and 10 to 20% for resins. The ternary diagram of saturates, aromatics and resin plus asphaltene fractions for the core extract samples (Set 2) is shown in Figure 3.3b. The core extracts samples are from 5 cores SSA, SSB, SSC, GAMM and INN, all from Canada except for the GAMM samples which are from China. The ternary diagrams show a very clear trend among 5 different core families where the samples from each core family plot close to each other. In general, the entire group seems to have a similar distribution which is located towards the bottom right of the ternary diagram showing compositions low in saturates and high in aromatic hydrocarbon fractions. Aromatic hydrocarbons are major components of the crude oils, which have been reported to represent typically from about 20 to 45% of the total hydrocarbons (Tissot and Welte, 1978). The GAMM core samples are distributed far from others at the middle of the diagram, corresponding to higher proportions of saturated hydrocarbon fractions which reach up to 33%.

SAMPLE	AVERAGE (%)			
	Sats	Aros	NSO	Asph
EN 149	28	51	15	6
EN 151	30	50	15	5
EN 154	37	42	13	8
EN 158	29	42	18	11
EN 168	24	49	18	9
EN 169	24	51	13	12
EN 174	37	45	13	5
H7	28	44	18	10
D13	27	43	18	11
BOSCAN	16	48	18	18
HEIDRUN	43	44	11	1
Cold Lake	25	32	30	14
Lloyminster	29	45	15	11
Douk Daka	44	23	20	13
TRY	36	37	17	10
SPY	35	39	19	7
BB#1	34	35	13	18
BB#2	34	39	16	11
BB#3	28	39	19	14
BB#4	24	44	14	19
BB#5	15	53	18	13
BB#6	31	48	16	4
BB#7	70	23	5	2
BB#8	21	49	19	11
BB#9	26	43	13	18
BB#10	14	46	20	21
BB#11	30	49	15	6
BB#12	26	35	19	20
BB#13	27	43	15	15
BB#14	14	51	18	17
BB#15	24	44	17	15
BB#17	34	48	11	6
BB#18	56	39	5	0
BB#19	35	39	15	11
BB#20	50	42	6	1
BB#21	25	47	13	15
BB#22	53	41	6	1
BB#23	32	46	13	9
BB#24	31	46	14	9
BB#25	36	46	12	6
BB#26	38	44	11	7
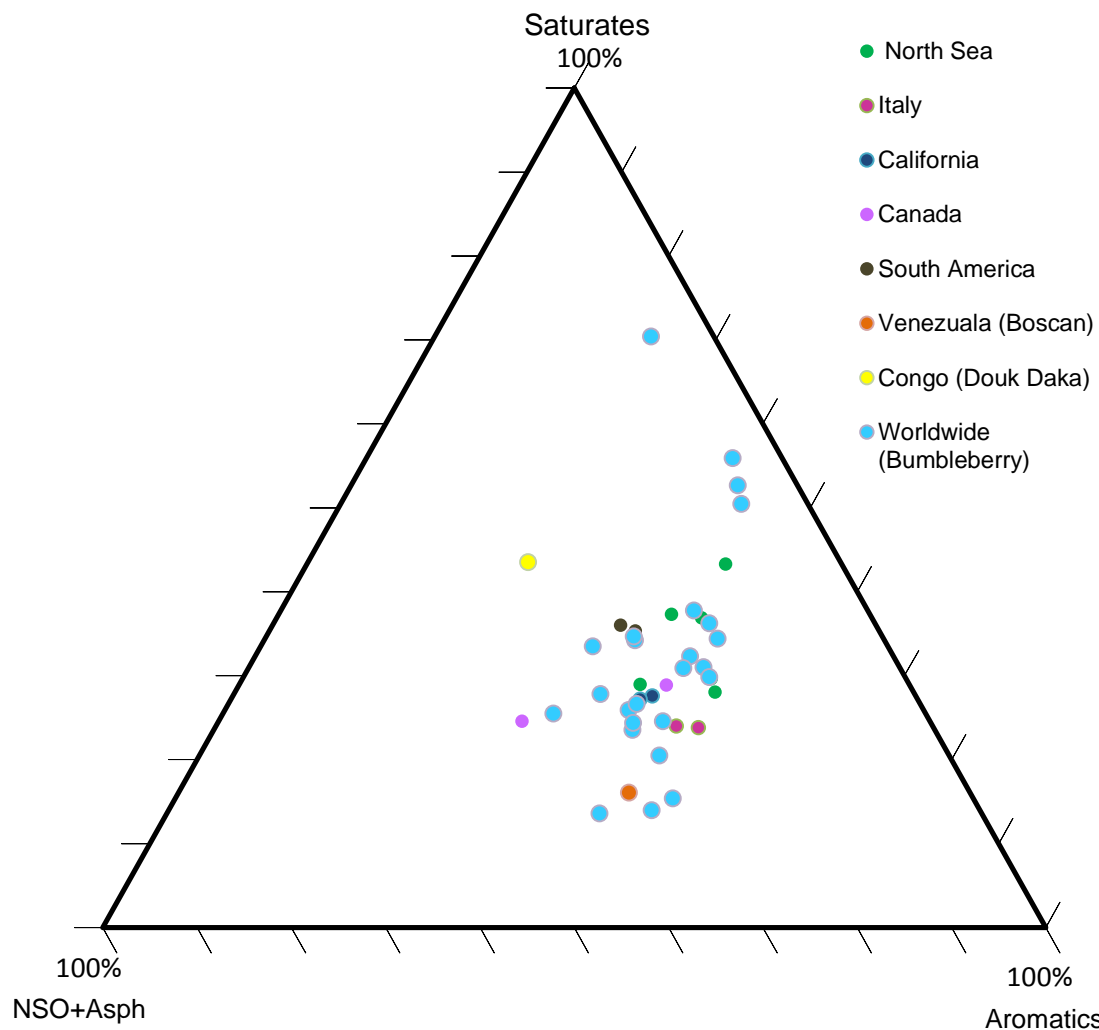
Table 3.2a Saturates, Aromatics, Resins and Asphaltene fractions by Iatroscan TLC-FID analysis for Set 1 (oils)

Figure 3.3a Ternary diagram of Saturates, Aromatics and Resin+ Asphaltene fractions by Iatroscan TLC-FID analysis for Set 1 (Oils)

SAMPLE	AVERAGE (%)			
	Sats	Aros	NSO	Asphlt
SSA#2	13	54	19	13
SSA#5	15	53	20	13
SSB#7	14	56	19	11
SSB#8	16	56	18	10
SSB#9	14	53	20	13
SSB#10	13	51	23	13
SSB#12	14	52	21	12
SSB#13	14	53	21	12
SSB#14	15	54	20	10
SSB#16	13	54	21	12
SSC#17	14	55	19	11
SSC#18	13	55	20	12
SSC#19	14	54	20	13
SSC#20	12	53	22	13
SSC#21	12	50	23	15
GAMM#23	24	36	26	15
GAMM#25	25	31	29	16
GAMM#31	33	32	19	16
GAMM#32	31	33	19	18
GAMM#33	30	35	19	17
INN#38	13	58	18	11
INN#39	13	57	17	13
INN#40	11	55	17	17
INN#41	11	54	17	17
INN#42	10	53	18	20
INN#43	11	54	19	16

Figure 3.3b Ternary diagram of Saturates, Aromatics and Resin + Asphaltene fractions by Iatroscan TLC-FID analysis for Set 2 (Core extracts)

Table 3.2b Saturates, Aromatics ,Resins and Asphaltene fractions by Iatroscan TLC-FID analysis for Set 2 (core extracts)

3.2.2 *Hydrocarbon biodegradation Assessment*

A total hydrocarbon (non-polar) fraction from 12 oil samples from the North Sea, Italy, California and Venezuela were analysed using GC-FID and GC-MS (SIM) (m/z = 57,85,91,128,142,156,170,178,191,192,217,218.) Their levels of biodegradation were then ranked according to the scheme of Peters and Moldowan (1993). The oil samples from Italy (EN 168 & EN 169) were undegraded to slightly degraded (PM=0-1) with a complete n-alkane envelopes in sample EN 168 showing that this oil is unaltered by microorganism whereas sample EN 169 experience a general depletion of *n*-alkanes.

The North Sea oils (NSO-1, Heidrun, EN 149, EN 154, EN 158, EN 174 & EN 151) have undergone from light to severe degradation (PM=1-10). The least biodegraded oil samples (NSO-1, EN 154, EN 158) appear to be slightly degraded (PM=1), showing some alteration of lower homologs of *n*-alkanes. Figures 3.3(b) and (e) indicate that although both oils samples (EN 154, EN 158) show some degradation of their lower *n*-alkanes, the TIC chromatogram of sample EN 158 has an unresolved complex mixture (UCM) or hump, suggesting that this oil is likely to be mixed with a more highly degraded oil or oils. The addition of a secondary fresh oil charge, can often complicate the existing simple biodegradation ranking of crude oils systems i.e. Larter et al. (2012). The Heidrun sample shows light biodegradation level PM=2/3 with evidence of appearance of UCM suggesting a historical charge of oil that was highly degraded in the reservoir. Oil samples EN 174 and EN 149 underwent a moderate biodegradation, with PM level 4/5 and 5, respectively. At this stage, all *n*-alkanes have been removed while their acyclic isoprenoids compound are significantly depleted leaving a big UCM hump in their total hydrocarbon chromatograms. Oil sample EN 151 appears to have experienced severe degradation of PM=10, with a large UMC and removal of *n*-alkanes, acyclic isoprenoids, steranes, diasteranes, hopanes and even their C_{26}-C_{29} aromatic steroids .

EN 158
(PM= 1,light)
(e)

Heidrun
(PM=2/3,light)
(f)

Boscan
(PM=2/3,light)
(g)

D13
(PM=4/5, Moderate)
(h)
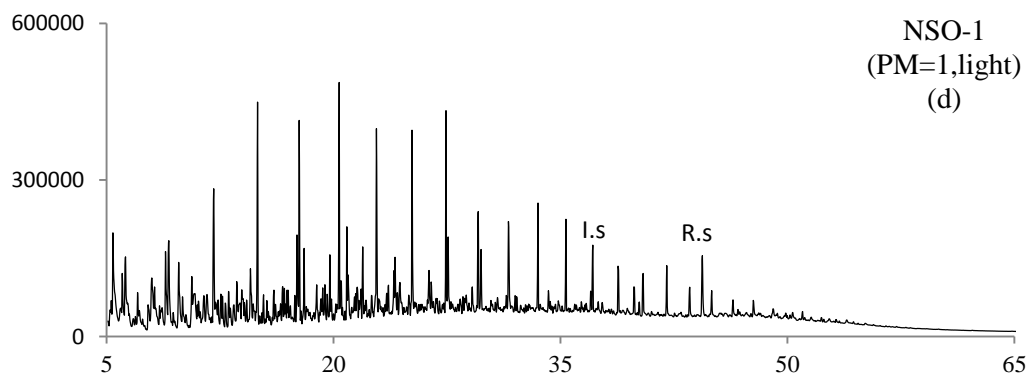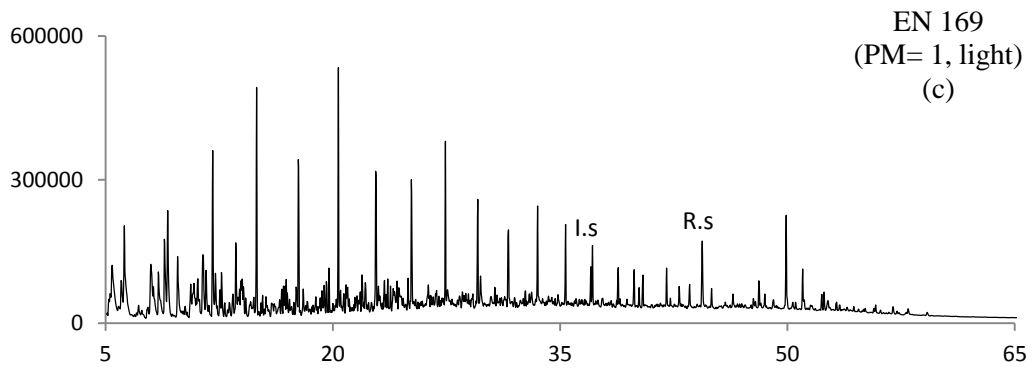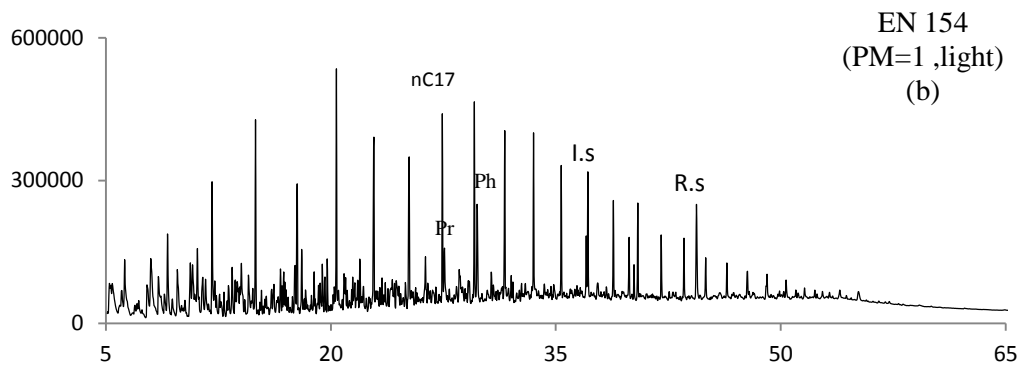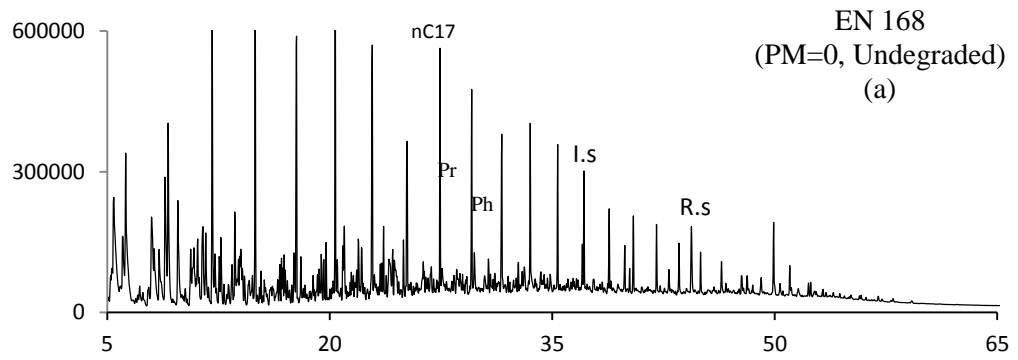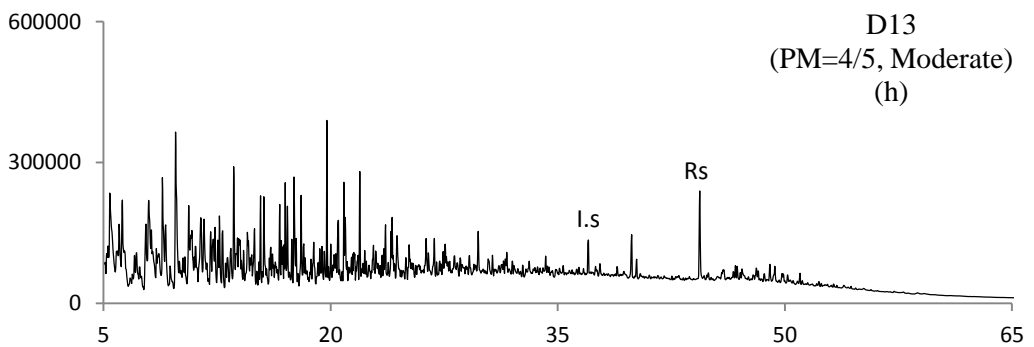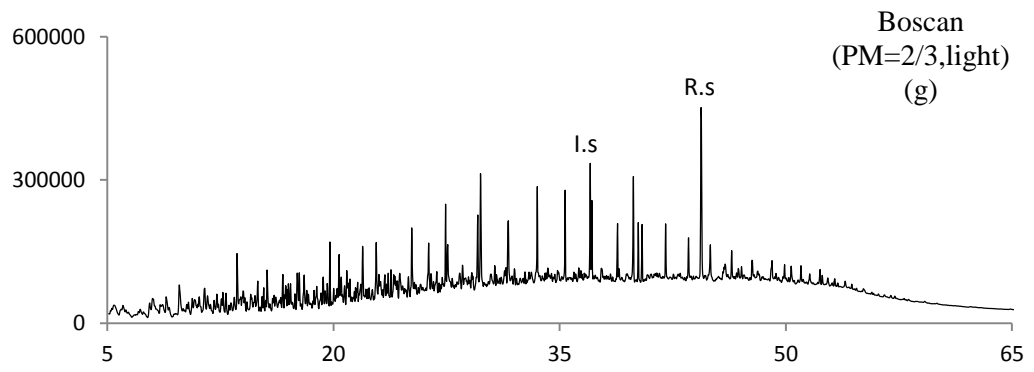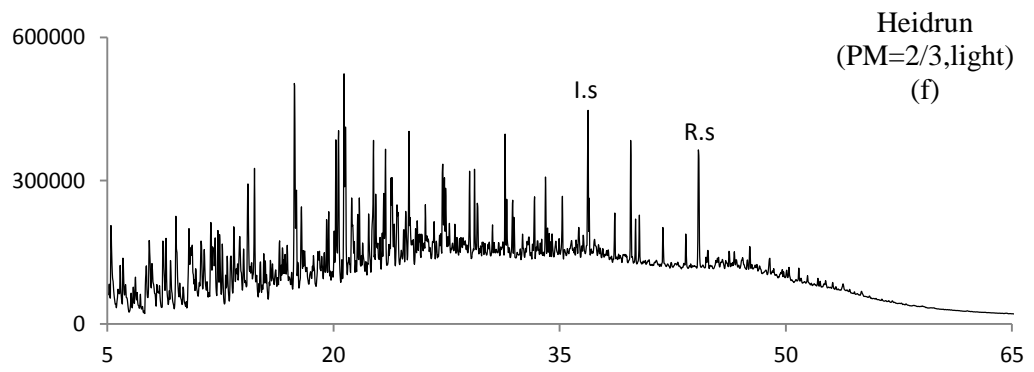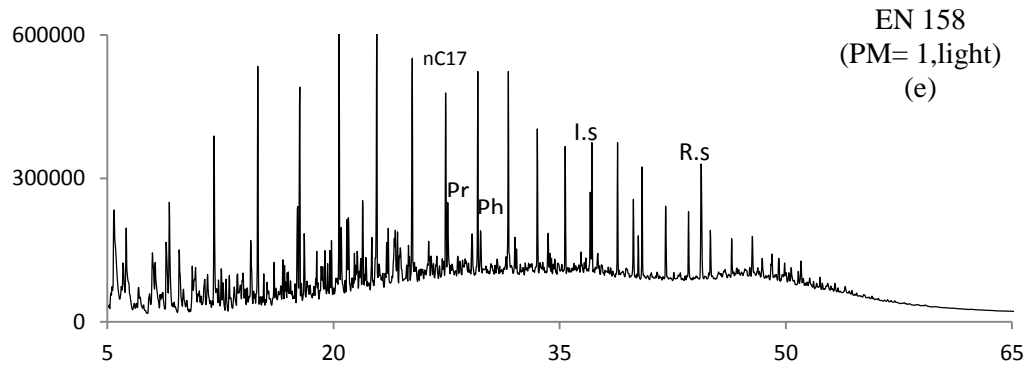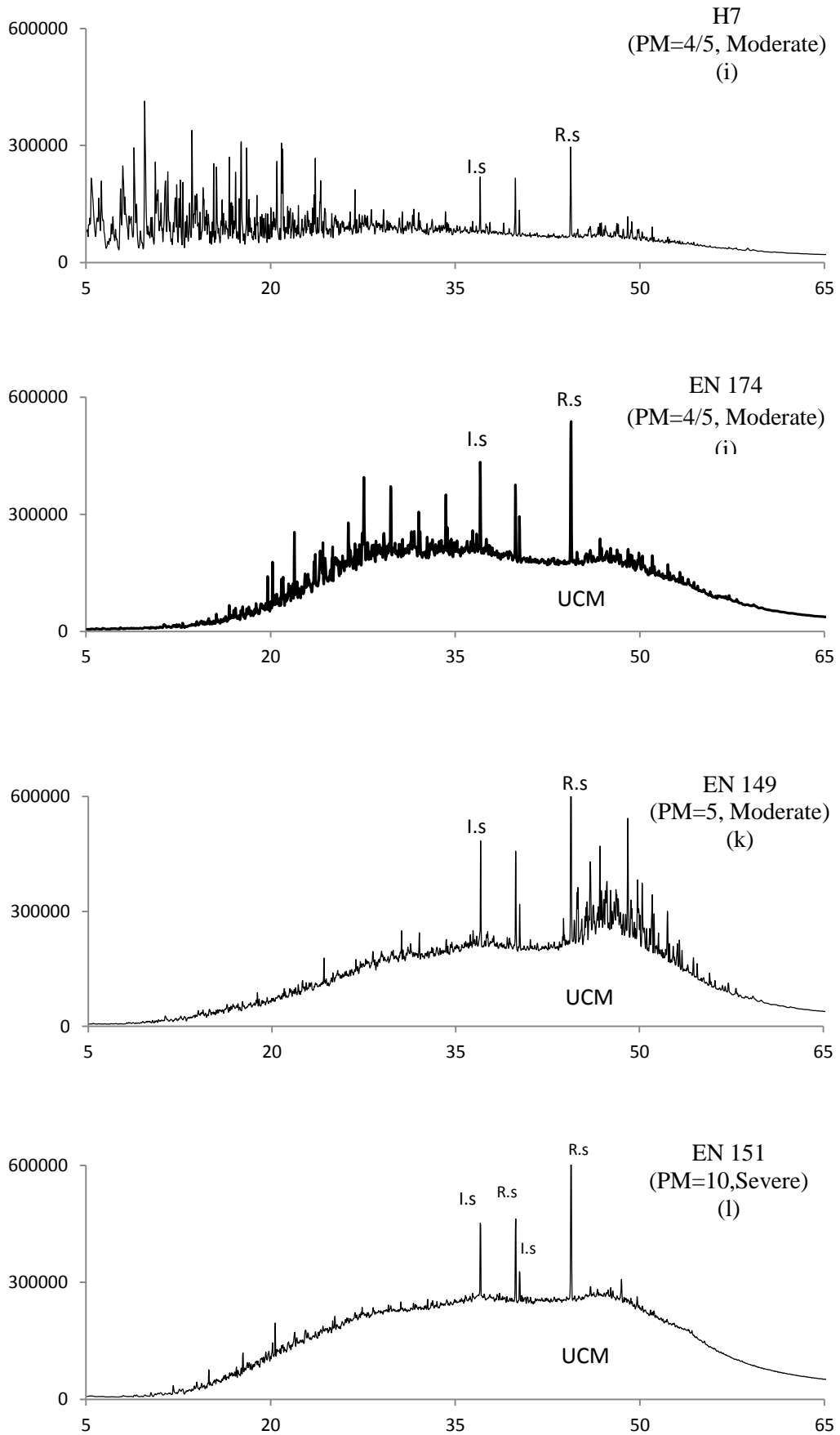
Figure 3.4 (a-l) Gas chromatograms (GC) of the total hydrocarbon fractions (non polar fraction) of oil samples. P.M=Peters and Moldowan (1993) level of biodegradation. I.S= Internal standard, R.S=Recovery standard, Pr=Pristane, Ph=Phytane.

The Californian oils D13 and H7 experienced moderate biodegradation (PM=4/5). Unlike the other oils similar level of moderate biodegradation, the acyclic isoprenoid compound class in both Californian oils were severely depleted, but the front end of gas chromatograms show traces of low molecular weight materials .The similar observation has been observed in the H7 oil sample by Taylor et al. (2001) who suggested that the addition of such non-degraded, low molecular weight material might due to fresh hydrocarbon migration into the reservoir.

The oil sample from Venezuela, (Boscan) has undergone light biodegradation with PM level of 2/3, though the presence of UMC in its chromatogram suggests that this oil is possibly mixed with more heavy degraded oil. The following figures show the example biomarker mass chromatograms: Figure 3.4 sterane (a), hopane (b), aromatic steroids (c), respectively, and non-biomarker mass chromatograms: Figure 3.5(a-c) naphthalenes and Figure 3.6(a-b) phenanthrenes, that were used.
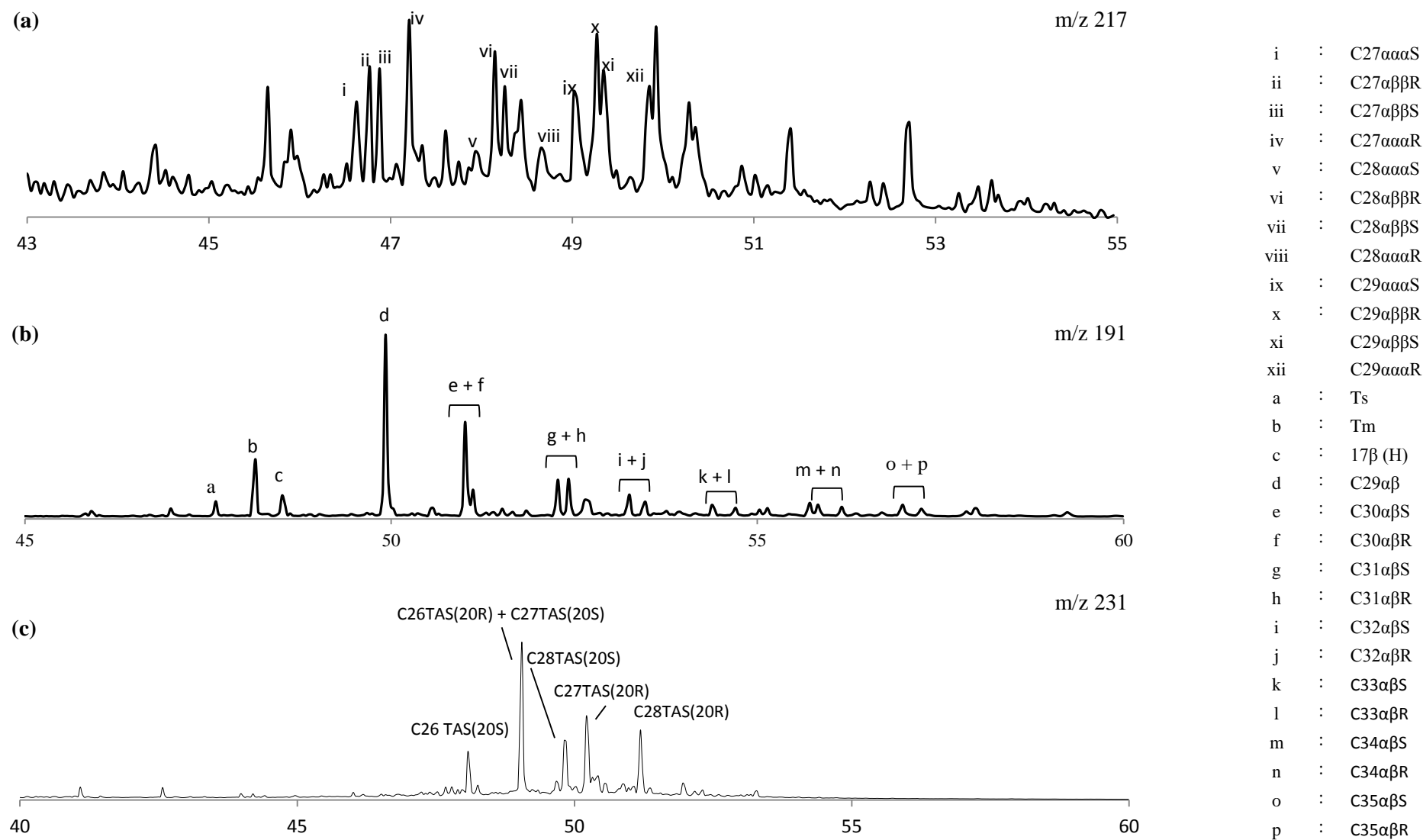
Figure 3.5 Mass chromatograms (m/z 217, 191, 231) displaying the distributions of steranes (a), hopanes (b) and aromatic steroids (c) in an undegraded oil (EN 168).
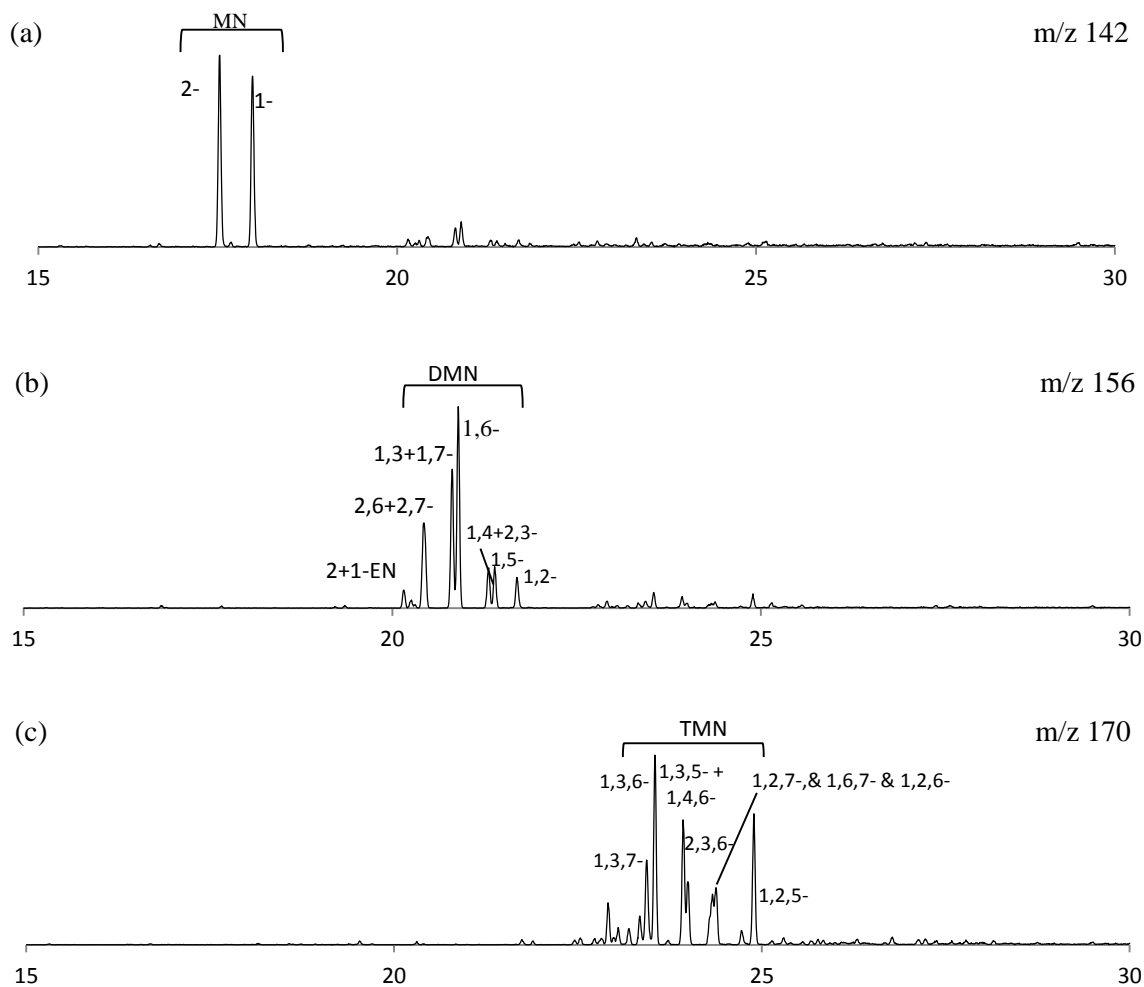
Figure 3.6 Mass chromatograms (m/z 142, 156, 170) displaying the distribution of methylnaphthalenes (a), ethyl &dimethyl naphthalenes (b), trimethylnaphthalenes (c) in undegraded oil (EN 168)
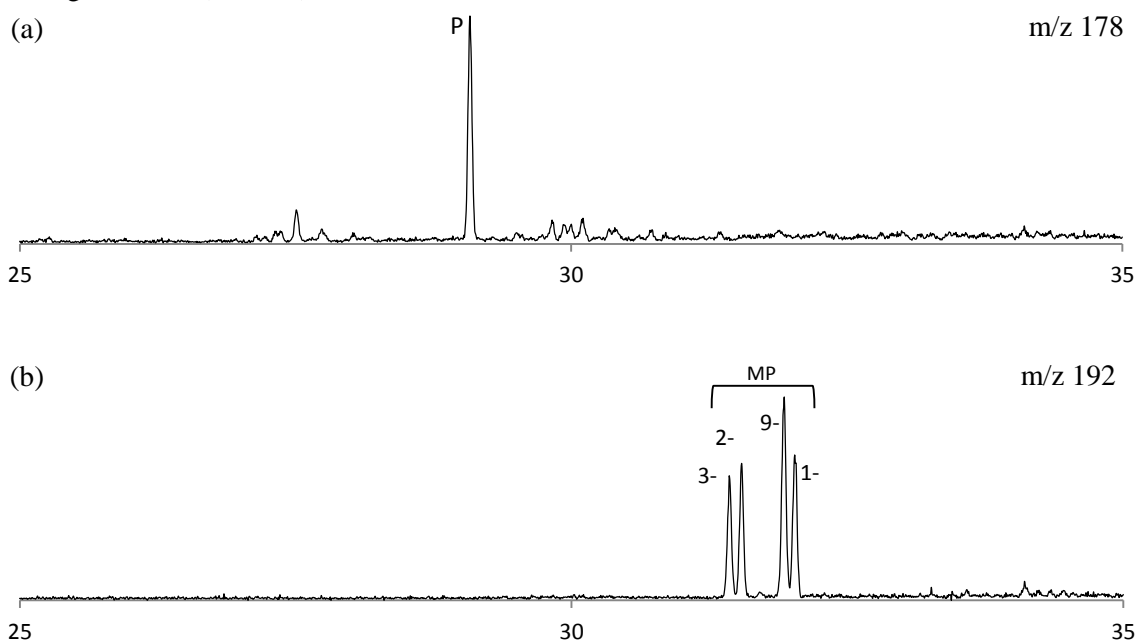
Figure 3.7 Mass chromatograms (m/z 178, 192) displaying the distribution phenanthrene (a) and methylphenanthrenes (b) in undegraded oil (EN 168)

SAMPLE	ORIGIN	NON-BIOMARKER MATURITY PARAMETER												BIOMARKER MATURITY PARAMETER				
		Pr/Ph	Pr/nC17	Ph/nC18	CPI	OEP(1)	OEP(2)	MPI-1	MPI-2	MPR	MNR	ENR	DNR-1	C31αβ(22S)/	C30βα/ C30αβ	Ts/ Tm	C29 20S/(20S +20R)	C29αββ/ (αββ(
EN 149	North sea	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.9	0.57	0.40	0.14	0.76	0.47	0.34
EN 151	North Sea	n.d	n.d	n.d	n.d	n.d	n.d	0.41	0.4	0.59	1.36	2	4.08	n.d	n.d	n.d	n.d	n.d
EN 174	North Sea	0.81	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.67	2	1.97	0.42	0.11	1.08	0.5	0.51
NSO-1	North Sea	1.21	0.47	0.5	0.28	0.97	1.03	0.58	0.6	0.91	1.14	1.6	3.75	0.44	0.10	1.11	0.55	0.48
HEIDRUN (1)	North sea	1.05	0.78	0.75	0.36	0.98	0.87	0.66	0.69	1.12	2.41	2.4	5.03	0.44	0.14	1.27	0.46	0.56
HEIDRUN (2)	North sea	1.12	0.78	0.79	0.37	0.93	0.92	0.62	0.61	0.98	2.45	2.4	5.58	0.43	0.15	1.45	0.47	0.55
HEIDRUN (2)	North sea	1.19	0.85	0.8	0.36	0.95	0.99	0.63	0.62	0.98	2.47	2.3	4.83	0.45	0.16	1.49	0.5	0.52
EN 154	North Sea	0.47	0.31	0.65	0.35	0.9	0.84	0.48	0.48	1.1	0.77	1.5	1.52	0.40	0.07	0.44	0.51	0.48
EN 158	North Sea	1.35	0.35	0.27	0.31	1.04	1.04	0.72	0.84	1.13	1.48	1.7	4.9	0.42	0.15	0.79	0.58	0.41
EN 168	Italy	0.59	0.14	0.27	0.31	0.99	0.92	0.8	0.94	1.24	1.07	2.5	2.91	0.50	0.08	0.24	0.49	0.5
EN 169	Italy	0.61	0.14	0.3	0.31	1	0.96	0.67	0.69	1.16	0.94	1.8	2.9	0.51	0.09	0.13	0.46	0.52
BOS(1)	Venezuela	0.41	0.76	1.78	0.35	0.92	0.95	0.78	0.75	1.25	1.09	2	2.96	0.38	0.11	0.19	0.49	0.47
BOS(2)	Venezuela	0.39	0.67	1.65	0.36	0.91	0.93	0.74	0.76	1.24	1.04	2.4	2.75	0.42	0.11	0.16	0.5	0.5
BOS(3)	Venezuela	0.39	0.83	1.66	0.4	0.95	0.87	0.77	0.77	1.28	1.03	1.6	3.51	0.42	0.10	0.17	0.5	0.49
H7	California	n.d	n.d	n.d	n.d	n.d	n.d	0.89	0.93	1.44	1.31	2.9	5.33	0.41	0.15	0.31	0.43	0.45
D13	California	0.81	2.32	n.d	n.d	n.d	n.d	0.89	0.99	1.61	1.26	2.1	5.67	0.37	0.13	0.57	0.46	0.43

Table 3.3 Biomarker biodegradation and thermal maturity parameters from (Peters et al., 2005). Note: Pr/Ph= pristine/phytane; Pr/nC17=pristane to n-C17 alkane ; Ph/nC18= phytane to n-C18 alkane; CPI=[(C25+C27+C29+C31+C33/C24+C26+C28+C30+C32)+(C25+C27+C29+C31+C33/C26+C28+C30+C32+C34)]/2 ; OEP(1)= (C21+6C23+C25)/ (4C22+4C24); OEO(2)= (C25+6C27+C29)/ (4C26+4C28); MPI-1= 1.5((2-MP+3-MP)/(P+1-MP+9-MP)); MPI-2= 3x(2MP)/(P+1MP+9MP); MPR= 2-MP/1-MP; MNR= 2MN/1MN; ENR=2EN/1EN; DNR-1= (2,6DMN+2,7DMN)/1,5-DMN; 22S/(22S+22R)Homohopane=C31αβ(22S)/ (22S+22R); Moretane/Hopane= C30βα/ (C30βα+C30αβ); 20S/(20S+20R)Sterane= C29ααα20S/(20S+20R); Bβ/(ββ+αα)isomerisation= C29αββ/(αββ+ααα).

3.2.3   *Hydrocarbon Thermal Maturation Assessment*

Maturity parameters measured using selected ion monitoring (SIM) gas chromatography mass spectrometry (GC-MS) from eleven oil samples from five different origins (North Sea, Italy, Venezuela and California) are listed in Table 3.3.

As thermal maturity increases, the *n*-paraffin envelope becomes displaced towards lower molecular weight homologues and the isoprenoid/n-paraffin ratio decreases (Peters and Moldowan, 1993). The North Sea (EN 154,EN 158, NSO-1, Heidrun), Italy (EN 168, EN 169) and Venezuela (Boscan) oil sets show that the ratios of Pr/nC_{17} and Ph/nC_{18} appear generally decreasing as maturity increases except samples EN 149, EN 174 and EN 151 from the North Sea and H7, D13 from California due to their ratios being unmeasurable. This was because they were affected by another process i.e. biodegradation (Peters et al., 2005). Excluding those highly biodegraded samples, the CPI ratio in the North Sea (EN 154, EN 158, NSO-1 and Heidrun), Italy (EN 168, EN 169) and Venezuela (Boscan) samples show unusually low value ranges from 0.28 to about 0.37, perhaps suggesting oils from carbonate source rocks or hypersaline environment (Peters and Moldowan, 1993), but this is unlikely for the North sea oils and their OEP-1 and OEP-2 ratios were about 1.0 suggesting mature marine sourced oils (Peters et al., 2005). The reason for the unsually low CPI values in these oils is uncertain, but perhaps removal of some *n*-alkanes has made other co-eluting compounds such as aromatic components normally present at much lower abundances than the n-alkanes, affect these parameters.

Aromatic hydrocarbon maturity parameters such as those based on methyl phenanthrenes (i.e. MPI-1, MP-2) and methyl naphthalenes, suggest that the North Sea oils are immature to early mature. Thermal maturity analysis was also done based on changes in the stereochemistry at chiral centres in steranes and hopanes such as the $C_{29}\alpha\alpha\alpha20S/(20S+20R)$ and $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ sterane parameters and $C_{31}\alpha\beta22S/(22S+22R)$ and $C_{30}\beta\alpha/(\beta\alpha+\alpha\beta)$ hopane and Ts/Tm ratios. The ratios of C_{31} $\alpha\beta$ 22S/(22S+22R) for the North Sea, Venezuela and Californian samples indicates exposure to very mild thermal stress (range 0.37 to 45), with the Italian oils barely having entered the oil generation window (range 0.5 to 0.51) which was consistent with the $C_{30}\beta\alpha/(\beta\alpha+\alpha\beta)$ hopane ratios, with low ratios of the less stable moretane to more stable hopane (ranging from 0.16 to 0.07). On the other hand, the North Sea oil set, except sample EN 149, had Ts/Tm ratios ranging from 1.08 to 1.49, suggesting high maturity oils, while other oil

sets generally contained Ts/Tm < 1, indicating low maturity, though source differences can affect this parameter (i.e. Peters et al., 2005). The $C_{29}20S/(20S+20R)$ sterane ratios for all samples show values (from 0.43 to 0.58) very close to, or having reached their thermal equilibrium ranges, while C_{29} $\beta\beta/(\beta\beta+\alpha\alpha)$ ratios (0.41-0.56) show the oils are close to or having entered the oil window, except oil sample EN 149 shows a low ratio possibly indicating slightly immaturity (Peters et al., 2005).

3.3   Summary of Hydrocarbon Analyses

Crude oil samples from the North Sea, Italy, California and Venezuela were analysed to determine their Saturates, Aromatics, Resin, Asphaltene (SARA) compositions, degree of biodegradation and thermal maturity. Bulk geochemical parameters together with biomarker and polycyclic aromatic compound distribution were utilised in an attempt to assess their thermal maturities.

The extent of biodegradation of the crude oils from the North Sea (NSO-1, Heidrun, EN 149, EN 174, EN 151) was highly variable ranging, from a light to severely degraded (PM level of 1 to 10) with oil samples (EN 154 and EN 158) indicated to have a experienced a low degree of biodegradation (PM level 1) but that mixing with more highly degraded oil may have occurred. The Italian crude oil analyses showed that the EN 168 oil did not appear to been biodegraded (PM level 0) as indicated by the normal distribution of n-alkanes from all oils while the EN 169 oil is slightly degraded (PM level 1). The Californian oils (D13 and H7) show moderate biodegradation (PM level 4-5), whereas the oil from Venezuela (Boscan) appears to experience a lighter biodegradation with PM level of 2-3.

The thermal maturities of the oils vary from intermediate to high maturity as measured from GC-MS analysis of sterane and terpane biomarker ratios. Oil samples from the North Sea appeared to range from immature to relatively mature. Crude oils from Italy are suggested to have experienced intermediate levels of thermal maturity. Finally, the thermal maturity of Californian oils is suggested to be a mid-mature whereas the Boscan oil, from Venezuala is immature to early mature. However, it is possible that some of these parameters (i.e. CPI, OEP, Pr/Ph, Pr/nC17, Ph/nC18, MPI, MNR) measured in some of the oils had been affected by biodegradation and/or mixing.

CHAPTER 4

TOTAL ACID NUMBER ANALYSIS

Chapter 4. Total Acid Number (TAN) Analysis

4.1 Introduction

ASTM Method D664 is the standard test method to measure the total acid number (TAN) of petroleum products by potentiometric titration, which can measure acid numbers from 0.05 up to 260 mgKOH/g oil. This standard method specifies the reagents that can be used for the titration, standardisation and the electrode electrolytes; it also specifies the preparation, maintenance and storage procedures for the electrodes and their cleaning. The method describes the auto-titration of oil samples (up to 20 g) dissolved in solvent mixture,(50% toluene and 49.5% propan-2-ol, 0.5% water), with a standardised alcoholic (anhydrous propan-2-ol) KOH solution, using a suitable glass electrode and calomel reference electrode. However, many titrator manufacturers have standard auto-titrator configurations which comply with the method's requirements for the potentiometer, electrode system, variable speed mechanical stirrer, burette (with CO_2 absorbing substance such as soda lime), stand and the beaker. Table 4.1 below shows the ASTM D664 recommended sample sizes needed to analyse certain acid number ranges of oils.

Acid Number	Sample size (g)	Weighing accuracy (g)
0.05 - < 1.0	20.0 ± 2.0	0.1000
1.0 - < 5.0	5.0 ± 0.5	0.0200
5.0 - < 20.0	1.0 ± 0.1	0.0050
20.0 - < 100.0	0.25 ± 0.02	0.0010
100.0 - < 260.0	0.1 ± 0.01	0.0005

Table 4.1 ASTM D664 recommended oil sample sizes

Nevertheless, there are limitations that arise using the standard ASTM method procedure, such as the requirement for a large amount of sample, which can be as high as 20 g of oil sample if acid number is less than TAN 1.0 gKOH/g oil. This requirement may be a constraint if it is necessary to perform other essential analyses on limited sample sizes (Fan and Buckley, 2007). This standard method reports a mediocre reproducibility for some analyses (Mahajan et al. (2006); Wang et al. (2008); for

instance in the ASTM D664 (1996) method, it is stated that reproducibility variations can be up to 44% for an automatic titration mode of fresh oils and additive concentrates at inflection points (5% under ideal conditions). However, there is no information on the variation of acid ranges that are observed in this standard method. In the ASTM D664 (2009) method it is stated that using a 20 g oil sample, the measurement reproducibility variation of oils with a TAN of 1.0 can be up to 28%, with those with a TAN of 0.1 it is up to 155% and further increases up to 296% for a TAN of 0.05 mgKOH/g oil.

Another limitation is that the procedure for TAN measurement was not originally intended for crude oils, heavy oils or their fractions (i.e. asphaltenes and maltenes), since they were designed for determining acidic constituents present in petroleum products, such as lubricants that were soluble or nearly soluble in mixtures of toluene and propan-2-ol. The procedure was also found not to manage to deal with asphaltene-precipitates fouling the electrodes thus leading to poor reproducibility, the presence of additives, salts etc., that lead to erroneous results. Fuhr et al. (2007) proposed some modifications to method ASTM D664 when applying it to heavy oil and bitumen samples. Also, in the ASTM D664 standard procedure, the titration inflection/end points (EP) may not always clear, and so (Fan and Buckley, 2007) proposed an improvement whereby the crude oil samples are spiked with an oil-soluble stearic acid, which resulted in sharper inflection points as well as improved accuracy of oil determination.

The aims of this section of work were:

I.   Development and validation of method based on ASTM D664, for measuring acid numbers of small sample sizes of heavy crude oil, maltene and asphaltene fractions.

II. Enabling the measurement of TANs on core extracts and thus allow any TAN gradient to be measured in reservoirs.

III. Determining the distribution of acidity in asphaltene and maltene fractions and their relative contribution to acidity of the bulk oil.

4.2 Results

4.2.1 Method development and modifications

4.2.1.1 General measurement procedures

Since the accuracy and reproducibility of TAN analysis is highly dependent on the glass electrode, careful steps must be taken in maintaining the electrode. These included firstly in the preparation of the electrode before/ between titrations and the regeneration of the electrode by filling the reference electrode with a fresh tetraethyl ammonium bromide (0.4 mol/l in ethylene glycol) which acts as the electrolyte. Preconditioning of electrodes in organic solvent is followed by distilled water for 10 to 15 minutes before titration is carried out. Secondly, calibration is performed with 179 μl, 895 μl and 1.79 ml of 0.1 M hydrochloric acid (HCl) which is expected to produce measured TAN values of 1, 5 and 10, respectively. Figure 4.1 below shows a typical standard calibration curve measured during analysis.
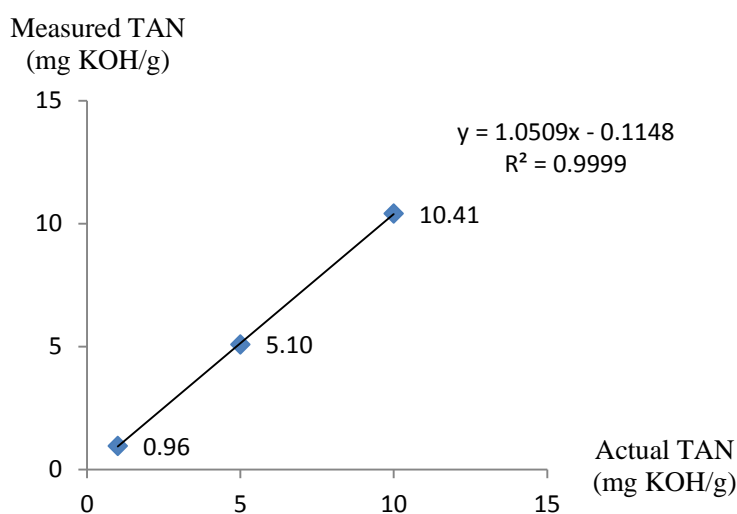
Figure 4.1 Standard/typical calibration curve of TAN 1, TAN 5 & TAN 10, 0.1M HCl

Thirdly, a careful cleaning procedure was undertaken after each titration in order to maintain the electrode performance. The electrode was rinsed with the toluene to remove any contamination caused by the previous titration (thorough rinsing of the electrode is needed for highly viscous oil samples). It is then gently wiped with wet tissue before being rinsed with titration solvent (toluene: isopropanol: water) and carefully re-wiped with a clean wet tissue. Finally, it was immersed in distilled water for at least 5 minutes before a blank titration was performed. Similar modifications to overcome ASTM D664 method limitations on heavy oils and bitumens have also been

proposed by (Fuhr et al., 2007) which mainly focused on initial sample handling during analysis. Other important practical precautions were also observed according to method ASTM D664.

4.2.1.2 Automatic versus manual end-point determinations

TAN values were measured using an automated analyzer (Methrohm 848 Titrino Plus) and an image of a result from the titrator is shown in Appendix B. The titration curve of samples sometimes gave ambiguous inflection points (EP1) and it was found that a manual check of the readings occasionally revealed incorrect automatic end-point determinations. If it is found to be necessary, a re-plot of the volume (ml) of KOH solution added versus the corresponding meter (mV) reading is carried out. Figure 4.2 below shows the example of titration curve for sample EN 174 before (a) and after (b) a re-plot.

(a)   (b)
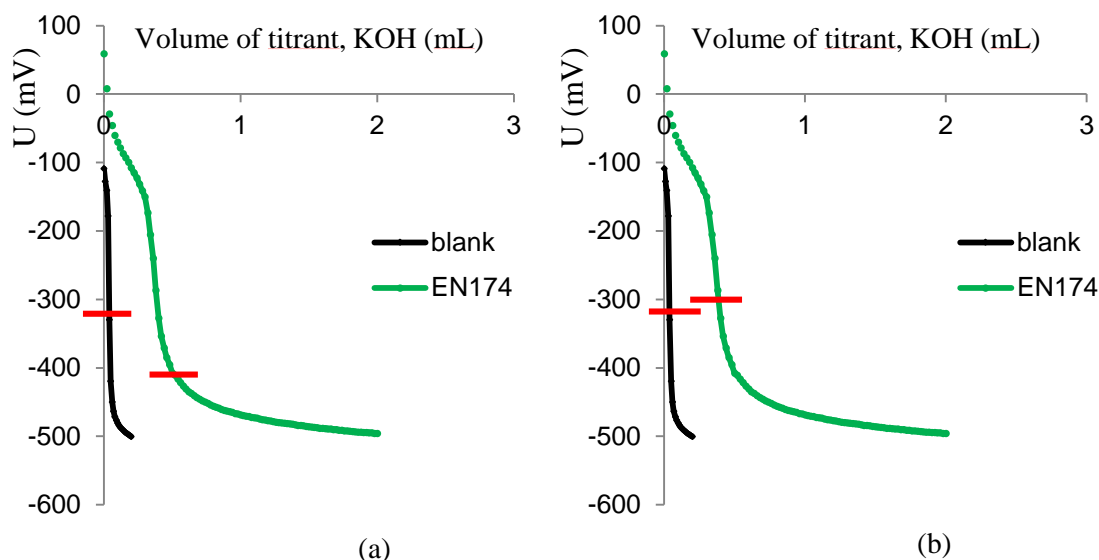
Figure 4.2 Titration curve for sample EN174 showing a TAN of 2.46 before re-plot **(a)** and **(b)** after re-plot (TAN 1.96)

Therefore, in the above example, the TAN of sample EN 174 (previously automatically recorded as 2.46) is manually determined from the correct inflection point (EP1) which should reflect the biggest potential difference response for a unit of KOH. The new TAN value is re-calculated by inserting the corrected EP1 value in the TAN equation formula (Eq. 1). As shown from both neutralisation curves in Figure 4.2, the TAN value changed from 2.46 to 1.96 as the position of inflection point changed.

	TAN mg KOH/g			Mean	SD	RSD
	1st reading	2nd reading	3rd reading			
Before re-plot	2.46	2.48	1.85	2.26	0.36	15.82
After re-plot	1.95	1.84	1.85	1.88	0.06	3.28

Table 4.2 Measured TAN values with mean, SD and RSD for sample EN174 before and after re-plot

In addition, the results from re-plotting the titration curve reduced the relative standard deviation (RSD) of the triplicate analyses from 15.82% to 3.28% suggesting that the repeatability of analysis has been highly improved after correction, although this was not always the case for all samples, but was noted in approximately 11 out of 33 determinations.

4.2.1.3 *Solvent volumes used for crude oil TAN determinations*

Volume (ml)	Mean (n=3)		SD		%RSD	
	D13	EN 149	D13	EN 149	D13	EN 149
25	1.18	1.12	0.26	0.17	22.02	15.17
35	0.99	1.10	0.23	0.09	23.54	8.37
50	1.17	1.11	0.19	0.05	16.58	4.52

Table 4.3 Effect of solvent volume on crude oil TAN determinations (average of three)

The effect of solvent volume on acid number measurement was evaluated on oil samples D13 and EN 149 by varying the volume of organic solvent from 25 ml, 35 ml and 50 ml as shown in Table 4.3. The results indicate that as the volume of solvent increases, the measurement standard deviation decreases. This suggests that an accurate TAN value can be better achieved in titrations with larger volumes of solvent. Although of those used, the 50 ml volume of solvent used appears to give the best reproducibility in the TAN titrations, in this study a solvent volume 35 ml was preferable due to the wide range of acid number of samples involved and that the Metrohm 848 Titrino Plus titration vessel could only take up to 75 ml solvent plus titrant at a time. Therefore a solvent volume of 35 ml was used to prevent a problematic situation such as a titration of high acid number sample that may cause an overload of solvent in vessel since the

higher the acid number, the more 0.1 M KOH titrant solution is titrated into the vessel. Furthermore, since the 35 ml solvent volume showed reasonably reproducible titration results, this reduced volume was preferable in order to reduce solvent waste.

4.2.1.4   Acid Spiking on TAN crude oils

Due to the ambiguous end-point (EP) issue in many of the TAN analyses, the acid spiking method i.e. Fan and Buckley (2007) was investigated using spiking agents (0.02M stearic acid, 0.02 M benzoic acid) in order to determine their effect on the TAN titration results and if it could improve the TAN measurements. (Refer to Methodology section 2.5.3 for spiking details)

Sample	EN 169			Boscan			Heidrun		
	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD
Standard method	0.13	0.04	31.22	1.66	0.02	1.2	2.62	0.02	0.79
Spiking with 1ml of 0.02 M stearic acid	0.19	0.09	46.78	1.83	0.15	8.42	2.71	0.06	2.24
Spiking with 1ml of 0.02 M benzoic acid	0.17	0.01	3.46	1.67	0.01	0.6	2.7	0.03	0.98

Table 4.4 Effect of acid spiking (1 ml of 0.02 M stearic acid and 0.02Mbenzoic acid, respectively) on standard TAN method results.

Table 4.4 shows a comparison of TAN measurement for three oils (EN 169, Boscan, Heidrun) together with their mean, SD, and RSD values, between the standard method, and the stearic acid and benzoic acid spiking methods. In general, the repeatability of TAN measurement was observed to be improved in the benzoic acid spiked samples, compared with the unspiked and stearic acid spiked samples. For example, for the low TAN oil sample EN 169, reproducibility was improved from 31.2% RSD (standard method) to 3.46% RSD in the benzoic acid spiked method. In addition, when comparing the reproducibility among spiking agents, samples spiked with benzoic acid appeared to be relatively consistent in all titrations (<3.5%) RSD, while the % RSD for samples spiked with stearic were <46.8%. The pKa of both spiking acids is relatively similar, (pKa stearic acid ~4.78, benzoic acid ~4.2), however the difference in molecular structure of benzoic acid (aromatic) and stearic acid (aliphatic) might be one of the possible reasons that causes different spiking effects on oil TAN measurement reproducibility. The improvement in reproducibility suggests that benzoic acid as a

spiking agent may enhance a well-defined and clear equilibrium point in oil TAN measurements.
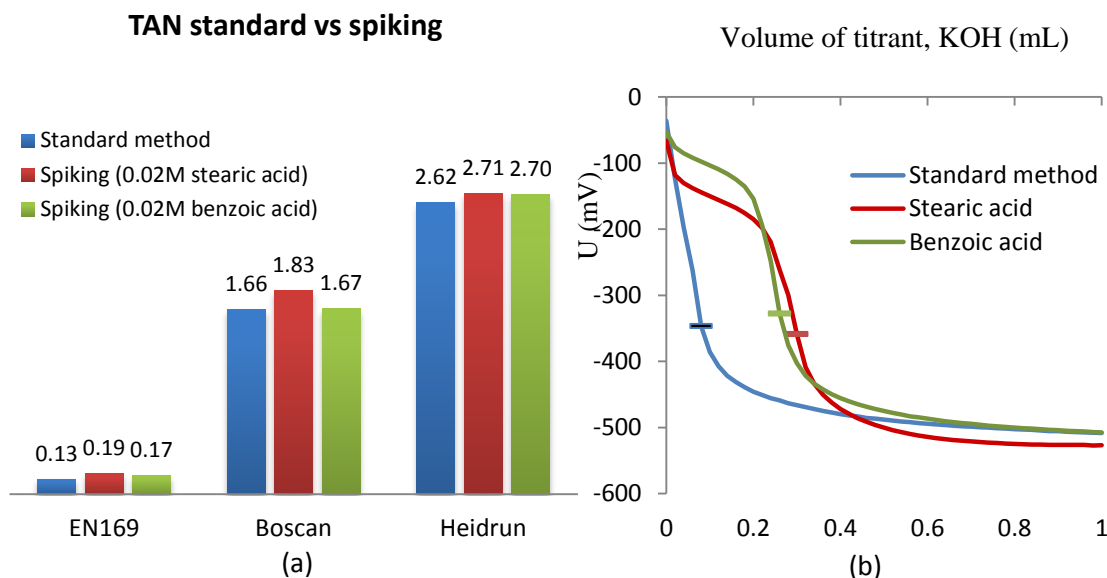
Figure 4.3 Histograms (a) and titration curves (b) of 35 mL organic solvent standard method, and 1 mL 0.02 M stearic acid and benzoic acid spiking solution methods for oil TAN.

Figure 4.3 above shows a histogram of TAN value measurements on three oil samples (EN 164, Boscan, Heidrun) corresponding to three different methods: a standard method (blue), 0.02 M stearic acid spiked method (red), 0.02 M benzoic acid spiked method (green). The TAN values of the higher TAN oil (Heidrun) from the three different methods are similar to each other suggesting no clear differences between these methods. The comparable observation also appears for the lower TAN sample (EN 169). Although according to standard method ASTM D664, a lower TAN sample (0.05 - < 1.0) requires up to 20 g of sample to be analysed, in this analysis only 1 g samples were used suggesting that a wide range of crude oil samples, from low to high TAN, may be satisfactorily measured using standard method without involvement of spiking agents.

Figure 4.3(b) shows the differences in the titration curves of the standard, stearic spiked, benzoic spiked analyses of low TAN sample, EN 169. The curves show an improvement in the definition of inflection/end point (EP1) of standard method < stearic acid spiked < benzoic acid spiked. It therefore appears that when measurements are made on 1 g quantities of low TAN oil samples, sharper and more well define EP1 occur when the sample is spiked with 0.02 M benzoic acid.

4.2.1.5   *Sample preparation and TAN analysis of asphaltenes*

It was necessary to develop a modification to the standard TAN method for the reason that asphaltenes are highly viscous solids which also have a poor solubility characteristics in the standard solvents used. Figure 4.4 below shows a modification of the sample preparation technique that is thought to be important in order to ensure all acidic components in the sample are fully dissolved in solvent before proceeding to titration.

Sample preparation

Crude oils, maltenes   Asphaltenes

- Dissolve oil sample (1 g) in 35 mL of TAN solvent
- Samples are sonicated at 40-50 °C for 10-15 minutes, to ensure oil and solvent are effectively mixed
- Titrate as soon as the sample is fully dissolved in the solvent

- Pre-dilute asphaltenes (100 mg) in toluene (10 ml)
- Samples are sonicated at 50-60 °C for 10-15 minutes to homogenise
- Add the homogenised asphaltenes + 10 mL toluene to 25 mL TAN solvent. (ratio now becomes 642:354:4)
- Titrate as soon as the sample is fully dissolved in solvent

Figure 4.4 Workflow of oils, maltenes, asphaltenes sample preparation for TAN analysis

The sample preparation modifications for asphaltenes involved pre-dilution with toluene (10 ml), which ultimately increased the usual toluene:isopranol:water solvent ratio,of 495:500:5 to 642:354:4 in order to enhance the solubility of the asphaltene aliquots (100 mg) analysed. The poor solubility of asphaltenes also required the application of heat and ultrasonic energy (for approximately 10-15 min) for effective mixing and homogenization. The titration was performed without any delay, in order to avoid any precipitation.

4.2.2 TAN repeatability and reproducibility

4.2.2.1 Crude oil TAN Analyses (May 2011)

Sample	Mean (TAN mgKOH/g)	SD	%RSD
EN 149	1.14	0.05	3.9
EN 151	7.58	0.08	1.1
EN 154	0.11	0.00	1.0
EN 158	1.24	0.02	1.2
EN 168	0.35	0.04	10.6
EN 169	0.13	0.04	31.2
EN 174	1.95	0.04	2.1
H7	2.19	0.04	1.9
D13	1.55	0.06	3.8
NSO	0.11	0.08	78.8
BOSCAN	1.66	0.02	1.2

Table 4.5(a) Table of crude oil TAN values (mean of 3) together with SD and %RSD values

Table 4.5(a) shows the results of TAN measurements and reproducibilities of eleven crude oils. The range of TAN values measured is from 0.11 to 7.58 mg KOH/g. Eight out of eleven oils shows a good repeatability (<4% RSD) for oils with TAN values higher than 1. This indicates a reasonable repeatability of ASTM method D664 for crude oils, even when only 1 g oil is used. The highest % RSD is typically for oils with TAN values lower than 0.4 mg KOH/g.

4.2.2.2 Maltenes TAN

Sample	Mean (TAN mgKOH/g)	SD	%RSD
EN 149	1.06	0.00	0.04
EN 151	6.85	0.17	2.40
EN 154	0.45	0.04	9.50
EN 158	0.89	0.07	8.10
EN 168	0.04	0.03	70.70
EN 169	0.14	0.05	36.10
EN 174	1.81	0.10	5.40
H7	1.17	0.11	9.50
D13	0.89	0.08	8.40
NS0-1	0.16	0.00	3.00
BOSCAN	0.78	0.08	10.70

Table 4.5(b) Table of maltenes TAN measurements (mean of 3) together with SD and % RSD.

The TAN data for maltene fractions together with their SD and %RSD values is shown in Table 4.5(b). The mean acid number value for all eleven maltenes sample was within the range of 0.04 to 6.85 mg KOH/g. Most (64%) samples in this set had TAN values below than 1 mg KOH/g, while the remainder were between 1.06 - 6.85 mg KOH. The best repeatability of 0.04% RSD, was on a relatively high TAN sample (EN 149), while the poorest (70.7% RSD) was on the lowest TAN (0.04 mg KOH/g) sample.

4.2.2.3 Asphaltenes TAN

Sample	Mean (TAN mg KOH/g)	SD	%RSD
EN 149	6.66	0.75	11.30
EN 151	21.24	1.73	8.20
EN 154	5.88	1.12	19.00
EN 158	4.19	0.48	11.50
EN 168	12.18	0.72	5.90
EN 169	na	na	na
EN 174	6.52	1.42	21.80
H7	4.57	0.66	14.50
D13	4.29	2.93	68.30
NS0-1	na	na	na
BOSCAN	3.13	0.19	6.10

Table 4.5 (c) Table of asphaltenes TAN reproducibilities together with mean, SD and % RSD.
na = not available

Table 4.5(c) above shows results of TAN analyses (mean, SD, % RSD) on 100 mg aliquots of the asphaltenes fractions from the intial oil set, using the modified ASTM D664 solvent ratio. The TAN values for this fraction were often higher than the crude oil from which they were derived. Hence in this set of sample the mean of TANs ranged from 3.13 to 21.24 mg of KOH/g asphaltene. The highest TAN values found in maltenes and asphaltenes samples came from highest TAN crude oil (EN 151) analysed. A total 89% of samples had reproducibilities better than 22% RSD and the best reproducibility was 5.9% RSD (from sample EN 168). Due to insufficient asphaltenes in them to isolate for analyses, asphaltene TAN data for samples NSO-1 and EN 169 was unavailable.

4.2.2.4 Crude oil TAN measurement long term repeatability

The TAN titration of the same set of samples was repeated three times under the same conditions over a period of 9 months in order to check long term analytical repeatability and validity of the results. Each of the titrations were carried out in triplicate and the average taken. Table 4.6 shows mean TAN values for eleven crude oils along with their SD and % RSD values.

Sample	Aug-10	Dec-10	May-11	Mean	SD	%RSD
EN 149	1.10	1.12	1.14	1.12	0.02	1.82
EN 151	7.91	7.50	7.58	7.66	0.22	2.83
EN 154	0.38	0.39	0.11	0.29	0.16	54.09
EN 158	1.16	1.24	1.24	1.21	0.05	3.76
EN 168	0.21	0.22	0.35	0.26	0.08	30.66
EN 169	0.07	0.19	0.13	0.13	0.06	44.12
EN 174	1.75	1.88	1.95	1.86	0.10	5.28
H7	1.70	1.89	2.19	1.93	0.25	12.80
D13	0.99	1.43	1.55	1.32	0.30	22.30
NSO	0.09	0.13	0.11	0.11	0.02	18.36
BOSCAN	1.51	1.69	1.66	1.62	0.10	6.02

Table 4.6 Oil TAN analysis reproducibilities measured in August 2010, Dec 2010 and May2011

From the data in Table 4.6, the higher TAN oils (>1.0 mg KOH/g) show generally good reproducibility (<6.02% RSD), with the best reproducibility (1.82% RSD) in sample EN 149. However, this is not the case for both Californian oil samples (H7, D13) with 12.80 and 22.30% RSD values, respectively. In addition, the TAN values of the Californian oil samples measured was getting higher with time. For example, when the first analysis of sample H7 was performed in August 2010 it gave a TAN value of 1.70. The second analysis (December 2010) using the same analytical conditions gave the TAN value of 1.89 and on the May 2012 measurement the TAN had increased again to 2.19 mg KOH/g. This increasing pattern is similar for both Californian oils. A possible reason behind this pattern might be due to the relatively high sulphur content in these samples and some of the sulphur compounds perhaps could have undergone chemical reactions (such as oxidation) to produce acidic species as the storage time increased. Oil samples with low TAN values (<0.3 mg KOH/g) show relatively poor reproducibility (up to 54.09% RSD). This low reproducibility of lower TAN oil is probably partly due to the small mass (1 g) of sample used, but is acceptable when compared to the standard method ASTM D664 (2009) which states that for the acid number ranges of 0.05 to <1.0 mg KOH/g oil, then using a 20 g sample, the reproducibility variations are from < 28% to as high as 296% (though around 5% are possible under ideal conditions). Also in absolute terms, a 50% measurement error on an oil of TAN 0.3 mg KOH/g is a small degree of acidity uncertainty which is not of great commercial significance. From the TAN analysis done, the standard ASTM D664 method could generally achieve good repeatability of TAN measurement on 1g aliquots of crude oils with acidity as low 0.1 mg KOH/g.

4.2.3. Comparison of TAN from Oil Company Assay data

Sample	TAN Assay	TAN measured (Aug 10, Dec 10, May 11)	% Difference
EN 149	1.40	1.12	20
EN 151	7.30	7.66	-5
EN 154	0.60	0.29	52
EN 158	1.19	1.21	-2
EN 168	0.72	0.26	64
EN 169	0.35	0.13	63
EN 174	1.80	1.86	-3
H7	1.75	1.93	-10
D13	1.25	1.32	-6

Table 4.7 Comparison between oil assay report TAN data and measured TAN

Table 4.7 above shows TAN value data on nine oil samples obtained from oil companies (though the measurements would have been mostly made by service companies on different samples of them) and TAN data measured in this work, together with the percentage difference of TAN measured from their corresponding assay report. Comparison between these data showed that the highest difference is with the three lowest acid numbers listed both in the assay report and measured TAN value of this sample set, (EN 154, EN 168, EN 169) with the difference of up to 64%. The five samples with highest TAN values show a relatively small differences (<10%) with the closest result only 2% different for sample EN 158 with TAN measured value of 1.21 mg KOH/g. These data again indicate that the method used to measure TAN on only 1 g oil samples in this work is reasonable and comparable method to conventional methods.

4.2.4 Distribution of acidity in crude oil maltene and asphaltene fractions

The TAN measurements on the maltenes and asphaltene fractions from nine oils together with their crude oil TANs, summed asphaltene and maltene TANs their fraction value to the oil's TAN, are shown in Table 4.8. From Table 4.8, the nine crude oil samples ranged in TAN from 0.11 to 7.58 mg KOH/ g oil. The highest oil TAN in the set of sample (EN 151) also had the highest TAN value in their asphaltene and maltene fractions when compared to the others. However, the lowest oil TAN sample (EN 154), it does not have the lowest asphaltene and maltene fraction TANs. These results indicate that other factors affect the individual distribution of acidity in oil fractions (maltene and asphaltene) and their contribution to the oil TAN value.

Comparing the TAN of the totaled oil fractions (A+M) and TAN of their corresponding crude oils, sample EN 174 shows comparatively similar values, while samples. EN 149, EN 151, EN 154 and EN 168 have totals slightly higher than their corresponding oils, and samples EN 158, H7, D13, Boscan had totals which were lower than their original oil TANs. A similar observation has been reported by (Barth et al., 2004), who suggested that a slightly higher TAN value of the sum of oil fractions when compared to the original oil may be caused by an oxidation process or contact with air during deasphalting procedure and might also due to the uncertainty during the ASTM D664 TAN determination on the asphaltene fraction.

The TAN values of the separated maltene and asphaltene fractions are shown in histogram below (Figure 4.5a). In general, asphaltenes TANs are much higher than their associated maltenes as shown in histogram (4.5a). Asphaltene TANs in this set of sample were up to 22 mg KOH/g (sample EN 151) while the related maltene fraction was approximately 7 mg KOH/g. Due to their much higher proportion than asphaltenes in the oils, maltenes contribute most of the acidity to the oils.

Sample	Crude Oil TAN (mg KOH/g oil)	Asphaltene (A) TAN (mg KOH/g A)	Percentage A in crude oil (%)	Maltene (M) TAN (mg KOH/g M)	Percentage M in crude oil (%)	Total oil TAN (A + M)	% TAN to oil Asphaltene (A)	% TAN to oil Maltene (M)
EN 149	1.14	6.66	4	1.06	96	1.28	21	79
EN 151	7.58	21.24	7	6.85	93	7.86	19	81
EN 154	0.11	5.88	9	0.45	91	0.94	56	44
EN 158	1.24	4.19	8	0.89	92	1.15	29	71
EN 168	0.35	12.18	5	0.04	95	0.65	90	10
EN 174	1.95	6.52	2	1.81	98	1.90	7	93
H7	2.19	4.57	9	1.17	91	1.48	28	72
D13	1.55	4.29	13	0.89	87	1.33	42	58
BOSCAN	1.66	3.13	10	0.78	90	1.02	31	69

Table 4.8 Contribution of asphaltenes and maltenes fractions to oil TAN, A=Asphaltenes, M=Maltenes.
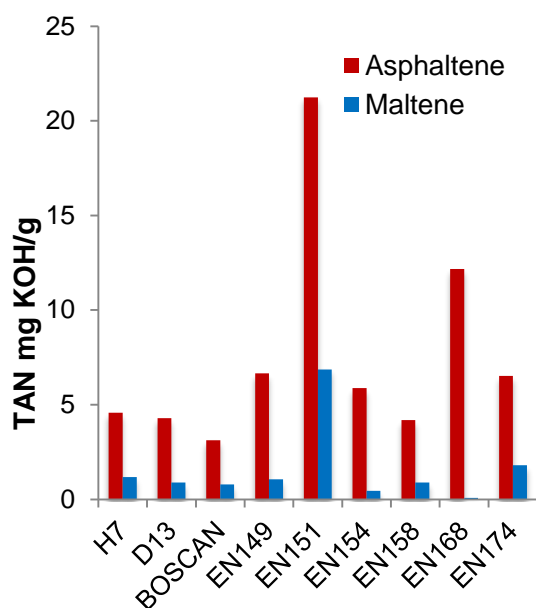
Figure 4.5 (a)
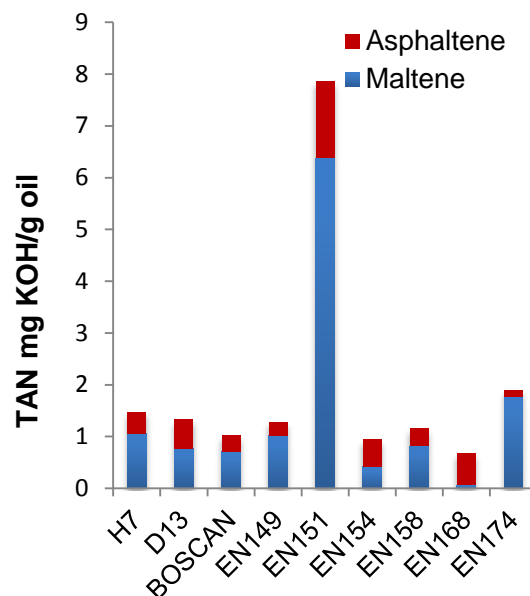
Figure 4.5 (b)

Figure 4.5 (a-b) Histogram of the distribution of TAN in asphaltene and maltene fractions (a) and (b) Histogram of the relative contribution of asphaltene and maltene fraction acidities to oil TAN

Further analysis of the relative contribution of these fractions to their corresponded TANs oil was plotted in Figure 4.5b above. Samples EN 168 and EN 154 revealed that > 50% of the acidity in those oils appeared to be in their asphaltene fractions. This suggests that in these samples, although the percentages of asphaltenes in these oils are less than 10%, more than half of acid functional groups in the whole crude oils are contained within them. This finding suggests that the acidity of the asphaltene fraction is one of the main controls on the acidity of certain crude oils.

4.3 Summary

ASTM method D664, although not originally designed for use on crude oils, was tested for its suitability for TAN measurements on crude oils, including heavy oils and crude oil fractions. The proposed modifications were then tested and the results were as follows:

The repeatability of TAN analysis was improved when EP1 point inspection was carried out and the data was replotted if necessary. From the results, eight out of eleven oils shows good repeatability (<4%) RSD for oils with higher TAN values. This result indicates reasonable repeatability of ASTM D664 to crude oils, even when only 1 g oil is use. The highest %RSD is typically for oils with lower TAN values (<0.4 mg KOH/g). The best repeatability of TAN measurement on 1 g of maltenes fraction is (2.43% RSD), is on a high TAN sample and the worst (81.9% RSD) is on a very low TAN sample. The determination of asphaltene TAN on samples as low as 100 mg by modification of ASTM method D664 has been achieved, with the best repeatability was 5.92% RSD, and the poorest was 68.34.

In general the maltene fraction contributes most in the acidity to crude oils, however in some samples (i.e. EN 168, H7, D13, EN 154) a large proportion of the oil TAN's acidity is contributed by the asphaltenes, even though they are quantitatively a small percentage of the oil in terms of weight.

CHAPTER 5

CARBOXYLIC ACID ANALYSIS

Chapter 5. Carboxylic acid analysis

5.1   Introduction

Numerous methods have been established for the extraction of carboxylic acids from crude oil. Examples of the extraction methods employed use: supercritical fluid (McDaniel and Taylor, 1999), ion-exchange resin in an aqueous medium using cyclohexane solvent (Ovalles et al., 1998), ion-exchanging resin in non-aqueous medium (Jones et al., 2001), and a new proposed solid phase extraction using non-aqueous medium with no involvement of hexane or cyclohexane solvents in their extraction procedure (Saab et al., 2005).

In this study, carboxylic acid fractions are isolated by adapting the non-aqueous ion exchange procedure developed by (Jones et al., 2001). The use of gas chromatography mass chromatography (GC-MS) is well suited for characterising naphthenic acid components at the molecular level, but due to their polarity the acids are usually derivatized to corresponding esters before GC-MS analysis. Nevertheless, a direct acid analysis is more desirable because it can provide rapid analysis without the concern of losing material through poor derivatisation efficiency. Consequently, other methods, such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT ICR MS), have been developed to provide highly detailed information on acidic species (see Chapter 6).

Although previously, the relationship between the molecular composition and the total oil acidity had not been considered, Meredith et al. (2000) showed a strong correlation (r^2=0.91) between the acidity (TAN mg KOH/g) and carboxylic acid content when using GC analysis of methyl esters of their isolated acids. Saab et al. (2005) confirmed the relationship with a strong linear correlation (r^2=0.96) between the acidity (TAN) and carboxylic acid fraction of their crude oils. Thus, these findings suggested that carboxylic acid fractions play a major role in acidity of crude oils and this strong correlation suggested that the acidity (TAN) of an oil may be controlled by its carboxylic acid content. Based on the assumption that 1 mole of potassium hydroxide (KOH) reacts with 1 mole of average carboxylic acids, Meredith et al. (2000) suggested a following formula:

$$\text{Calculated TAN:} \quad \frac{(\text{Acid conc.}/334) \times 57}{1000}$$

Where, 334 is the molecular weight (Mw) of an "average acid compound", C_{22} with three saturated ring structure attached with an alkyl side chain and one carboxylic acid group, while 57 is the molecular weight of 1 mole of KOH.

The aims of this section of work were:

I.   To investigate the generality of the relationship between the concentration of isolatable carboxylic acids in an oil and its acidity on a sub-set of the oils from this project.

II. To investigate the effects of biodegradation maturity process on the amounts of carboxylic acids in oils.

III. To test the predictability of oil Total Acid Number (TAN) using the concentrations of the carboxylic acid fractions.

5.2 Results

5.2.1 Carboxylic Acid Fraction Data

The results obtained from carboxylic acid fraction analysis, using gas chromatographic quantitation, of 10 selected crude oils of various origins and acidity including some from the North Sea (UK and Norway) and Italy, with TAN showed values ranging from 0.11 to 7.66, and are presented in Table 5.1 below.

	Origin	TAN	Total carboxylic acids (µg/g)	*n*-acids (µg/g)
NSO-1	North Sea	0.11	194	2
HEIDRUN	North Sea	2.64	3241	2
EN 151	North Sea	7.66	10391	0
EN 158	North Sea	1.21	325	12
EN 174	North Sea	1.86	1137	8
EN 168	ITALY	0.26	159	1
#3	Worldwide	6.05	3286	107
#8	Worldwide	4.35	410	17
#10	Worldwide	0.63	502	18
#21	Worldwide	0.20	229	12

Table 5.1 List of samples with their origin, TAN values and total acid and *n*-acid concentrations. (µg/g)

As can be seen from the Table 5.1, approximately 30% of the samples consist of low acidic oils <0.5 and other 70% are considered as high acidic oils sample. In general, the total carboxylic acids in high acidity oils range from 325 to 10391 µg/g, while low acidity oil samples contain much lower carboxylic acid fraction concentrations ranging from 159 to 229 µg/g. For example, the high acid samples of EN 151, #3 and Heidrun, shows substantially higher amounts of total carboxylic acid fractions (10391, 3286, 3241 µg/g) respectively, than the other lower acidity samples.

However, this relationship between total carboxylic acid content and acidity is not the case for the total amounts of n-acids and acidity, and there is no clear trend in these data (Table 5.1). Further analysis on the correlation of total carboxylic acid fractions and total n-acids fractions and their corresponding TAN values and origins are shown in section 5.4.

Figures 5.1(i-x) show gas chromatograms of carboxylic acid (as methyl esters) fractions isolated from ten oil samples, listed in a sequence of increasing TAN. The peaks due to the internal standard of 5β-Cholanic acid (IS) and surrogate standard of 1-phenyl-1-cyclohexane carboxylic acid (SS) appeared at 23.32 and 51.5 min. retention time (*Rt*), respectively. Some of the lower acidic oils appeared to be dominated by *n*-fatty acid components while higher acidic oils tend to be dominated by an unresolved complex mixture (UCM) consistent with higher levels of biodegradation in higher acid oils.
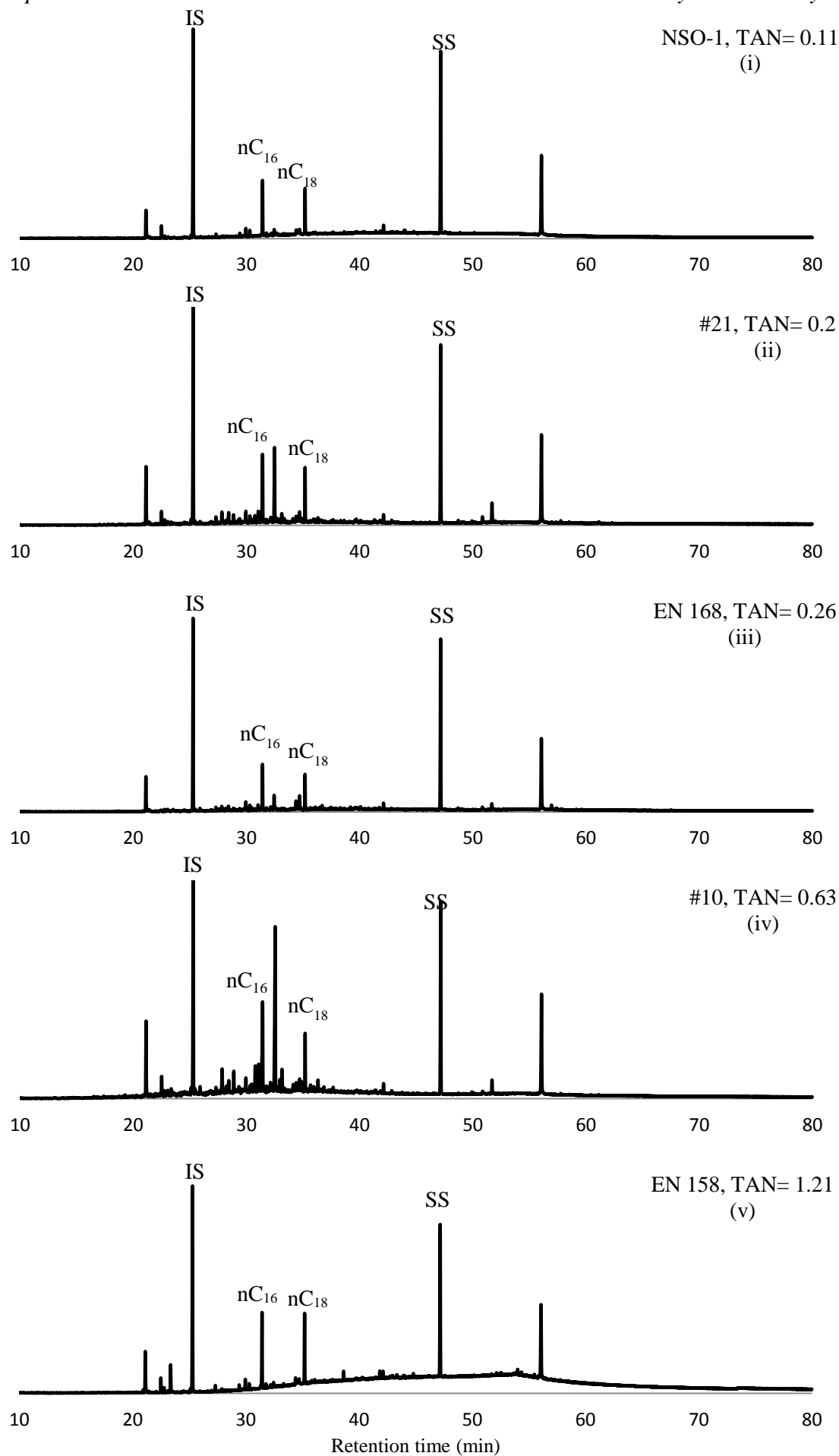
Figure (i-v): See figure legend next page
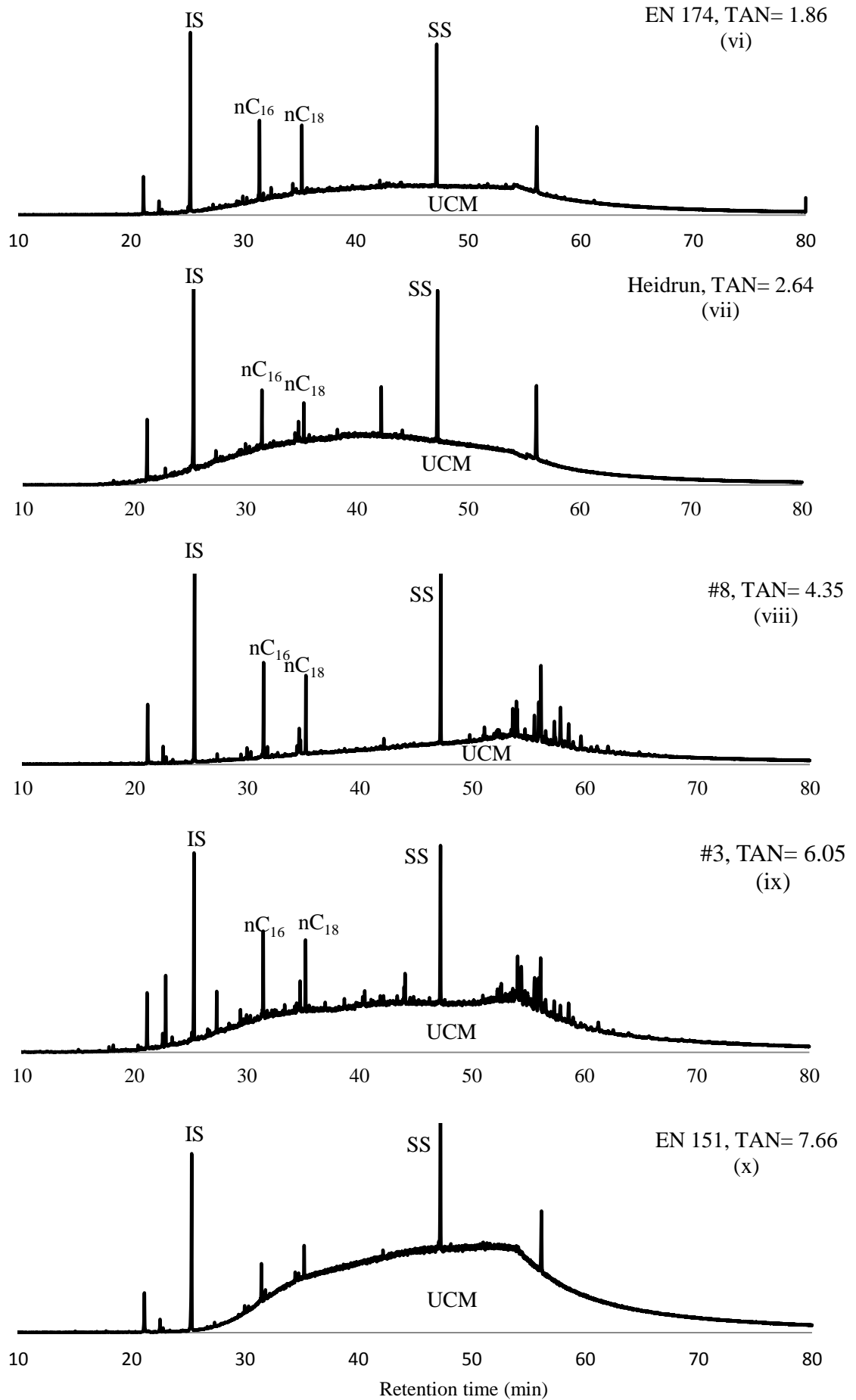
Figure 5.1 (i-x) Gas chromatograms showing oil sample carboxylic acid fractions (as methyl esters). IS and SS are internal standard (methyl ester of 1-phenyl-1-cyclohexane carboxylic acid) and surrogate standard (5β-cholanic acid)

5.2.2   *Total carboxylic acid concentration vs TAN*
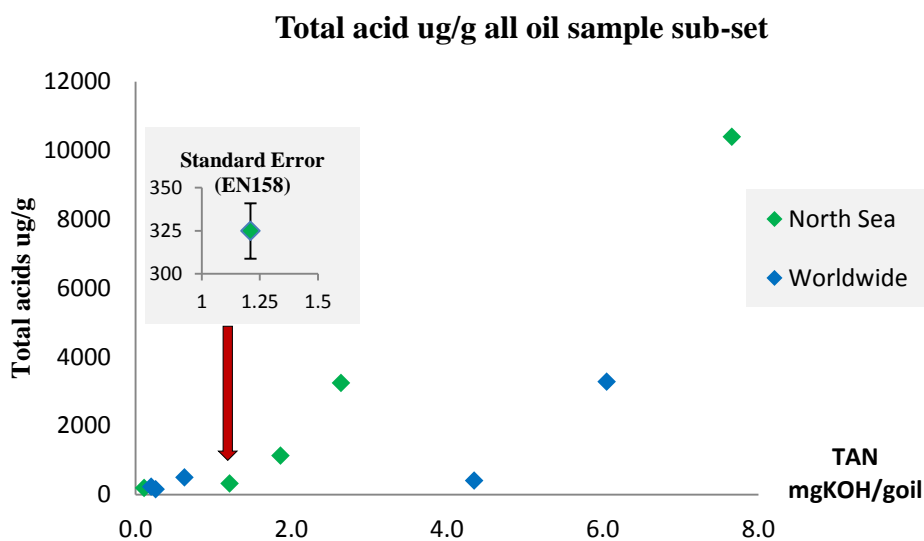
Figure 5.2 Concentration of total carboxylic acid fractions (µg/g) vs Total Acid Number (TAN). Standard Error for sample EN158 (SE=16)

A plot of carboxylic acid fraction concentrations and oil acidity (TAN) is shown in Figure 5.2. A triplicate analysis was done on one of the North Sea samples, (EN 158 with TAN of 1.21), in order to assess the reproducibility of the analysis, and a standard error of 16 ug/g was measured on an average concentration of 325 ug/g (see also Figure 5.2).

Figure 5.2 shows a positive trend in oil carboxylic acid fraction concentrations as the acidity of oil samples increases. This finding is in agreement with the findings by Meredith et al. (2000) who found a strong correlation of increasing carboxylic acid concentration and increasing acidity in their 34 oil samples from different geological settings, source environments, maturities and post-emplacement alteration effects. However, this relationship in the samples from this present study is not as strong, probably due to the smaller data set. However, better trends are seen when samples of similar origin only (i.e. North Sea) are compared with improvement of correlation coefficient (r^2) from 0.69 to 0.98.

5.2.3   Total n-Acid Concentrations vs TAN

n-acids ug/g all oil sample sub-set
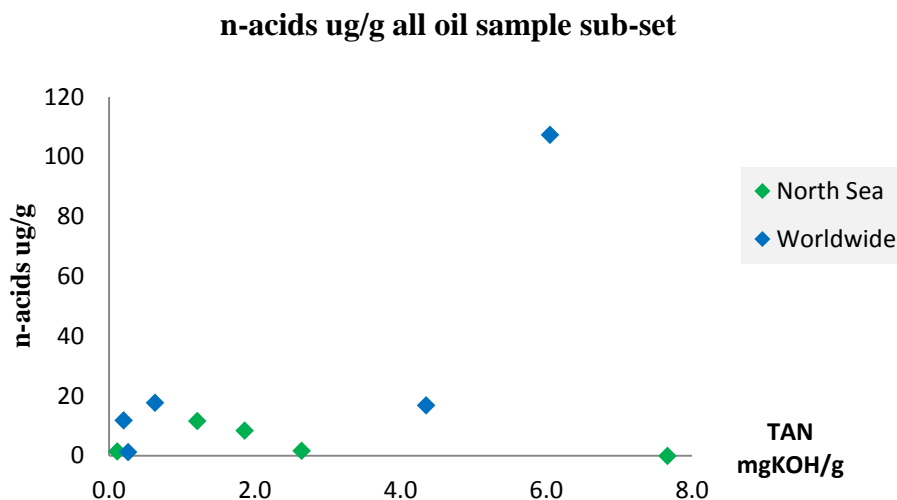
Figure 5.3 Concentration of n-acids µg/g vs acid number (TAN)

Figure 5.3 shows no clear relationship between the concentration of saturated *n*-acids and acid number (TAN) suggesting that *n*-acids does not have a major effect on the acidity of crude oils. A possible explanation for the observed results is that *n*-acids are highly affected by the biodegradation process. This is also consistent with the findings of others (Jaffé and Gallardo, 1993; Barth et al., 1998; Meredith et al., 2000) where total *n*-acids showed a limited relationship with oil acidity. Biodegradation processes could affect this observation where increasing biodegradation results in an increased size of the unresolved complex mixture (UCM) as well as potentially leading to the loss of *n*-acids. A strong correlation of the acidic component in oils with biodegradation in oils has been observed in the following plotted Figure 5.4 and also been proved by others i.e. Behar and Pelet (1984).

5.2.4 Total Carboxylic Acid Concentration vs Biodegradation

Total acids (ug/g)
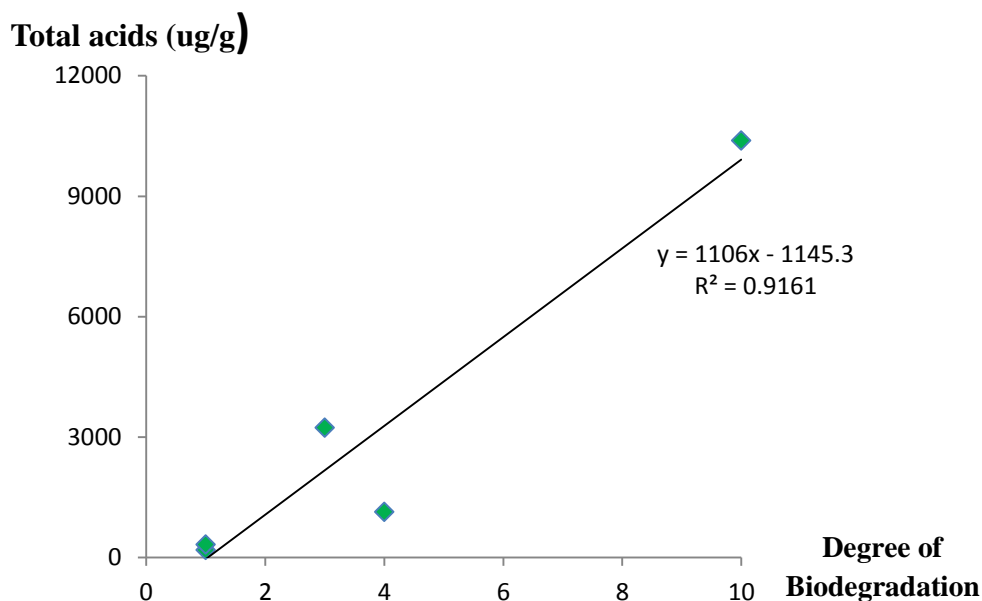
Figure 5.4 Concentration of total carboxylic acid (µg/g) vs degree of biodegradation using (PM level) in North Sea oils.

The relationship of degree of biodegradation on concentration of carboxylic acids in North Sea oils (NSO-1, Heidrun, EN 151, EN 158, and EN 174) has been plotted in Figure 5.4 according to the Peters and Moldowan (1993) scale. The trend of increasing concentrations of carboxylic acid fractions as the biodegradation (correlation coefficient of r^2=0.92) indicates that biodegradation might be one of the main process that controls the concentration of carboxylic acids fraction in these crude oils in confirmation of the findings of those of (Meredith et al., 2000; Dou et al., 2008). However, this strong relationship in North Sea samples have limitation, due to the smaller data set (n = 4).

5.2.5   Total Carboxylic acid content vs Thermal Maturity
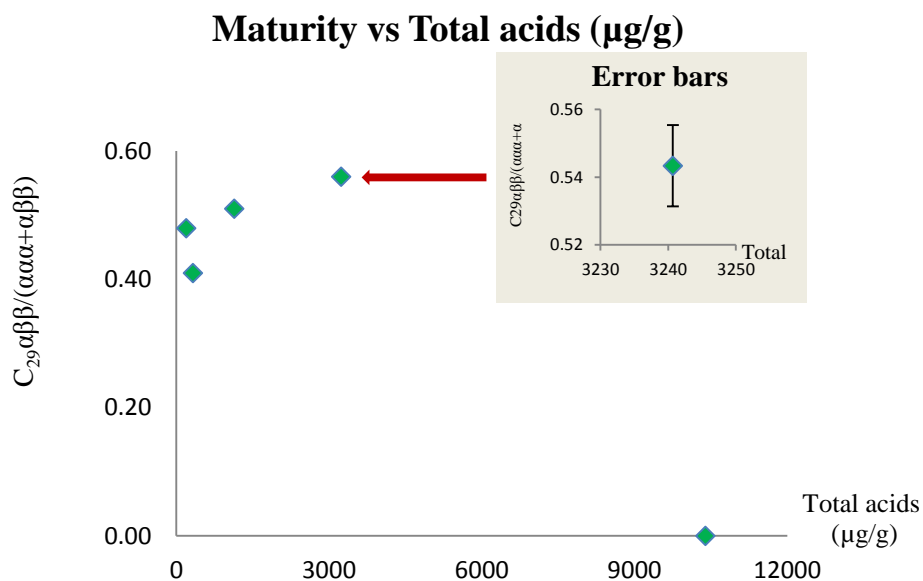
Figure 5.5 Thermal maturity (C$_{29}$αββ/(ααα+αββ)) vs concentration of carboxylic acid fraction (µg/g) in North Sea oils.

Figure 5.5 shows the relationship between a C$_{29}$ sterane biomarker thermal maturity parameter and the concentration of carboxylic acids in North Sea oils sample (NSO-1, Heidrun, EN 151, EN 158, EN 174). Unlike the clear relationship between concentration of carboxylic acids with the degree of biodegradation shown in Figure 5.4, the same samples shows no clear relationship between the carboxylic acid concentrations and the maturity assessed using a sterane maturity parameter (C$_{29}$ αββ/(ααα+αββ)). This indicates that thermal maturity is not a main process that controls the acidity in these crude oils and is similar to the findings have been reported by (Meredith et al., 2000; Dou et al., 2008).

5.3   Predicted Total Acid Number

Sample	TAN (mgKOH/g oil) (ASTM D664)	TAN (mgKOH/g oil) Predicted	% (Pred. vs measured)
NSO-1	0.11	0.03	30
HEIDRUN	2.64	0.55	21
EN 151	7.66	1.77	23
EN 174	1.86	0.19	10
EN 158	1.21	0.06	5
EN 168	0.26	0.03	10
#3	6.05	0.56	9
#8	4.35	0.07	2
#10	0.63	0.09	14
#21	0.20	0.04	20

Table 5.2 Predicted Total Acid Number (TAN)

Table 5.2 shows the measured Total Acid Number (TAN) and predicted TAN calculated assuming a C_{22} saturated tricyclic monocarboxylic acid structure compound, with a molecular weight (Mw=334) according to the average acid in crude oils that controls the TAN of oils (Meredith et al., 2000).

As shown in Table 5.2 above, the TAN measured by ASTM D664 ranges from 0.11 to 7.66, while the predicted TAN is much lower ranging from 0.03 to 1.77 mg KOH/g. Although the previous results (Figure 5.2) showed that oil carboxylic acid content correlates well with TAN, these low values of predicted TAN compared to the ones measured by ASTM D664 suggest that this C_{22} compound previously suggested as an average acid is not the main acidic compound that controls the acidity in this set of oils. In this oil set, the percentage of oil TAN that would be contributed by this average tricyclic acid compound structure was less than 30% of its measured TAN, indicating that more than 70% of oil TAN was contributed by other acidic compounds in this set of oils. This observation was also noted by Meredith et al. (2000) in some of the oils they analysed and they suggested that a low contribution of isolated carboxylic acid fraction might due to the average structure being incorrect in molecular weight or that other carboxylic acidic compounds might be a major controls to their oil TAN.

5.4 Summary of Carboxylic Acid Analysis

Analysis of isolated carboxylic acid fractions from 10 oils of different origins, including those from different source depositional environments, levels of biodegradation and thermal maturity, using a non-aqueous solid phase extraction (SPE) separation method, revealed that the concentration of total carboxylic acids increased as the total acid number increased which indicated that these acidic compounds may be a major control on the acidity in crude oils. The concentration of *n*-fatty acids on the other hand showed no clear relationship with TAN which suggests that these acyclic acids do not have a major effects on oil acidity in this set of sample.

The degree of biodegradation of the oil samples, assessed using the scale of Peters and Moldowan (1993), shows a positive correlation with the concentrations of their total carboxylic acid fractions, which indicates that biodegradation is one of the major processes that controls the concentration of carboxylic acids in this set of crude oils, confirming similar findings by previous work (i.e. Meredith et al., 2000). The thermal maturity of the oils analysed had no clear relationship with their measured concentrations of carboxylic acids.

The TAN prediction formula based on measured carboxylic acid content suggested by (Meredith et al., 2000), was applied to this set of samples, though it predicted less than 30% of the values of the measured Total Acid Numbers, indicating that factors other than those considered in the formula were affecting TAN in these samples.

CHAPTER 6

FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY ANALYSIS

Chapter 6. Characterisation of crude oil naphthenic acids by negative ion ESI-FT-ICR MS

6.1 Introduction

Negative ion electrospray Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis of crude oil and its fractions selectively ionise strong acid i.e. carboxylic acids which are usually naphthenic acids, weak acids such as phenolic compound and neutral (non-basic) nitrogen species (i.e. carbazoles, indoles, pyrroles) as noted previously (Qian et al., 2008; Mapolelo et al., 2011). The molecular composition of petroleum homologous compounds can be expressed as $C_nH_{2n+z}X$, where n is the carbon number and X refers to functional groups or heteroatom, nitrogen, sulphur or oxygen (N,S,O) while z referred to as the hydrogen deficiency index (Barrow et al., 2003; Hsu, 2010). Thus, the empirical formula for the carboxylic acids (likely naphthenic acids) may be described by $C_nH_{2n+z}O_2$. Petroleum acid characterisation in crude oils by FT-ICR MS has been reported in a number of studies, i.e. by (Qian et al., 2001a; Hemmingsen et al., 2006) the effects of thermal maturity (Hughey et al., 2004; Smith et al., 2009), biodegradation (Kim et al., 2005; Liao et al., 2012) and geochemical origins (Hughey et al., 2002) have also been investigated by this method.

The ultrahigh resolving power and mass accuracy of FT-ICR MS allows petroleum components to be categorised according to their compound "class" as this refers to the number and type of X components, i.e. the elemental composition with the same number and type of heteroatoms ($N_nS_sO_o$) and also ring "types" which refers to the double bond equivalent (DBE) or z number which indicates the number of rings plus double bonds and can be used when describing the carbon number distributions for each compositionally distinct group of components i.e. (Hughey et al., 2001; Marshall and Rodgers, 2004) z can be used as a measure of aromaticity characteristic of a molecule, as the value becomes negative, the more aromatic a species becomes. DBE is also a convenient measurement of aromaticity as the value become higher with increasing in number of rings plus double bonds a compound has. DBE is defined as the number of hydrogen atom lacking from an elemental composition in comparison to the corresponding saturated molecule with otherwise identical numbers of carbon and heteroatoms (Al-Hajji et al., 2008). The DBE of compound can be calculated using following formula;

$$\text{DBE of } (C_c H_h N_n O_o S_s) = c - h/2 + n/2 + 1 \tag{1}$$

Every additional double bond or ring in the molecule will reduce the number of hydrogen atoms by two. DBE can be calculated from z number

$$\text{DBE} = -(z - n - 2)/2 \tag{2}$$

Where n is the number of nitrogen atoms. Details of hydrogen deficiency were described in Hsu (2010). With the elemental composition of a molecule determined by FT-ICR MS, a general molecular structure of the species can be obtained using the DBE value and carbon number (Shi et al., 2010). For example, in Figure 6.1 below, for a compound with an empirical formula of $C_n H_{2n+z} O_2$ (belonging to the "O_2 class"), acyclic acids have a DBE=1, z=0, as it contains one carbonyl group with a double bond and no rings. Naphthenic acids with two rings and one carbonyl group double bond have a DBE=3, and z=-4 while O_2 class compounds that contain one aromatic ring structure have a DBE 5 and -z=-8. Thus, naphthenic acids and aromatic acids can have the same number of DBE (DBE value of 5 and z value of -8) may comprise a naphthenic acid structure with four rings or an alkyl monoaromatic carboxylic acid.
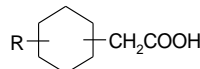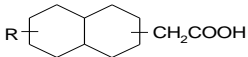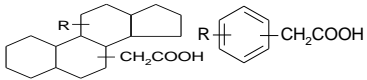
z	DBE	Examples of structure for O_2 compound class
0	1	RCOOH
-2	2	
-4	3	
-6	4	
-8	5	

Table 6.1 Examples of structures of O_2 class compounds with their corresponding hydrogen deficiency (z) and double bond equivalent (DBE) values.

The aims of this section of work were:

I.   To investigate the types of carboxylic acids in crude oils using FT-ICR MS and particularly those correlated with the oil acidity (TAN).

II.   To investigate the distribution of petroleum acids in the asphaltene and maltene fractions of crude oils using FT-ICR MS and how they contribute to the whole oil TAN.

6.2 Samples

A set of 6 crude oil samples (see Table 6.2) from the UK North Sea and California were subjected to TAN value measurement by a modified ASTM D664 method (described in Chapter 4). The maltenes and asphaltene fractions from each oils were also isolated and analysed in order to investigate the distribution of acidic species corresponding to acidity (TAN).

Sample	Origin	TAN mg KOH/g sample		
		Whole oils	Maltenes	Asphaltene
EN 154	North Sea	0.11	0.45	5.88
EN 149	North Sea	1.14	1.06	6.52
EN 174	North Sea	1.94	1.81	6.66
EN 151	North Sea	7.58	6.85	21.24
D13	California	1.55	0.89	4.27
H7	California	2.19	1.17	4.57

Table 6.2 List of samples (oils, maltenes and asphaltenes) along with their origin and TAN measured according to the modified ASTM D664 method.

6.3   Results

6.3.1   FT-ICR MS on North Sea samples

6.3.1.1   Heteroatom species distribution: North Sea oils
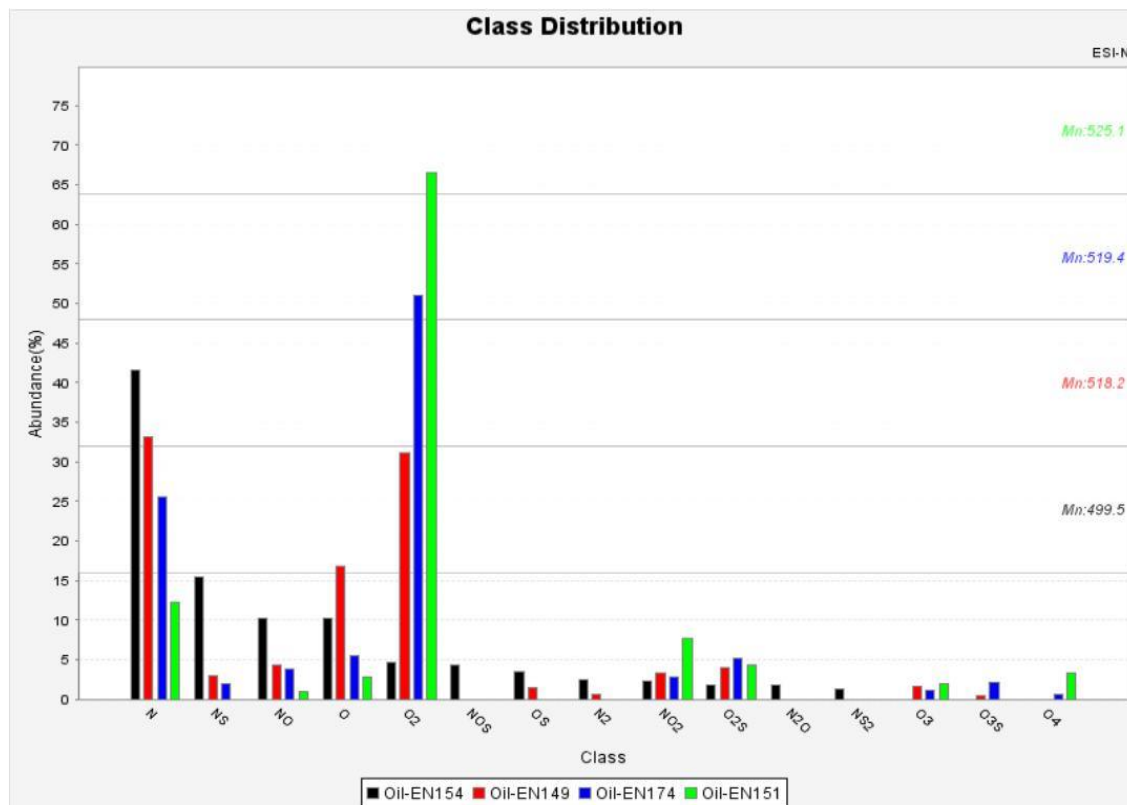
Figure 6.1 Distribution of heteroatom classes in North Sea oils sample set.

Figure 6.1 shows the distribution of heteroatom species contained in a set of four crude oils in a sequence of increasing TAN (EN 154<EN 149<EN 174<EN 151), obtained using negative ion (-ESI) ESI FT-ICR MS. The analysis identified 15 different main heteroatom compound classes (N, NS, NO, O, O_2, NOS, OS, N_2, NO_2, O_2S, N_2O, NS_2, O_3, O_3S and O_4). In general, the O_2 compound class appeared to be the most abundant (up to 67%) in this set followed by N >O >NO_2 >O_2S >NS, while other compound classes are in relatively low (below 5%) abundance. A positive trend of increasing of O_2 compound class was observed with increasing acidity (TAN value). On the other hand, the N compound class distribution showed the opposite trend from that of the O_2 compound class with the increasing of TAN. Another observation is that, lower TAN oils contain a relatively wider distribution of heteroatom species than higher TAN oils. The lowest acid EN 154 oil contained 12 main compound species, with more than 60% of total species being N-containing (i.e. N, NS, NO, NOS, N_2, NO_2, N_2O and NS_2). The

highest acid EN 151 oil, had only 8 main heteroatom compound species and most of the compounds are O-containing species (O, O_2, O_3, and O_4). A possible explanation for this is that the sensitivity of detection for each individual compound in the ESI-MS analysis depends on the ionisation efficiency (Hemmingsen et al., 2006) and since the relative abundance is scaled separately for each mass spectrum, the relative abundance is thus affected by the increases in the amounts of other classes. The reduction of the number of heteroatoms with increasing TAN could also be related to the limited dynamic range in FT-ICR MS. Naphthenic acids have good selectivity to ionisation in an ESI source, and so other species would be supressed and some of them might be undetectable, by addition of naphthenic acid (O_2) or other species to the mixture (Kim et al., 2005; Liao et al., 2012). When comparing the percentage abundance of O_2 class compounds in each of the oils, the percentage of abundance increases as the TAN is increased from 5% for sample EN 154 (TAN 0.11) to 31% for EN 149 (TAN 1.14) to 51% for EN 174 (TAN 1.94) and finally to 67% for EN 151 (TAN 7.58).
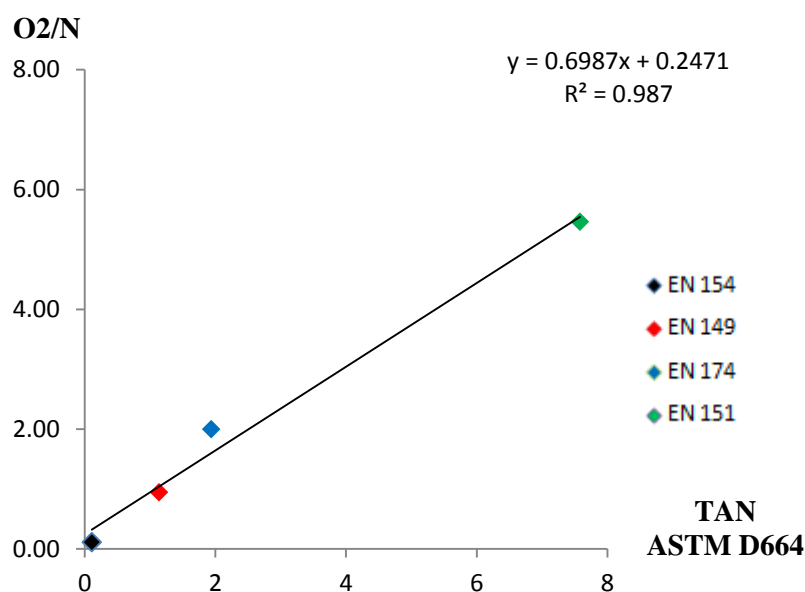
Figure 6.2 Correlations between O_2/N compound class ratio and TAN value for the

From Figure 6.2 it is clearly seen that the amount of O_2 species relative to N species greatly increases as TAN increases (ratio of O_2/N used for consistency purpose). A strong correlation with an $r^2=0.987$, suggests that that the O_2 compound class (i.e. carboxylic acids) is the main compound class that controls the acidity in the North Sea oils set. These results directly support the studies of (Meredith et al. (2000); Saab et al.

(2005); Vaz et al. (2013a)) who used FT-ICR MS, and proposed that the carboxylic acid fraction is a major contributor to their oils TAN.
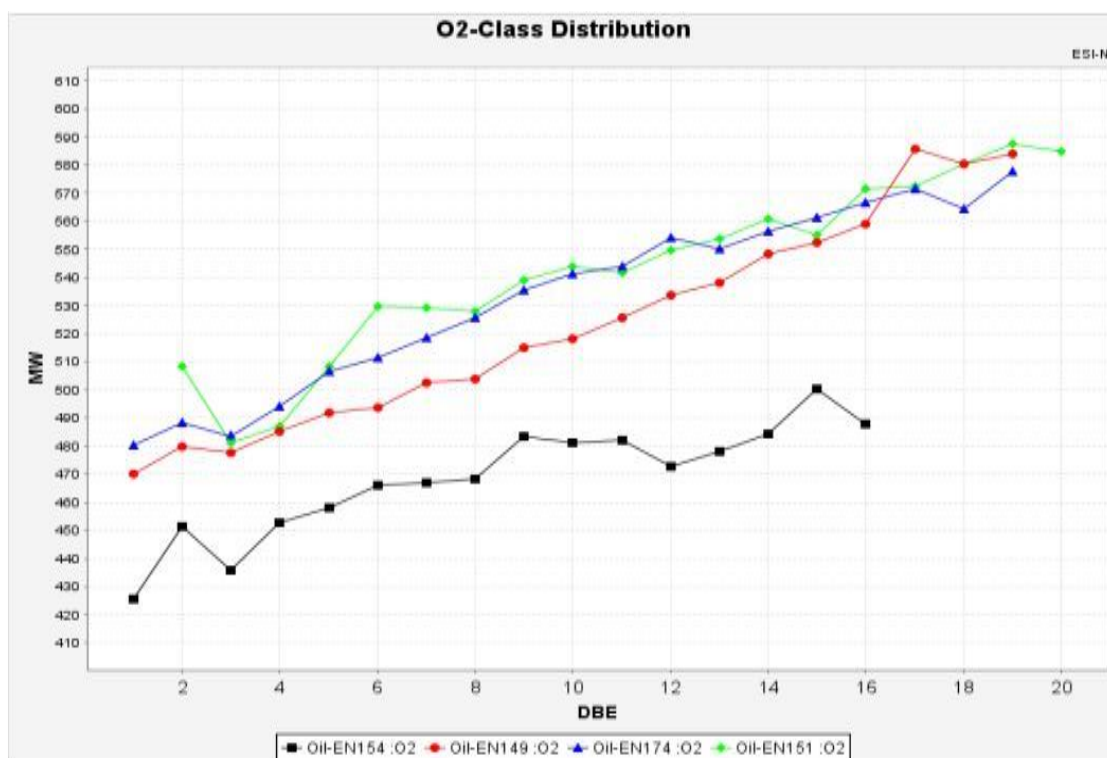
Figure 6.3 DBE distributions of O_2 compounds corresponding to their molecular weight (Mw) for North Sea oil sample set

Figure 6.3 shows that the molecular weights of the O_2 class compounds in the North Sea oils are distributed from 425 to 558. The samples plot in a sequence of increasing TAN (i.e. EN 154 lowest and EN 151 highest TAN), with a clear correlation seen as the molecular weight increases when TAN increases, i.e. O_2 class compounds with the same DBE show increasing molecular weight as oil TAN increases. This indicates more molecular structures with additional alkyl group in higher acidity oils. However, above a TAN value of 2.0, the trend is not as clear as that for the lower TAN samples. This observation is similar to the all O_2 class compound distributions for the other DBE compounds between samples with a TAN of 1.94 (EN 174) and a TAN of 7.58 (EN 151).
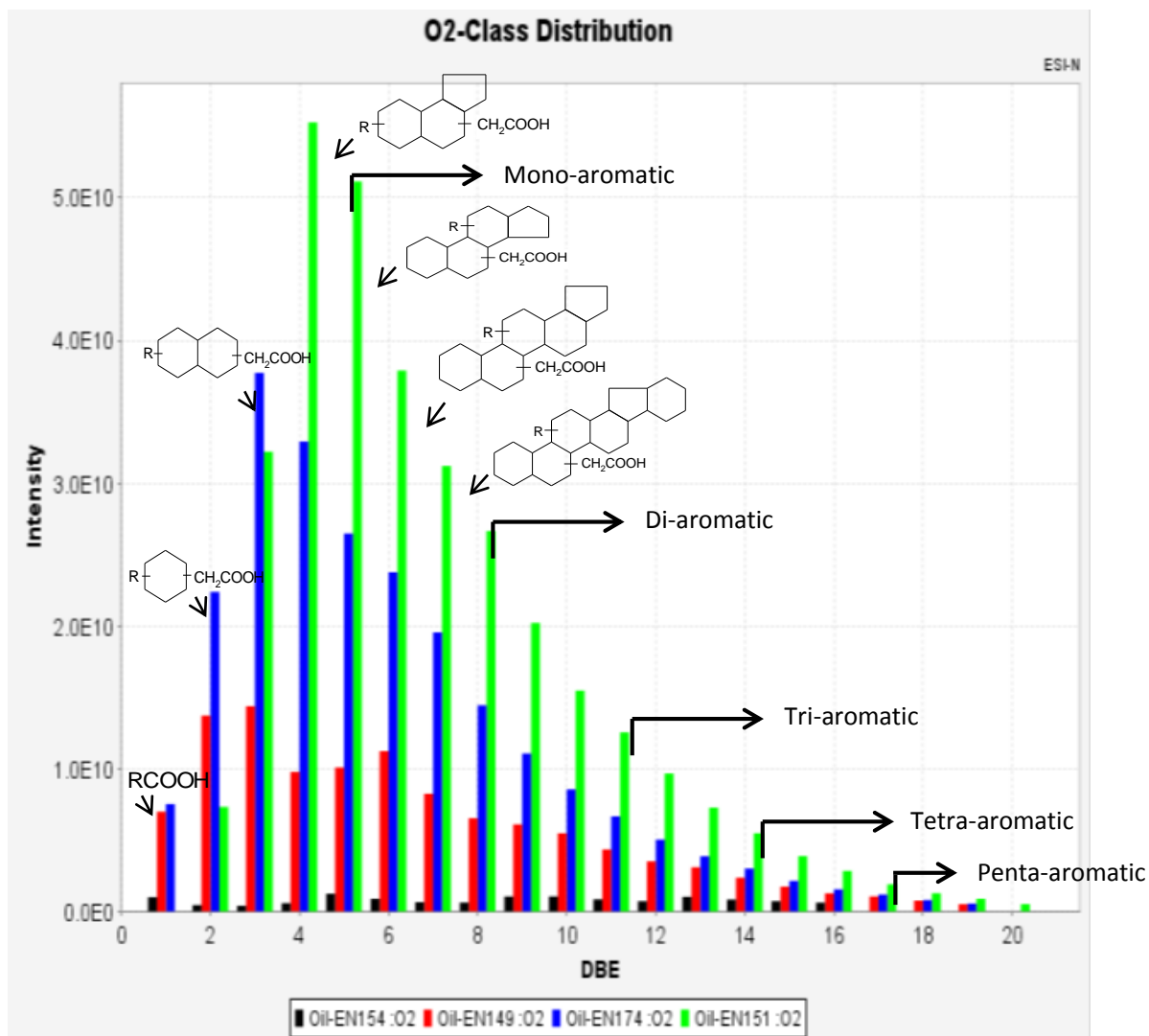
Figure 6.4 DBE distribution for the O_2 heteroatom class in the North Sea oil samples.

Figure 6.4 shows the DBE distribution of the O_2 compound class from the North Sea oils plotted in a sequence of increasing acidity (TAN). From the graph, the lowest acid oil EN 154 (TAN 0.11) is distributed from DBE=1 to DBE=16, two samples EN 149 (TAN 1.14) and EN 174 (TAN 1.94) are distributed from DBE=1 to DBE=19 while the highest acidity sample EN 151 (TAN 7.58) is distributed from DBE=1 up to DBE=20. This observation shows that the higher acidity oils contain a wider distribution of O_2 acid species than the lower acidity oils and confirm the previous observation made from Figure 6.3. The peak trend shows a shift of O_2 class intensity increasing towards 1) higher TAN oils, 2) higher DBE class: indicating O_2 acid structures with more rings and more aromatic as TAN increases. Based on the distribution from DBE=1 to DBE=20, the acids identified in the North Sea oil set are: saturated acyclic acids, 1 to 6 ring naphthenic acids, and 1 to 5 ring aromatic acids which is similar to findings by Hughey et al. (2002) in their low maturity, lacustrine oil from China. O_2 species with DBE=4,

which corresponds to a three ring naphthenic acids molecular structure, dominates sample EN 151 in the North Sea oil set, while O_2 species with DBE=3 which can be assigned as a two ring naphthenic acids molecular structure, appear to be the most abundant species in both oils EN 149 and EN 174. Further details of the O_2 compound class DBE distribution together with carbon number is shown in Figure 6.5. The $C_nH_{2n+2}O_2$ species in the high TAN EN 151 oil range from DBE = 2 to DBE = 20 with a predominant intensity of DBE = 4.
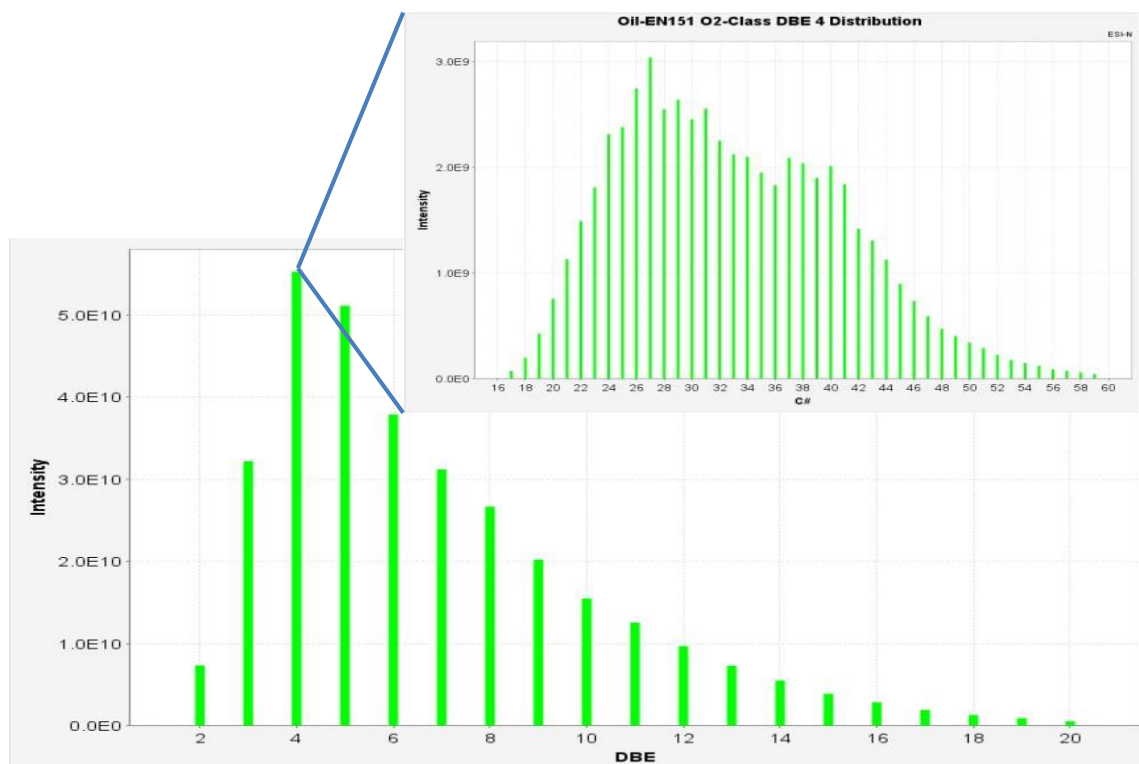
Figure 6.5 DBE distribution for members of the O_2 heteroatom class for sample EN151 (TAN7.58). (Top) Carbon number distribution for O_2 species with DBE=4

A wide range of DBE (2-20) compounds suggest that this high TAN EN 151 oil contains a variety of cyclic to polycyclic naphthenic and aromatic to polyaromatic acids (1-6 cyclic to penta-aromatic rings) of $C_nH_{2n+z}O_2$ general formula, though the highest relative intensities are concentrated in lower double bond equivalents (DBE=4-6). The intensities gradually decrease towards higher DBE acid structures which indicates that acid species with relatively small molecular structures and low DBE values control the acidity in this North Sea oil set and not the multiaromatic (higher DBE) structures. In Figure 6.5 (top), the DBE=4 carbon number distribution for that high acidity EN 151 oil suggests that the possible acid structures include naphthenic acids with 3 cyclic rings

with a carbon number distribution ranging from C_{17}-C_{59} with a subsidiary peak at C_{27}. Thus, the molecular formula of this latter acid is $C_{27}H_{48}O_2$ and some example possible molecular structures are shown in Figure 6.6.
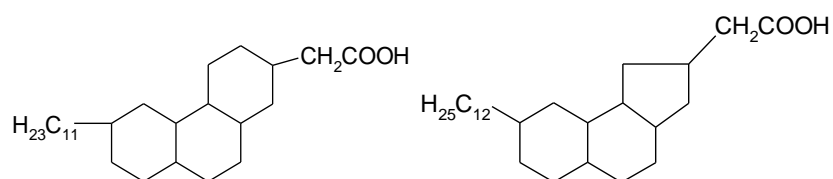
Figure 6.6 Example possible molecular structures for $C_{27}H_{48}O_2$ species with DBE=4 for sample EN151 (TAN 7.68)

The next most abundance series in this sample is DBE=5, which could correspond to a core of four saturated rings with an acid group. Another possible structure that shares the same DBE=5 would be a mono-aromatic acid.

6.3.1.2   Heteroatom species distribution: North Sea Maltenes samples
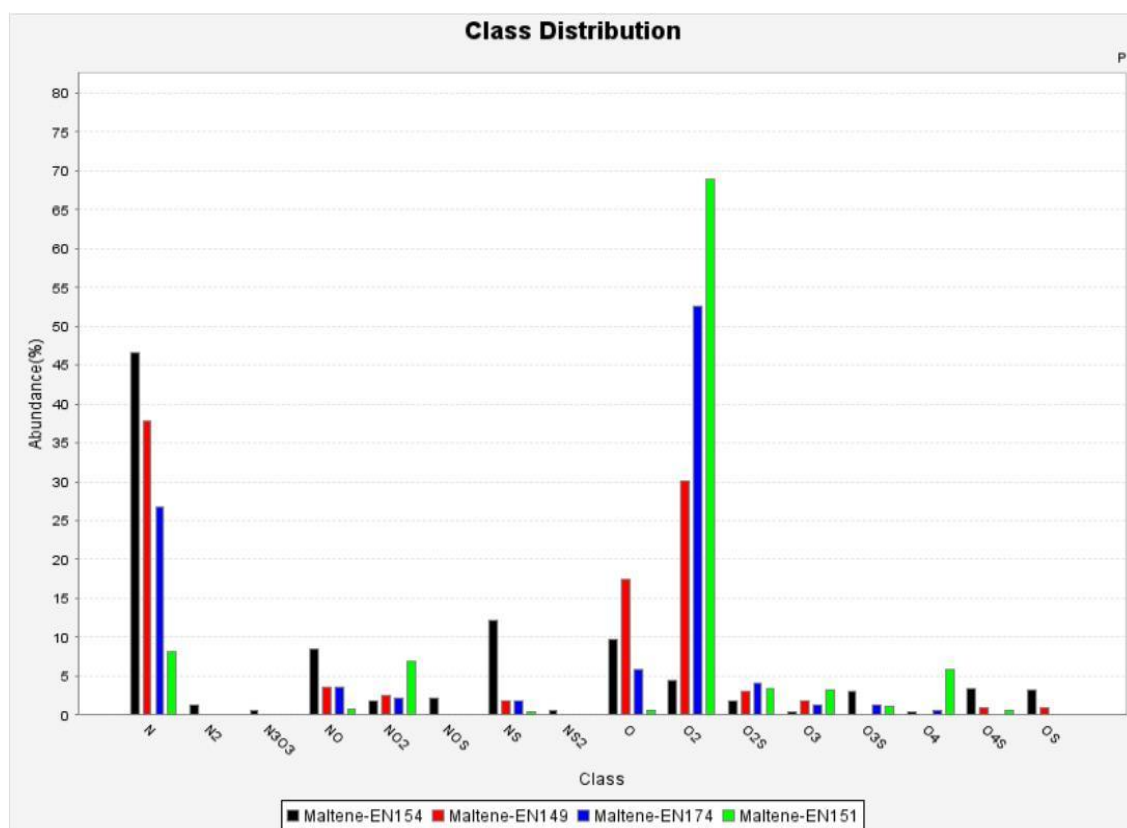
Figure 6.7 Distribution of heteroatom classes in North Sea maltenes sample set.

A total of 16 NSO heteroatom species (N, N_2, N_3O_3, NO, NO_2, NOS, NS, NS_2, O, O_2, O_2S, O_3, O_3S, O_4, O_4S, OS) are identified in the North Sea maltenes fractions analysed (Figure 6.7). Their relative abundances in the maltenes fraction of this sample set is plotted in sequence of increasing maltenes TAN, where EN 154 < EN 149 < EN 174 < EN 151 with TAN values of 0.45, 1.06, 1.81 and 6.85, respectively. From the above distribution, O_2 is the most prominent species amongst them. An increasing trend of abundance of O_2 species as the acidity (TAN) increases, can also be clearly seen, beginning from 5% for EN 154 to 30% for EN 149 to 53% for EN 174 and finally to 69% for EN 151. This observation suggests that O_2 group comprise mainly of molecules with a COOH (carboxylic acid) functional group. The second most abundant group is neutral nitrogen, N, which are believed to be mainly made up of pyrrole, carbazoles, indole groups (Teräväinen et al., 2007) A decreasing trend of relative abundance of N group species as acidity (TAN) increases is clearly seen from the above figure, which is an opposite trend compared to the O_2 species. This decreasing trend may in part be explained by the sensitivity for detection of each individual compound in the ESI MS analysis being dependent on the ionisation efficiency and abundant highly ionisable

groups may suppress the ionisation of other species present. For example, carboxylic acids exhibit higher ionisation, efficiency than other weak acids such as phenol, or thiophenes accounting part for the dominance of carboxylic compounds (Hemmingsen et al., 2006). However, the O-containing compounds with a formula of $C_nH_{2n+z}O$, showed no clear trend as acidity increased and these are likely corresponding to phenols and aromatic alcohols (DBE > 4) or aldehydes (for N_1 DBE < 4) (Kim et al., 2005). Thus, while phenols are acidic, this unclear trend suggests that O-containing species are not the main acid species that controls the high acidity in this set of maltenes fractions, which is in agreement with the findings of Meredith et al. (2000) who found no correlation of phenol concentrations measured by GC-MS in oils, with the acidities of the oils.
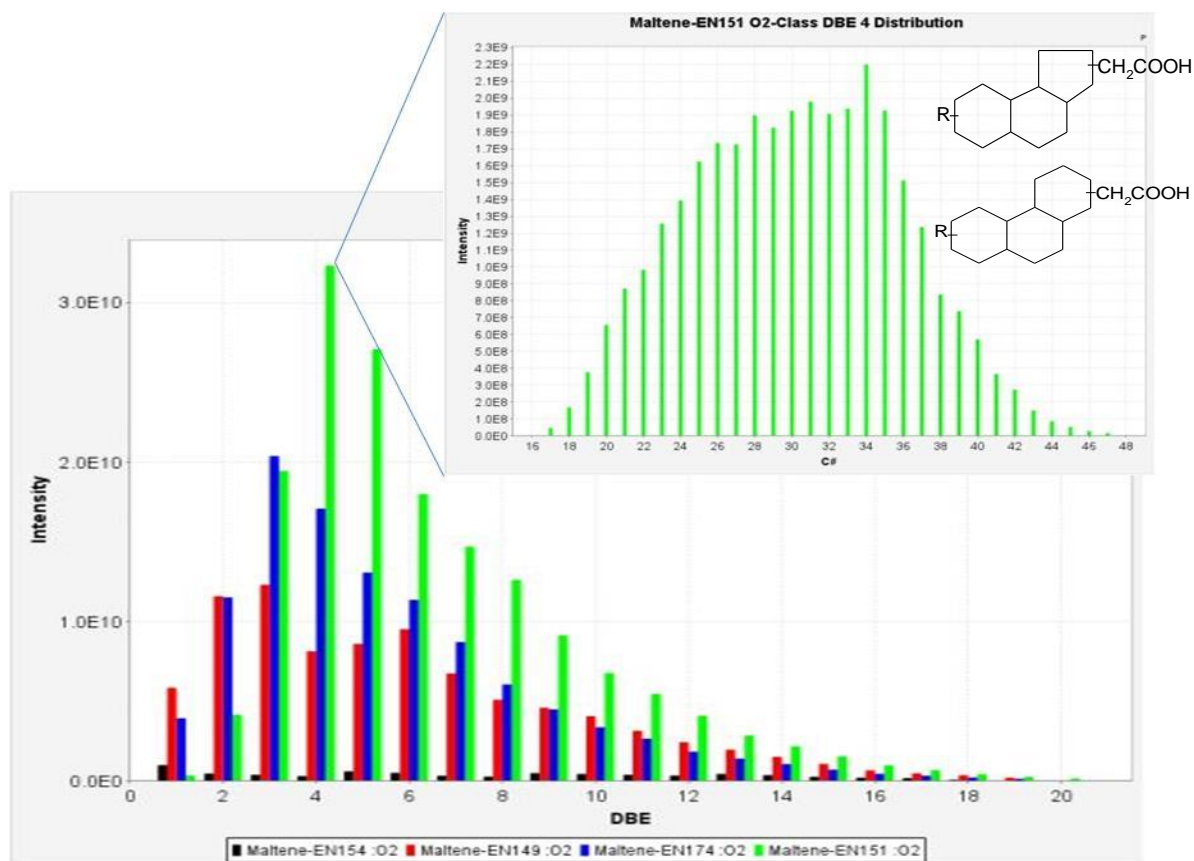
Figure 6.8 DBE distribution of the O_2 heteroatom compound class for the North Sea maltenes sample set (main) and (top) carbon number distribution for O_2 species with DBE=4 (high acidity maltenes sample EN151)

The DBE distribution of O_2 species versus their intensity in the North Sea maltenes is shown in Figure 6.8 in a sequence of increasing sample TAN. In general, DBE of $C_nH_{2n+z}O_2$ species in the North Sea maltenes are distributed from DBE=1 to DBE=20, which is comparable to the DBE distribution to their corresponding oils (see Figure 6.4) The compound type distributions for maltenes (Figure 6.7) and their corresponding oils (Figure 6.1) also exhibit high similarity. A likely explanation for this is that since the maltenes fractions generally comprise more than 90% of whole oils (Groenzin and Mullins, 1999) they are therefore likely to be similar to their corresponding whole oil compositions. The low acidity maltene sample (EN 154) has a low intensity distribution from DBE=1 to 17, but unlike in the other samples the acyclic fatty acids (DBE=1) are the most abundant (Figure 6.8). The O_2 species of the EN 149 and EN 174 maltenes sample are distributed from DBE=1 to 19 with the DBE=3 class (corresponding to 2 rings naphthenic acids) most abundant, while for the highest TAN maltene (EN 151) a wider distribution (DBE=1 to 20) is identified, with highest concentration of DBE=4 species. These DBE=4 species correspond to 3 ring naphthenic acid molecules that have a carbon number distribution ranging from C_{17} to C_{47}, with the highest intensity at C_{34} (Figure 6.8). This observation indicates more polycyclic and polyaromatic acids structures are found in higher acidity maltenes. These observations suggest that although the North Sea maltenes fractions contain a wide distribution of the $C_nH_{2n+z}O_2$ molecular species, from acyclic up to 6 ring aromatic systems (DBE=20), the O_2 species in this sample set are mainly concentrated in a low ringed naphthenic acids (< DBE=5), indicating that their high acidity (TAN) may be controlled by a low ring number naphthenic acid structures.

6.3.1.3   Heteroatom species distribution: North Sea Asphaltenes
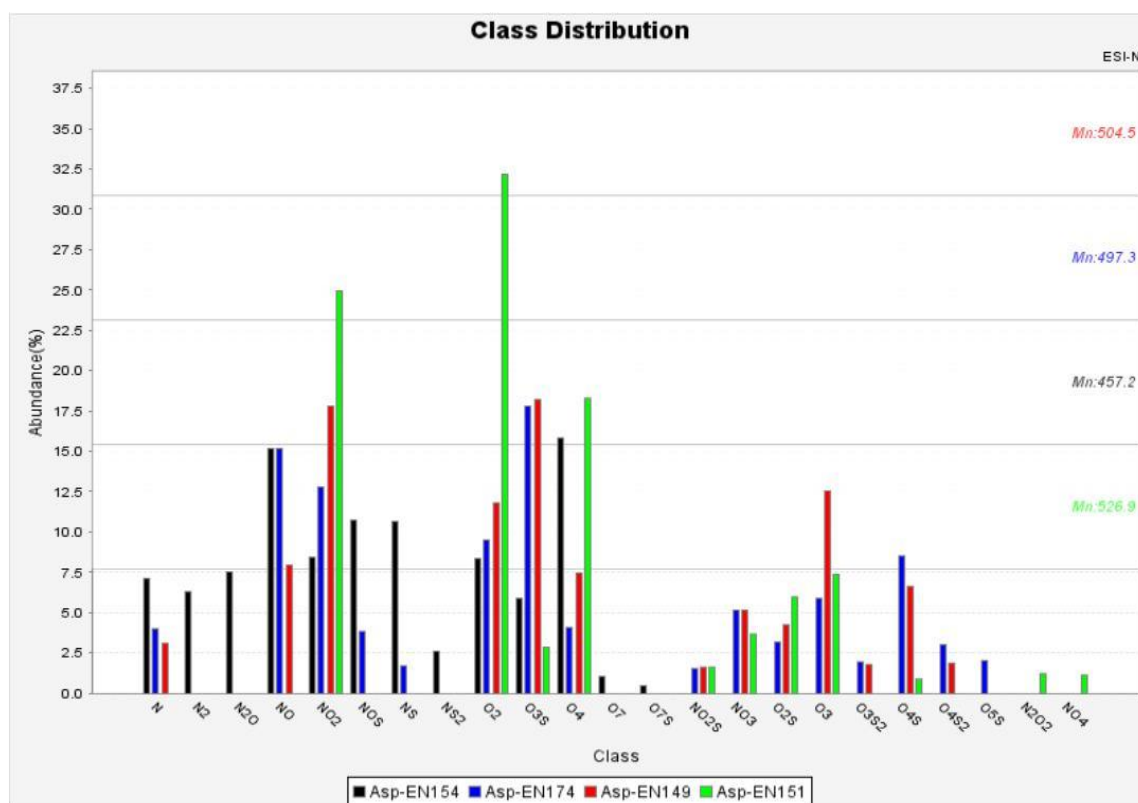
Figure 6.9 Distribution of heteroatom classes in North Sea asphaltenes sample set.

The distribution of acidic heteroatom classes in the North Sea asphaltene fractions is shown in Figure 6.9, in a sequence of increasing TAN i.e., EN 154 (TAN 5.88), EN 174 (TAN 6.52), EN 149 (TAN 6.66) and EN 151 (TAN 21.24). The figure shows an extremely complex variety of heteroatom species identified in asphaltene fractions, including 23 species of strong acids, weak acids and non-basic nitrogen-containing species (N, N_2, N_2O, NO, NO_2, NOS, NS, NS_2, O_2, O_3S, O_4, O_7,O_7S, NO_2S, NO_3, O_2S, O_3, O_3S, O_3S_2, O_4S_2, O_5S, N_2O_2, NO_4). A complex variety of heteroatom species in asphaltene has been reported in previous work by Klein et al. (2006b) where their asphaltene deposit sample found to be dominant in species that contain multiple heteroatoms and those that contain oxygen. Among these, the O_2 compound class appeared the most prominent, with a clear trend of increasing percentage abundance from 8% for EN 154, to 9% for EN 149, to 12% for EN 174 and to 32% for EN 151 as the asphaltene samples TAN values increase. This indicates that the O_2 species (probably as carboxylic acids) is one of the main species that controls the acidity in this asphaltenes set of sample. The next most abundant species is NO_2, presumably pyrrole and indole benzolog components that contain carboxylic acid functional groups. A clear trend of increasing in percentage abundance of this compound class is seen as the

acidity of the asphaltenes samples increase from 8.5% to 13% to 18% and finally to 25% in the sequence of increasing TAN samples, which also suggest that this species may be one of the species that controls the TAN of asphaltenes. Although, this class (NO_2) has a relatively low abundance (<8%) in their corresponding parent oil, and maltenes fraction (Figures 6.1 and 6.9, respectively). The highest acidity asphaltenes (EN 151) contain relatively high abundances of O_2, O_4, O_2S, N_2O_2 and NO_4 species. However, no clear trend of abundance was observed in O_4 species as the acidity increases, since the lowest acidity asphaltenes (TAN 5.88) contained 16% O_4 species, but as the sample TANs increased to 6.52 and 6.66, the percentage abundance of O_4 dropped to 4% and 7%, respectively, and finally as the TAN increased to 21.24, the O_4 percentage increased back up to 18%. This lack of correlation suggests that the O_4 compound class does not have a major control on the acidity (TAN) of North Sea oil asphaltenes. On the other hand, the lowest TAN asphaltenes sample (EN 154) appears to have a highest relative abundance of N, N_2, NOS, NS, NS_2, O_7, O_7S species compared to other asphaltene samples. O_7 species were observed only in EN 154 and were not in any of the other oils.
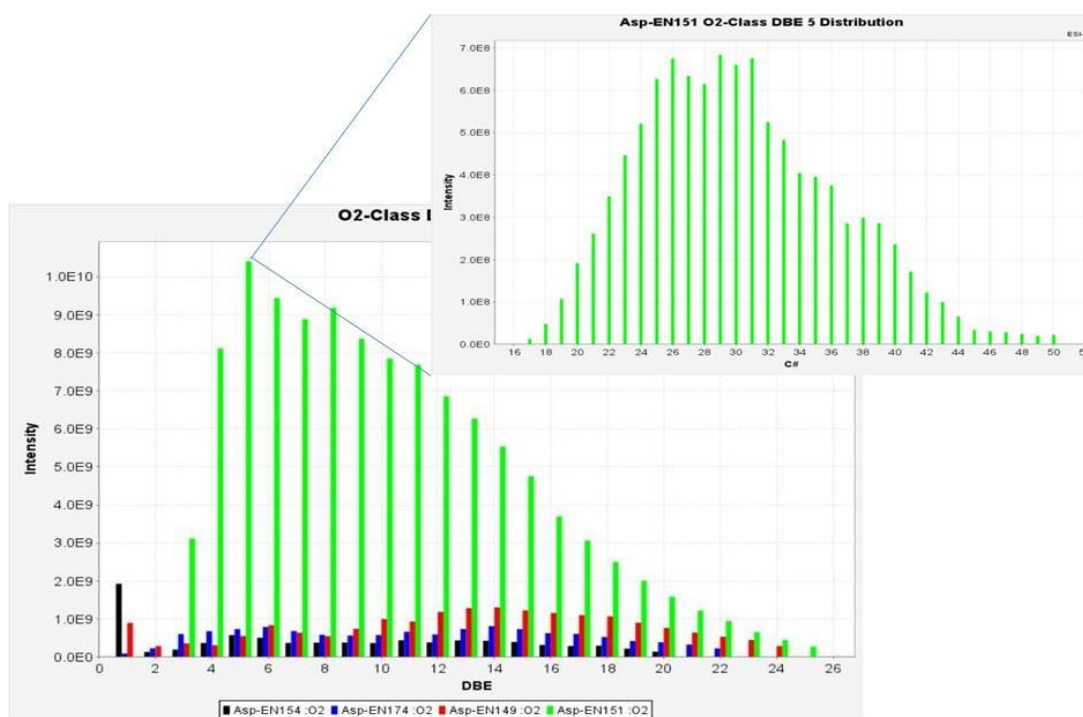
Figure 6.10 DBE distributions for members of O_2 heteroatom compound class for the North Sea asphaltenes sample set. (Top) Carbon number distribution for O_2 species with DBE=5 (high acidity asphaltenes sample EN151)

The DBE distribution of O_2-species in North Sea asphaltenes is shown in Figure 6.10. In general, the distribution of $C_nH_{2n+z}O_2$ species is distributed from DBE=1 to 25. The distribution of O_2-species in the lowest TAN sample (EN 154) is from DBE=1-20, in the EN 174 sample from DBE=1-22, while in the next highest TAN sample (EN 149) it is from DBE=1-24 and finally for highest acidity (TAN) sample (EN 151) the O_2-species is distributed from DBE=3-25. These distributions showed that as the acidity of asphaltenes increases, the O_2 species DBE distribution increases, suggesting increasing aromatic systems with O_2 acid groups in this North Sea asphaltenes set, where DBE values of up to 25 correspond to a 7 aromatic ring core structure. Figure 6.10 shows $C_nH_{2n+z}O_2$ species with DBE=5 to be the most abundant acidic species with carbon number ranging from C_{17} to C_{50} where C_{26}, C_{29} and C_{31} are most dominant. There is a significant difference of the relative intensity for most of O_2 class DBE distributions between the highest acidity asphaltene (EN 151) and the other samples (EN 154, EN 149, EN 174). This observation may be explained by EN 154, EN 149, EN 174 samples having only slight differences in their TAN values (of 5.88, 6.52 and 6.66, respectively), thus the relative intensity of DBE distribution of O_2 class also only slightly increases, while there is a big acid value (TAN) gap between those three samples (TAN <6.67) and that of sample EN 151 (TAN=21.24). These observations provide evidence that the high acidity of North Sea asphaltenes are controlled by O_2 species (mostly polycyclic and aromatics acids).

6.3.2   FT-ICR MS on Californian samples

6.3.2.1   Heteroatom species distribution: California oils
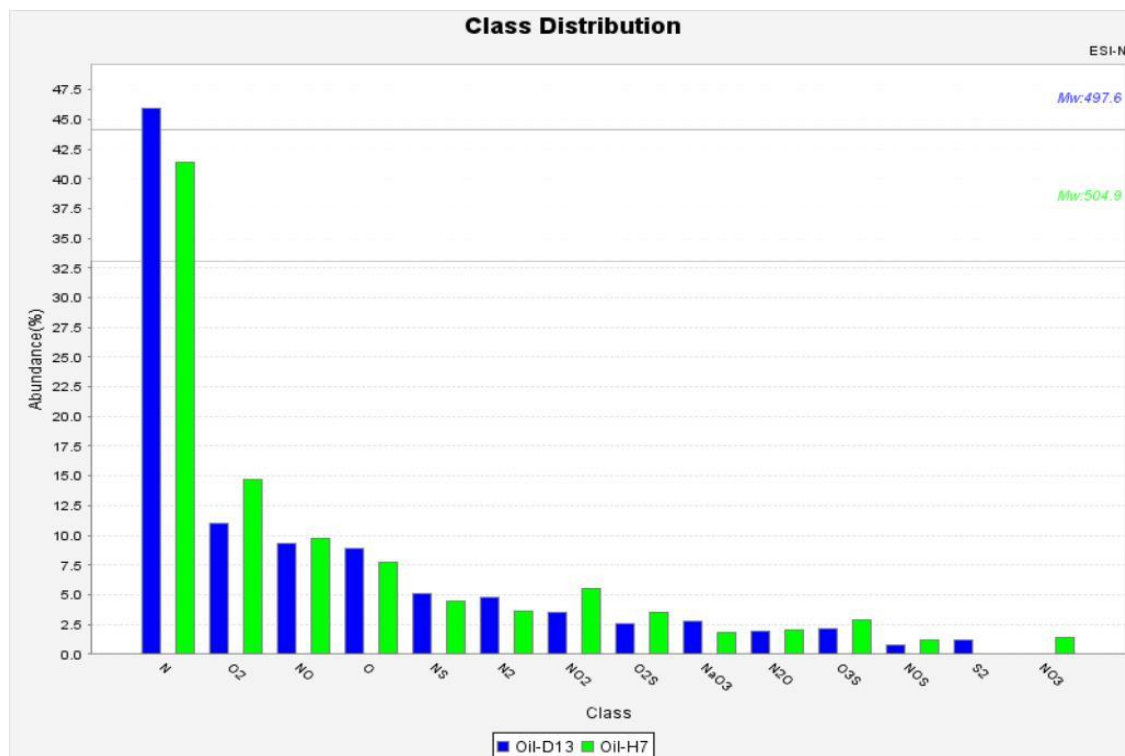
Figure 6.11 Heteroatom class distributions in the Californian oil samples.

Detailed acidic polar compositions of the Californian oil samples derived by (-) ESI FT-ICR MS are shown in Figure 6.11 above. The samples are plotted in a sequence of increasing TAN, where the TAN values are 1.55 and 2.19 for samples D13 and H7, respectively. The Californian oils contained a total of 14 different heteroatom species of strong acids, weak acids and non-basic species with 11 common compound classes, N, N_2, N_2O, NO, NO_2, NS, NOS, O, O_2, O_2S, O_3S . The S_2 class appears only in D13 and not in H7 and the NO_3 class appears in H7 and not in D13, though both these two heteroatom classes have low percentage abundances (<1.5%). Neutral nitrogen, N compounds dominated in both samples with up to 46% abundance (presumably pyrrole and carbazole homologues). The second most abundant species is the O_2 compound class where in the higher TAN H7 sample, they are 4% higher than in the sample D13 oil. A similar increase of O_2 species as the TAN increased was noted in the North Sea oil set, suggesting that O_2 compound class might also affects the acidity in these oils. Although the Californian oils are considered high TAN, the percentage of abundance of strong acid O_2-species was only < 15% for sample H7 (TAN of 2.19) compared with the North Sea oil samples of comparable TAN (i.e. EN 149, 1.14, and EN 174, 1.94) which

shows O_2 species with 31.20% and 51.06 % abundances, respectively. This observation may indicate that the O_2 species abundance may not be the only control on their high acidities.
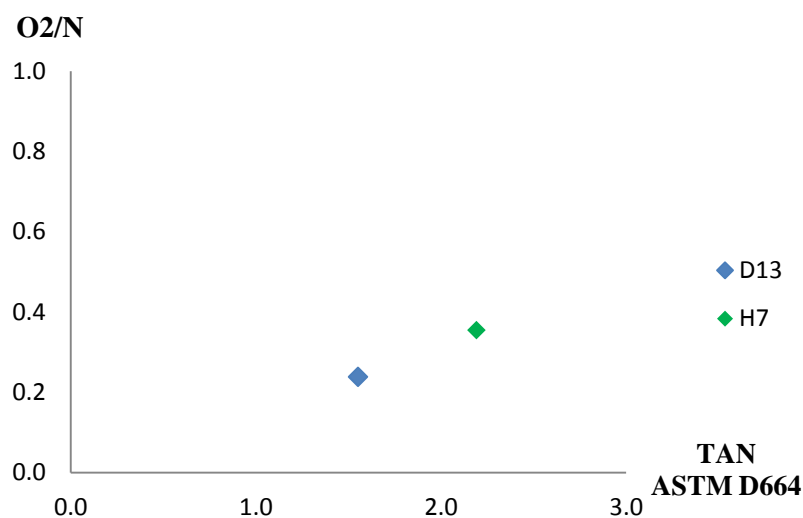
Figure 6.12 Plot of O_2/N and TAN values for the Californian oil samples

Figure 6.12 shows the O_2/N species ratios for the Californian oils plotted against their corresponding TAN values which shows that their TAN increases as their O_2 species relative abundance increases. However, unlike the approximately one to one correlation between O_2/N to their TAN values seen in North Sea oil sample set (see Figure 6.2), the O_2/N ratio in the Californian oils appears to be ~7 times lower. This observation is consistent with the previous observation from Figure 6.11, where the relative abundance of the O_2 compound class is not as prominent in the Californian oils as the North Sea oil sample set. This also suggests that O_2-compound class (mainly naphthenic acids) may not be the only major acidic class compound that controls the TAN of these Californian oils and that other acidic species may also contribute to their high acidity. This result supports the work by Smith et al. (2008) which claimed that naphthenic acids may not be the sole cause of high TAN and also the suggestion of Meredith et al. (2000) that some sulphur compounds may effect oil TAN.
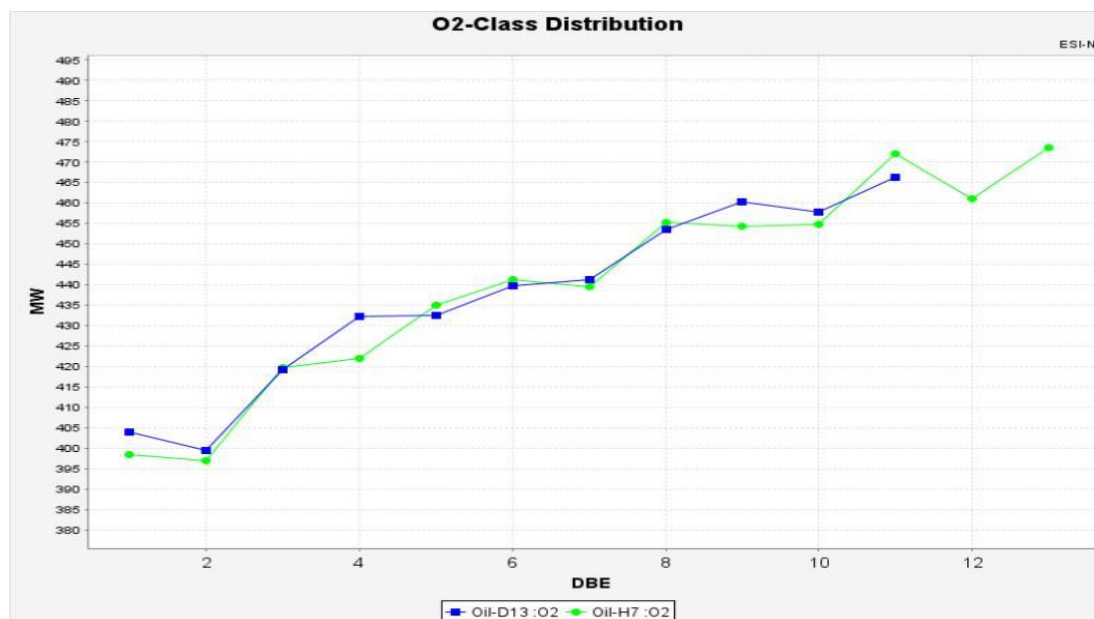
Figure 6.13 DBE distributions of O_2 compounds in the Californian oil samples plotted against their molecular weight.

Figure 6.13 shows the O_2 compound class DBE distributions in the Californian oil samples plotted against their molecular weight. Although the O_2 compound class appears not to be the only main controller of in acidity in these Californian oils, the molecular weights (Mw) of the species in this compound class ranged from 398 to 475 with the highest TAN oil (H7) having a higher Mw species than the lower TAN sample (D13). This range of O_2 species in this sample set is smaller than that in the North Sea oil set, which was from approximately 470 to 560, indicating that molecular structure of O_2 species in the Californian oils were of lower complexity and less aromatic than the O_2 acid species in acidic North Sea oils, though the reasons for this require further investigation.
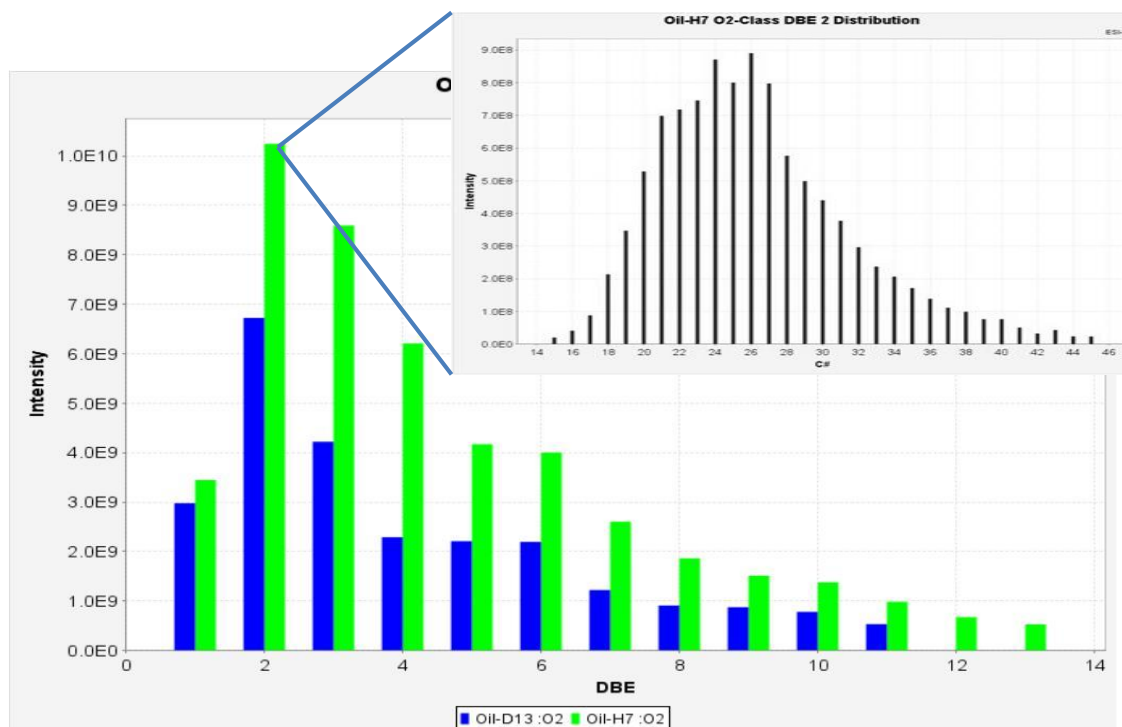
Figure 6.14 Distribution of DBE for members of O_2 heteroatom class for Californian oils sample set. (Top) Carbon distribution for O_2 species with DBE=2 (high acidic oil sample)

The intensity of the O_2 compound class with their DBE distribution in Californian oil is shown in Figure 6.14. The higher acid sample (H7) with a TAN of 2.19 contains a wider DBE distribution (1-13) compared to sample D13 with a TAN 1.55 with DBE values between 1 to 11. Both oils are dominated by DBE=2 O_2 species with which are believed to be naphthenic acids with one cyclic ring structure, followed by DBE=3 two ring napthenic acids. These most abundant one ring naphthenic acids (DBE=2) have C number ranging from 15-45, centred at C_{26} and C_{27} (Figure 6.14 top).

6.3.2.2   Heteroatom species distribution: California maltenes
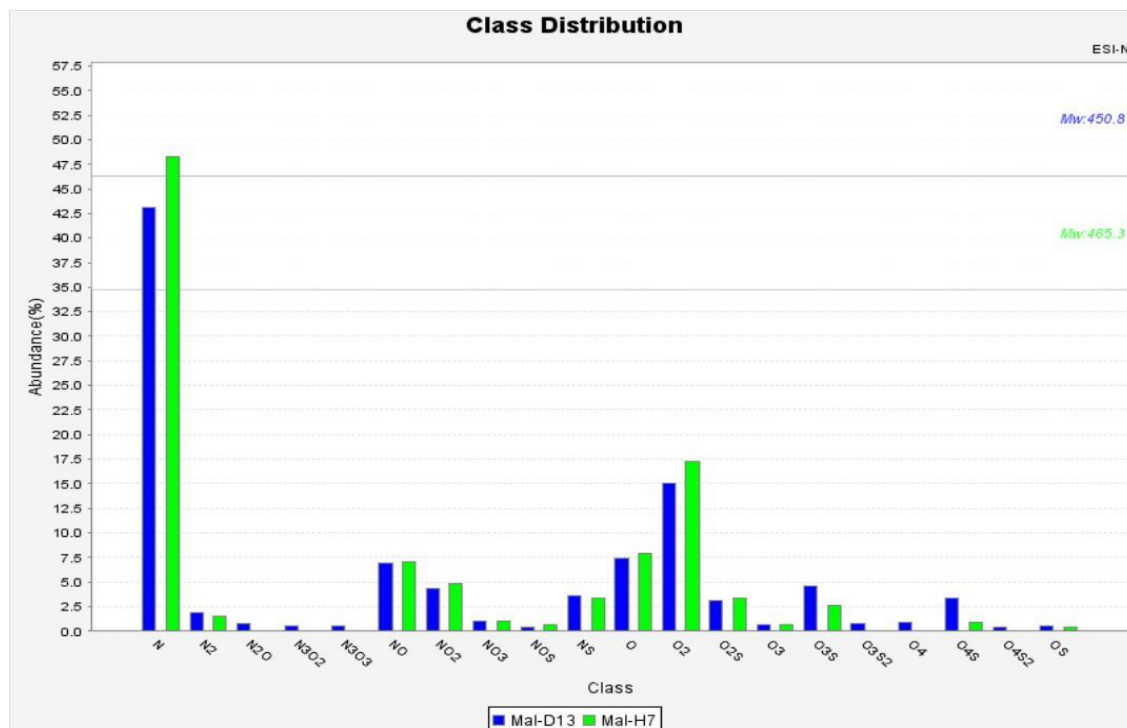
Figure 6.15 Distribution of heteroatom classes in Californian maltenes sample set.

The acidic polar compound compositions of the Californian oil maltenes samples derived by (-) ESI FT-ICR MS are shown in Figure 6.15 above where the samples are plotted in a sequence of increasing TAN. From the figure, a total of 20 different heteroatom species are distributed with 14 similar heteroatomic compounds (N, N_2, NO, NO_2, NO_3, NS, NOS, O, O_2, O_2S, O_3, O_3S, O_4S, OS) found in both maltenes amples. While N_2O, N_3O_2, O_3S_2, O_3S_2, O_4, O_4S_2 classes not detected in the H7 maltenes, this sample shows relatively slightly higher N_1-class (48%) and O_2 class (17%) compounds than that of D13. The neutral nitrogen N1 class dominated in both samples, with up to 46% abundance in the D13 sample, presumably due to the presence of pyrrole and carbazole homologue). The O_2 compound class was the second most abundant, with an increasing abundance from 15% for D13 to 17% for H7 as the maltenes TAN increased. The next most abundance species were O and NO, but these compound classes appeared to have no clear correlation with maltene acidity, though this observation might be due to limitations in sample numbers since only two maltenes samples were in this sample set. However, the O and NO compound classes also gave a similar unclear correlation in the previous North Sea maltenes set, thus it suggests that these species are not the main species that control the acidity in maltenes.
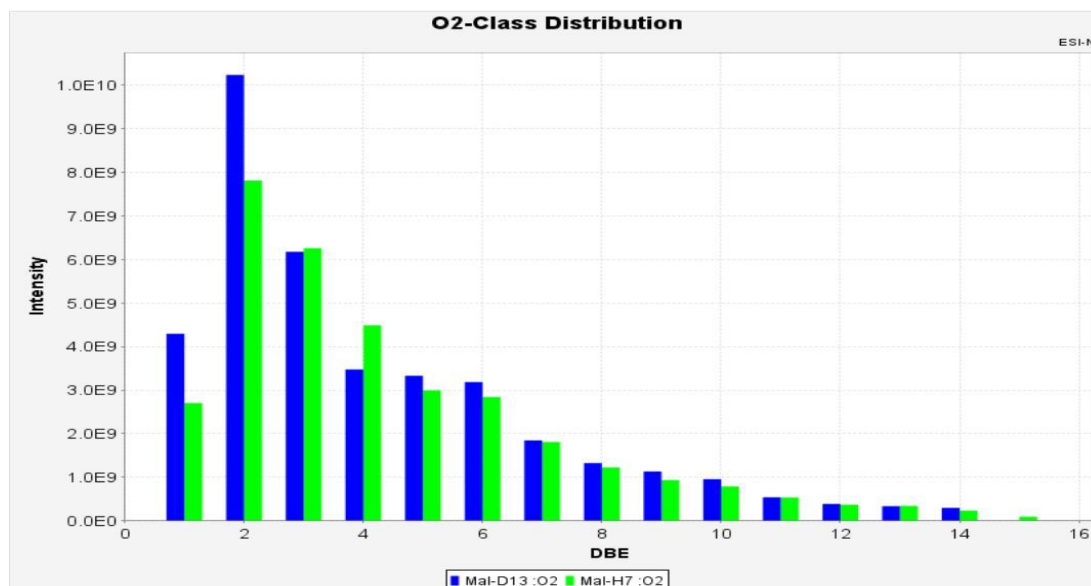
Figure 6.16 O_2 compound class DBE distributions for the Californian oils maltenes.

Figure 6.16 shows distribution for the plots of O_2 class DBE intensities in the Californian maltenes samples. The ranges of DBE for this set are from 1 to 15 with the maximum intensity at 2, which suggests one saturated ring naphthenic acids. DBE values of 1 to 15 indicate a distribution of carboxylic acid structures ranging from acyclic up to tetra-aromatic acids. With the abundance of low ring number naphthenic acids (< 1double bond + 3 aromatic rings), this observation is comparable with the O_2 species DBE distributions of their corresponding crude oils where the (1 double bond + 1 cyclic ring) acid structure appeared to be the most prominent. However, the intensity of O_2 species in the lower TAN D13 sample appeared as the most prominent compared to the H7 sample in most of the DBE range which is contrast to that observed in the North Sea samples. This observation again may suggest that these O_2 species (naphthenic acids) are not be the only species that responsible for controlling the acidity in these Californian samples.

6.3.2.3   Heteroatom species distribution: California asphaltenes
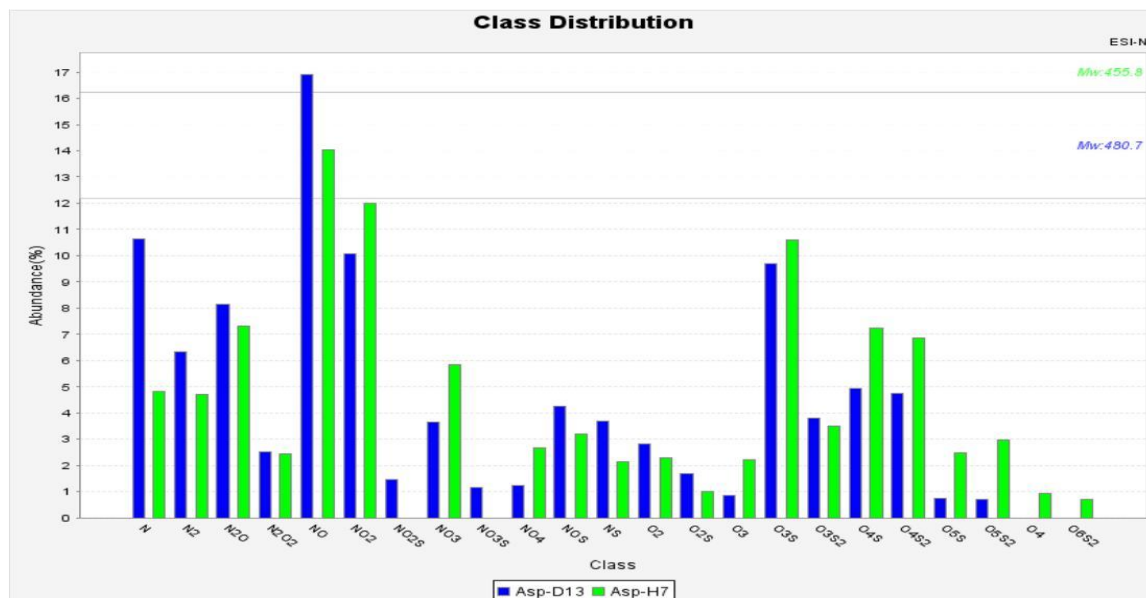
Figure 6.17 Distribution of heteroatom classes in Californian asphaltenes sample set.

The heteroatom species distribution for the Californian asphaltene samples is shown in Figure 6.17 above, in sequence of increasing TAN where the Asp-D13 TAN value is 4.27 and that of asp-H7 is 4.57. In general, the asphaltenes for this set of fractions contain up to 23 heteroatom species. The species in highest relative abundance is the NO species, which decreases as asphaltene, TAN increases. The next most abundant are the acidic NO_2 and O_3S species, which increase in abundance as the asphaltenes TAN increases. These compound classes might therefore be ones that contribute to the acidity in this sample set. The strong acid species, O_2 appear approximately only relative abundance levels of 3% and 7% in samples D13 and H7, respectively. This indicates that the carboxylic acid (including the naphthenic acids) may not be the main species responsible for the acidity in these Californian asphaltenes. Due to the highly complex variety of multi-heteoatom species in these Californian asphaltenes and the small sample set, no clear trend is observed in their DBE distributions (Figure 6.18).
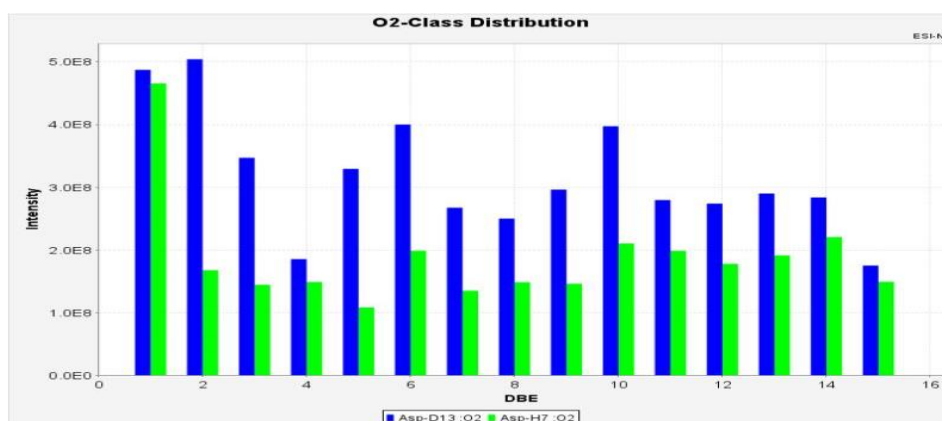
Figure 6.18 O_2 compound class DBE distributions of the Californian asphaltene samples.

6.3.3 *Distribution of heteroatomic compounds in oil, maltene and asphaltene fractions of North Sea samples*
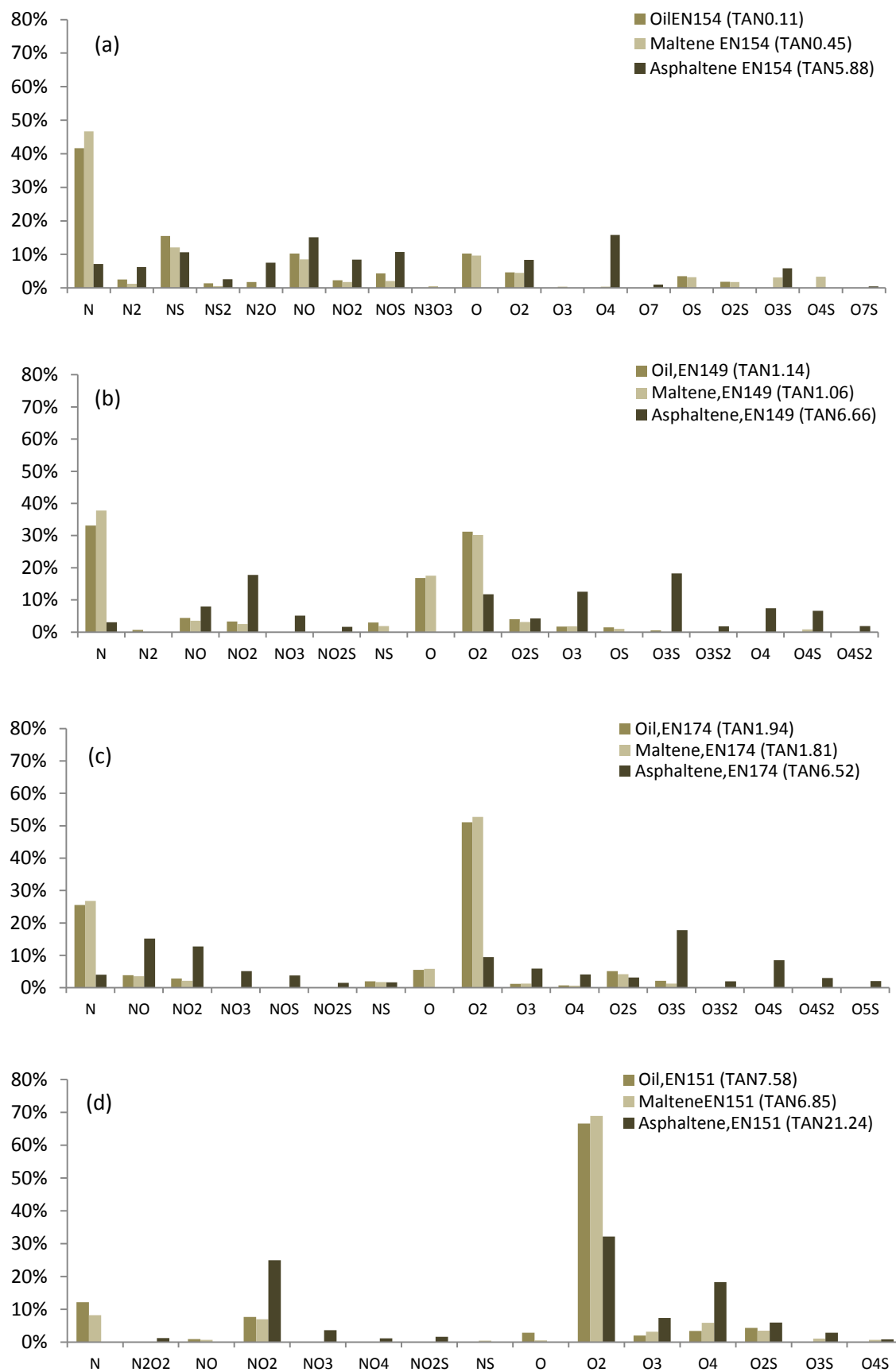
Figure 6.19 Distributions of heteroatomic compounds in oils, maltenes and asphaltenes in the North sea sample set. (a) EN154, (b) EN149, (c) EN174, (d) EN151 (samples listed in sequence of increasing biodegradation) 109

The distribution of heteroatomic compound classes in oils and their maltene and asphaltene fractions for samples EN 154, EN 149, EN 174 and EN 151 are shown in sequence of increasing TAN in Figure 6.19 (a-b). In general, in oils and their fractions with higher TAN values, the relative abundance of O_2 species becomes more prominent compared to lower TAN samples. This may also be a reason for lower detection of other different heteroatomic species in the high TAN samples; although the amounts of them may be comparable, the high ionisation efficiency of strong acids (such as naphthenic acids) in the samples suppresses the ionisation of other species. This, could explain why a low TAN sample (i.e. EN 154) shows a quite a large variety of heteroatomic species (up to 19 species) compared to other samples. When we observe the heteroatom distributions among fractions, the maltene fraction are likely similar to their corresponding crude oil. Asphaltenes on the other hand, show a larger diversity of heteroatomic compounds and a higher relative abundance of multiply oxygenated species than their corresponding oils and maltenes. Moreover, there is no stand out species appear, suggesting that high acidities in asphaltenes, unlike those in the crude oils and maltenes, are contributed by many of acidic NSO polar compound classes. For example, EN 154 asphaltenes (TAN 5.88) contain comparable percentage abundances of O_4, NO, NOS, NS and O_2 species while a very high TAN (21.24) asphaltene sample, EN 151, contain mainly O_2, NO_2 and, O_4 species.

6.*3.4 Distribution of heteroatomic compounds in oil, maltene and asphaltene fractions of Californian samples*
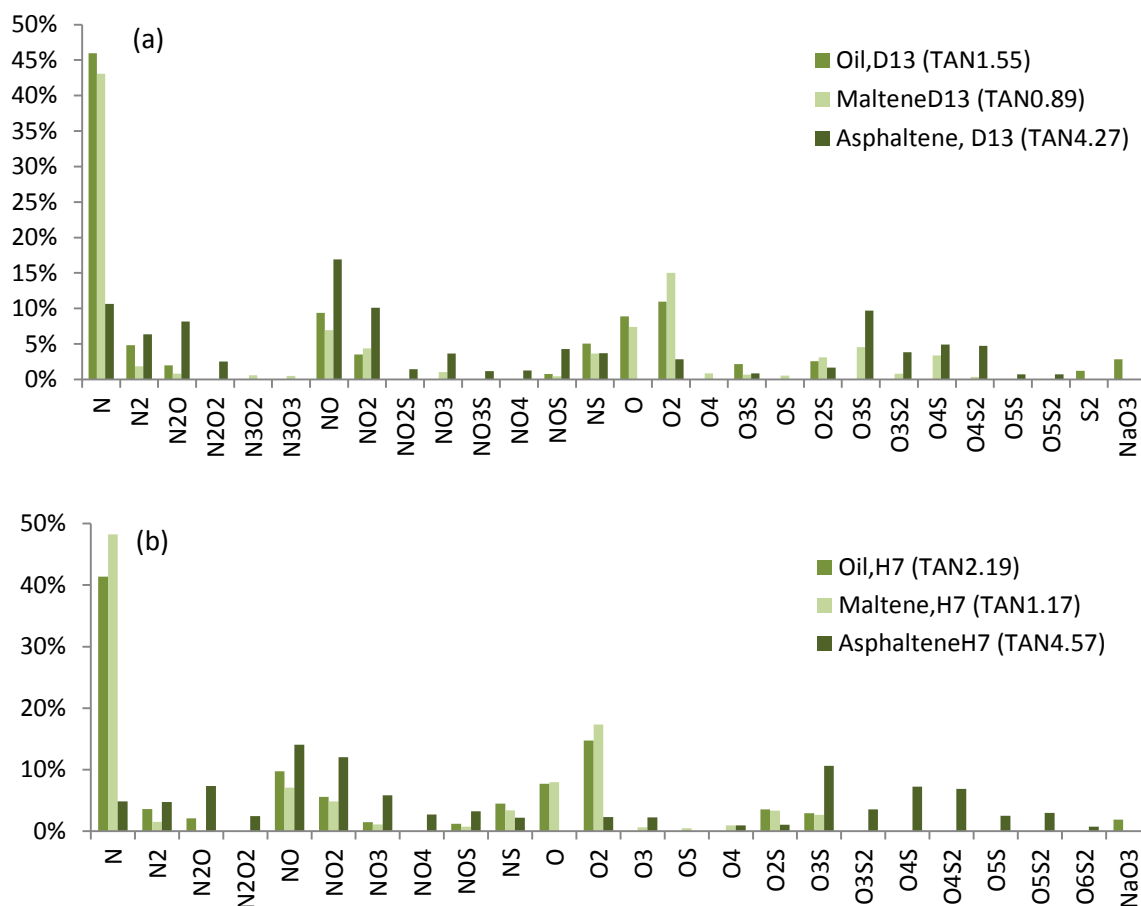
Figure 6.20 Heteroatomic compound distributions in oils, maltenes and asphaltenes from Californian samples (a) D13, (b) H7,

Figure 6.20(a-b) shows the distribution of heteroatomic species in oils, maltenes and asphaltene fractions of Californian samples D13 and H7. Compared with the previous North Sea sample distributions, these samples show higher varieties (up to 24) of heteroatom containing species. The distributions amongst these oils and their fractions show that although their TAN values are high (1.55 and 2.19 for D13 and H7 oils, respectively), both of these sample show a relatively low abundance of O_2 species, (11%, 14%, respectively) and prominent N-containing species (46, 41% abundance, respectively). This observation is in contrast with the North Sea oil samples that have a comparable TAN values (1.94 for EN 174), which show an abundance of O_2 species up to 51%, while N-containing species are only approximately 25%. This suggests that the high TAN values of the Californian samples is affected by other compound species in addition to the O_2 species (mainly naphthenic acids). Also, almost all of the O_2 species in the Californian oil samples are present in maltenes fractions rather than asphaltene fractions.

6.4   Summary of FT-ICR MS analysis

The detailed of compositional distribution of heteroatomic compound classes that contribute to the high Total Acid Number (TAN) values in two sets of oils and their maltenes and asphaltenes fractions, from different geological origins (North Sea and California), has been investigated by negative ion electrospray ionisation (ESI) coupled with high field 12T Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS or FT-ICR MS).

In the North Sea set, a total of 26 heteroatomic compound classes has been identified in the crude oils and their fractions: N_2, N_2O, N_2O_2, N_3O_3, NO, NO_2, NO_2S, NO_3, NO_4, NOS, NS, NS_2, O, O_2, O_2S, O_3, O_3S, O_3S_2, O_4, O_4S, O_4S_2, O_5S, O_7, O_7S, OS. The O_2 class (presumably "COOH" carboxylic acids) are the most dominant compound class among others. This observation applied to the North Sea oils and also in their maltenes and asphaltenes fractions. A strong correlation, (r^2: 0.989) of the O_2/N ratio to corresponding oil TANs (measured by a modified ASTM D664 method) indicates that the O_2 compound class is the main one that controls the high TAN in this sample set. A further analysis of compositional information on the O_2 compound classes suggest that the molecular structure of the O_2 class species in North Sea oils and maltenes set ranged from DBE 1 to 20, which correspond to structures of saturated acyclic acids, 1 to 6 cyclic acids, cyclic and aromatic acids and 1 to 7 ring aromatic acids. Their DBE distribution in asphaltenes fractions ranged from 1 to 25. with a possible structures ranging from acyclic, cyclic and up to 7 ring aromatic acids. As the TAN increases, the DBE distribution shifts to higher values suggesting that molecular structures were shifted to higher aromatic structures in high TAN samples. High TAN values in the oils corresponded to DBE=4 O_2 species, consistent with tricyclic acids with carbon numbers ranging from 17 to 59. High TAN maltenes corresponded to abundances of tricyclic acids (DBE=4) with carbon numbers ranging from 17 to 47, while high TAN asphaltenes contained abundant O_2 species of tetracyclic acids or monoaromatic acids (DBE=5) with carbon numbers from 17 to 50. Thus, high acidity in North Sea oils maltenes and asphaltenes are correspond to abundances of 3 to 4 ring naphthenic acids.

In the Californian crude oils and their fractions, a total of 30 heteroatomic compound classes has been identified: N, N_2, N_2O, N_2O_2, N_3O_2, N_3O_3, NaO_3, NO, NO_2, NO_2S, NO_3, NO_3S, NO_4, NOS, NS, O, O_2, O_2S, O_3, O_3S, O_3S, O_3S_2, O_4, O_4S, O_4S_2, O_5S, O_5S_2,

O_6S_2, S, S_2. Unlike North Sea set, the high TAN Californian oils and maltene fractions have the N compound class as the most dominant, followed by the O_2 compound class, though the relative abundance percentage of the N compound class decreases as TAN values increase. The O_2 compound class abundance increases as oil TANs increase although the relative abundance percentages (~11-15%) of this compound class is less than those (31-51%) of North Sea samples comparable TAN values. The Californian samples show much lower (~6 times less) O_2/N ratio values compared to equivalent TAN North Sea sample values, supporting indications that O_2 species are not the only compound class controlling the acidity in the Californian oils, maltenes and asphaltenes. The next most abundant compound classes are the O and NO species, however the correlation of these compound classes to the oil TANs are not clear, and the percentage abundances of these classes are low (<10% total abundance).

The O_2 compound class in Californian oil and maltenes fractions are distributed from DBE 1 to 15, which correspond to structures ranging from saturated fatty acids and up to 4 ring aromatic acids. This distribution indicates that the Californian oils contain lower ringed aromatic acid structures compared to the North Sea oils. The O_2 species structures that dominate in these samples correspond to one ring naphthenic acids (DBE=2) with carbon numbers distributed from 15 to 45. Asphaltene fractions on the other hand appear to have more complex heteroatomic compound compositions with no significant prominent compound class except the NO class, which appears to decrease in relative abundance as TAN increases. The low (<3%) relative abundance of the O_2 compound class suggests that this species does not have a major control on the acidity of these Californian asphaltene fractions. The combination of multi-hetroatomic compound classes in these asphaltenes might contribute to their TAN values. Thus for the Californian oils, it is believed that although naphthenic acids appear to contribute to their acidity, other species also have a major contribution to their high TAN values.

CHAPTER 7

FOURIER TRANSFORM INFRARED SPECTROSCOPY ANALYSIS

Chapter 7. Fourier Transform Infrared Spectroscopy Analysis

7.1 Introduction

FTIR has previously been used in a number of studies related to acidity and the characterisation of acidic species, especially as an initial screening of acid content in crude oil (Tomczyk et al., 2001), functional group distribution analysis in oils and isolated acid fractions (Saab et al., 2005; Li et al., 2010) and in comparisons of Total Acid Number (TAN) value measurements (Meredith et al., 2000; Zhang et al., 2006; Li et al., 2010). FTIR also has been used for determination of relative contents of oil carboxylic acids and to confirm the occurrence of high acid contents in their distillation cut samples (Olsen, 1998).

As acidity in crude is believed to be mainly contributed by carboxylic acid groups (Muller et al., 2009), and this functional group has been observed to be increased in high acidity oils and especially in highly biodegraded oils (Barth et al., 2004). Carbonyl group (C=O) absorption frequency band ranges reported to appear from 1800-1600 cm^{-1} Li et al. (2010) with a strong band of C=O *str* appear at 1700 cm^{-1} (Kemp, 1991). Others typical functional groups contained in crude oils and their absorption frequencies are shown in Figure 7.1
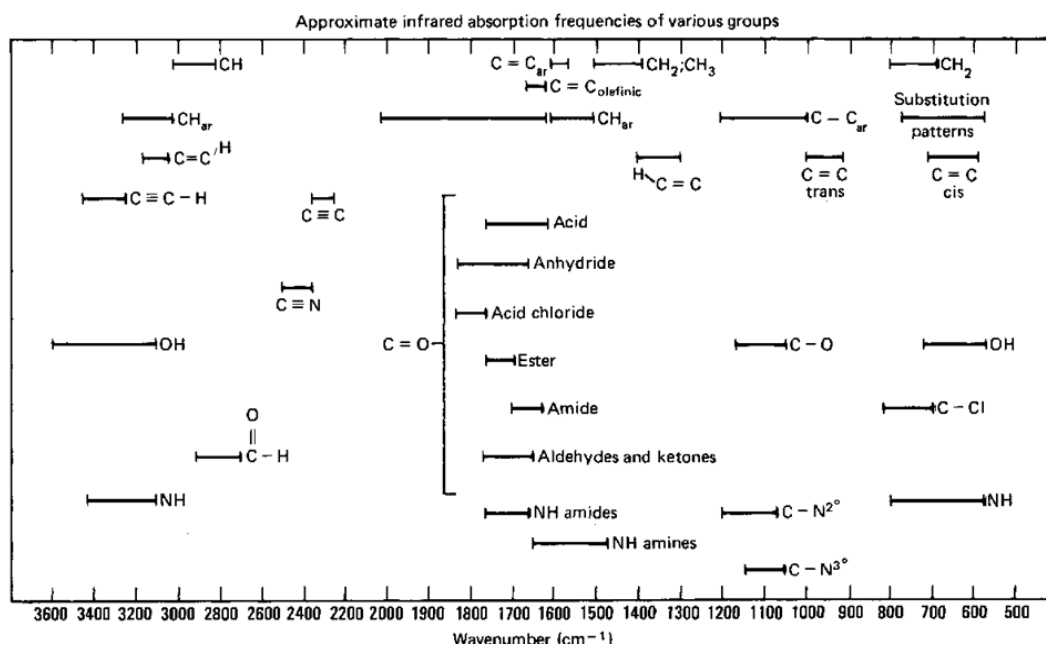
Figure 7.1 Infrared absorption frequencies of various functional groups (Zubrick, 1997)

Single-bounce Attenuated Total Reflectance (ATR) FTIR sampling accessories (such as the ThermoNicolet Smart Orbit) and multi-bounce HATR accessories (such as the ThermoNicolet Smart ARK) were introduced due to their advantages such as requiring little or no sample preparation, resulting in less time consuming analyses and also often a smaller sample size is needed compared with other techniques (Thermo Scientific Sampling Catalog for FT-IR). Multi-bounce HATR accessories have higher sensitivity than single bounce ATR and can be suitable for liquids and thin films. The spectral range measurable using ATR depends on the crystal material used. ATR using a diamond crystal can measure spectral ranges around 500-4000 cm^{-1} and ZnSe crystals from 600-4000 cm^{-1} (Thermo Scientific Sampling Catalog for FT-IR). Li et al. (2010) for example, used single-bounce ATR sampling accessories for their acid determination. This chapter describes the results of an investigation of these two types of sampling accessories in order to assess their usefulness for measuring carboxylic acid contents of crude oils, core extracts, bitumens, maltenes and asphaltene fractions.

The main aim of this section of work was to investigate the usefulness of FTIR for quantitatively measuring carboxylic acid components in oils, bitumens, core extracts, and their maltene and asphaltene fractions from different geological environments, with different degrees of biodegradation and maturites and with different Total Acid Number (TAN) values. As part of this, single-bounce and multi-bounce ATR accessories were tested and compared for their effectiveness and reproducibilities for these carboxylic acid acid measurements in such samples.

7.2   Results

7.2.1   *Typical spectra for crude oils, maltenes and asphaltenes*
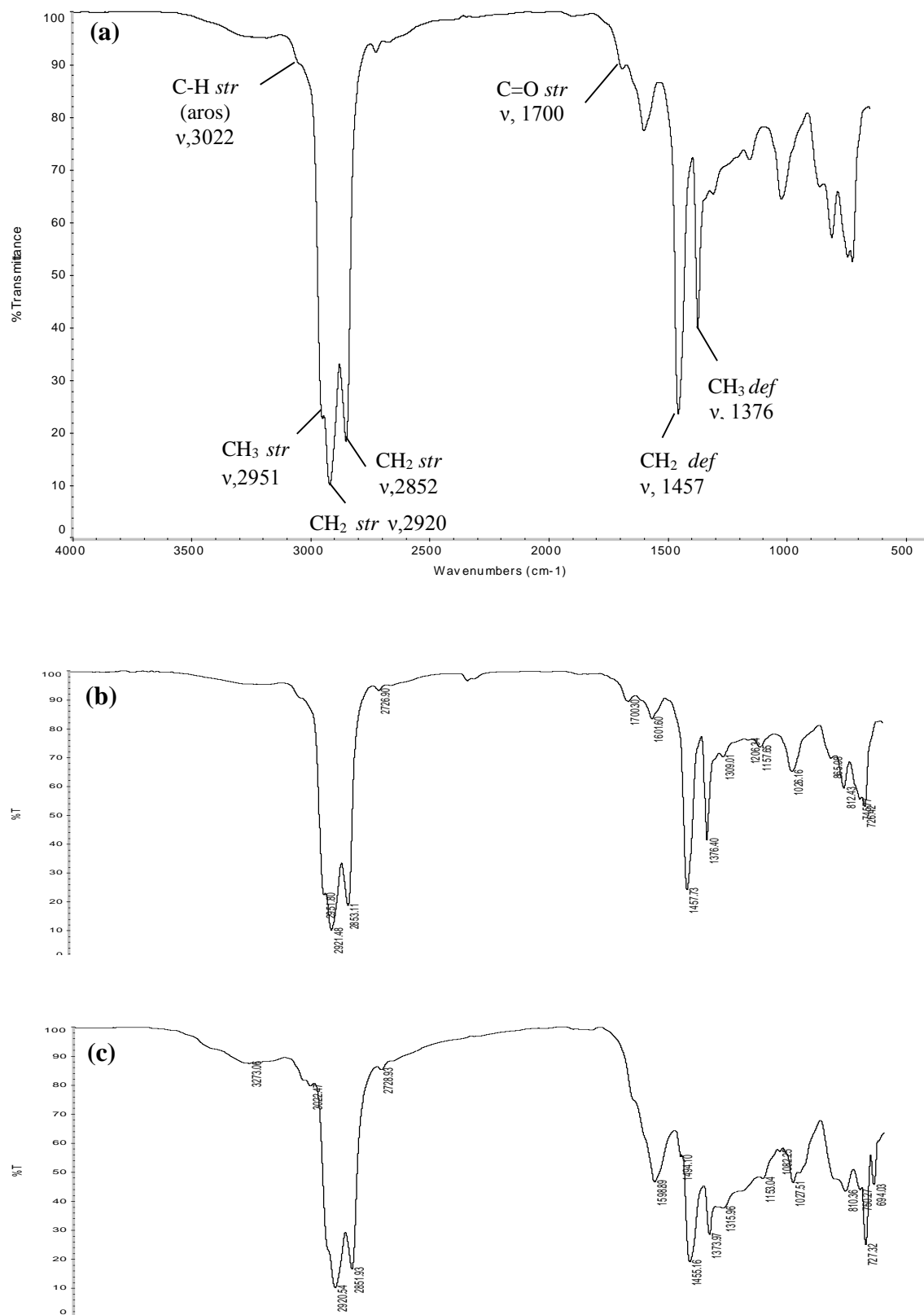
Figure 7.2(a-c) Typical ATR FT-IR spectra of a (Boscan) crude oil (a), and its maltene (b) and asphaltene (c) fractions, displayed as Transmittance (%T). The spectra obtained using the Smart ARK HATR sampling accessory (multi-bounce).

The infrared spectra between 4000 cm^{-1} and 500 cm^{-1} of typical crude oil (a) and their maltene (b) and asphaltene (c) fractions of the same oil (Boscan) are shown in Figure 7.2. In general, the IR spectra of crude oils contain characteristic major vibrational bands for aliphatic and aromatic carbon-hydrogen bonds and smaller ones due to carbonyl functional groups and they are similar to the spectra obtained on their corresponding maltenes and asphaltenes fractions. Main vibration bands include very strong aliphatic hydrocarbon CH_3, CH_2, CH_2 stretching (2951, 2920, 2852 cm^{-1}) and CH_2, CH_3 bending (1457, 1376 cm^{-1}). The medium-strong intensity band that appears approximately at 1700 cm^{-1} can indicate the C=O stretching signal of carboxylic acid functional groups. Absorptions around 1600 cm^{-1} possibly indicates the presence of aromatic ring C=C stretching (Barth et al., 2004). A small shoulder that appears at 3022 cm^{-1} and numerous signals below 900-700 cm^{-1} indicate aromatic C-H streching bonds .

Although crude oil and maltene fraction spectra have similar features, spectra obtained from asphaltene fractions show a wide O-H stretching signal from 3100 to 3500 cm^{-1} with maximum peak intensity at 3273 cm^{-1} (i.e. see Figure 7.2c). The absence of a clear carboxylic acid signal at 1700 cm^{-1} may often be due to the overlapping of the signal with that of the high intensity of aromatic ring C=C at 1599 cm^{-1}. The intensity of the numerous bands below 900 cm^{-1} is much higher in asphaltenes than in oils or maltenes which may suggests more aromatic ring structure distributed in asphaltene fraction.

7.2.2 Multi-bounce vs single-bounce ATR
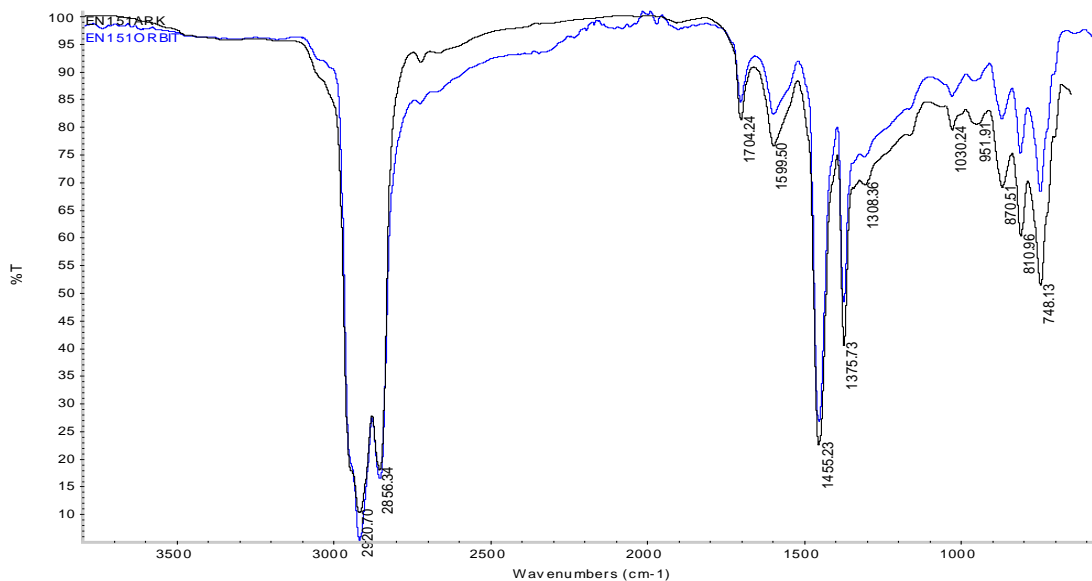
Figure 7.3 Combined FTIR spectra (in %T, transmission format) of sample EN151 measured using single-bounce ATR (Orbit) and multiple-bounce ATR (ARK) sampling accessories which in blue and black lines, respectively.

FTIR analysis on the same sets of crude oils, maltenes and asphaltenes was carried out using two different ATR sampling accessories, the single-bounce (Smart Orbit) and the multi-bounce (Smart ARK) in order to investigate the performance of these two accessories for oil acidity analysis. Figure 7.3 above shows comparison of spectra of an oil sample (EN 151) measured using single-bounce and multi-bounce ATR accessories. The single-bounce (Smart Orbit) exhibited generally less clear signal intensities compared to the spectra obtain using the multi-bounce (Smart ARK) accessory which had greater ATR crystal contact with the sample (broader sampling area), and also enabling multiple internal reflections of the IR beam through the sample. Thus, the multiple bounce accessory was the more sensitive of the two tested. On the other hand, the spectra obtained using both accessories were similar and contained all the same characteristic of functional group signals. This may suggest that despite their disadvantages, with only one aliquot of sample required, single-bounce ATR accessories still produce a good qualitative measurement analysis especially for initial screening test analysis, while, multi-bounce accessories may offer better measurements for both qualitative and quantitative analysis of oil samples.

7.2.3 FTIR for acidity measurement

Figure 7.4 (a-b) presents the FTIR absorbance spectra obtained from crude oils with different TAN values ranging from 0.11 to 7.66 mg KOH/g. As shown in Figure 7.2, an absorption band indicating the presence of a C=O stretching band corresponding with those found in carboxylic acids, appears at 1700 cm^{-1} in the spectra and shows increased intensity of up to 63% as TAN increases from 0.11 to 7.66 mg KOH/g. The lowest TAN oil (NSO-1) shows lowest relative absorbance of carboxylic acid group while highest acidity oil (EN 151) shows highest absorbance. This observation indicates that acidity in this oil set is correlated with the concentration of carboxylic acids in the oil, thus supporting our previous interpretation on carboxylic acid data presented in Chapters 5 and 6 and is also consistent with previous reports (Olsen, 1998; Zhang et al., 2006; Li et al., 2010) that that concentration of carboxylic acids in oils increase as oil TAN increases.
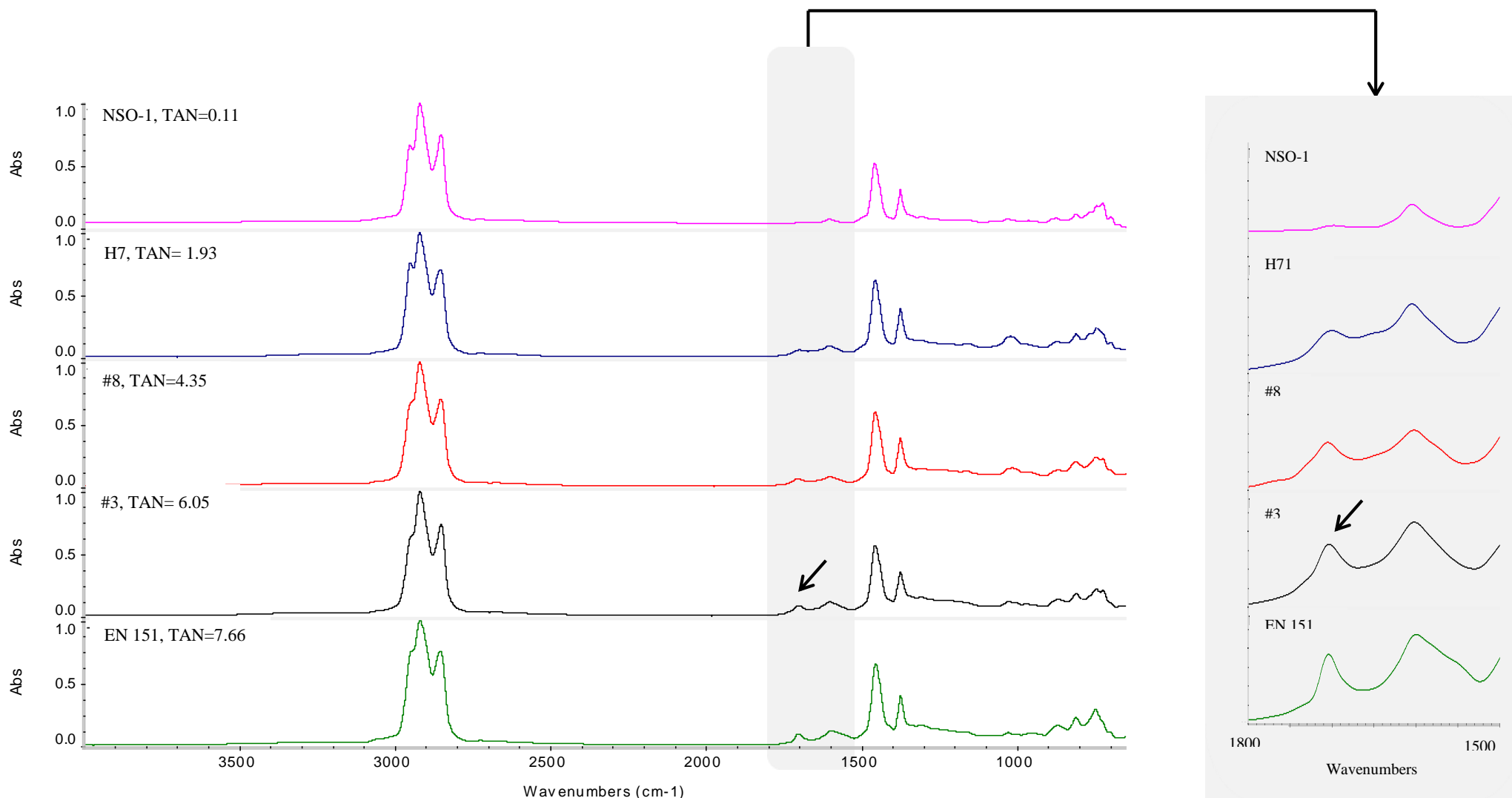
Figure 7.4 Variation of FT-IR spectra of crude oils samples with increasing Total Acid Number (TAN). The spectra were obtained using the Smart ARK HATR sampling accessory.

7.3 Total Acid Number (TAN) measurement using FTIR spectroscopy

ASTM D664 is a standard test method for the measurement of the acid number of petroleum and petroleum products by potentiometric titration. This method offers an acceptable repeatability with but with often only mediocre reproducibility. However there are some major limitations with this method such as unclear end points, the need for large sample sizes, the sensitivity of the electrodes and it is also quite slow and time-consuming. Since the method was originally designed for petroleum products and lubricants, some modifications are required in order to efficiently apply it to crude oils. Alternatively, FTIR spectroscopy offers a fast and accurate analysis method compared to the ASTM D664 method. Therefore this section presents the development of a rapid method for the determination of TAN on conventional and heavy crude oils, which focused on the carbonyl functional group (C=O) infrared absorption around 1700 cm^{-1} and its relationship to TAN, using FTIR spectroscopy.

7.3.1 Calibration of FTIR using benzoic acid spiking in oil sample EN 169

Benzoic Acid (mg)	EN 169 TAN (mg KOH/g)	Norm. abs. (1770-1650 cm^{-1})
0.22	1.34	1.32
0.72	3.05	1.58
1.29	6.57	1.97
2.11	8.88	3.13
2.08	9.68	3.02
2.10	9.70	2.89
6.06	29.21	7.20

Normalised C=O (1770-1650 cm^{-1})

$y = 0.2149x + 0.9157$
$R^2 = 0.9896$

Actual TAN mgKOH/g oil

Table 7.1 Table showing the amounts of benzoic acid spiked into oil EN 169 and their corresponding TAN values and normalised carbonyl absorbance (1770-1650 cm^{-1})
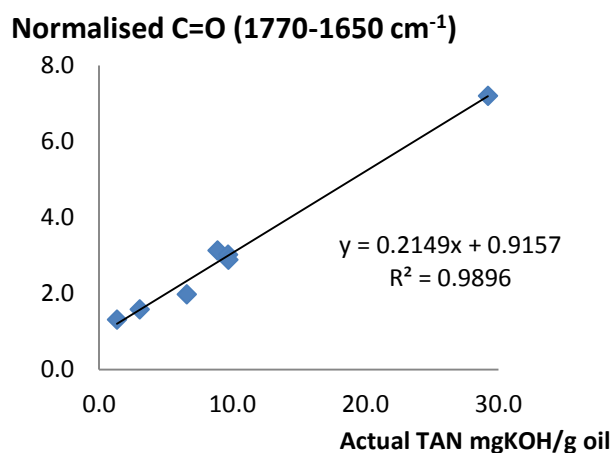
Figure 7.5 Plot of TAN determined using ASTM D664 vs. normalised carbonyl absorbance (1770-1650 cm^{-1}) in sample EN 169 spiked with known amounts of benzoic acid

Freshly prepared EN 169 crude oil samples (with a TAN of 0.13 mg KOH/g oil) were spiked with a series of known amounts (0.22 - 6.06 mg) of benzoic acid as shown in Table 7.1. Each oil sample was divided into two for TAN determination using the

ASTM D664 standard method and for FTIR measurement. It was found that these calibration standards had TAN values ranging from 1.34 to 29.21 mg KOH/g and that this, when plotted against the carbonyl absorption band (1770-1650 cm^{-1}) normalised against the C-H *str* absorption band (2920 cm^{-1}), corresponded well, with with a strong correlation coefficient of r^2=0.99 as shown in Figure 7.5.

7.3.2 Correlation of normalised carbonyl (C=O) vs TAN for a global oil calibration set

Figure 7.6(a) Plot of Total Acid Number determined using ASTM D664 vs. normalised carbonyl absorbance at 1770-1650 cm^{-1} in a 36 crude oil calibration set using a multibounce HATR accessory. Samples D13 and TRY: triplicate analysis

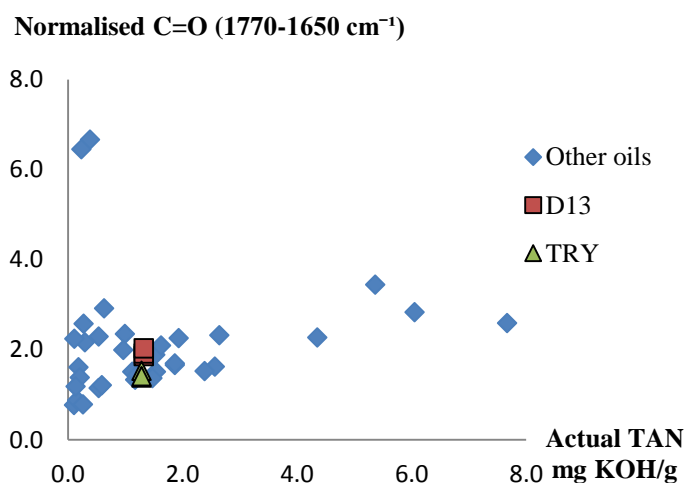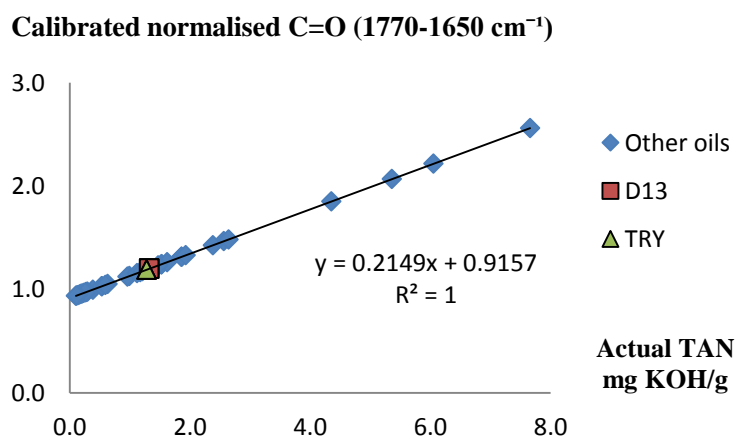**Figure 7.6(b)** Calibrated plot of Total Acid Number determined using ASTM D664 vs. normalised carbonyl absorbance at 1770-1650 cm^{-1} in 36 crude oil calibration set using multi bounce HATR accessory. Samples D13 and TRY: triplicate analysis

A simple plot of Normalised C=O region (1770-1650 cm^{-1}) / C-H str (2920 cm^{-1}) against their corresponding TANs in order to see the relationship between this peak to TAN value is shown in Figure 7.6(a). This plotted graph (without calibration) shows that as acidity increases, the normalised C=O region is slightly increased although the correlation is not strong. Figure 7.6(b), shows the same graph after calibration (using y= 0.2149x +0.9157).

7.3.3   *Total Acid Number (TAN) measurement by FTIR spectroscopy using multivariate analysis*
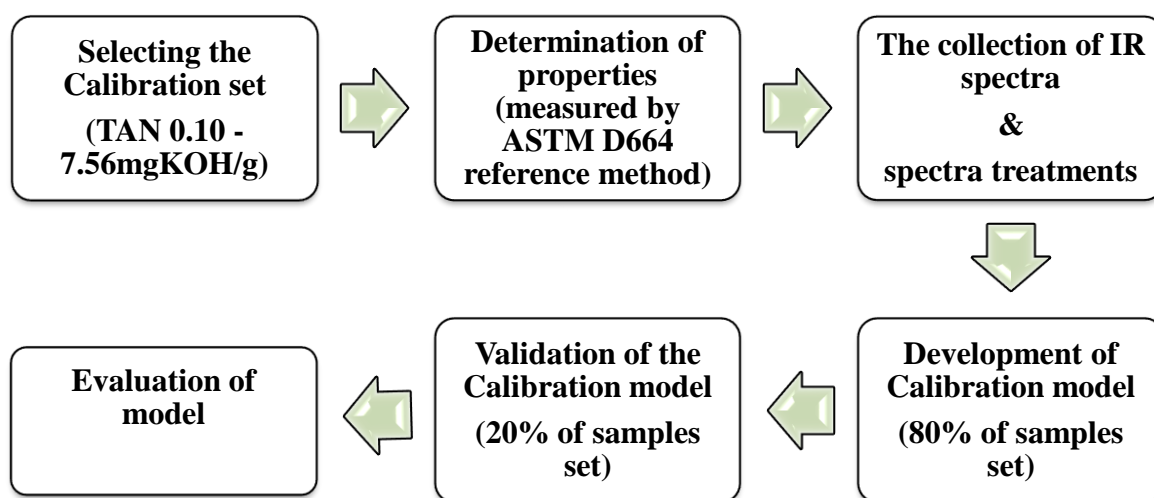
Figure 7. 7 Schematic diagram of work flow of TAN prediction using FTIR spectroscopy combined with multivariate analysis

Figure 7.7 above shows a flow work used in TAN prediction using FTIR spectroscopy combined with multivariate analysis. The steps involved were firstly 36 oil samples were analysed using the Smart ARK HATR accessory and 41 samples using the Smart Orbit ATR, for a calibration set selected to represent the range of oil TAN values from 0.10 to 7.56 mg KOH/g measured by the ASTM D664 standard method. The spectra of the samples were collected using a Thermo Nicolet 6700 FTIR spectrometer (as described in the previous methodology section 2.9) and were pre-processed (i.e. baseline correction, smoothing, normalisation, main IR band identification) using Thermo Scientific OMNIC software. This treatment was necessary in order to provide uniform spectra for comparison, as well as to avoid any abnormal results in the original data set. The quantitative evaluation of the specific region of interest (in this case

carbonyl region from 1770-1650 cm^{-1}) was carried out by using a multivariate Partial Least Squares (PLS) regression method using Pirouette 4.0 (Infometrix Inc.) software. Briefly, the procedure used 80% of the oils, to produce the multivariate calibration from the spectral absorbance patterns especially in the C=O region (1770-1650 cm^{-1}) and build a regression model against the actual/ absolute TAN measured by the ASTM D664 standard method. The created calibration model, also known as predictive model, was validated before use, by testing the remaining 20% of the oil samples of already known TANs values. Finally, the evaluation of this model was performed by randomly selecting a few samples as test samples and re-development of the calibration model with the remaining samples using the same procedure. Multivariate regression model are evaluated based on the r^2 correlation value between the predicted TAN value by FTIR and actual TAN value measured by the ASTM D664 method, which should be as close as possible to 1.

The results of the calibration of the relationship between the reference/measured values of ASTM D664 TAN and the FTIR predicted TAN values using partial least squares regression using the carbonyl region of interest, by single bounce ATR and multi bounce HATR accessories are presented in Figure 7.8a and Figure 7.8b, respectively. The results for both crude oils and bitumens shows that the C=O absorbances (1770-1650 cm^{-1}) from the multi bounce HATR accessory strongly corresponds to their TAN values measured by the ASTM D664 method, with an r^2 correlation coefficient 0.943 compared to single bounce ATR accessory which produced r^2 correlation coefficient of 0.812. Supported by the triplicate analysis shows in Table 7.2(a) for single bounce and 7.2(b) for multi bounce, the single bounce accessories appear to give a higher value of relative standard deviation of (reproducibility,% RSD, < 26) compare to multi bounce accessory shows an improvement on reproducibility with (%RSD, < 3). High RSD suggest that, single bounce accessory may not offers a good repeatability and reproducibility analysis of acidity due to the small contact area of sample-crystal (diamond) during analysis thus make this accessory low in sensitivity. On the other hand, multi bounce may offers a good repeatability and reproducibility analysis of acidity due to a broad sampling area, sample-crystal (ZeSe) provide a high sensitivity of the analysis compare to single bounce accessory. The comparison of predicted results from both accessories has suggested that the best TAN prediction model is achieved by using multi bounce accessories combined with multivariate analysis.
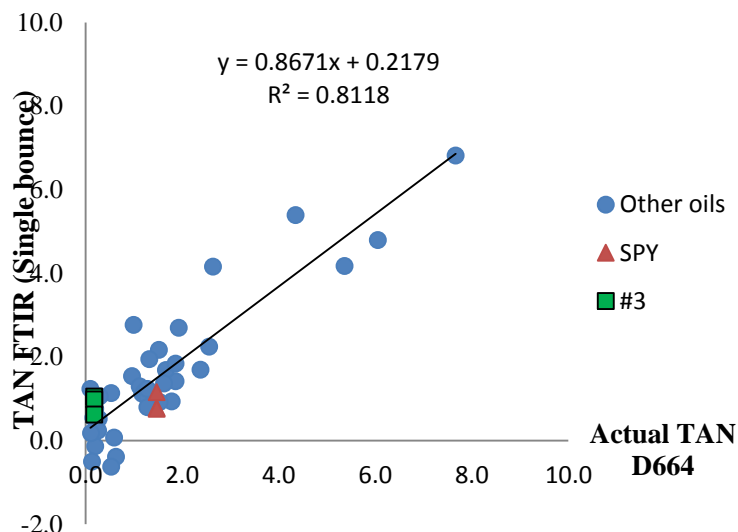
Figure 7. 8(a) Plot of TAN values measured by ASTM D664 vs predicted TANs from single bounce ATR FTIR

Sample	Predicted TAN Mg KOH/g			Mean	SD	RSD
	1st	2nd	3rd			
SPY	0.79	1.17	0.77	0.91	0.23	24.88
#3	1.06	0.99	0.63	0.89	0.23	25.62

Table 7. 2a Reproducibility of TAN prediction using the Smart Orbit (Single bounce ATR) accessory.
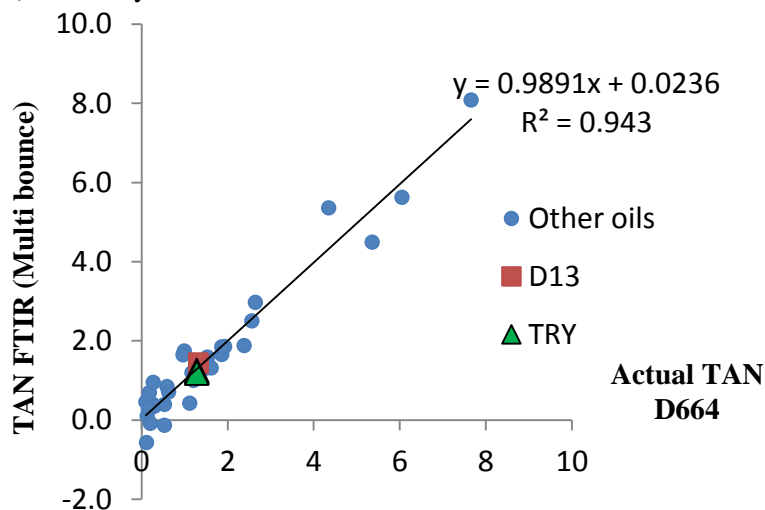
Figure 7. 8b Plot of TAN values measured by ASTM D664 vs Predicted TANs (Multi-bounce HATR) FTIR value

Sample	TAN Predicted mgKOH/g			Mean	SD	RSD
	1st	2nd	3rd			
D13	1.42	1.43	1.46	1.44	0.02	1.45
TRY	1.25	1.22	1.19	1.22	0.03	2.40

Table 7. 2(b) Reproducibility of TAN prediction using the Smart ARK (Multi-bounce HATR) accessory.

Similar work on the development of TAN determinations using FTIR spectroscopy has been reported by Dong et al. (2000) on lubricant samples and recently on distillation residues by Parisotto et al. (2010). Both of those TAN determinations were developed using multivariate calibration involving partial least squares (PLS) regression. The former work involves specifically focused only on the contribution of the carboxylic acid functional group in the 1603 -1560 cm^{-1} region for their lubricants,while the latter work, involved a calibration model using a three variables selection model with interval Partial Least Squares (iPLS), synergy interval Partial Least squares (siPLS), and backward interval Partial Least Squares (biPLS). Although the data processing was similar to the work done on lubricants by Dong et al. (2000), this work has offers a much more rapid procedure by using current state-of-the-art single ATR and multi bounce HATR FTIR accessories which allow much less complicated sample preparation steps than that used by Dong et al, (2000), and resulted in a fast and cheap method for measuring crude oils TAN values.

7.4 Summary of FTIR analysis

Acid components in samples of oils, bitumens, core extracts, maltenes and asphaltenes fractions were characterised using FTIR, showing an increasing of intensity of absorption by carbonyl functional group (C=O) from carboxylic acids (which appears at approximately 1700 cm^{-1}), as their TAN values increased. This data supported previous findings in this thesis that carboxylic acids are one of the major controls on the acidity in oil samples analysed.

With simple sample preparation (~3-5 min) per sample, both single bounce (Smart Orbit ATR), and multi-bounce (Smart ARK HATR) sampling accessories proved to be useful for the FTIR measurements of carboxylic acids and acidity in oils, bitumen, core extracts and their fractions (maltenes and asphaltenes). Compared to the single bounce accessory, the multi bounce accessory was more sensitive and better for quantitative measurements of carboxylic acids in the oils and their fractions examined.

The method for determination of TAN values of crude oils and bituments was developed using FTIR spectroscopy with little or no sample preparation involved. Single bounce attenuated total reflectance (ATR) and multi-bounce Horizontal Attenuated Total Reflectance (HATR) accessories in the mid-infrared region, combined with multivariate data analysis software (Pirouette), using multivariate Partial Least Squares (PLS) regression, enabled correlation of their infrared spectra with their TAN values. PLS was employed for data modelling using the spectral region of interest from 1770-1650 cm^{-1}, Using multi-bounce HATR accessory, the model predicted the measured TAN values with a strong r^2correlation coefficient of 0.943, suggesting that this is a possible alternative technique to replace the time-consuming ASTM D664 potentiometric titration standard method for measuring the Total Acid Number in crude oils and bitumens.

CHAPTER 8

CONCLUSIONS & FUTURE WORK

Chapter 8. Conclusions and Future Work

The main findings from the analyses of the oils in this study by FT-ICR MS and FTIR, and their isolated carboxylic acid fractions by GC and GC-MS, were that carboxylic acids (mainly occurring as naphthenic acids) are the principal types of acidic compounds that contribute to the acidity in crude oils and bitumen. Thus, in this work there is an increasing trend of the concentrations of the carboxylic acids as their oil total acid number (TAN) values increase. This finding supports the observations by Meredith et al. (2000) based on the analysis isolated acid fractions by GC alone. A major geochemical control on the oil acidities and carboxylic acid compositions in this study was the extent of biodegradation of the oils, although crude oils from different sources had varying heteroatomic, including acidic, species. A method for determining the acidity of small samples of oils and oil fractions, including asphaltenes was developed and it was found that not only were asphaltenes generally much more acidic than the maltenes, in some oils the asphaltenes were a major contributor to the oil TAN values.

In order to measure the TAN values on small quantities (1 g or less) of crude oils, bitumens and crude oil fractions, a method based on a modification of the ASTM D664 potentiometric titration standard test method, was developed as part of this study (as described in Chapter 4) . The method generally achieved repeatability of between 1.0 to about 78.8 %RSD for TAN measurements on samples with acidities as low as 0.1 mg KOH/g and with good repeatability (< 4%) RSD for oils with TAN values higher than 1, even when only 1 g samples are used. The modified ASTM D664 method was demonstrated to be effective for TAN measurement on core extracts thus allowing "TAN gradients" to be measured in reservoirs, which can provide information potentially useful for exploration and production purposes.

TAN measurements were made on crude oil maltenes fractions, which had values between 0.07 to 6.85. The measurement repeatability was between 2.43% RSD (on a high TAN maltenes sample) and 81.9% RSD (on a very low TAN sample). A TAN measurement method has also been developed for asphaltenes, which have poor solubility characteristics in the standard TAN method solvents. This involved sample pre-dilution with toluene, whisch ultimately increased the organic solvent ratio from 495:500:5 to 642:354:4 (toluene:isopropanol:water). The TAN range of the asphaltene fractions measured was from 3.13 to 21.24. The measurement repeatability was between

5.92, and 68.34% RSD (with the latter being on a poor solubility sample). The number of asphaltenes sample measured in this study was limited might be improved in future study with addition of more samples that represent a wide variation in TAN. Thus, this considered as one of the future attention that should be focused on the improvement of the repeatability and the accuracy of analysis of Total Acid Number of asphaltenes.
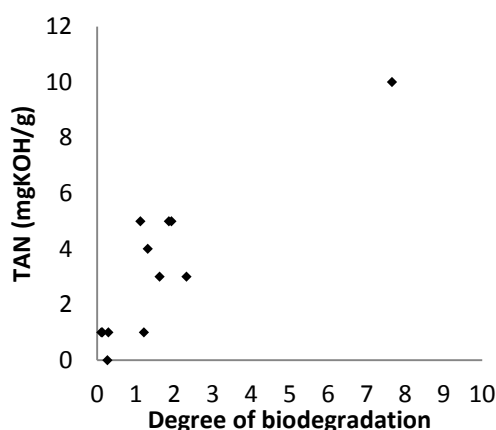
Figure 8.1 (a) Degree of biodegradation using (PM level) vs oil TAN (this study)
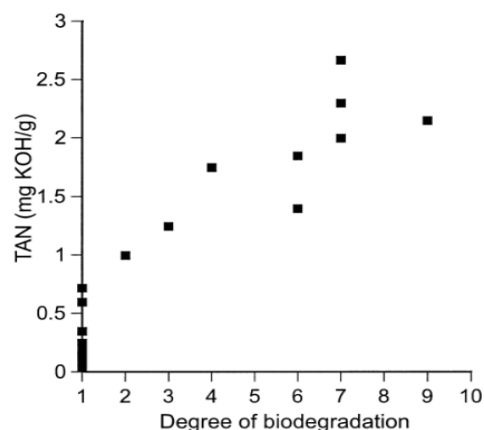
Figure 8.1 (b) Degree of biodegradation using (PM level) vs oil TAN (Meredith et al. (2000) data

The extent of biodegradation of the crude oils analysed varied considerably (as shown in Chapter 3), ranging from none to severely degraded (PM level of 0 to 10) with some samples apparently mixed (i.e. lightly + highly degraded oil). The relationship between biodegradation level and acidity in this set of samples showed that biodegradation is a major control on oil TAN, with correlation coefficient of $r^2 = 0.78$ (Figure 8.1a). This finding supported the work of Meredith et al. (2000) (see Figure 8.1b) where TAN in their oil set also increased with increased biodegradation, although there is some degree of scatter ($r^2 = 0.74$).

This present study demonstrates an increasing trend of concentration of isolated carboxylic acid fractions as the oil TANs increase (as shown in Chapter 5), also suggesting that these acidic compounds may be a major control on the acidity in crude oils and supporting the previous findings of Meredith et al. (2000). The concentration of

n-fatty acids, on the other hand show no clear relationship with TAN which suggests that these acyclic acids do not have major effects on oil acidity in this set of samples. Selected North Sea oil samples (EN 168, EN 154, EN 174, EN 151) and Californian oils (H7, D13) together with their fractions (maltenes and asphaltenes) were analysed using a negative ion electrospray Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The FT-ICR MS data from both sample sets shown in Chapter 6, have a clear correlation with whole oil TAN values measured using the modified ASTM D664 method. Maltene and asphaltene fraction FT-ICR MS data also correspond well with TAN values. North Sea oil fraction data indicate that the O_2/N species ratio (derived from FT-ICR MS) in asphaltenes can be up to 10 times higher than in their corresponding maltenes and crude oil. A strong correlation (r^2=0.997) between acidity and O_2 compound class (carboxylic acids) abundance, suggests that this is the main compound class affecting the acidity in the North Sea oil set. These results also support the findings of others (Meredith et al., 2000; Saab et al., 2005; Vaz et al., 2013b) that the carboxylic acid fraction (mainly naphthenic acids) is a major contributor to the oil TAN. Although the data shows an increase in acid structure complexity (becoming more highly aromatic) as TAN increases, highly aromatic acid species do not greatly contribute to the high acidity in crude oils. Highly acidic oils contain relatively high amounts of DBE 4 and DBE 5 class compounds, which correspond to 3 and 4 ring naphthenic acids. In contrast, the FT-ICR MS data for the Californian oils shows that the O_2 class is not likely to be the main compound class responsible for the high TAN of these samples, although there is a positive correlation as TAN increases. It has been suggested that other factors, possibly sulphur compounds may play an important role the in high acidity of such samples (i.e. Meredith et al., 2000). Further work, on such samples would be required in order to more fully understand the contributions to their acidities.

FTIR spectroscopy has been demonstrated (in Chapter 7) to be an effective analytical tool for the analysis of acidic components in oils, bitumens, core extracts and oil fractions with TAN values ranging from 0.04 to 12.18. The findings shows that total acid number is closely related to the abundance carbonyl functional group (C=O) that absorbs in the 1770-1650 cm^{-1} wavenumber range of IR spectra. Absorption in this region corresponded well with TAN values using both single bounce (Smart Orbit) ATR, and multi-bounce (Smart ARK) HATR sampling accessories, although the multi-bounce accessory is more sensitive and better for quantitative measurements compared

to single-bounce ATR. Based on these findings, a model predicting TAN values with a strong correlation ($r^2 = 0.943$), on crude oils and bitumens have been developed. This model was constructed in the mid-infrared region using the multi-bounce HATR accessory, combined with multivariate data analysis (Pirouette software), using multivariate Partial Least Squares (PLS) regression on spectral region of interest from (1770-1650 cm^{-1}). This model based method could provide a rapid and economic alternative method to replace the classical ASTM D664 potentiometric titration TAN measurement method for oils and bitumens, which minimises sample handling and also toxic solvent usage and disposal. Further calibration of the model for oil fractions (maltenes and asphaltenes) with more samples in the calibration set would probably allow improvement of what has already been developed.
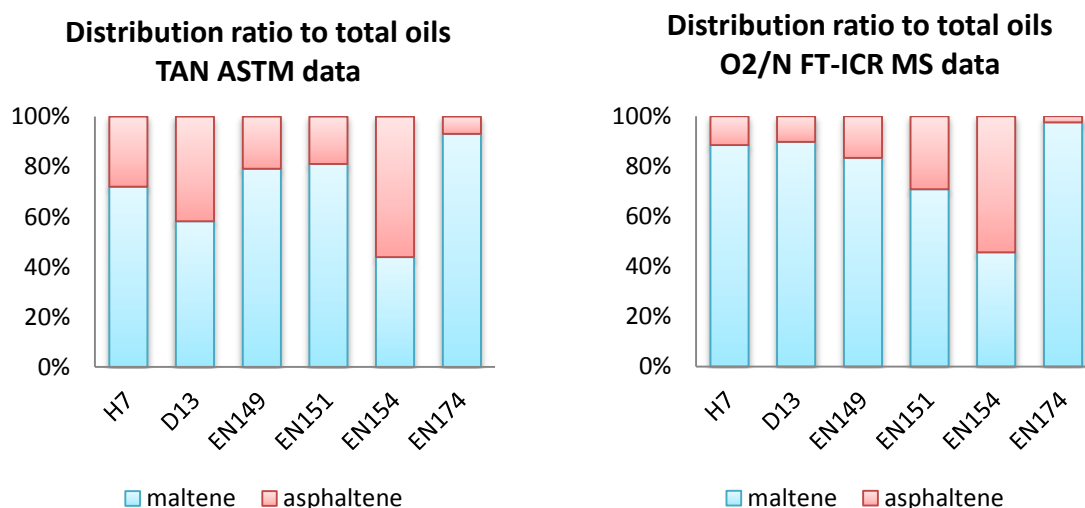
Figure 8.2 (a) Distribution of acidity of oil fractions to total oils using modified ASTM D664 data

Figure 8.2 (b) Distribution of acidity of oil fractions to total oils by FT-ICR MS derived O_2/N data

One of the interesting findings in this study was obtained from analysis of the acidity distribution in the oil fractions. Although asphaltene TAN values are typically much higher than those of the corresponding maltene fractions, due to the generally low proportion of asphaltenes in oils, the maltenes usually contribute most of the acidity to the oil TAN. However the findings in this study show that some oils (i.e. EN154, EN168 , D13) have highly acidic asphaltenes that make up more than 40% of the oils acidity, even though they are quantitatively a small percentage of the oil in terms of

weight. The maltene and asphaltene modified ASTM D664 TAN distribution data and O$_2$/N FT-ICR MS data (Figure 8.2) showed a similar trend, supporting the findings of the TAN distributions in the oil fractions found in this study. The variations in acidity and acidity distributions between the maltene and asphaltene fractions of different oils may be due to both biodegradation and source effects, since biodegradation level alone does not correspond to these differences. From the broader perspective, the discovery of highly acidic asphaltenes in some oils but not others, has implications not only for exploration, but also for acidity reduction (and hence value upgrade) in those oils. Thus, further investigation of these preliminary findings should be undertaken with a larger, well constrained oil sample set in order to distinguish these effects.

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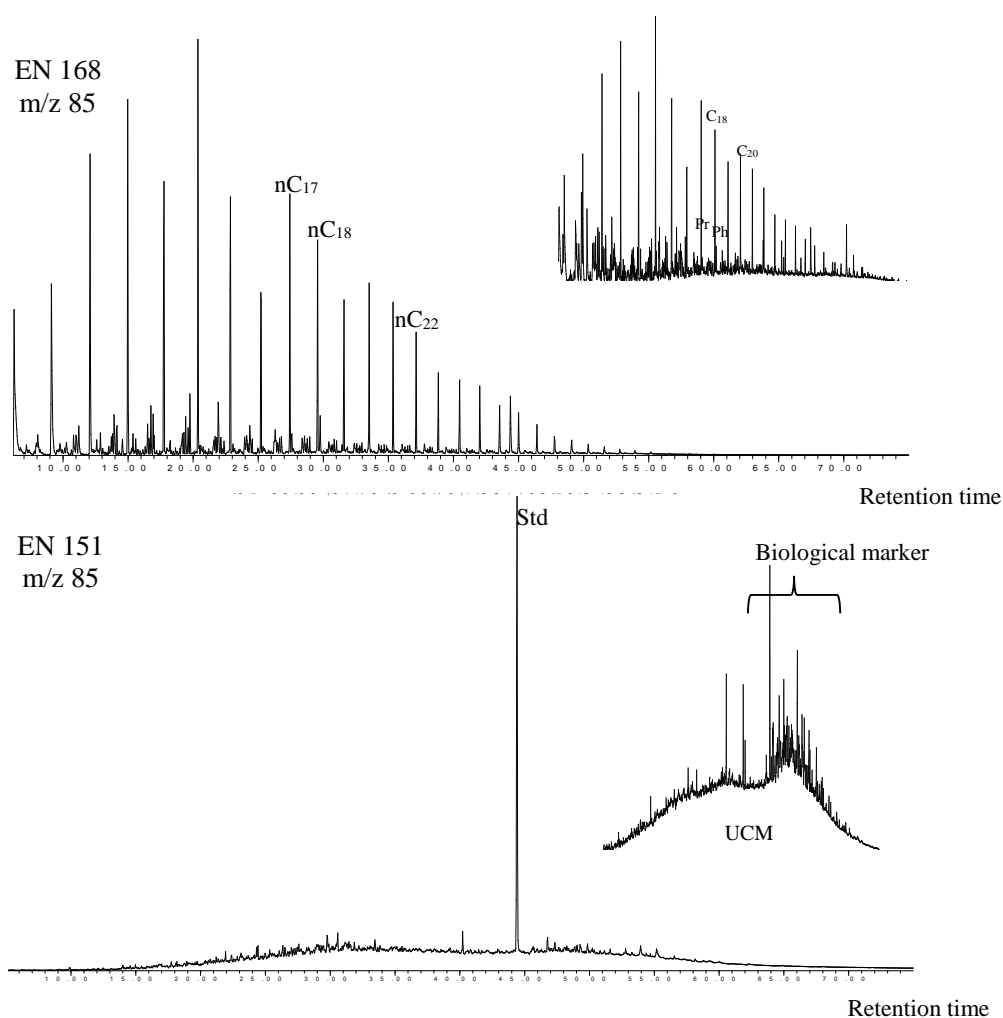
APPENDICES

Appendices A

Bulk Composition Analysis Of Crude Oils

1. Example of Iatroscan TLC-FID chromatogram for oil sample EN 168
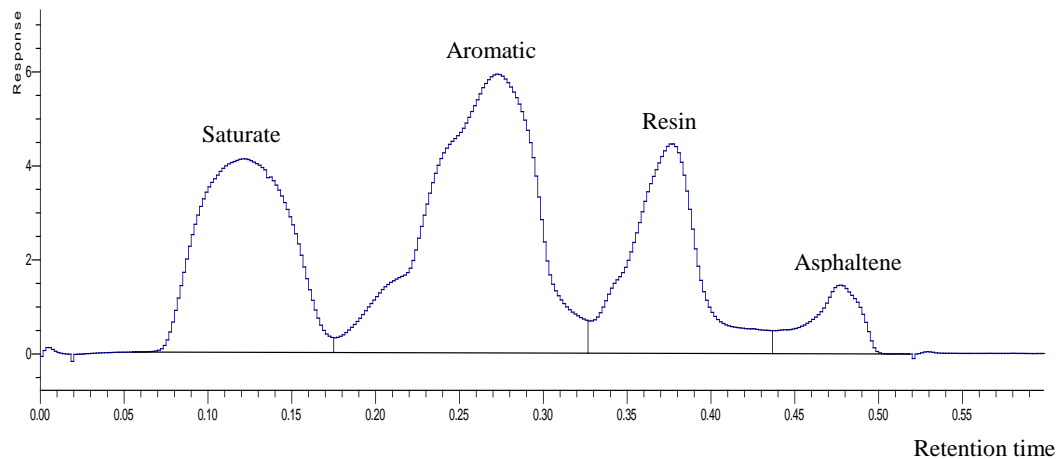
2. Example mass chromatogram (m/z 85) and gas chromatogram (inset) for samples EN 168 (undegraded) and EN 151 (severely degraded)

Appendices B

Total Acid Number Analysis on Crude Oils, Bitumens, Core Extracts and Their Fractions

1. Total Acid Number (TAN) results: A full list of all samples TAN measured according to the slightly modified (as described above) ASTM D664 standard method, are presented below. Selected samples (with an asterisk) were run in triplicate (and the means reported) in order to monitor the reproducibility of the results.

Set 1: Total Acid Number (TAN) results for sample set 1 (crude oils)

SAMPLE	TAN mgKOH/g
(*)EN 149	1.12
(*)EN 151	7.66
(*)EN 154	0.29
(*)EN 158	1.21
(*)EN 168	0.26
(*)EN 169	0.13
(*)EN 174	1.86
(*)H7	1.93
(*)D13	1.32
(*)NSO-1	0.11
(*)Boscan	1.62
(*)Heidrun	2.62
Cold Lake bitumen	0.53
Lloydminster	0.59
Doukdaka M2	2.38
(*)TRY	1.28
(*)SPY	1.47
(*)BB1	1.52
BB2	1.95
BB3	6.06
BB4	0.18
BB5	1.75
BB6	0.93
BB7	0.22
BB8	4.39
BB9	0.27
BB10	0.63
BB11	0.96
BB12	0.38

BB13	0.23
BB14	2.72
(*)BB15	1.66
BB16	0.11
(*)BB17	0.53
BB18	0.19
BB19	5.30
BB20	0.10
BB21	0.20
(*)BB22	0.33
BB23	1.53
BB24	2.56
(*)BB25	0.16
(*)BB26	1.17

Set 2: Total Acid Number (TAN) results for sample set 2 (core extracts)

SAMPLE #	TAN mgKOH/g
SSA1	2.27
SSA2	2.55
SSA3	2.53
SSA4	3.60
(*)SSA5	2.01
SSA6	3.08
SSA7	3.30
SSA8	3.92
SSA9	3.99
SSB10	3.84
SSB11	3.26
SSB12	3.89
SSB13	3.98
SSB14	4.59
SSB15	3.77
SSB16	3.69
SSB17	3.92
SSB18	4.09
SSB19	2.88
SSC20	3.56
SSC21	4.00
SSC22	3.29
SSC23	3.45
SSC24	4.30
GAM25	2.89
GAM26	3.61
GAM27	3.99
(*)GAM28	3.88
GAM29	3.80
GAM30	4.98

GAM31	6.29
GAM32	8.97
GAM33	1.21
GAM34	1.56
GAM35	1.16
GAM36	1.38
GAM37	1.96
GAM38	2.86
GAM39	2.95
GAM40	1.77
INN41	0.62
INN42	0.64
INN43	0.91
INN44	0.93
INN45	0.62
INN46	0.90

2. Snapshot of raw data taken from titrator data file. Red circle shows the TAN value measured& calculated by automatic titrator
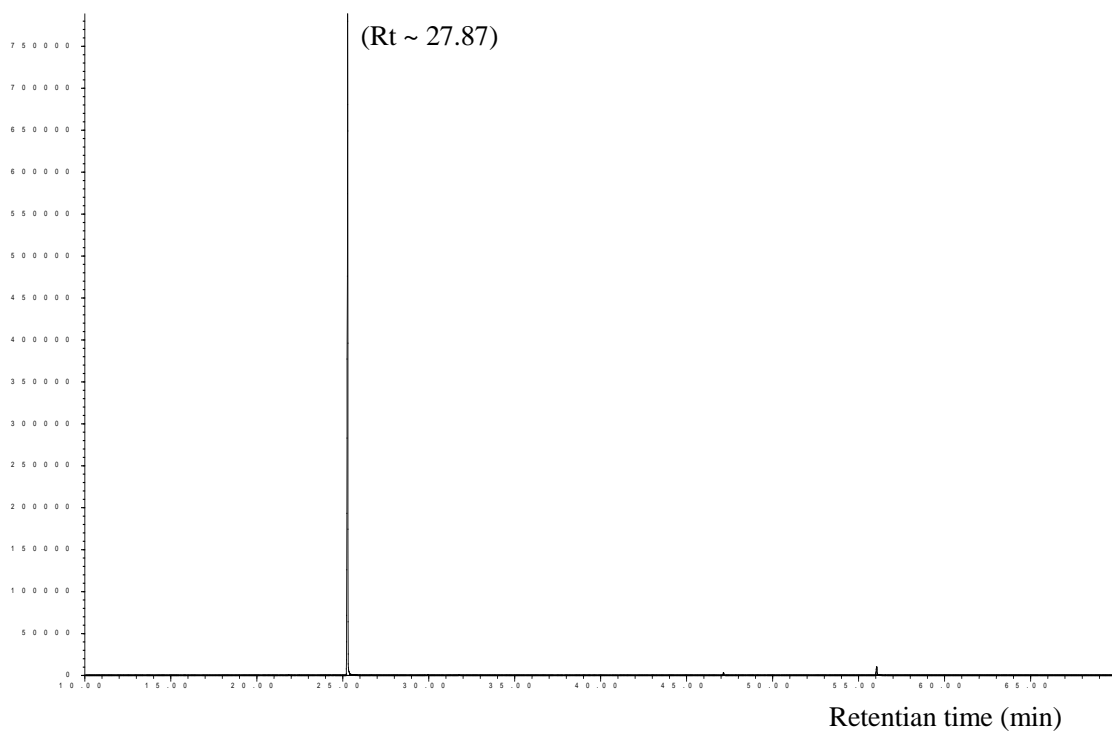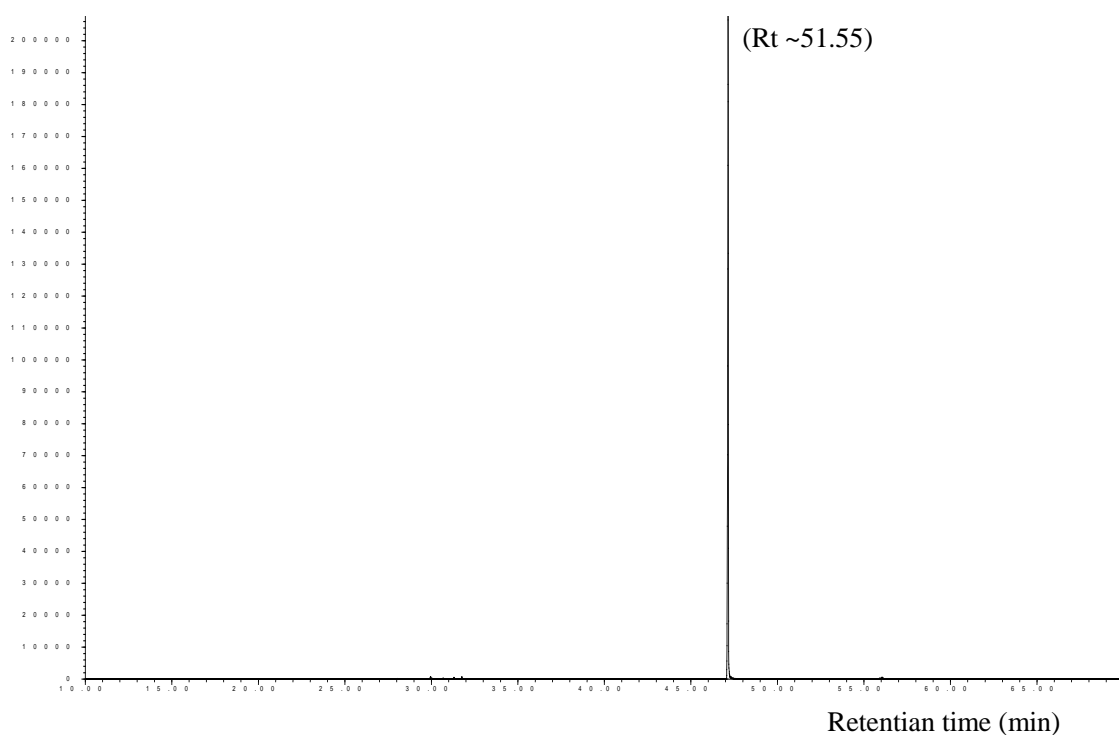
Appendices C

Carboxylic Acid Analysis on Crude Oils

1. Mass chromatogram (m/z 159) showing 1-phenyl-1-cyclohexane carboxylic acid Internal Standard (I.S)

(Rt ~ 27.87)

Retentian time (min)

2. Mass chromatogram (m/z 217) showing 5β-cholanic acid Surrogate Standard (S.S)

(Rt ~51.55)

Retentian time (min)

3. Carboxylic acid analysis data of North Sea samples showing TAN values (mg KOH/g), degree of biodegradation (PM level) , total acids (ug/g), *n*-acids (ug/g) and sterane maturity ratio $C_{29}\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$.

Origin		TAN	PM level		*Total* acids (ug**/g**)	*n*-acids (ug/g**)**	**C29ab**
UK	NSO	0.11	1	light	194	2	0.48
uk	HEIDRUN(1)	2.64	3	light	3241	2	0.56
uk	EN151	7.66	10	severe	10391	0	0.00
UK (west shetland)	EN158	1.21	1	light	325	12	0.41
uk	EN174	1.86	4to5	moderate	1137	8	0.51

4. Concentration of total carboxylic acid fractions (µg/g) vs Total Acid Number (TAN) for North Sea only set

Total acids for North Sea only set

$y = 1444.8x - 837.59$
$R^2 = 0.9767$
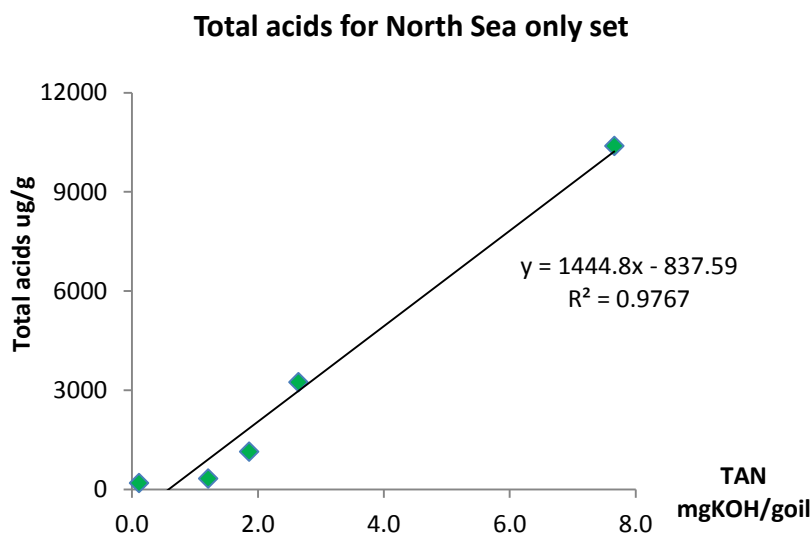
Appendices D

Bulk Fourier Transform Ion-Cyclotron Resonance Mass Spectrometry Analysis on Oils and Their Fractions

1. Photograph of the University of Calgary, FT-ICR MS
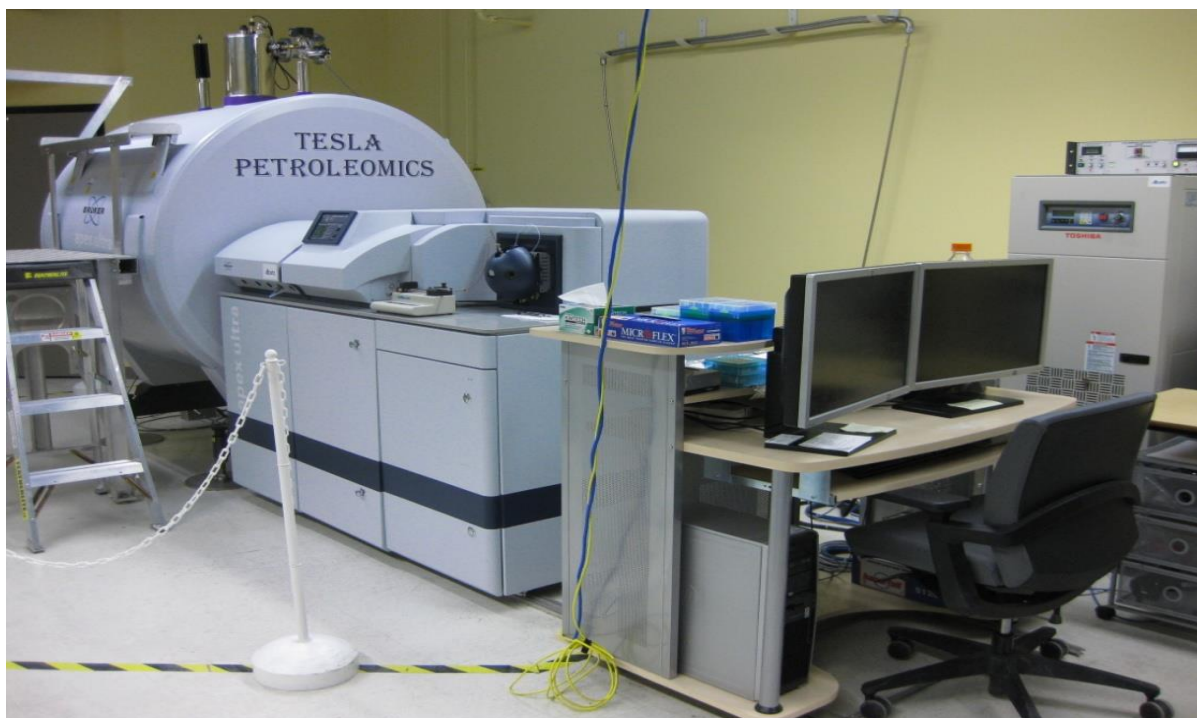
2.Broadband electrospray ionization FTICR mass spectrum of sample EN 174.

List of heteroatoms species for North Sea oils

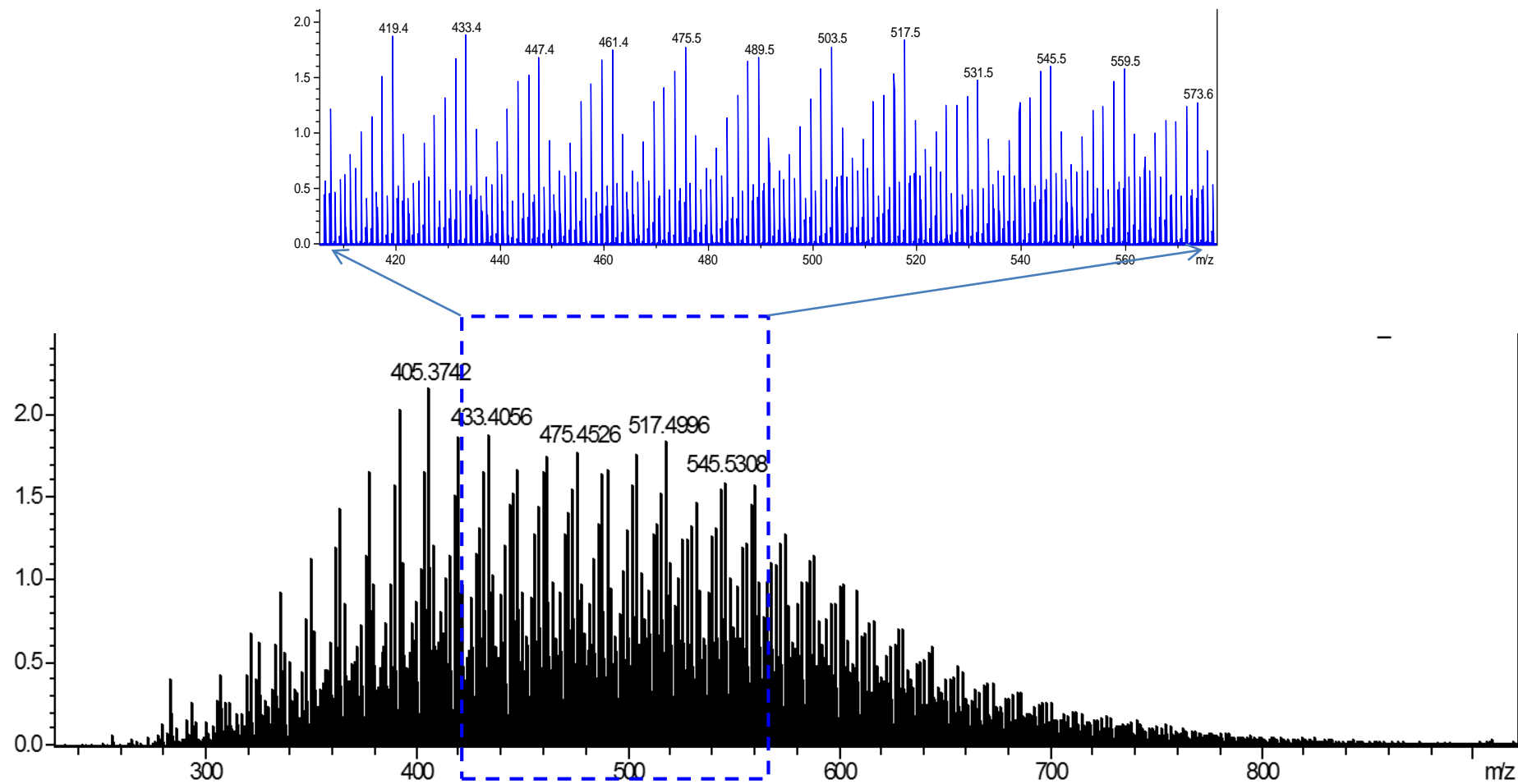| EN 154 (TAN0.11)		EN 149 (TAN1.14)		EN 174 (TAN1.94)		EN 151 (TAN7.58)	
species	% abundance	species	% abundance	species	% abundance	species	% abundance
N	41.64	N	33.11	O_2	51.06	O_2	66.56
NS	15.46	O_2	31.20	N	25.55	N	12.19
NO	10.29	O	16.80	O	5.53	NO_2	7.70
O	10.27	NO	4.39	O_2S	5.15	O_2S	4.35
O_2	4.68	O_2S	3.96	NO	3.87	O_4	3.39
NOS	4.32	NO_2	3.27	NO_2	2.87	O	2.87
OS	3.51	NS	2.96	O_3S	2.15	O_3	2.01
N_2	2.51	OS	1.48	NS	1.96	NO	0.93
NO_2	2.30	O_3	1.68	O_3	1.16	-	-
O_2S	1.83	N_2	0.68	O_4	0.71	-	-
N_2O	1.79	O_3S	0.48	-	-	-	-
NS_2	1.41	-	-	-	-	-	-

List of heteroatoms species for North Sea maltenes

EN 154 (TAN0.45)		EN 149 (TAN1.06)		EN 174 (TAN1.81)		EN 151 (TAN6.85)	
species	% abundance	species	% abundance	species	% abundance	species	% abundance
N	46.70	N	37.75	N	26.81	N	8.19
N_2	1.25	NO	3.49	NO	3.54	NO	0.68
N_3O_3	0.54	NO_2	2.53	NO_2	2.15	NO_2	6.97
NO	8.55	NS	1.88	NS	1.73	NS	0.49
NO_2	1.73	O	17.50	O	5.81	O	0.56
NOS	2.10	O_2	30.15	O_2	52.68	O_2	68.91
NS	12.12	O_2S	3.11	O_2S	4.18	O_2S	3.45
NS_2	0.57	O_3	1.75	O_3	1.25	O_3	3.14
O	9.65	O_4S	0.87	O_3S	1.23	O_3S	1.05
O_2	4.52	OS	0.97	O_4	0.62	O_4	5.91
O_2S	1.78	-	-	-	-	O_4S	0.66
O_3	0.40	-	-	-	-	-	-
O_3S	3.10	-	-	-	-	-	-
O_4	0.43	-	-	-	-	-	-
O_4S	3.34	-	-	-	-	-	-
OS	3.22	-	-	-	-	-	-

List of heteroatoms species for North Sea asphaltenes

EN 154 (TAN5.88)		EN 174 (TAN6.52)		EN 149 (TAN6.66)		EN 151 (TAN21.24)	
species	% abundance	species	% abundance	species	% abundance	species	% abundance
N	7.15	N	4.01	N	3.08	N_2O_2	1.22
N_2	6.27	NO	15.18	NO	7.95	NO_2	24.93
N_2O	7.56	NO_2	12.77	NO_2	17.75	NO_2S	1.59
NO	15.13	NO_2S	1.52	NO_2S	1.65	NO_3	3.63
NO_2	8.46	NO_3	5.15	NO_3	5.13	NO_4	1.14
NOS	10.70	NOS	3.81	O_2	11.76	O_2	32.16
NS	10.61	NS	1.70	O_2S	4.27	O_2S	5.98
NS_2	2.60	O_2	9.46	O_3	12.53	O_3	7.34
O_2	8.33	$O2S$	3.15	O_3S	18.23	O_3S	2.83
O_3S	5.86	O_3	5.91	O_3S_2	1.75	O_4	18.31
O_4	15.82	O_3S	17.75	O_4	7.42	O_4S	0.87
O_7	1.02	O_3S_2	1.98	O_4S	6.63	-	-
O_7S	0.48	O_4	4.07	O_4S2	1.84	-	-
-	-	O_4S	8.48	-	-	-	-
-	-	O_4S_2	3.03	-	-	-	-
-	-	O_5S	2.05	-	-	-	-

List of heteroatom species for Californian oils

D13 (TAN1.55)		H7 (TAN2.19)	
class	% abundance	class	% abundance
N	45.96	N	41.38
O_2	10.96	O_2	14.70
NO	9.36	NO	9.72
O	8.88	O	7.70
NS	5.05	NO_2	5.53
N_2	4.81	NS	4.46
NO_2	3.51	N_2	3.59
O_2S	2.56	O_2S	3.51
NaO_3	2.82	O_3S	2.91
N_2O	1.98	N_2O	2.06
O_3S	2.18	NaO3	1.85
NOS	0.74	NOS	1.17
S_2	1.19	NO3	1.42

List of heteroatom species for Californian maltenes

D13 (TAN4.27)		H7 (TAN4.57)	
species	% abundance	species	% abundance
N	43.10	N	48.25
N_2	1.86	N_2	1.49
N_2O	0.82	NO	7.05
N_3O_2	0.58	NO_2	4.84
N_3O_3	0.51	NO_3	1.06
NO	6.95	NOS	0.71
NO_2	4.37	NS	3.38
NO_3	1.03	O	7.93
NO_S	0.45	O_2	17.32
NS	3.64	O_2S	3.32
O	7.38	O_3	0.63
O_2	15.02	O_3S	2.63
O_2S	3.12	O_4S	0.93
O_3	0.67	OS	0.44
O_3S	4.56	-	-
O_3S_2	0.79	-	-
O_4	0.84	-	-
O_4S	3.39	-	-
O_4S_2	0.37	-	-
OS	0.55	-	-

List of heteroatom species for Californian asphaltenes

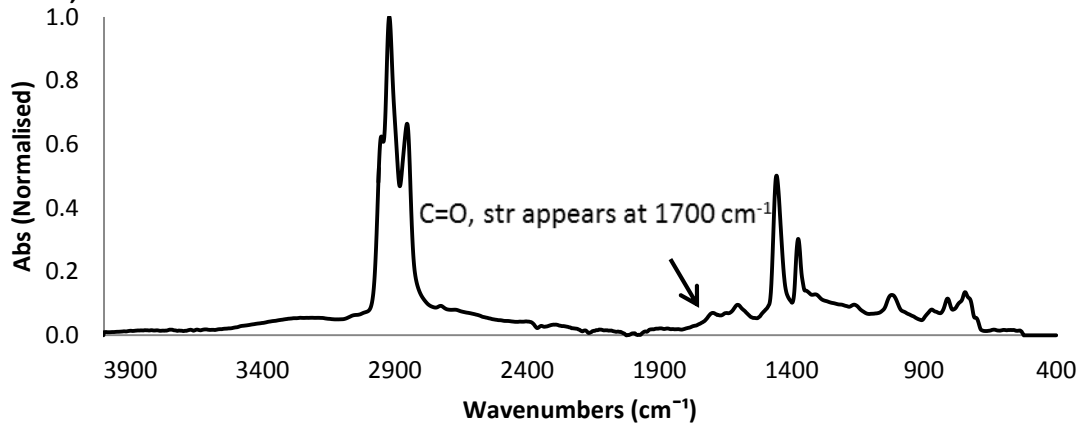| D13 (TAN4.27)		H7 (TAN4.57)	
species	% abundance	species	% abundance
N	10.62	N	4.81
N_2	6.34	N_2	4.71
N_2O	8.16	N_2O	7.30
N_2O_2	2.52	N_2O_2	2.45
NO	16.90	NO	14.04
NO_2	10.08	NO_2	12.01
NO_2S	1.45	NO_3	5.82
NO_3	3.64	NO_4	2.68
NO_3S	1.15	NOS	3.21
NO_4	1.25	NS	2.16
NOS	4.26	O_2	2.28
NS	3.69	O_2S	1.00
O_2	2.83	O_3	2.21
O_2S	1.67	O_3S	10.62
O_3	0.85	O_3S_2	3.51
O_3S	9.69	O_4	0.93
O_3S_2	3.81	O_4S	7.22
O_4S	4.93	O_4S_2	6.87
O_4S_2	4.73	O_5S	2.49
O_5S	0.73	O_5S_2	2.95
O_5S_2	0.71	O_6S_2	0.71

Appendices E

Fourier Transform Infrared Analysis On Crude Oils And Their Fractions

1. FTIR normalised absorbance spectra of Set 1 samples (obtained using Smart ORBIT accessory)
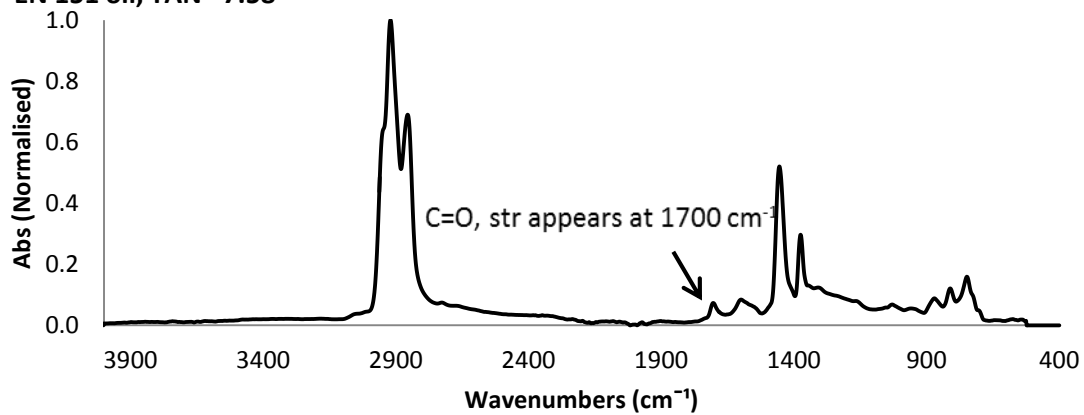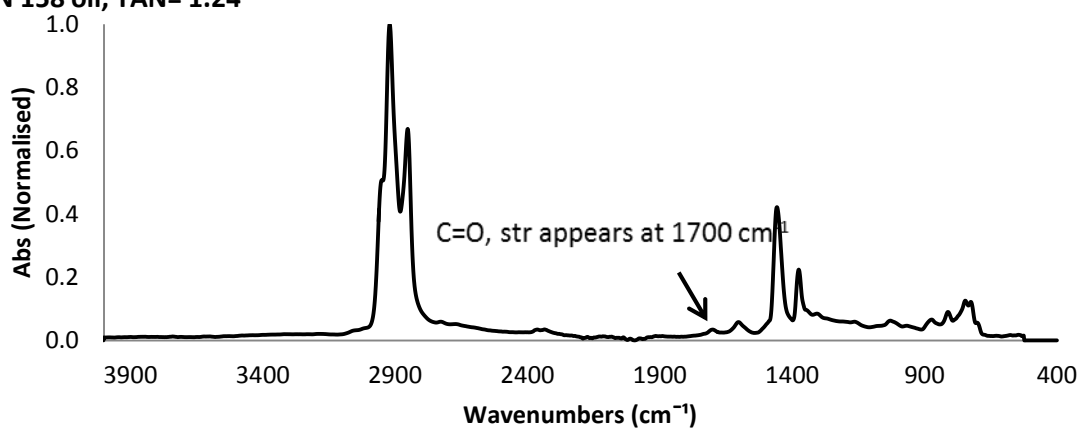
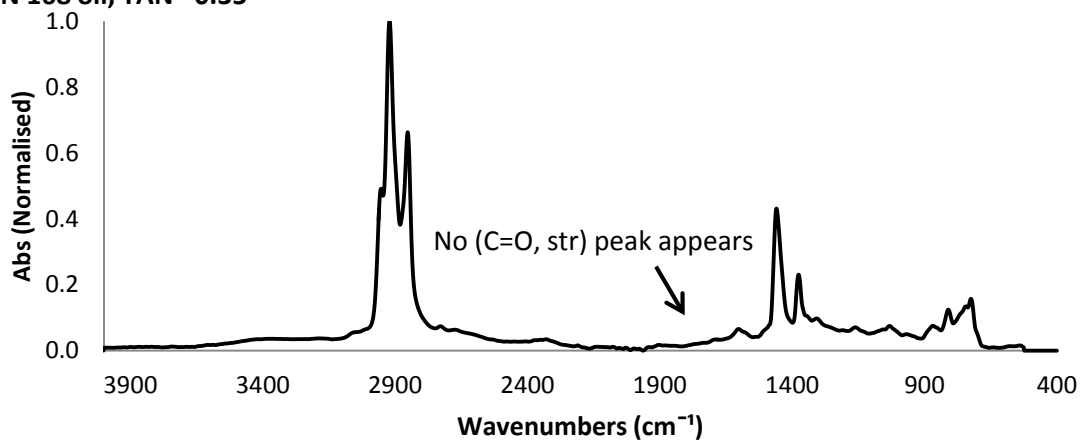   a. Oils

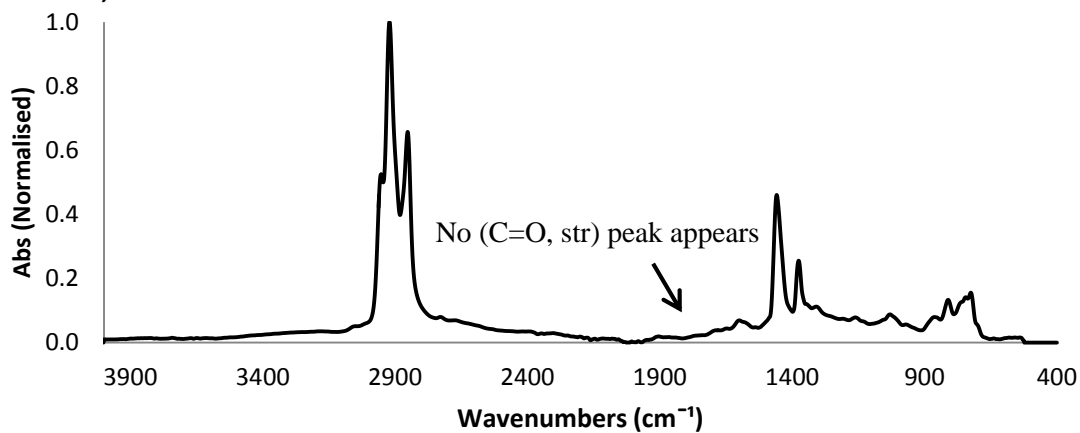**Boscan oil, TAN=1.66**
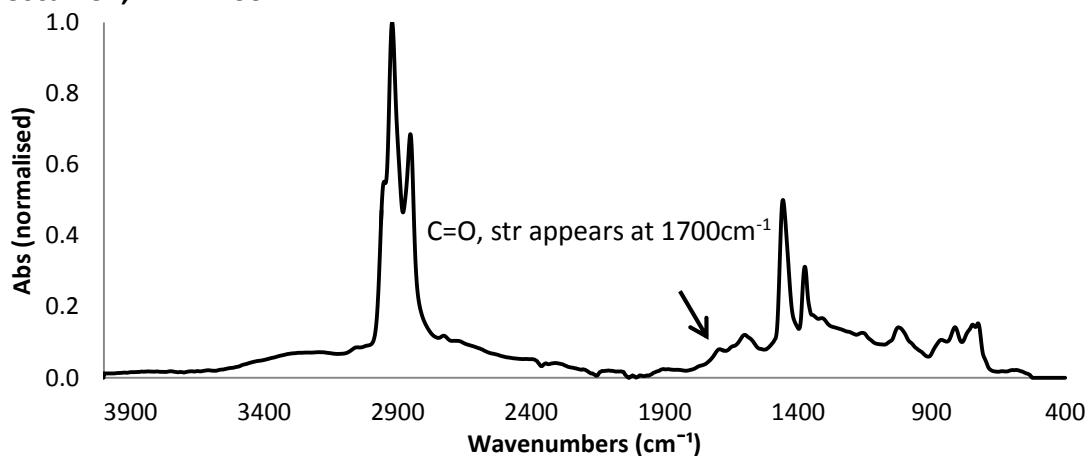
D13 oil, TAN= 1.55

EN 151 oil, TAN= 7.58

C=O, str appears at 1700 cm⁻¹

EN 158 oil, TAN= 1.24

C=O, str appears at 1700 cm⁻¹

EN 168 oil, TAN= 0.35

No (C=O, str) peak appears

EN 169 oil, TAN= 0.13

No (C=O, str) peak appears

EN 174 oil, TAN= 1.95

C=O, str appears at 1700 cm^{-1}

H7 oil, TAN= 2.19

C=O, str appears at 1700 cm^{-1}
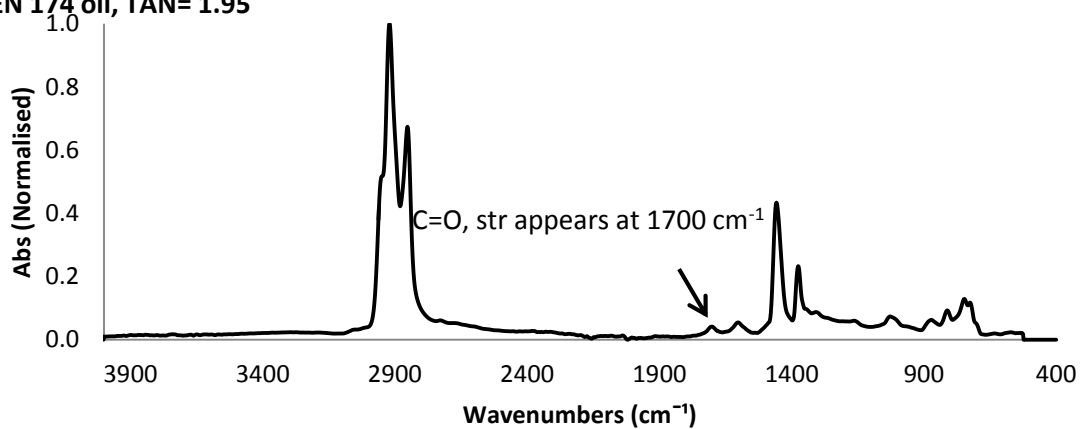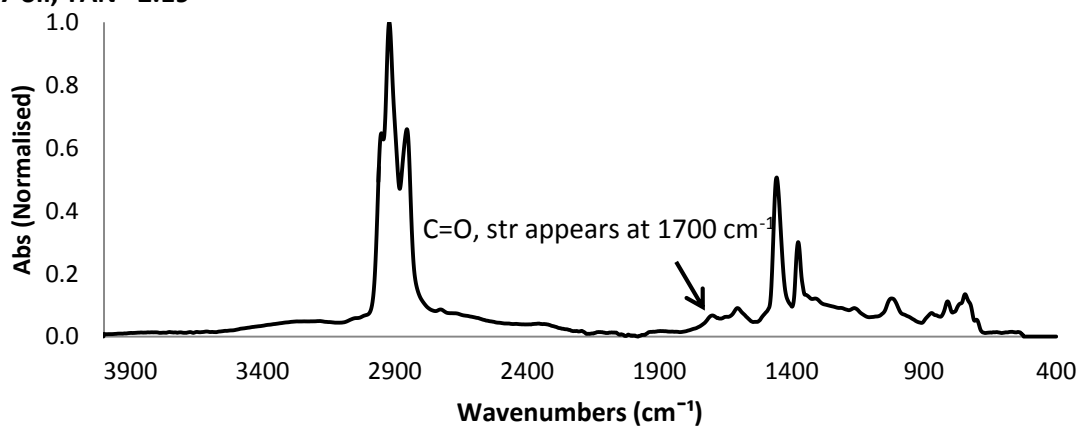
2. Calibration data
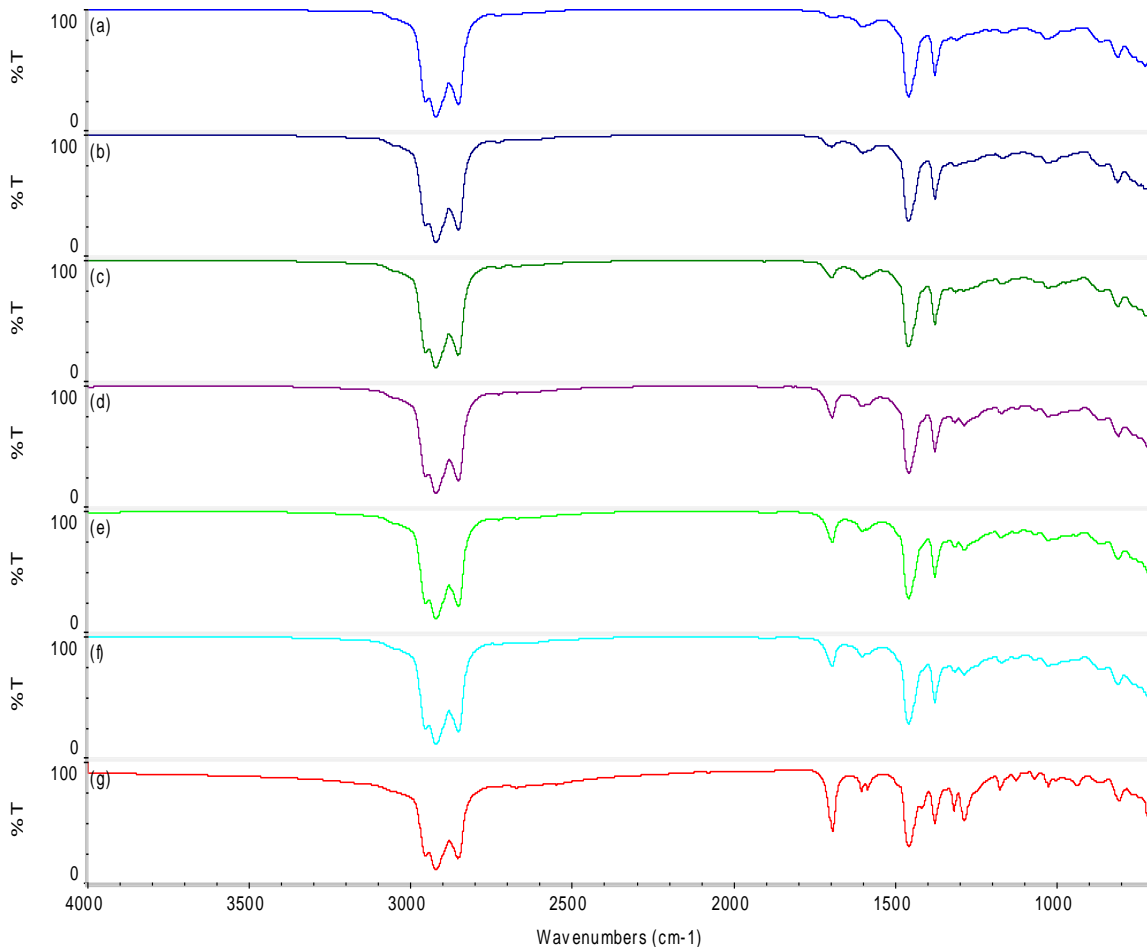
	BENZOIC ACID		
	mass oil(g)	**Benzoic acid mass (g)**	**TAN (mgKOH/g)**
(a)	1.001	0.0022	1.34
(b)	1.0249	0.0072	3.05
(c)	0.9946	0.0129	6.57
(d)	1.076	0.0209	8.88
(e)	1.0072	0.0208	9.68
(f)	1.0135	0.0210	9.70
(g)	0.9993	0.0606	29.21

TAN (mgKOH/g)

$y = 480.88x - 0.2266$
$R^2 = 0.9967$

Benzoic acid (g)

The end