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Aristotle University of Thessaloniki
Kapodistrian University of Athens
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Democritus University of Thrace

DISSERTATION:

CHEMISTRY OF CRUDE OIL – THE ROLE OF CHROMATOGRAPHIC AND
SPECTROSCOPIC TECHNIQUES AND SPECIATION OF N- AND O-CONTAINING
COMPOUNDS IN HEAVY DISTILLATES

Submitted by

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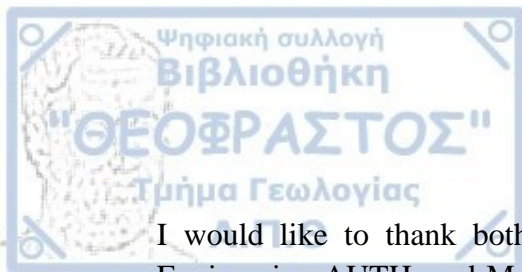
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Abstract

Petroleum is a naturally occurring mixture that consists of thousands of distinct hydrocarbon and heterocyclic molecules. It is well known that the crude oil composition has a conspicuous impact on its quality, on the refining processes and the production, thus it changes its economic value. The present study aimed to provide a wide presentation of the petroleum chemistry and the importance of composition analysis in the crude oil fractions, with emphasis to the heavy distillates. The most important chromatographic and spectroscopic techniques used in heavy crude oil are presented, such as Thin-Layer Chromatography (TLC), High Performance Liquid Chromatography (HPLC), Gas Chromatography (GC), Infrared spectroscopy (IR), Raman, Nuclear Magnetic Resonance (NMR) and Mass Spectroscopy (MS), along with examples of their applications. In addition, the determination of undesirable species like the nitrogen and oxygen containing compounds in the heavy distillates, is discussed and explained in detail. Applications of lately used techniques for the speciation of N- and O-containing compounds are also presented.

<u>Nomenclature</u>

CN: Cetane Number

COSY: Correlation Spectroscopy

DEPT: Distortionless Enhancement by Polarization Transfer

GASPE: Gated Spin Echo

MON: Motor Octane Number
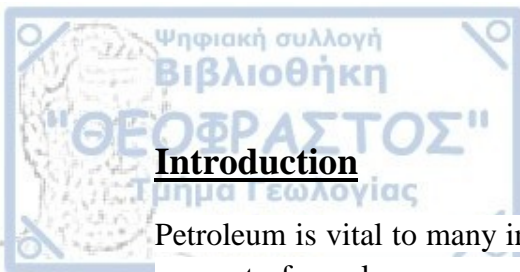
RI: Refractive Index

RON: Research Octane Number

RVP: Reid Vapor Pressure

SARA: Saturates, Aromatics, Resins, Asphaltenes

TAN: Total Acid Number

TBP: True Boiling Point

Introduction

Petroleum is vital to many industries and in the manufacture of a wide variety of materials. It accounts for a large percentage of the world's energy consumption, and thus is a critical concern for many nations. Despite all of the efforts to enable efficient and cleaner energy sources, crude oil is still the primary raw material in the production of fuels (da Cunha et al., 2016). As the worldwide supply of light crude oil decreases, the need to utilize heavy oils is becoming more and more necessary (Wood et al., 2008). The great challenge for the crude oil industry nowadays is to refine large quantities of heavy crude oils and to transform them into specialized refined products to meet the market's demands. In this regard, all the crude mixtures should be converted from heavy fractions to light distillate products in multiple complex refining steps (Silva et al., 2011).

It is well known that gas oils from heavy oils are difficult to convert because conventional catalysts are deactivated by the high levels of unwanted impurities, such as nitrogen compounds. These impurities not only affect the conversion processes but also cause environmental pollution. For that reason, it is of paramount importance to gain the optimum information about species that interrupt the refinery processes and apply a specialized removal treatment. Notwithstanding the foregoing, it is necessary to make periodic reviews and to characterize these oils in terms of chemical structure, physical and chemical properties, in order to obtain products with high quality and in accordance to the environmental specifications.

In general, the available and more widely used instrumental analysis techniques do not provide highly detailed analysis of the composition (i.e. identification of each individual group), owing to the high number of compounds in heavy oils. Until now, the possibilities of analysis are mainly group type quantifications, like the typical SARA fractions (Saturates, Aromatics, Resins, Asphaltenes). However, the need for a quantitative characterization of specific compounds, like the nitrogen- and oxygen-species, has lead to a further research of new techniques that would provide a complete and quick determination of these compounds (N.E. Oro, C.A. Lucy, 2013).

In order to understand the importance of analysis and the chemical composition of the crude oil, we have to give an extensive explanation of the petroleum chemistry and the different types of compounds it contains. After that, there will be a detailed presentation of the crude oil and its fractions and the analytical methods used for heavy oils.

PART 1:

Theoretical Approach

Chemistry and Analysis of Heavy Oils

1.1 Petroleum Chemistry

The different types of compounds in petroleum can be classified into two major groups, the hydrocarbons and the compounds containing hetero-atoms. Hydrocarbons contain only carbon and hydrogen. Compounds with heteroatoms on the other hand, also contain sulfur, nitrogen, oxygen, vanadium, nickel or iron (S.K. Panda, 2010). The general formula is $C_nH_{2n+z}X_aY_bZ_c$, in which X, Y and Z are the hetero-atoms, z is the deficiency value of hydrogen, and a, b and c are the number of hetero-atoms. The first compound group, the hydrocarbons, can be subdivided into different categories of compounds as follows (Beens, 2000):

1.   **Acyclic alkanes** (also called paraffins), branched or normal (also called iso- or normal), with the general formula of C_nH_{2n+2}.

2.   **Cyclic alkanes** (also called naphthenes). Depending on how many saturated rings they contain, they can be called as mono-naphthenes (one ring) or poly-naphthenes (more than one rings). There may be one or more paraffins attached to the naphthenic ring. The ring contains either five or six carbon atoms and the general formula for mono-naphthenes is C_nH_{2n}, for di-naphthenes C_nH_{2n-2}, for tri-naphthenes C_nH_{2n-4}, etc.

3.   **Alkenes** (also called olefins). Branched, normal or cyclic. They normally don't exist in the crude oil and the straight-run products of crude oil distillation, but they exist in large quantities in processed products, especially those obtained by thermal or catalytic cracking. The general formula for mono-olefins is C_nH_{2n}, for di-olefins or naphthenic mono-olefins C_nH_{2n-2}, etc.

4.   **Aromatics** (compounds that contain at least one benzene ring). They may have one or more paraffins or naphthenes attached to the ring. Mono-aromatics are compounds that contain one benzene ring, di-aromatics contain two benzene rings, etc. The general formula is C_nH_{2n-6} for mono-aromatics with alkyl substitution (paraffin attached), C_nH_{2n-8} for mono-aromatics with one naphthenic ring, etc.

In Figs. 1 and 2 it is well observed that as the number of carbon atoms increases, the number of isomers grows, which means that the number of different structures rises. In crude oil, there are compounds that may have more than 70 carbon atoms, signifying that the number of possible isomers grows beyond comprehension and the mixture becomes exceedingly complex.

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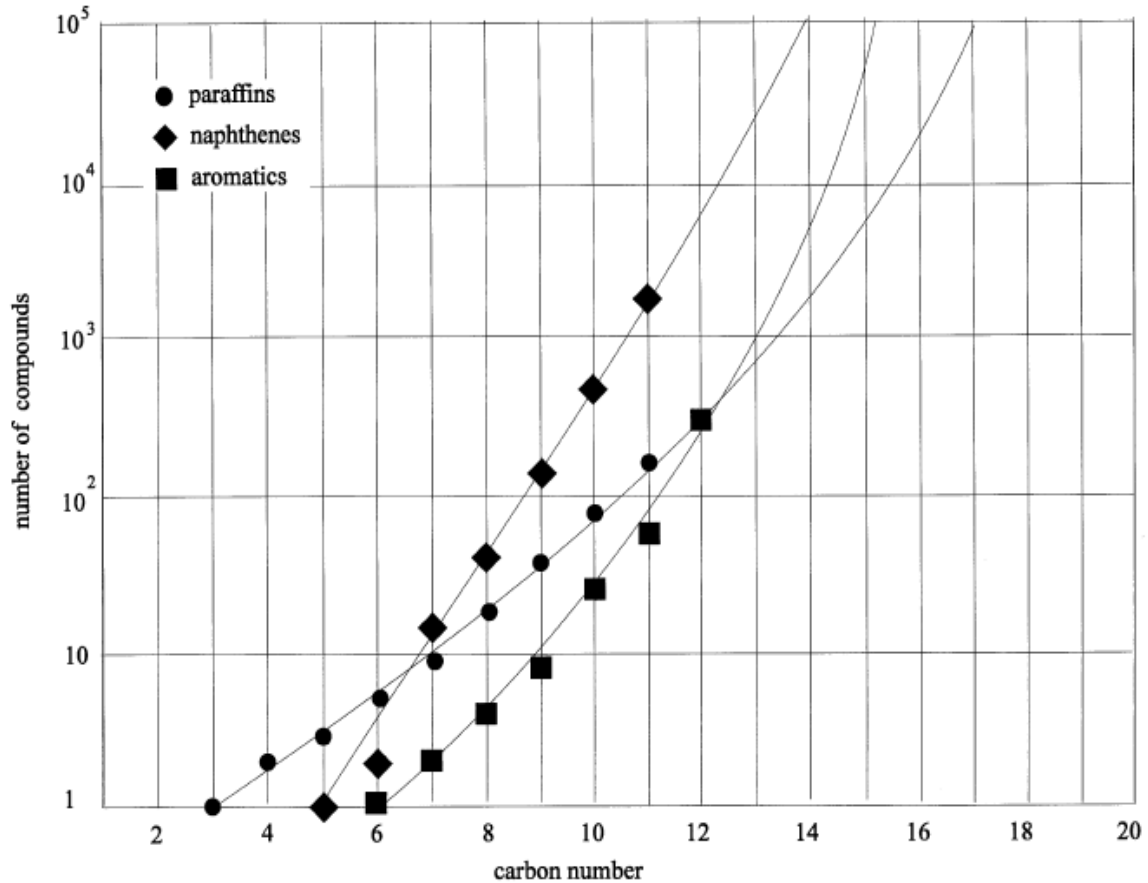
Fig. 1. The number of possible hydrocarbon isomers (Beens, 2000).

The second compound group, containing heteroatoms, can be classified according to the containing hetero-atom as follows (Beens, 2000):

1. **Sulfur-containing compounds.** These are usually present in higher percentage than the other compounds. Their occurrence in petroleum products is extremely undesirable for different reasons. The main reasons are the conversion of sulfur into SO_2 and SO_3, which cause are considered environmental pollutants, and also the detrimental effects of sulfur on catalysts used in different processes of crude oil refining. Another important reason is that most of the sulfur compounds are very malodorous, especially hydrogen sulfide and mercaptans. Generally, they can be categorized into 3 main groups : thiols (also called mercaptans) in the form of R-S-H (R being an alkyl substituent), sulfides in the form of R-S-R` or disulfides (R-S-S-R`), and thiophenes (R-C_4H_3S), that can have one or two attached benzene rings and are called benzothiophenes (R-C_8H_5S) or dibenzothiophenes (R-$C_{12}H_7S$) respectively (Silva et al., 2011).

Fig. 2. The number of possible sulfur-containing isomers (Beens, 2000).

2. **Nitrogen-containing compounds.** They normally exist in lower concentrations than the sulfur compounds, but are regarded as undesirable when they are present in fossil fuels and in their processed fractions, due to the problems they may cause:
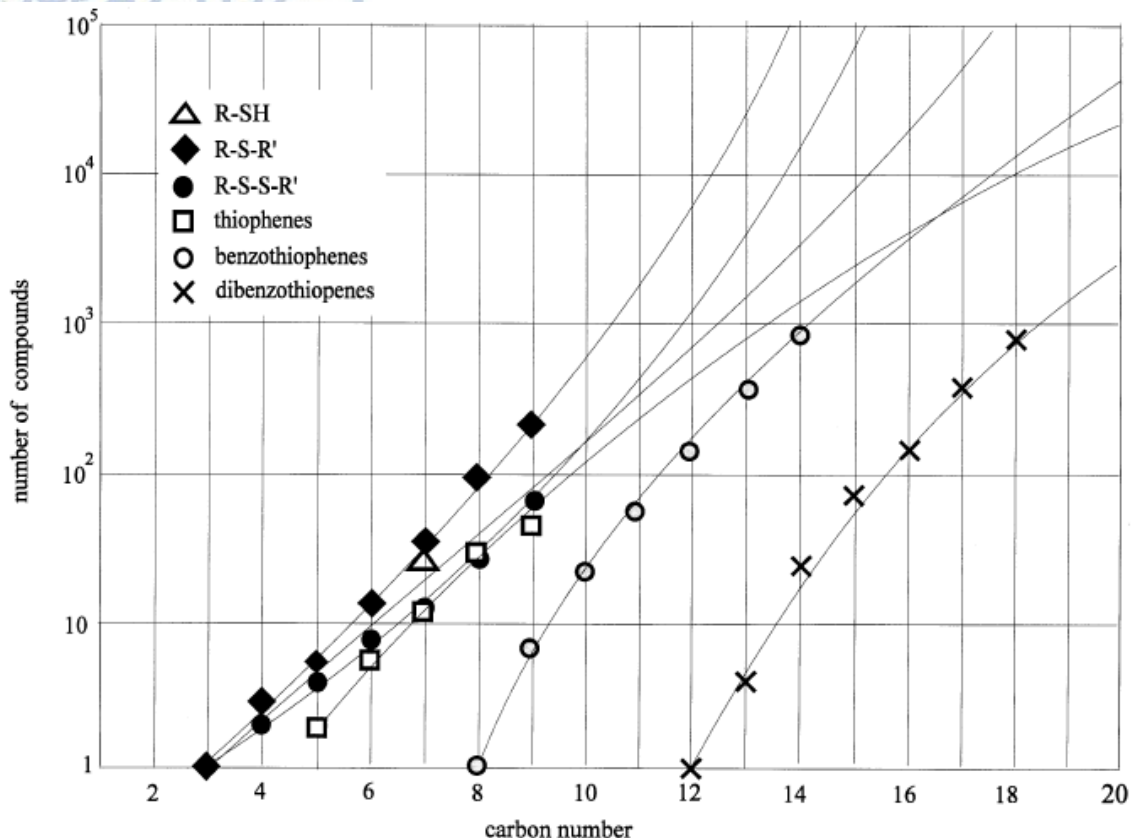
❖ to human health, some of them are toxic and mutagenic,

❖ to the environment, their combustion leading to the formation of NOx and consequently contributing to acid rain (Mao J., 1995) ,

❖ to refining processes, like catalyst poisoning (Yang H., 2004), fouling, corrosion of refinery equipment (e.g. storage tanks and piping) (Batts BD, 1991), color and gum formation in transportation fuels and eventually in motor engines. They are also refractory to hydrotreating (Kabe T., 1999; Kanda W., 2004), preventing the efficient upgrading of feedstocks (e.g. middle distillates to transportation fuels) (Mushrush GW, 1991). Therefore, the detailed characterization of their chemical structure, and not only of the total amount of nitrogen, is considered a crucial issue to better understand and improve hydroconversion processes (Adam F., 2007).

N-containing compounds in crude oil fractions are conventionally parted into non-basic or neutral such as indoles and carbazoles (e.g. pKa of indole of 3.6), weakly basic such as hydroxyquinolines, hydroxypyridines and anilines (e.g. pKa of aniline of 4.6) and basic such as pyridines, quinolines, phenanthrolines and acridines (e.g. pKa of pyridine of 5.25). They are present at concentration as low as 0.1–2.0 wt.% (Flego and Zannoni, 2011). There will be a more detailed discussion below about the quantification of these groups, and the methods used for their identification.

3. Oxygen-containing compounds. There are five groups of oxygen compounds, some of which can be present in the form of their respective acids or salts (Beens, 2000):

- ❖ naphthenic acids,
- ❖ phenols,
- ❖ fatty acids,
- ❖ furans and
- ❖ phenyl ketones.

The oxygen compounds that are usually being identified are phenols and acids, since these are usually found in a higher percentage in the crude oil distillates. Two detailed studies about the determination of these compounds will be presented in part II.

4. The most common metals present in the petroleum fractions are vanadium, nickel and iron. They are present in very low concentrations and in the form of organic metal complexes (porphyrins etc) (Beens, 2000).

1.2 Crude oil

Crude oil is a dark black liquid at normal (atmospheric) conditions (i.e. room temperature and pressure) with a smelly odour that is caused by the sulfur-containing compounds (R.I. Botto, 2003). It is lighter than water, it has a high viscosity and is highly flammable. In order to exploit it, crude oil must be extracted from the earth to the surface and undergo various steps of processing or refining (Borgund et al., 2007).

The main content of crude oil consists of complex heavy hydrocarbon chains, while light hydrocarbons may also be present in smaller quantities. Other elements like sulfur, nitrogen, oxygen, are also present in minor quantities and have a great effect on its quality. More precisely, crude oil can be characterized as "sweet" crude oil if the sulfur (S) content is below a specified percentage by weight, usually around 0.45% or 0.46%, or "sour" crude oil if its sulfur content is above that percentage. Crude oil is almost entirely composed of the following four types of hydrocarbons: paraffins (alkanes), olefins (alkenes), napthenes (cycloalkanes) and aromatics (derivatives of benzene) (Kassinis, 2015).

Fig. 3. Sweet and sour crude oil.
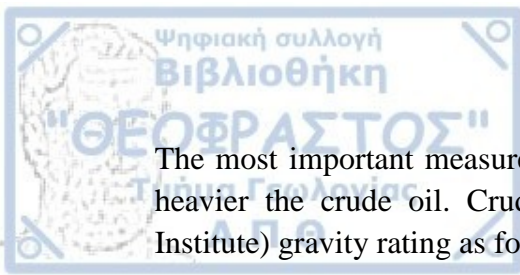
The most important measure of crude oil is the API gravity. The lower the API gravity, the heavier the crude oil. Crude oil is classified according to its API (American Petroleum Institute) gravity rating as follows (Petroleum.co.uk, 2017):

1) Light crude oil (API > 31.1)
2) Middle crude oil (22.3 > API > 31.1)
3) Heavy crude oil (API < 22.3)
4) Extra heavy crude oil (API < 10)

Light crude oil is considered to be better as long as it contains fractions that make up gasoline. On the other hand, heavy crude oil and extra heavy crude oil are considered to be lower quality oils. The difference of these several types of crude oil is mostly related to the location of the found reservoir, since different circumstances result in different composition and properties. In this content, crude oil can be divided into the following types (Petroleum.co.uk, 2017):

❖ Brent, a mixture of crude oils produced from North Sea oil fields. It is classified as Light Crude and has low sulphur (S) content.
❖ West Texas Intermediate (WTI) is the US reference crude oil. It is classified as Light Crude (lighter than Brent) and has low sulphur (S) content.
❖ OPEC Crude Basket is a mixture of –on average- 15 different crude oils produced by member countries of OPEC. It is classified as Light Crude (lighter than Brent and WTI) and has a lower sulphur (S) content.
❖ Dubai Crude is the crude oil generally from Dubai and Oman. It is available on "spot" markets.

The first stage of the treatment of crude oil is related with the separation of the different types of hydrocarbons, which is achieved by distillation in a fractionation column. Fractional Distillation is the process of separating component substances of the liquid crude oil through their vaporization points. Lighter hydrocarbons have lower vaporization points, which means that they evaporate at lower temperatures. With this physical separation process, it is quite easy to achieve the separation of crude oil into different fractions.

During the distillation of crude oil, the first products collected are butane (C_4H_{10}) and lighter hydrocarbons, which go directly for gas processing to recover the various gasses (butane, propane, ethane, methane). Next fraction collected is naphtha, which is used for making gasoline following catalytic reforming. Heavier hydrocarbons follow such as kerosene, that undergoes hydrotreating to produce jet fuel, which is further processed in catalytic cracking. The residue that remains is used to make coke following a process known as coking. Coke is a solid fuel that can be made by heating coal in the absence of air so that the volatile components are driven off (Kassinis, 2015).

After the separation of the different components of crude oil, the processes that follow concern the refining of the distillates. The main final products of crude oil refining, as shown in Table 1, are LPGs (Liquefied Petroleum Gas), Gasoline, Kerosene, Fuel Oil (Diesel), Lubricating

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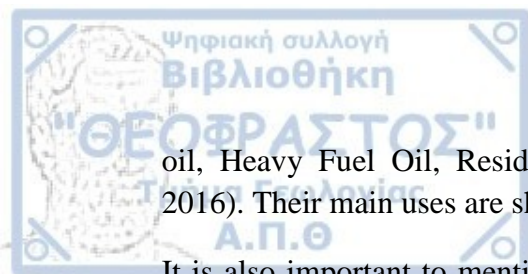
oil, Heavy Fuel Oil, Residuals (coke, asphalt, tar, waxes) (Lemonidou, Lappas, Vasalos, 2016). Their main uses are shown in Fig. 4.

It is also important to mention four main parameters used to characterize these products and their efficiency. One of them is the Research Octane Number (RON), which is a standard measure of the performance of a fuel. The higher the octane number, the more compression the fuel can withstand before igniting, consequently the better the quality of the fuel. Therefore, RON represents the behavior of the gasoline engines that require higher compression ratios and is used to characterize the performance of lighter fractions (Morganti et al., 2013). Motor Octane Number (MON) is another type of octane rating, but is used to evaluate the performance of gasoline engines with a higher speed. Depending on the composition of the fuel, the MON of a modern pump gasoline will be almost 8 to 12 octane units lower than the RON, but there is no direct relation found between RON and MON (Morgan et al.,2010). Pump gasoline specifications typically require both a minimum RON and a minimum MON. At the same time, cetane number (CN) is an indicator of the combustion speed of diesel fuels and represents the behavior of diesel engines (Janecek, 2017). Diesel engines do not compress the fuel, but rather compress air and then inject fuel into the air which was heated by compression. Likewise, the higher the cetane number, the better the quality of the diesel fuel. Finally, another parameter is the Reid Vapor Pressure (RVP), which is a common measure of the volatility of gasoline (Flecher, 1997). High levels of vaporization are desirable for winter starting or operation, and lower levels are desirable in avoiding vapor lock during summer heat. Fuel cannot be pumped when there is vapor in the fuel line (summer) and winter starting will be more difficult when liquid gasoline in the combustion champers has not vaporized.

Table 1. Oil products boiling range.

| Product	Hydrocarbon Content	Boiling Range
Petroleum Gas	Small alkanes (1-4 C)	< 40°C
Naphtha	Mixture of alkanes (5-9 C)	60°C - 100°C
Gasoline	Mixture of alkanes & cycloalkanes (5-12 C)	40°C - 205°C
Kerosene	Mixture of alkanes & aromatics (10-18 C)	175°C - 325°C
Diesel	Liquid alkanes (12 C +)	250°C - 350°C
Lubricating oil	Long chain alkanes, cycloalkanes, aromatics (20-50 C)	300°C - 370°C
Heavy Fuel Oil	Long chain alkanes, cycloalkanes, aromatics (20-70 C)	370°C - 600°C
Residuals – coke, asphalt, tar, waxes	Multiple-ringed compounds (70 C +)	> 600°C

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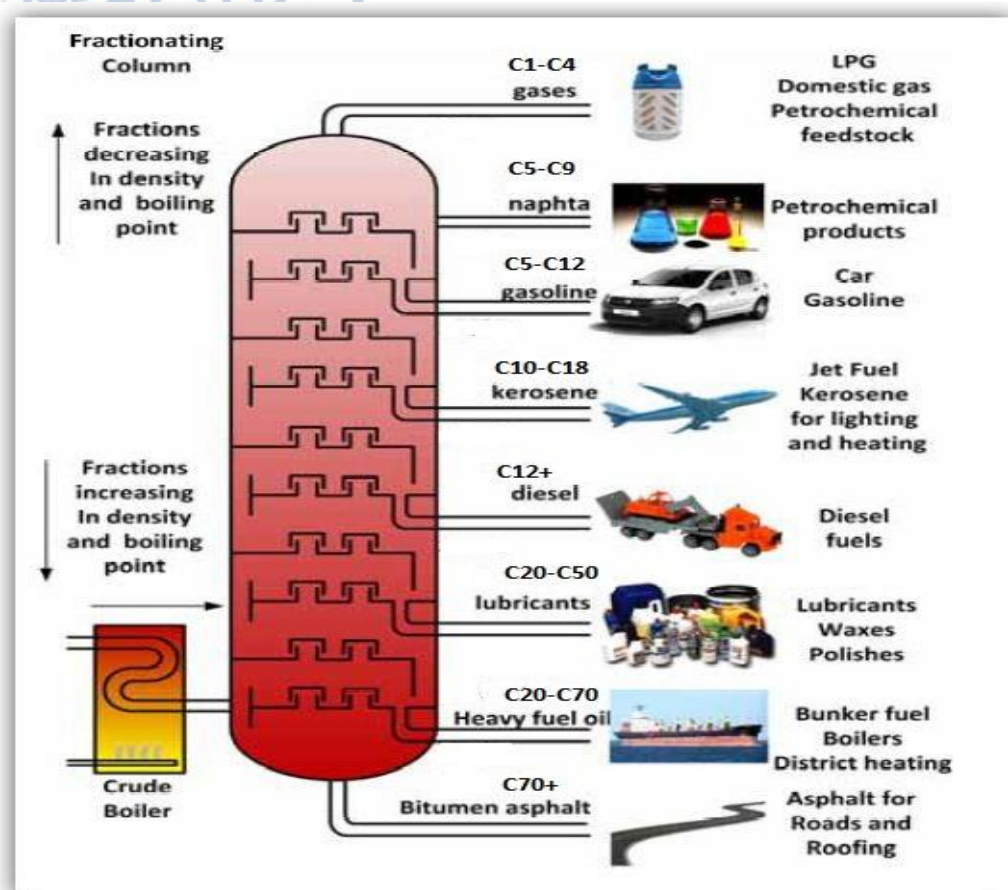
Fig. 4. Fractions of crude oil and their uses after the refining processes (Georgakopoulos, 2016).

Petroleum products are usually grouped into four categories: light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, jet fuel, diesel), heavy distillates (lubricating oil, heavy fuel oil) and residuals (wax, asphalt) (Aitani, 2012). The characterization of heavy petroleum fractions is developing into a major analytical research issue, due to the fact that they contain hundreds of long chain compounds that do not allow the quantification of impurities such as nitrogen and oxygen containing compounds. For this reason, this study is focused on techniques used in the analysis of heavy samples and the implementation of innovative techniques used for the determination of nitrogen and oxygen species.

1.3 Quality of petroleum and importance of composition analysis

There are many factors affecting the quality of crude oil. Some of them are the origin of the crude oil, its density, and its composition. For the reason mentioned previously, it is of vital importance to collect the optimum data for every component in the crude oil mixture. Of course the separation and identification of every single compound in crude oil is an impossible idea, since it is a very complex sample consisting of hundreds of compounds. Usually, what we receive from a crude oil analysis is the general distribution of compounds and there are

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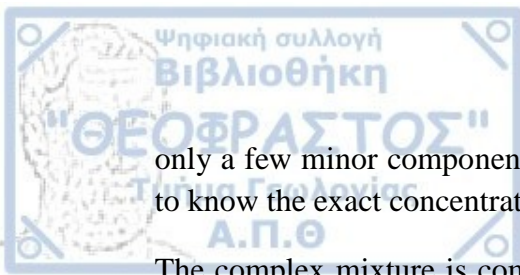
only a few minor components, like the sulfur, nitrogen and oxygen species, for which we aim to know the exact concentration.

The complex mixture is composed of many compounds, ranging in size from the smallest to large compounds where the quantity of carbon atoms varies. It has different quantities of various compounds and special properties depending on the geographical source. It is necessary to characterize these substances in terms of chemical structure and their physical and chemical properties. The heavier the crude oil, the more complicated its composition and the variety of the compounds. The identification and quantification of asphaltenes, sulfur, nitrogen, oxygen and metal ions are the path to heavy oil characterization.

The composition analysis of heavy crude oils is a vital problem in the petroleum industry, since there are many compounds like polyaromatics that are considered to be toxic or carcinogenic (Doan, 1995). In addition, sulfur, nitrogen and heavy metals, that are present in higher concentrations in heavy crude oils, have environmental implications and cause huge problems in the refining process due to the corrosion and poisoning of the catalysts (Peinder et al., 2009). Ashapltenes on the other side, cause environmental and refining problems, due to their tendency to flocculate and precipitate. High concentrations of these compounds can lead to a greater formation of coke or the deactivation of catalysts (Behera, 2008), which can have unfavorable effects on the smoke point of a jet fuel (Cookson, 1990) or affect the combustion process in various motors (Lee, 1999). The presence of heavy aromatic compounds can also have a negative effect on the cetane number of a diesel.

The characterization of the crude oil is done at a primary stage through some tests like True Boiling Point (TBP), and then with the help of chromatographic and spectroscopic techniques for a better understanding of the chemistry of each petroleum fraction. If there is a considerable amount of information about the chemical properties of each fraction, then we're in position of improving the quality of the final petroleum products.

Some of the most common analyses performed in all refinery laboratories are the determination of density, refractive index (RI), viscosity, flash point and the cold-flow properties, like the pour point and cloud point (Beens, 2000). The TBP allows the evaluation of the composition, the properties, the behavior during storage or use, and the optimization of refinery processes. TBP is an excellent way to characterize heavy crude oil, but the main problem associated with this analysis is the long time needed to obtain the final results (Silva et al., 2011). Other tests and analysis that can be done, like viscosity-gravity constant, correlation index, K-UOP factor and other ASTM and IP methods, even though they are not so time consuming, they give only a general idea about the composition and properties of crude oil. In consequence, the purpose is to develop an improved quantification analysis, using known technologies able to efficiently evaluate the crude oil, and contribute to the time reduction of analyses, to the cost reduction and to give online information. The main techniques used in the petroleum industry for this purpose are discussed in the next section.

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1.4 Main chromatographic – spectroscopic techniques used in heavy crude oil analysis

There are many methods used in the petroleum industry that give us the opportunity to classify the chemical compounds present in crude oil and draw some conclusions concerning their properties. The main techniques used to analyze qualitatively petroleum fractions are chromatographic methods, like thin-layer chromatography (TLC), high performance liquid chromatography (HPLC), gas chromatography (GC), and some spectroscopic methods like infrared spectroscopy (IR), Raman, nuclear magnetic resonance (NMR) and also mass spectroscopy (MS).

1.4.1 Thin Layer Chromatography (TLC)

In TLC, an adsorbent material is used as a stationary phase on a glass plate. The development of the chromatogram occurs as a mobile phase that percolates through the stationary phase. In fact, TLC can be considered as an open column chromatography method, which is, however, faster and more suitable than analogous low pressure chromatography methods. The separation of the components is achieved through adsorption, distribution, ion exchange or with a combination of these (Papadogiannis, Samanidou, 2001). The thin-layer chromatography technique is easy and simple to use, and the separation capacity that can be achieved is too high, especially with the coating materials of the high performance plates (HPTLC). It is quite sensitive and we can separate several compounds in a short time. These compounds can then be recovered and studied more extensively. Quantification of the compounds, that are separated as stains, can be done with great precision with special instruments, called Scanning Densitometers. There is a variety of plate coating materials and solvent systems, which are used to develop the chromatogram. By choosing the right combination, we can even achieve a more speciated separation.

Regularly used solvents are hexane, benzene, dichloromethane, trichloromethane, tetrachloromethane, ethyl acetate, dioxane, isobutanol, acetone, isopropanol, ethanol and methanol. Although, using mixtures of solvents is preferable because it is a way to ensure the required properties for the chromatographic separation. As for the stationary phase, in the case of petroleum analysis, the usually employed stationary phase is silica or alumina put on a glass, aluminum or plastic plate (Silva et al., 2011). TLC is also often used along with other chromatographic and spectroscopic techniques, in order to get better results of the separation and gain extra information for the isolated compounds. There has been no precise quantitative analysis achieved with TLC till now, and this is why it is more often used as a qualitative analysis (Simanzhenkov, 2003). In heavy distillates, TLC is used for the characterization of semi-volatile and non-volatile products and in the separation of compounds like asphaltenes, which have a high boiling point. Efforts are made to improve the TLC technique for quantification purposes, such as the combination of TLC with a flame-ionization detector (TLC-FID), which helped in the distinction between hydrocarbon groups, like saturates, aromatics and polars in heavy oil (Fig. 5).

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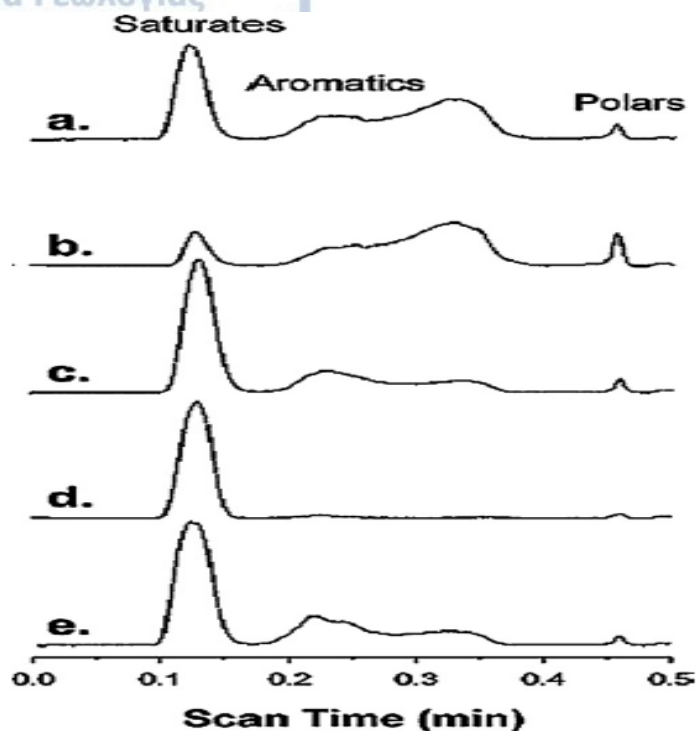
Fig. 5. Example of a TLC-Fid chromatograms of 500 N VGO cut and its fractions. Chromatogram (a) VGO, (b) extract, (c) raffinate, (d) wax and (e) base oil (B.N. Barman, 2005).

1.4.2 High Performance Liquid Chromatography (HPLC)

Compared to other chromatography techniques, HPLC differs because of the fact that small-grained fillers are used and high pressure is applied. With the HPLC technique, faster and more efficient separation of mixtures can be achieved. Like in all chromatographic techniques, separation is the result of the combined action of a stationary and a mobile phase. The sample is inserted at the top of the column and with the help of the mobile phase its components move and finally elute in sequence. The analysis time is usually small (a few minutes), while accuracy and repeatability are very good (Papadogiannis, Samanidou, 2001).

HPLC is known to be a useful method for the analysis of compounds that do not present enough volatility to be analyzed by GC. Crudes with composition consisting of 80% of heavy fractions need temperatures above 350°C to vaporize (Silva et al., 2011). For this reason, HPLC is a more efficient way to analyze such crudes than typical GC. Application of HPLC for the analysis of oil samples has many advantages, good separation of heavy oil fractions and precise analysis in a very short time are some of them. The main disadvantage is that depending on the used detector [e.g. UV absorption (UV), refractive index (RI) or fluorescence (F)] there are some compounds which are impossible to identify. Yet it should be mentioned, that RI is not very sensitive and the temperature variation can affect the output of the recorder (Kenkel, 1994). Even though HPLC is widely used in analyzing group of

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compounds, such as paraffinic, naphthenic and aromatic, it is not recommended for analyses of individual compounds. This is because HPLC is not able to separate compounds that present identical boiling point range. However, some examples of HPLC uses in the bibliography include the identification of molecular types in non-volatile feedstocks, in the study of asphaltene fractions (Speight, 2001) and in the identification of aromatic groups (mono, di-, tri-aromatics) (Papadakis et al., 2001). An example of an HPLC chromatogram with a UV detector is given in Fig. 6.
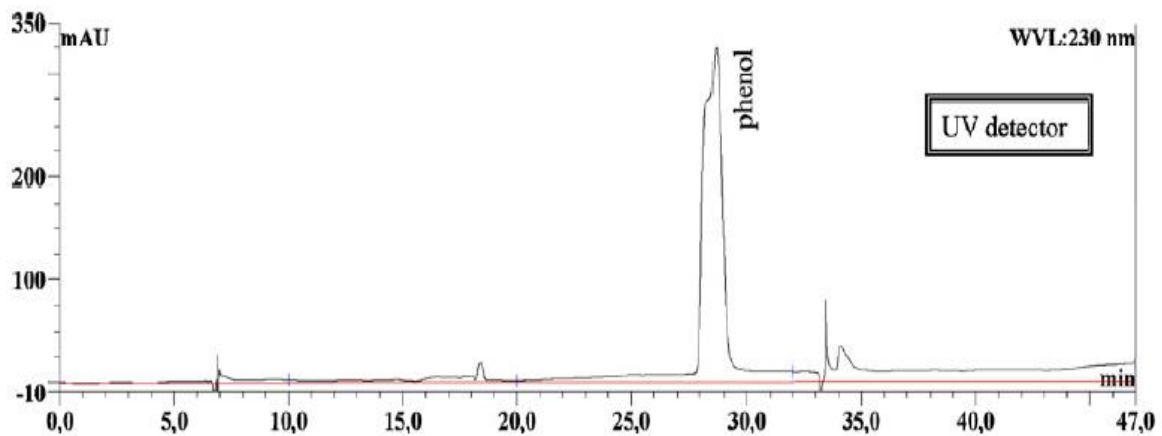
Fig. 6. A chromatogram of a mixture of four standards (phenol, octadecane, octadecanoic acid and 1,12-dodecanedioic acid) using an analytical HPLC column and a UV detector (Borgund et al., 2007).
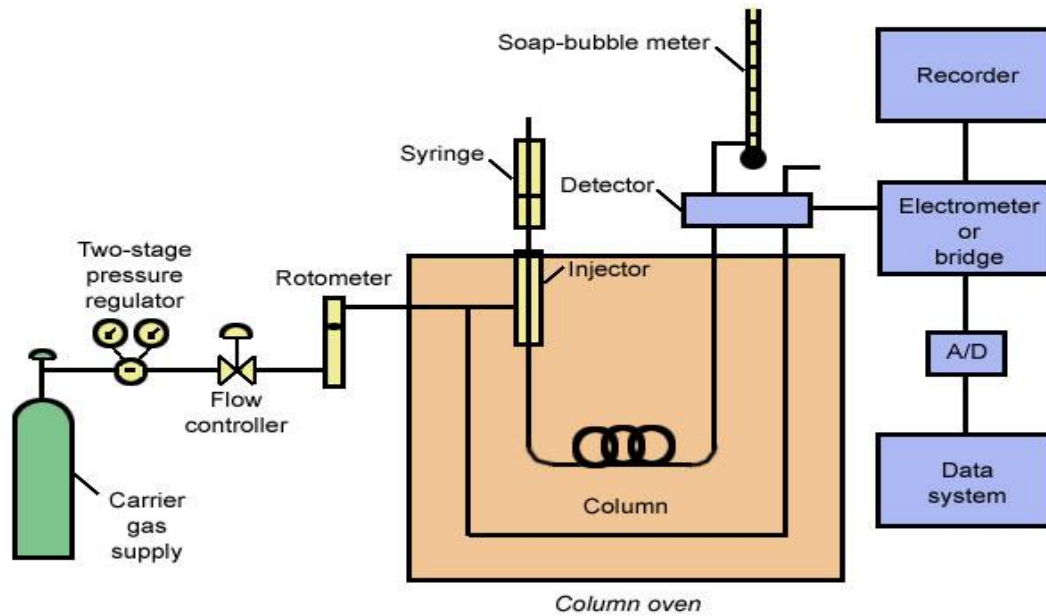
1.4.3 Gas Chromatography (GC)

GC is commonly used for the separation and analysis of complex mixtures of many components that can be vaporized without decomposition. The sample in this technique is carried through a column by a moving phase, which is a gas (Papadogiannis, Samanidou, 2001). The time required by the chemical constituents of the sample to pass through the column depends on their chemical and physical properties and on the interaction with the stationary phase, which is usually solid. Retention time is the time needed for each compound to leave the column. The separated substances coming out of the column are detected and represented by an electronic signal.

There are different detectors used in the GC technique. There is the Flame Photometric Detector (FPD), the Flame Ionization Detector (FID) and the Thermal Conductivity Detector (TCD). They have different sensitivity, which means that the smallest quantity of compounds they detect is different, and the selectivity also differs (type of compound). FID is generally a universal detector, and it is used in the analysis of organic substances such as benzene in gasoline according to the ASTM D3606 method (Simanzhenkov, 2003). The FPD is used in the identification of organic compounds that contain sulfur or phosphorus as in the case of

heavily biodegraded spill samples (Silva et al., 2011). TCD on the contrary, is not very sensitive but it is quite selective and is widely used in the analyses of crude oil fractions or products. Except for these detectors, there are others like the electron trap detector and nitrogen/phosphorous thermo ionic detector, that are used depending on the compound under investigation (Papadogiannis, Samanidou, 2001).

Gas Chromatograph Schematic

Fig. 7. Schematic of a typical Gas Chromatograph (Slh.wisc.edu, 2017).

In general, the GC method has many benefits, like the short time needed for the analysis to be completed and the small amount of sample required. But it must be mentioned that this method is not very good for the analysis of heavy crude oil fractions, since all the compounds analysed by GC must be in the gaseous phase and need to have a boiling temperature less than 350°C (Altgelt, 1994). Only the light fractions, like gasoline, kerosene or diesel have a boiling point smaller than 350°C. The heavy fractions, instead, have a distillation temperature much higher than 350°C. This means that the GC technique is not appropriate because of the existence of heavy compounds and their low volatility, and is most often used for light (Fig. 8) or middle distillates. There are different ways that GC method is being used in the petroleum industry. Some examples of GC applications in the crude oil characterization would be ASTM D2163 for the analysis of gaseous boiling range, ASTM D2427 method of gasoline boiling range, ASTM D3524 method for the analysis of diesel fuel and ASTM D3606 for the aviation gasoline.

The high number of isomers in heavy crude oils make the separation and identification of these compounds with conventional GC a difficult task (Andersson, 1992) as the co-elution of different compounds may cause false results in the analysis.
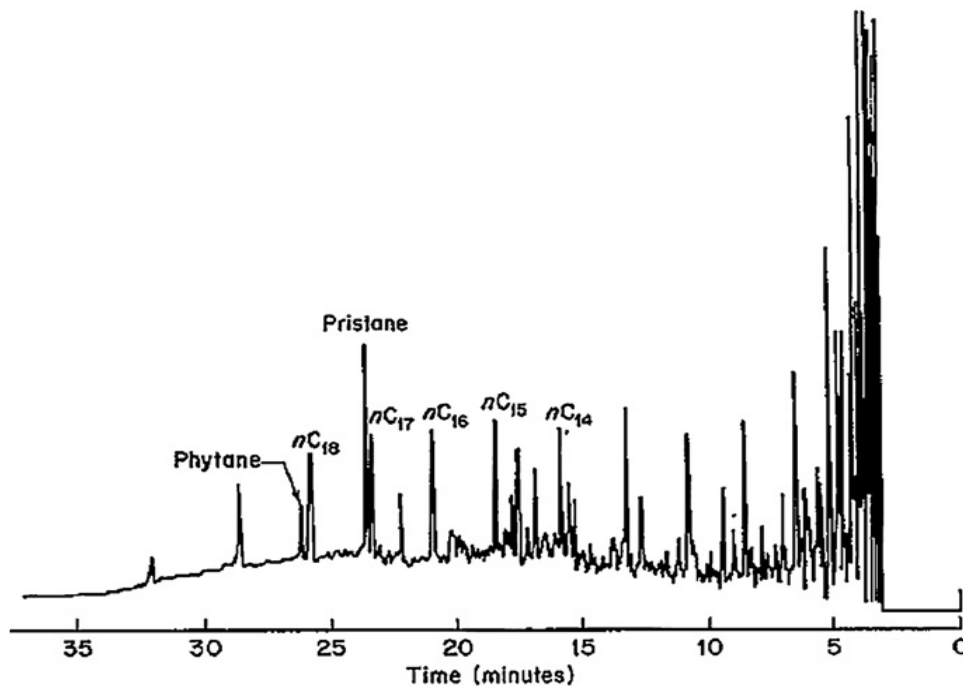
Fig. 8. An example of a GC spectrum of a light Nigerian crude (fraction with a boiling point temperature < 343ºC) (Silva et al., 2011).

1.4.4 GC x GC technique

The limitations of conventional GC can be overcome with the application of the two dimensional gas chromatography (GCxGC) technique. In this technique, isomeric and homologous compounds tend to cluster in specific areas of the chromatographic space, allowing better identification, especially in combination with different selective detectors (Flego and Zannoni, 2011). GCxGC is one of the main analytical methods used in heavy crudes, especially in the speciation of N-containing compounds that will be extensively discussed in part II.

Comprehensive gas chromatography is a major analytical technique with superior peak capacity and resolution compared to other chromatographic techniques. The sample in this technique is separated on two columns of different polarity connected by a device called modulator. A typical GCxGC system (Fig. 9) consists of an injector, a primary oven which houses the secondary oven as well, two columns of different polarity and dimensions housed in the respective ovens, a modulator which is located between the two columns and the

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detector. The 'heart' of the separation lies at the selected combination of columns and the modulator. Commonly, the 1st column is apolar/low polarity and the 2nd column is polar for an orthogonal system, while the opposite combination concurs with a non-orthogonal or 'reversed-phase' system. In the 1st column the compounds are separated by their volatility (and/or polar interactions), while other mechanisms are employed in the 2nd column, such as π-π interactions, hydrogen-bonding and steric effects. The modulator's function is to periodically trap the effluent coming out of the 1st dimension column and then release it into the 2nd dimension column (Michailof, 2016).
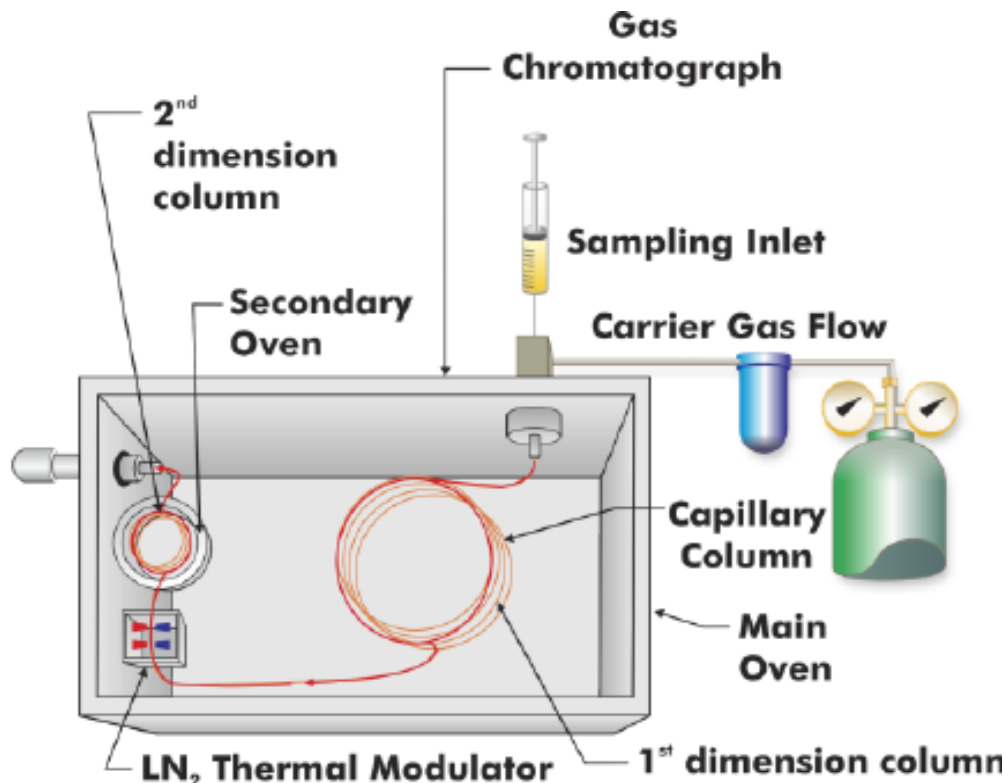
Fig. 9. Schematic of a GCxGC system.

GCxGC offers a high ordering of the separated species in the two dimensional plane. For example, the di-aromatics in Fig. 10 are not only separated from the saturates and mono-aromatics, but are grouped in a band from which more chemical information can be extracted. The different groups of di-aromatics, naphthalene (No. 23), the methylnaphthalenes (No. 24 and No. 25), the naphthalenes with substituents with two carbon atoms (No. 27), with three carbon atoms (No. 28) and with four carbon atoms (No. 29) are clearly recognized (Beens, 2000).
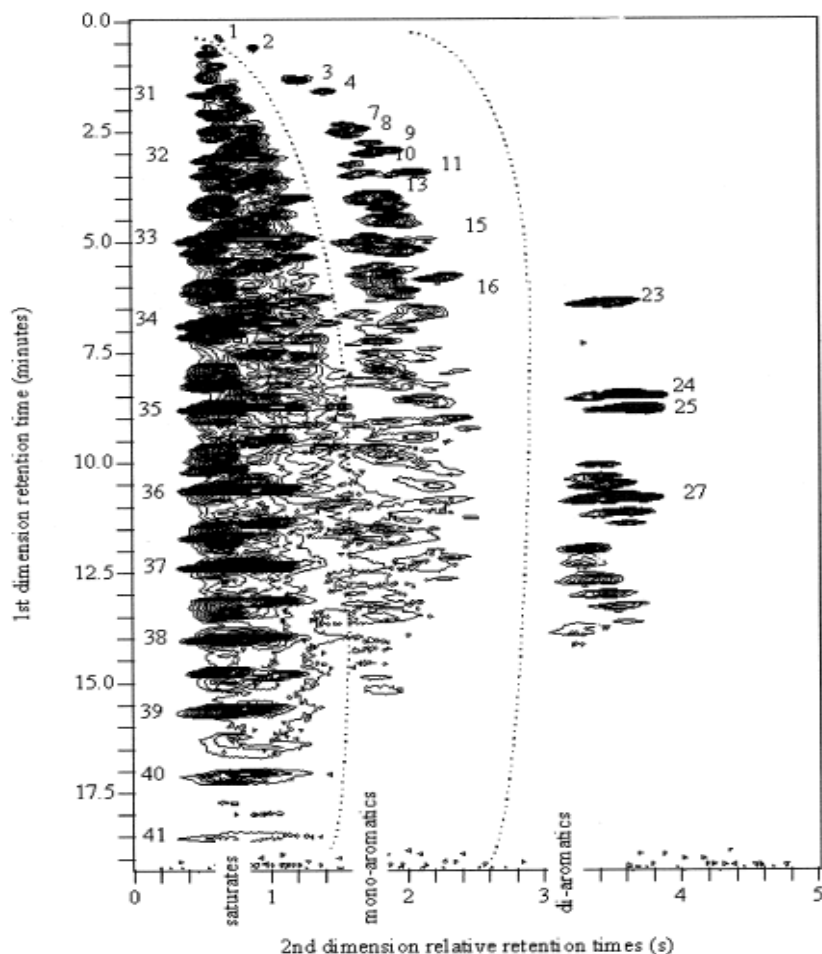
Fig. 10. Contour plot of a GCxGC separation of a heavy gasoil. 1. Benzene, 2. Toluene, 3. Ethylbenzene+para+meta-xylene, 4. Ortho-xylene, 7-13. C_9 aromatics, 15.C_{10} mono-aromatics, 16. C_{11} mono-aromatics, 23. Naphthalene, 24. 2-methylnaphthalene, 25. 1-methylnaphthalene, 27. C_2 naphthalenes, 28. C_3 naphthalenes, 29. C_4 naphthalenes, 30-41. n-C_8 though n-C_{19} (Beens, 2000).

1.4.5 Infrared spectroscopy (IR)

IR is one of the most important techniques used to receive information about the hydrocarbon skeleton and functional groups (like hydroxyl or carbonyl groups) of compounds in complex mixtures. With this method we are able to measure a great number of structural parameters like the paraffinic or naphthenic character, aromatic hydrocarbons and methyl group content. It also gives information about functional features of different petroleum constituents, the nature of polymethylene chains and the nature of polynuclear aromatic systems. In addition, it is partly responsible for the aging determination of oils related to the oxidation of carboxylic acids (Gautam et al., 1998). There are many advantages in this method, but the main one is that it offers the possibility to analyze the hydrogen bonding in the crude oil mixture. IR spectroscopy is considered to be more of a qualitative technique, rather than a quantitative one. Even though IR spectroscopy is more widely used in the study of middle distillates, there are some applications of IR in the analysis of heavy crude oil fractions (Fig.11). An example

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of an IR application is the study of spilled oils (derivatives from crude), but only in the definition of the chemical classes to which their components belong, since a more specific determination is not an easy task, especially in heavy products. That is the reason why IR spectroscopy should be combined with other spectroscopic techniques, to counteract these limitations (Aske et al., 2002).
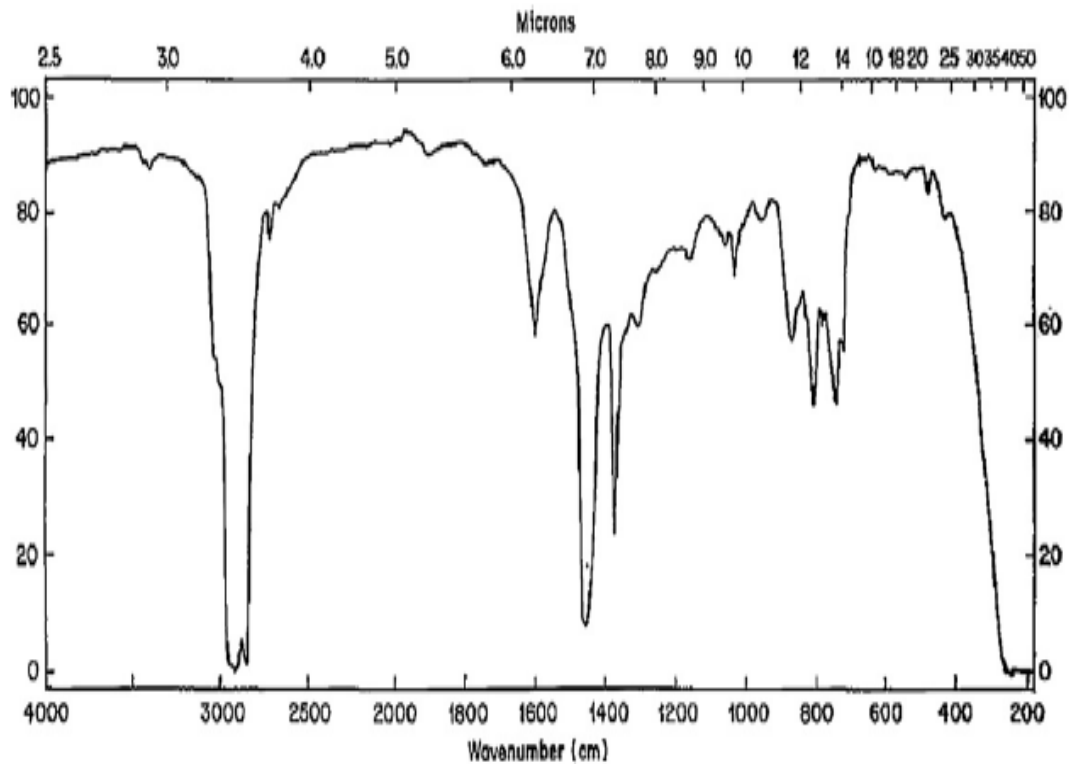

Fig. 11. Example of an IR spectrum of a heavy fuel oil (Silva et al., 2011).

1.4.6 Raman spectroscopy

The technique of Raman spectroscopy is used to observe the vibrations of the molecules bonds and to quantify the needed energy to change the ground state of a chemical compound. The Raman effect occurs whenever there is a change in the polarization of the compound, and it can actually give more thorough information than infrared spectroscopy (Papadogiannis, Samanidou, 2001). The results of these techniques are quite similar and are usually combined to achieve a more clear view of the analysis of the petroleum samples. There are applications of Raman spectroscopy in the determination of aromatic and olefinic compounds in complex hydrocarbon mixtures. The advantages in this kind of analysis are that there is no need for sample preparation and that it is quicker, if compared with other similar techniques. Nonetheless, it is not the best choice for crude oil characterization, because of the weak signal obtained in the Raman spectrum. Besides, the natural fluorescence of some hydrocarbon components may be another limitation, since it leads to problems in the identification of the signals when the components are irradiated by visible lasers (Simanzhenkov, 2003). These

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methods give a more detailed analysis when applied to light elements, like gasoline (Fig. 12), gas oil, jet, kerosene and diesel, or in combination with Fourier transform. Applications of FT-Raman spectroscopy were useful in the determination of the octane number (RON), the motor octane number (MON), the pump octane number (pump) and the Reid vapour pressure (RVP) (Cooper et al., 1995).
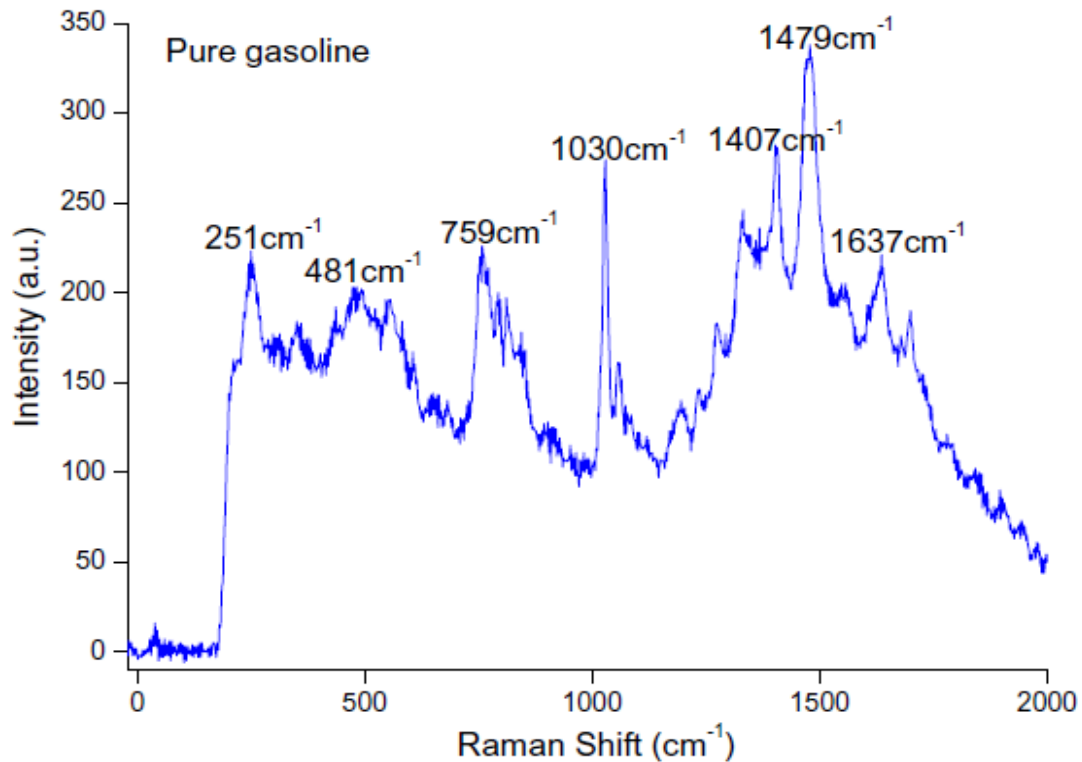

Fig. 12. Raman spectrum of pure gasoline (Qing Ye et al., 2009).

1.4.7 Mass spectrometry (MS)

MS gives information about the structure of the compounds by assigning their molecular formula based on the molecular weight. Various MS ionization methods are used, like the electron impact (EI), chemical ionization (CI), field ionization (FI), fast atom bombardment (FAB) and others. An important technique is EI-MS, which is characterized by the existent of a set of electrons with high energy that will contact with the molecules of compounds and will cause their fragmentation (Kenkel, 1994). Typically, each compound has a characteristic fragmentation of the molecule that provides a specific signal. For example, in alkyl chains the most evident fragments are the ones caused by the loss of CH_3, C_2H_5 or C_2H_4. Fragments with four carbon atoms are an example of the most common ions of paraffins. Yet, there are fragments with C_2, C_3 or C_5. Monoalkylbenzenes are identified by the characteristic fragment of C_6H_5. Similar examples of typical fragments related to monoalkylnaphthenes, monoalkylphenanthrene, monocyclic alkanes or other molecules, are found in the literature (Altgelt, 1994). Due to the complexity of the heavy petroleum fractions and the variety of

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compounds, it is obvious that there are many fragmentation patterns that are impossible to distinguish. As a result, EI-MS is not frequently used in the heavy petroleum analysis. The most frequently used MS techniques in the analysis of heavy crude oil is NF-MS (non-fragmenting MS), which is also called "soft ionization". These techniques create a simpler spectra, if compared with the resulting spectra from the fragmentation (Skoog, 1998). A good example would be the difficult identification of aliphatic hydrocarbons, because their fragmentation does not follow any given pattern. Another disadvantage is that compounds that appear to have the same chemical formula, such as sulfur and nitrogen compounds, are very hard to analyze. On the contrary, compounds like the aromatics have a good behavior in the spectra and are not hard to identify, especially with techniques like "soft ionization". When the boiling point of the sample increases, the identification with MS techniques is even more difficult, on account of the increase in the number of types of different compounds and the high number of produced fragments. In brief, aromatic hydrocarbons, sulfur or nitrogen compounds are complex compounds to be analyzed by the MS method. To receive more accurate information about all the heavy crude oil fractions it is important to use MS conjugated with other techniques. MS is very often used in combination with chromatographic techniques, like GC or HPLC, in order to obtain better information about the sample to be analyzed and to use the advantages of both techniques. In Fig. 13, a broadband mass spectrum (a) of a crude oil sample is given, which was zoomed (b, c) in order to be able to observe several hydrocarbons in the mixture. $C_{31}N_{40}N_1$ is the most numerous of the bunch, but the sample also contains $C_{30}H_{52}N_1$, $C_{28}H_{44}N_1S_1$ and $C_{29}H_{32}N_1S_1$, among others.
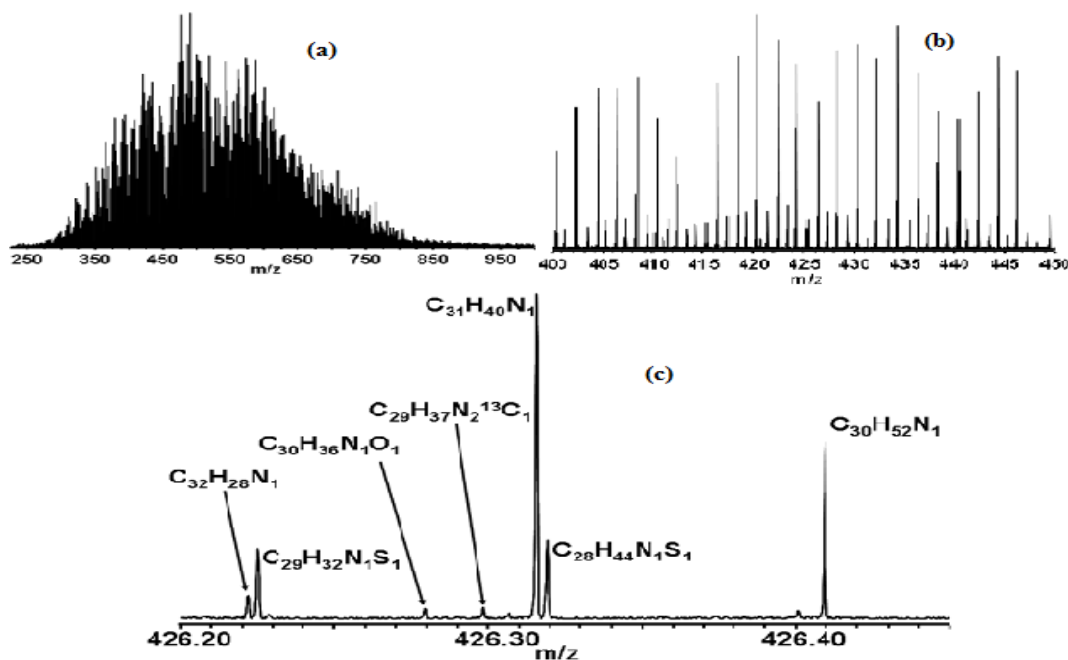
Fig. 13. (a)broadband mass spectrum of a crude oil sample, (b) enlarged region of the mass spectrum of the same sample, (c) enlarged region of the mass spectrum of the same crude oil sample, identifying individual hydrocarbons (observed from: nationalmaglab.org).

1.4.8 Nuclear magnetic resonance spectroscopy (NMR)

NMR spectroscopy is lately one of the most important techniques in the study of heavy petroleum fractions. It has many advantages, like the short time of analysis, as it provides an analysis in only a few minutes per stream, and that it can be performed in a continuous and online way. Another advantage is that it can analyze dark and opaque samples, like the crude oil. NMR is a rapid and non-invasive process that offers great analysis of the chemical nature of individual types of hydrogen and carbon atoms, in complex petroleum samples and in the products obtained from the refining processes (Gautam et al., 1998), combined with the ability of analyzing groups, like aliphatic, aromatic and other. Nonetheless, there are disadvantages in NMR spectroscopy, like the high cost, the risk of magnetic disturbances and the overlap of frequency ranges. The overlap is the reason why the analysis of the spectra is quite painful. Then again, there have been made efforts to improve NMR with the use of some techniques like DEPT, GASPE, COSY, etc. Moreover, there is a need for a statistical approach of the information given by NMR to correlate the spectral data with the characterization of crude oil. NMR has been suggested as one of the most powerful methods for industrial analysis. It has been widely used in the analysis of carbon and hydrogen content in the middle distillates, but the first time it was used in the analysis of heavy oil fractions was in 1959 (Sau et al., 2005). Since then, NMR spectroscopy has been repeatedly and successfully applied in the characterization and identification of heavy crude oil fractions. In the long run, it contributes to obtain information about the structural characteristics, to estimate the molecular weight and to analyze the effects in some refining processes. In figures 14 & 15, typical ^{13}C NMR and ^{1}H NMR spectra for Saturates, Aromatics, Resins, Asphaltenes (SARA) fractions are given.
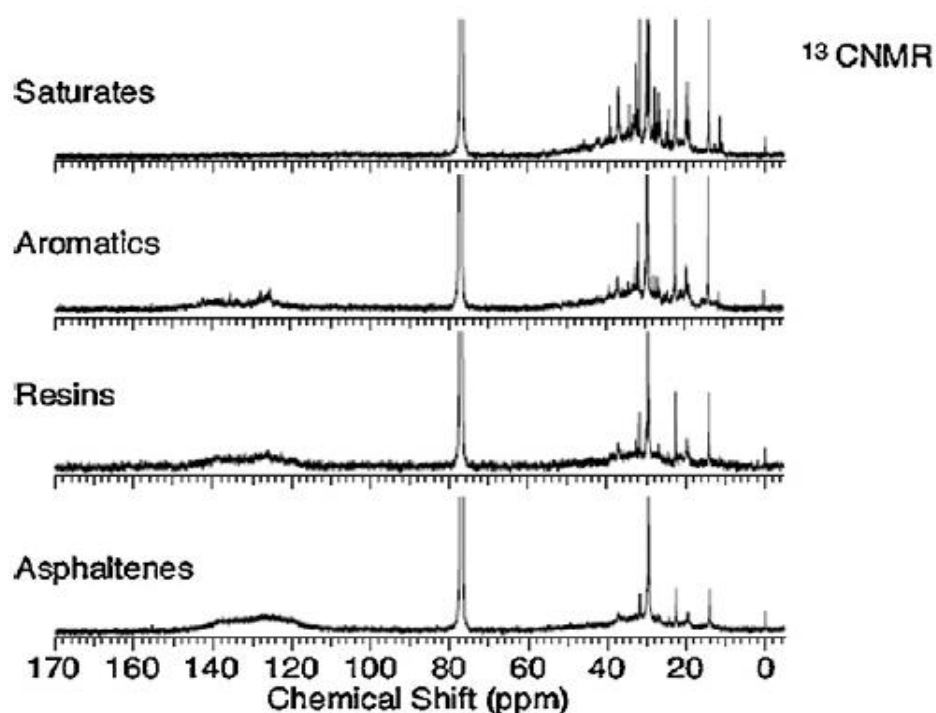

Fig. 14. Typical ^{13}C NMR spectra for SARA fractions, obtained in a Varian Unity Inova 400MHZ spectrometer with a 5 mm 4 nucleus probe (S.L. Silva et al., 2011).
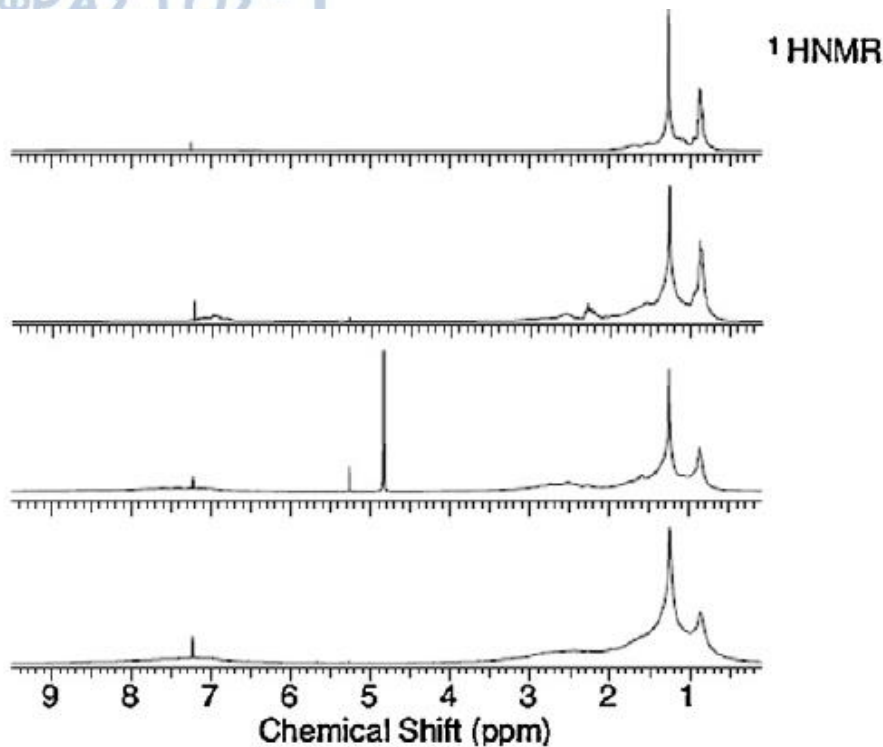
Fig. 15. Typical ¹H NMR spectra for SARA fractions, obtained in a Varian Unity Inova 400MHZ spectrometer with a 5 mm 4 nucleus probe (S.L. Silva et al., 2011).

On the whole, both chromatographic and spectroscopic techniques provide valuable information for the under investigation compounds, yet in most cases their combination achieves better analysis results and maximizes the obtained data. The usually followed path of analysis is using a chromatographic technique as a primary separation method and then choose a spectroscopic technique like NMR to obtain more specific information about the structure or the molecular weight of the analysed compounds. Considering the above, these techniques can be applied for the analysis of the compounds with hetero-atoms after suitable preparation of the samples. The applied analytical techniques are described in Part 2.

PART 2:

Speciation of Nitrogen and Oxygen containing compounds in heavy distillates

2.1 Determination of N- and O- containing compounds

As mentioned in part I, nitrogen species are undesirable in fossil fuels and in their processed products, due to the problems they cause to human health, the environment (formation of NOx) and the refining processes.

The negative implications they have on the refining of heavy cuts is of paramount importance (Sau et al., 2005). Neutral N-compounds are actually considered as refractories to hydroconversion reactions. At the same time, basic ones show an inhibitive behavior towards the hydrotreatment step (Chishti, 1999; Jimenez et al., 2007), especially in hydrodesulfurization reactions. In addition, they poison the acidic catalysts sites during hydroconversion processes (Sau et al., 2005). Not to mention, the presence of basic nitrogen-containing compounds increases the catalyst deactivation by coking. As a matter of fact, a detailed characterization of nitrogen species in heavy petroleum cuts is necessary in order to better understand the reactions implemented during these processes.

From the viewpoint of monitoring the quality of raw materials and products in the petrochemical industry, there is a need to develop analytical methods for the identification and quantification of these species even if they are present in trace quantities. These new analytical methods must focus not only on the quality of the results but also on practical aspects targeting the reduction of sample preparation time and complexity. Currently, complex procedures and time consuming protocols are used to enable the determination of nitrogen compounds, including separating the neutral from the basic fraction of analytes (da Cunha et al., 2016). However, in practice, procedures are hard to replicate and lead to inconsistent results.

In the case of oxygen-containing compounds, like phenols, acids, furans or ketones, their presence in petroleum streams is not found to be poisonous to processing catalysts. The main compounds of this category that are being identified and quantified are acids and phenols.

The characterization of acidic compounds in petroleum is usually undertaken to explain physical or technical properties of the crude, like corrosion (Turnbull et al., 1998), emulsion stability (Ese, 2004), or wettability change of solid surfaces by adsorption (Standnes, 2003; Borgund, 2009). The most used measure of the acid content in crude oil samples is non-aqueous titration which gives a Total Acid Number (TAN) (Annual Book of ASTM Standards, 1989). Yet, this value does not provide any information about the composition of the acids found in the samples, and does not correlate well with the degree of corrosion caused by oils of different acidities (Tomczyck et al., 2001). With this in mind, there is a need for more detailed analysis that will provide more information that could be possibly correlated with the physical effects of the acids. The total acid content of most crudes is generally low, but may reach as much as 3%, as in some California crudes.

Phenols are generally known to have a major impact on the technical properties of petrochemicals, especially on lubricity, storability and "gum" formation (sticky polymers that can clog pipelines and pumps). Chloro- and nitrophenols are also important targets in many environmental studies (Wasinski, Andersson, 2007). Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds and are of no commercial value.

Heavy crude oil fractions have a heavier molecular composition. That "heaviness" is caused by the high concentrations of mainly two types of compounds: asphaltenes and resins (Fig. 16). They are typically compounds with a highly polar terminal group that frequently contains an oxygen, sulfur or nitrogen, as well as of a long chain with alkyl groups. Due to their complexity, it is impossible to characterize them without a good pre-fractionation step, like liquid–liquid extraction, solvent extraction or preparative liquid chromatography (prep-LC). Lately, prep-LC has been the most used technique, because of its many advantages. There are plenty of separation and identification schemes using activated neutral oxide aluminum or modified silica to separate into neutral and basic nitrogen compounds (Conceição Oliveira et al., 2004).
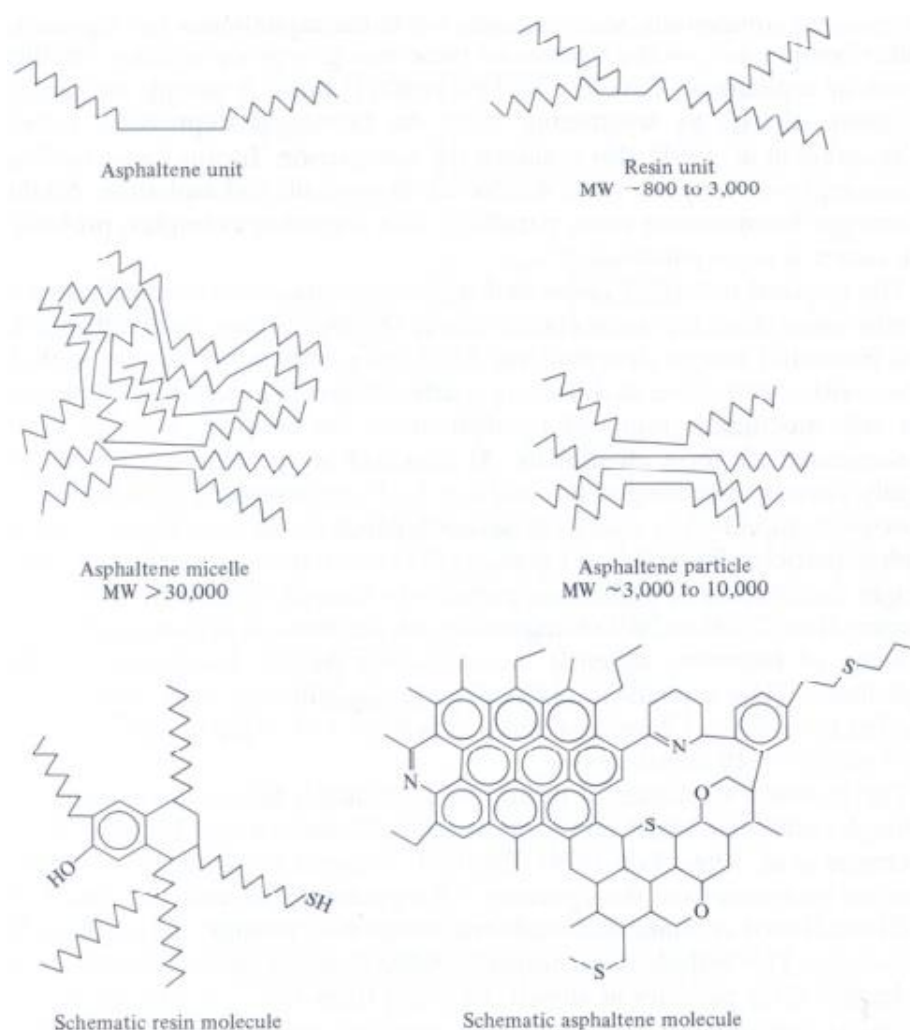
Fig. 16. Schematic of resin and asphaltene molecules (Hunt, 1995).

Applications of different techniques used lately for the determination of N- and O-containing compounds will be presented and discussed in the following paragraphs. Summaries of the conditions and sample preparations in each technique for the nitrogen species are given in Table 2.

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Table 2. Techniques used for the determination of N- containing compounds and sample preparation methods.

Analysis technique	Sample Preparation method	Compounds analysed	Column	Chromatographic technique - Conditions	Compounds identified	Literature
Comprehensive GCxGC–MS	Dilution in 74 mg/ml CH_2Cl_2 before analysis.	Indoles, Carbazoles, Anilines, Quinolines, Morpholine, Tributylamine	Primary column (boiling point separation): HP-1MS (25m, I.D. 0.2 mm, 0.33μ) Secondary column (polarity separation): DB-1701 (1.6m, I.D. 0.1mm, 0.10μ)	Primary column: 50 °C to 280 °C → 3.0 °C/min 280 °C to 300 °C→ 1.0 °C/min Final isotherm at 300 °C of 10 min Secondary column: +8 °C	Carbazole	C. Flego, C. Zannoni, 2011
High temperature comprehensive GCxGC/NCD	Ion exchange chromatography to separate basic nitrogen compounds from the neutral ones: • Resin Amberlyst A15 in glass column • Hydrocarbons, neutral species: methanol. • Basic species: dichloromethane/ammonium, methanol/ammonium Dilution of neutral and basic fractions in toluene.	Basic fraction: Acridines Neutral fraction: Carbazoles	Primary column: DB5-HT 30m x 0.32mm x 0.1μm Secondary column: BPX-50 1.5m x 0.1mm x 0.1μm	Oven temperature: 90-360 °C →2°C/min	Carbazole, Tetrahydrocarbazole, Benzocarbazole, Dibenzocarbazole	T. Dutriez et al., 2011

HPLC system with ultraviolet (UV) + refractive index (RI) detectors.	Samples treated with large amounts of n-pentane to remove asphaltene fraction. Solids removed with ultra-centrifugation and resin fraction analysed.	Total Nitrogen content	20mm x 250 mm NH_2 column with hexane as mobile phase	Flow rate of 5 mL/min. After 25 min, methyltertbutylether as second solvent. UV → 240-400 nm	Pyrrole, Pyridine	J. Woods et al., 2008
GCxGC coupled to time-of-flight mass spectrometry detector	Samples diluted 40-fold with dichloromethane	Indoles, Carbazoles, Quinolines, Anilines	Primary column: IL59 (ionic liquid GC column) Secondary column: DB-5MS (5% diphenyl-95% dimethylpolysiloxane)	Initial oven 50°C → 3°C/min Secondary oven +35°C to primary	Indole, Carbazole, Quinoline, Aniline and other.	F. Cappelli Fontanive et al., 2016
Reverse-phase HPLC with fluorescence detector	Dilution in isooctane. Dilution in detergentless microemulsion (DME): 1% of sample in DME - 0,1% of sample in DME	Carbazoles, Quinolines, Indoles, Acridines, Anilines	Column: 4.6 x 250 mm Eclipse Plus C18 with 5μm particle size. Mobile phase: water and alcohol mixture.	Column at 15°C Better detection at 220nm.	Carbazole, 3-ethylcarbazole, 9-methylcarbazole, 9-ethylcarbazole, Quinoline, Benzoquinoline, Indole, Acridine, 3-methylindole, N,N-dimethylaniline	A.L.M.C. da Cunha et al., 2016

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Combined GC-MS/AED	SPE method to separate into basic and non-basic fractions: • 200μl of sample syringed on top of the SPE cartridge holding 3g of attapulgus clay • 1st solvent: n-pentane (20ml) (hydrocarbons elute) • 2nd solvent: DCM (40ml) • 3rd solvent: 95:5 THF/water mixture • 4th solvent: Acetone (40ml)	Carbazoles, Pyrroles, Anilines, Quinolines, Indoles, Acridines	Identical columns on both instruments → RESTEK 10,526 , 60.0m x 250.00μm x 0.25μm	GC-AED: Initial flow: 2.2ml/min Cavity temperatures set at 350°C GC-MS: Flow: 40.7 ml/min	36 alkylcarbazoles	Y. Briker et al., 2003

As it can be seen from Table 2, GCxGC is the most common technique used for the determination of nitrogen species. The preparation of the crude oil sample is in most cases a simple dilution in a solvent, or a separation into basic and neutral fractions (through methods like SPE or ion exchange chromatography).

The identification of the N-species is based on the different polarities of the compounds. For example, in the GCxGC plot, the non-aromatic nitrogen compounds (tributylamine, morpholine, N-methylmorpholine) elute in the general area of paraffinic species, tributylamine is a little more polar than linear alkanes (<500 ms), while morpholine elutes near the cyclic alkanes (500-1500 ms). Increasing the polarity, quinoline and aniline elute in the 4000-5000 ms range and indole and carbazole elute in the upper limit of the 2D plot. The quantification of these compounds is usually achieved with the help of different mathematical formulas and the calibration parameters. The elution map of the N-species in a GCxGC plot is given in Fig. 17 and an example of a GCxGC plot is shown in Fig. 18. Also, the chemical structures of the most often identified nitrogen species in the crude oil are shown in Fig. 19.
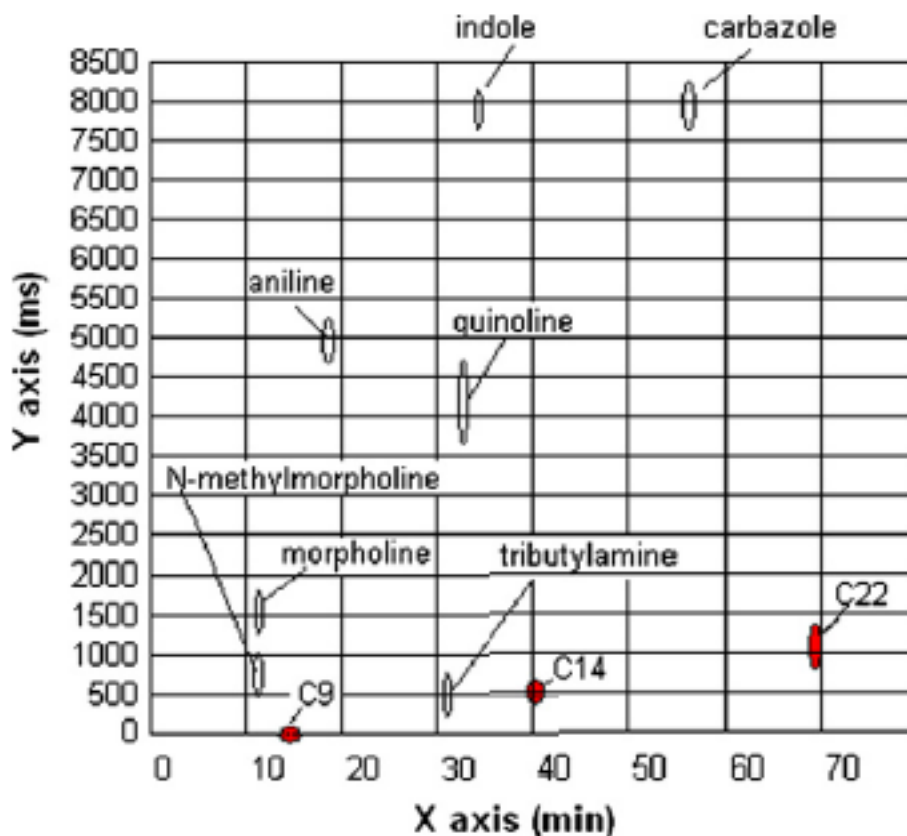

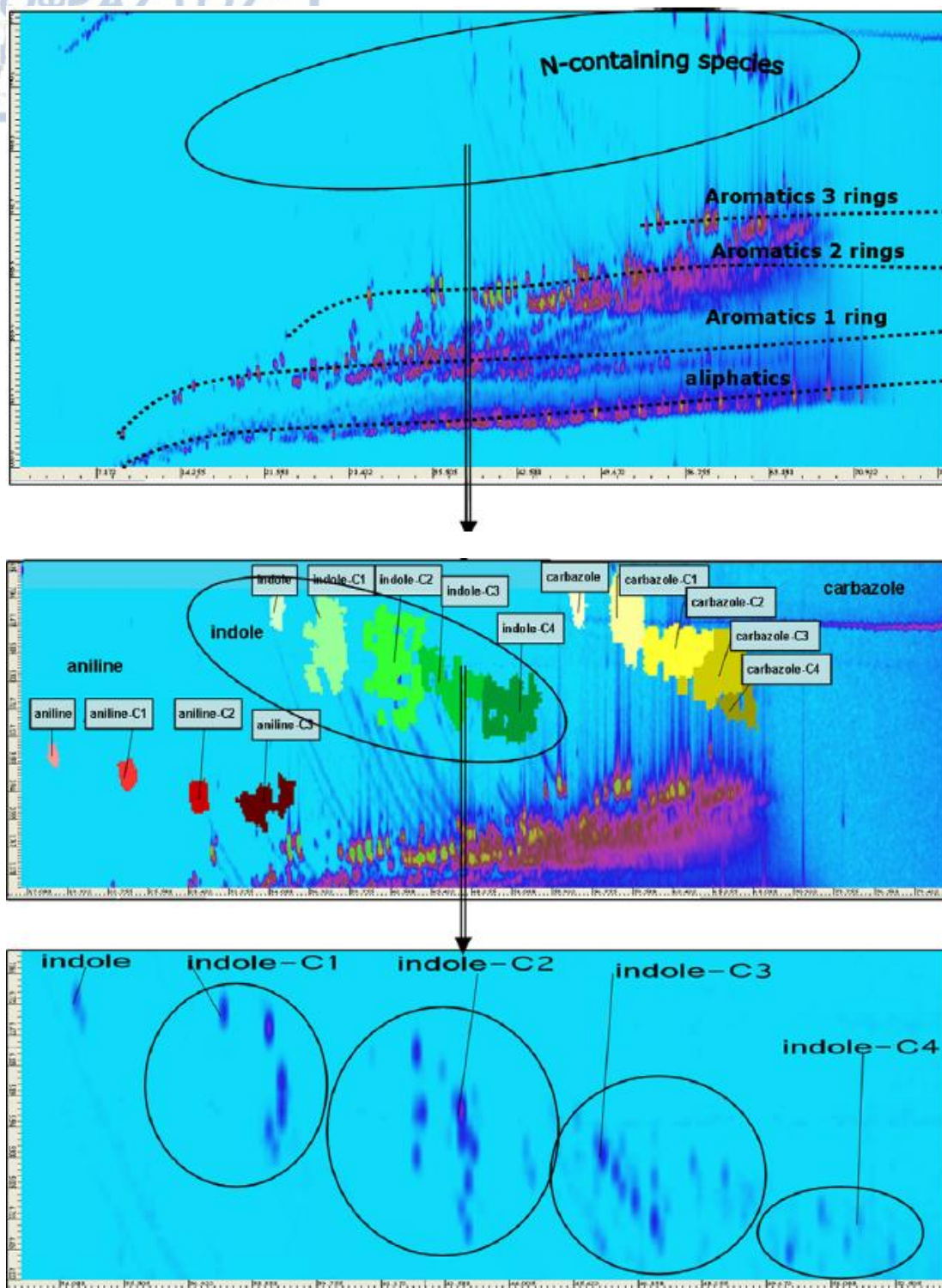**Fig. 17. Elution map of N-containing compounds in a GC x GC plot.**

Fig. 18. Example of a GCxGC plot: general map (top), details of the N-species area (middle) and distribution of indole family into derivatives with aliphatic substitutes at C_x atoms.

Tributylamine   **Morpholine**   **Quinoline**

Aniline   **Indole**   **Carbazole**
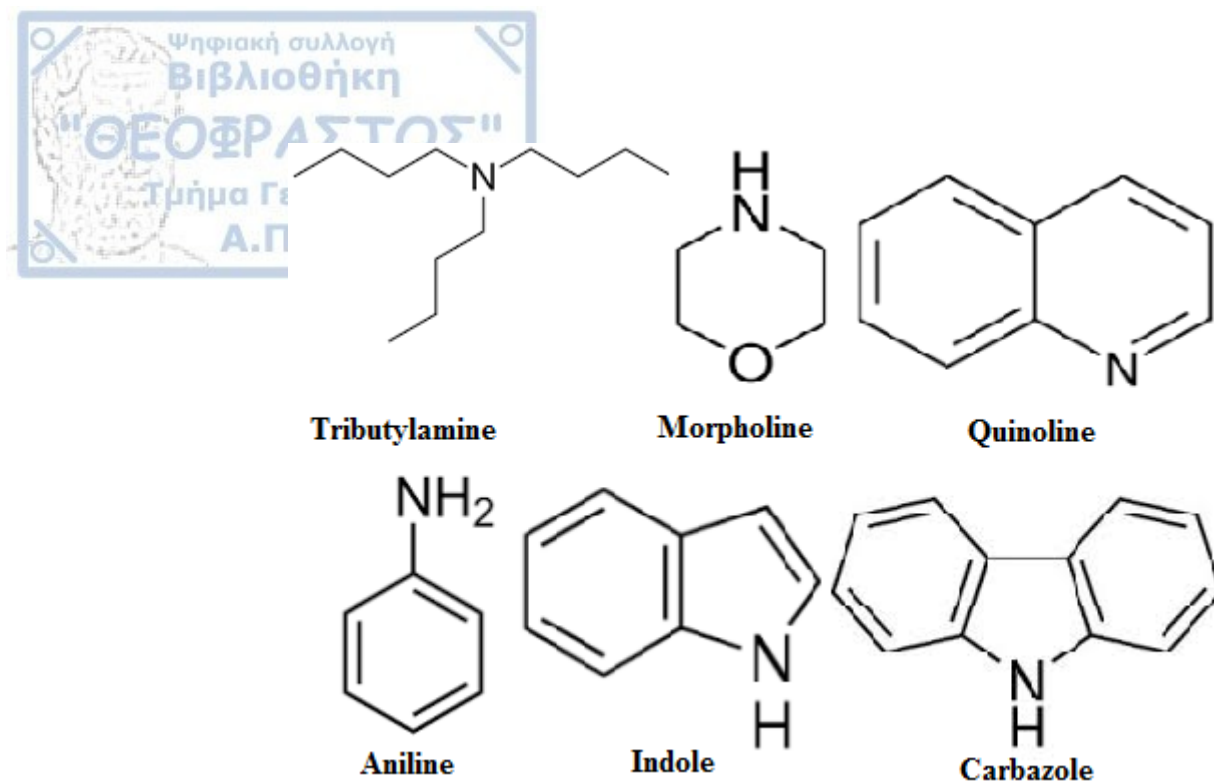
Fig. 19. Chemical structures of the most common nitrogen species in crude oil.

Some quantitative results are given in Tables 3 and 4. In the first case, in the heavier sample (B), 653 wt.ppm of carbazole-like species were identified. In the second case, 601 ppm of nitrogen were found in the neutral fraction of the N-species (VGO supplied by IFP Energies Nouvelles Lyon).

Table 3. N content in sample A (365ºC- cut) and sample B (365ºC+ cut) (C. Flego and C. Zannoni. 2011).

N content (wt. ppm) in sample A and in sample B.

	Indole-like species (wt. ppm)	Aniline-like species (wt. ppm)	Carbazole-like species (wt. ppm)	Total amount N (wt. ppm)
Sample A	215	47	753	1015
Sample B	–	–	653	653

Table 4. Group type quantification of N-compounds in a heavy VGO by HT-2D-GC-NCD combined with a previous ion-exchange chromatography (T. Dutriez et al., 2011).

Family	SR VGO		
	In neutral fraction (% N)	In basic fraction (% N)	Total (ppm N)
Neutrals			601
Carbazole	42.6		256.1
Tetrahydrocarbazole	3.7		22.0
Benzocarbazole	49.6		298.4
Dibenzocarbazole	4.1		24.5
Basics			235
Acridine		n.d.	–
Tetrahydroacridine		n.d.	–
Benzoacridine		n.d.	–
Dibenzoacridine		n.d.	–

n.d.: not determined.

The quantification of N-compounds in petroleum materials is therefore quite challenging and some recent papers have approached the subject for a selective speciation. Although this approach is a great improvement due to the sole determination of the total N amount or the discrimination between total and basic N, yet it does not give reason of the potential interference from the petroleum matrix. In addition, the use of one selective detector needs a preliminary and not exhaustive activity of assignment of the peaks on the basis on retention times of specific standard solutions or with the help of complementary analyses in the presence of mass spectrometer detector.

Another suitable technique is the HPLC that also seem to give satisfactory results. The sample preparation is also a simple dilution, which means that the procedure is not time consuming. The separation and distribution of the nitrogen compounds in the HPLC chromatogram is based as well on the polarity of the compounds. Even though HPLC is a technique that usually provides separation, identification and also quantification of each component in a mixture, it seems that in the case of high complexity mixtures like the heavy distillates, there is a need for supplementary techniques to achieve quantitative analysis.

Moreover, it must be mentioned that the spectroscopic techniques described in Part 1, are usually used in terms of verification of the results obtained from the chromatographic techniques. In general, the spectroscopic techniques are used to achieve a more detailed characterization and collect more information about the chemical structures of the analysed compounds.

As for the determination of oxygen-containing compounds, there is a paucity of literature even in the case of the middle distillates. Consequently, only one successful application was found for the identification of oxygen species in the heavy distillates. In addition, an interesting method for the fractionation of the crude oil acids into four fractions was obtained from the literature. This method is simple and rapid and can be used as a sample preparation for further analysis of the acidic compounds (oxygen-containing species). Both techniques are presented in Table 5 and Table 6, and will be discussed in the next paragraphs.

Table 5. Determination of oxygen species through Ligand Exchange Chromatography.

Main chromatographic technique	Steps (Columns/ Conditions)	Sample preparation	Compounds identified	Literature
Ligand exchange chromatography (LEC)	1. Isolation of the fraction of aromatic compounds through a modified SARA fractionation using liquid chromatography on alumina 2. LEC on a palladium-bonded stationary phase to obtain different structural isomers (1.2mL/min flow rate, 254nm) 3. Methyl iodide derivatization (30mg of each sample treated with an excess of methyl iodide and silver tetrafluoroborate in 1,2-dichloroethane for 48hr) 4. Characterization by positive ESI FT-MS (2μL/min ,spray voltage 4.5kV)	(no preparation)	Dibenzofuran Phenol Naphthol	S.K. Panda et al., 2010

The identification of the O-compounds is achieved due to the different polarities they have. This technique can only identify the oxygen compounds and is not able to provide quantitative results. In that case, there is a need for a supplementary technique that will allow the quantification of these compounds.

Table 6. Fractionation of crude oil acids into four fractions with HPLC.

Main chromatographic technique	Columns/ Conditions	Sample preparation	Fractions obtained	Literature
Normal phase HPLC	Cyano columns and guard columns Light scattering detector ELSD and UV detector Flow rate: 2ml/min	Ion exchange method for acid extraction. Dissolution in dichloromethane : methanol, 93:7 (v/v)	1. Non-polar compounds 2. Carboxylic acids 3. Phenolic compounds 4. Polyfunctional compounds	A.E. Borgund et al., 2007

In this technique, an ion exchange method is used as an acid extraction procedure. Then the obtained acid extract is analysed with HPLC and separated into four fractions: the non-polar compounds, the carboxylic compounds, the phenolic compounds and the polyfunctional compounds. The simplification of the acid composition enables the more detailed chromatographic analysis by supplementary techniques, like GC-MS, GCxGC etc. The chemical structures of the most often identified oxygen species in the crude oil are shown in Fig. 20.
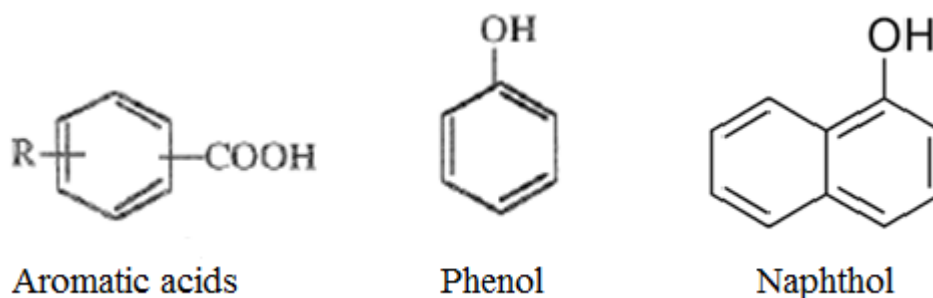
Fig. 20. Chemical structures of the most common oxygen species in crude oil.

Conclusion

This dissertation thesis aimed to provide a wide presentation of crude oil and its chemistry, the importance of composition analysis and the quality control of petroleum fractions with emphasis to the heavy distillates, which are not easy to analyze due to the complexity and variation of compounds that need to be identified. There was an attempt to summarize the most important chromatographic and spectroscopic techniques used in heavy crude oil analysis, such as Thin-Layer Chromatography (TLC), High Performance Liquid Chromatography (HPLC), Gas Chromatography (GC), Infrared spectroscopy (IR), Raman, NMR and Mass Spectroscopy (MS). In addition, different applications of each described analytical method were given, along with examples of chromatograms and spectrums for each case.

Moreover, after an extended study of a considerable amount of literature, a number of research studies based on the speciation of nitrogen and oxygen-containing compounds in heavy distillates were chosen to be presented in detail. The analysis and characterization of heavy distillates is in general a great challenge for the petroleum industry, even more when there is a need for determination of specific compounds like N- and O-compounds in such complex samples. There were a few successful endeavors of determining different nitrogen and oxygen compounds in heavy distillates and most of them used a combination of methods to achieve better separation and analysis results. The most famous methods among them were GC x GC and HPLC, sometimes used in combination with a spectroscopic technique like MS. Generally speaking, the analysis of nitrogen and oxygen species is yet quite limited in heavy samples and there is a need in developing new methods that would not only achieve the determination and quantification of these compounds, but would also be simple and rapid for the industry requirements. It can be expected that future studies will consolidate the earlier researches described in this dissertation and will be directed towards their improvement or the development of new more efficient, detailed and reliable methods for the determination of these specific species in complex samples, such as the heavy distillates.

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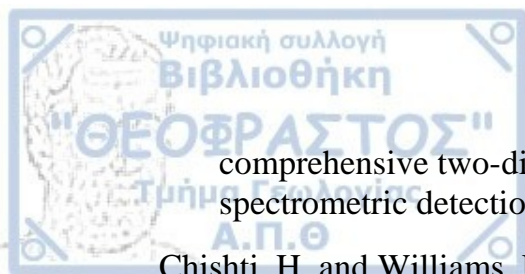
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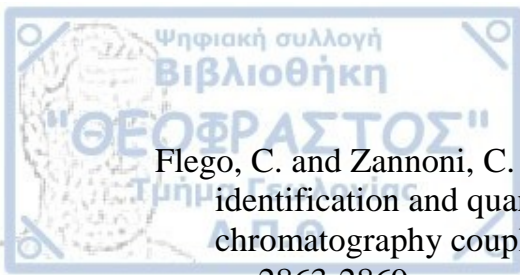
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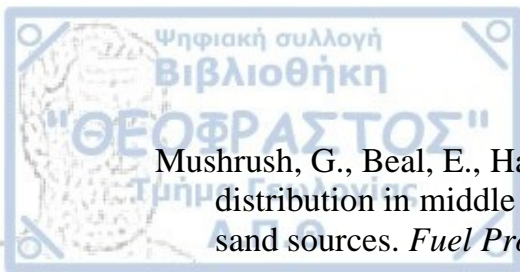
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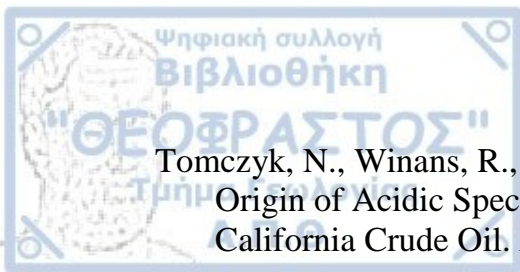
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