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The Use of Aromatic Biomarkers in the Geochemical Characterization of Oil Application to Prinos Basin Oils

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Thesis

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Chapter 1

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I seem to have been only
like a boy playing on the
seashore, and diverting
my
finding a smoother pebble
or a prettier shell than
ordinary, whil
ocean of truth lay all
undiscovered before me.

J

Chapter 2

Abbreviations

- N = Naphthalene
- MN = Methylnaphthlene
- EN = Ethylnaphthalene
- DMN = Dimethylnaphthalene
- TMN = Trimethylnapthalene
- TeMN = Tetramethylnaphthalene
- DBT= Dibenzothiophene
- P = Phenanthrene
- An = Anthracene
- BF = Benzofurans
- Flu = Fluorene
- Fla = Fluoranthanes
- Pyr = Pyrene
- Chry = Chrysene
- B[b]Fla = Benzo[b]Fluoranthane
- B[ejk]Fla =Benzo[e,j,k]fluoranthrane
- B[k]Fla = Benzo[k]fluoranthrane
- B[e]Pyr = Benzo[e]pyrene
- B[a]Pyr = Benzo[a]pyrene
- Pery = Perylene
- MPery = Methylperylene
- Ipyr = Indeno[1,2,3-cd]pyrene
- DB[a,h]An = Dibenz[a,h]anthracene
- B[g,h,i]Pery = Benzo[ghi]Perylene
- B[a]An = Benzo[a]anthracene
- TAR = Terigenous to Aquatic Ratio
- CPI = Carbon Preference Index
- OEP = Odd to Even Predominance

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Chapter 3

Abstract

This study focuses on the geochemical evaluation of oils based on the composition of the aromatic fraction. A method was developed using Gas Chromatography - Mass Spectrometry (GC-MS), for the qualitative and quantitative determination of the aromatic compounds. The method was applied on a set of ten samples from five different wells (K1, PN2, SK4, PB, and E1) of the Prinos basin (Greece). The analysis was carried out using the GC-MS analyzer GC: 7890A, MS: 5975C from Agilent Technologies. The aromatic compounds were identified based on their MS spectrum using Qualitative Analysis B.07.00 and quantified with MS Quantitative Analysis B.07.00 software packages. A series of 70 compounds were identified and evaluated as biomarkers, including naphthalenes, cadalene, dibenzothiophenes, phenanthrenes, anthracenes, pyrenes, perylene, fluoranthrenes, florenes, chrysenes and their alkylated versions. The findings of the aromatic biomarkers analysis certify the already existing geochemical information related to Prinos basin, and substantiate that the oils are nonbiodegradated and immature. They were formed in shale and carbonate source rock formations, with more terrestrial and less marine contribution of organic material, in a saline-hypersaline environment. In addition the polyaromatic hydrocarbons are found to be mostly combustion-derived and less from natural biological precursors.

Chapter 4

Introduction to Oil Generation and Biomarkers

4.1 Biogenic Formation of Oil

PETROLEUM consists of thousands of components, the majority of which are saturated hydrocarbons ,cycloalkanes/napthenes , aromatics, and asphaltenes. The main sources of these hydrocarbons are biomass compounds from bacteria, phytoplankton, zooplankton, terrestrial higher plants, and angiosperms. Many investigations have been published, proving that the compound sources of the hydrocarbons are mainly proteins, lignin, lipids and carbohydrates. Solar energy stored inside molecules with photochemical procedures like photosynthesis is eventually preserved inside the chemical bonds of hydrocarbon molecules.

With the proper chemical and biochemical reactions, lipids, proteins and lignin, in the state of diagenesis, can be transformed into geopolymers – forming kerogen. The procedure of converting kerogen into other lighter hydrocarbon molecules in the state of catagenesis, due to changes of temperature conditions is called maturation. The molecular forces of kerogen compounds break due to pyrolysis phenomena, resulting in lighter compounds. Maturation is a significant procedure studied in oil exploration and petroleum engineering because it provides crucial information about oil generation process and possible oil reserves.

In chemical fossils, also known as biomarkers, are chemical compounds that can be found inside oil mass or in source rock extracts. They appear to have a significant resemblance to relative biomolecules, which proves the biological nature of the petroleum. Biomarker molecules are usually characterized by chemical stability, which is the reason why geoscientists can still find these molecules; otherwise these compounds would biodegrade during the catagenesis and diagenesis processes, resulting

in lighter hydrocarbons. Most of the biomarkers are not identical with their relative biomolecules, as there are some small differences in their chemical composition, isomerization, or both. This difference, for instance, can be either the addition or the removal of methyl groups, or the changes in stereo-isomerization of the molecules.

Factors that cause these reactions are changes in temperature, depth, and the effect of the nature and chemistry of the environment in which the organic matter is accumulated. Temperature is the main factor responsible for the breakdown or dislocation of the chemical bonds between carbon atoms. In addition, the chemical conditions of the environment with its acidic parameters or the type of organic material accumulated in the basin, play a decisive role for the formation, of the oil and determine values of the ratios between the different compounds, as well as the isomers of petroleum and its biomarkers.

Biomarkers disclose the history of the oil that is generated and can give information about the source rock. They mainly provide information about the level of biodegradation of the oil, the precursor organic matter that was used to form the kerogen, the state of thermal maturation of kerogen, and the conditions and type of the basin in which the organic matter was accumulated.

Almost all of the different compound groups of biomarkers have been studied for years including normal and branched alkanes, terpenoids (such as steranes and diasteranes), hopanes, and aromatic/polyaromatic hydrocarbons. The last category will be discussed further later on in this study. Application of geochemical analysis procedures for qualitative and quantitative analysis of polyaromatic hydrocarbons will be used for the geochemical evaluation of the Prinos basin.

4.2 Kerogen

Kerogen is a solid organic matter found in sedimentary rocks. There are different types of kerogens that occur in nature, and the best method to classify kerogens in petroleum geoscience is to create the graphical plot developed by *Dirk Willem van Krevelen (1950).*[1] Plotting the dimensionless parameters of the Hydrogen Index (HI) and Oxygen Index (OI) data from kerogens onto the Van-Krevelen diagram, one can observe the classification of the different potentials of the kerogen in order to produce oil. Also, the Van-Krevelen diagram can define the path and the state of maturation process of a kerogen, while the HI and OI are being reduced. There are four types of kerogen; Tissot describes the first three types.

Kerogen also respects the Arrhenius law, in that the maturation process leads to the production of more thermally stable components, exactly like the Arrhenius exponential equation. The most important variable of this procedure is temperature. The effect of temperature according to the Arrhenius law has an inverse exponential

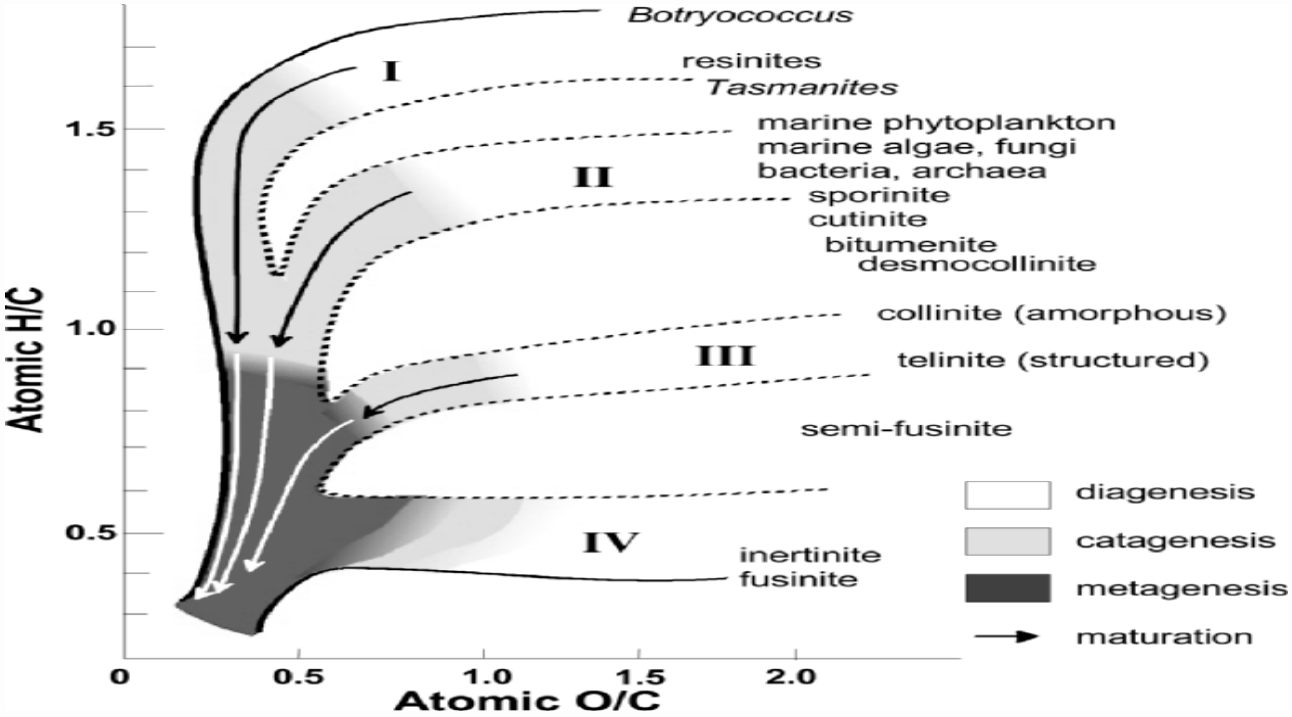


Figure 4.1: Van Krevelen diagram [1]

power of Euler's constant (e).

Temperature is the most significant parameter for maturation of oil in sediments. With the continuous increase of sediment depth, the temperature conditions of the organic matter trapped inside the rock matrix increases. In studding kerogen byproducts, one can extrapolate information about the precursor molecules, organic matter, thermal stress, biodegradation level and temperature.

4.2.1 Type I

Sapropelic Kerogens

High concentrations of the HI ratio are usually over 1.5 with a relative low initial OI ratio of less than 0.1. This type of kerogen is related to lipid precursors that predominantly have many aliphatic chains and a few aromatic rings. The aliphatic hydrocarbon chains have a HI almost equal 2, while the aromatic rings have a HI of less than 1. Since the values of the hydrogen are relatively high, this kerogen appears to have a very high oil and gas generation potential, with relatively larger amounts of volatile compounds than the other types of kerogen.

4.2.2 Type II

Planktonic or Sulfurous Kerogens

This type of kerogen is typically derived from lipids of very specific algae (i.e. Botryococcus or Tasmanites), or generally from lipid-rich microorganisms. Type II kerogens are characterized by marine organic material, usually found in reducing environments with a high relative quantity of sulfur. The HI of planktonic or sulfurous kerogens is usually less than 1.5, with an OI between 0.03-0.18. This type of kerogen is associated with oil and gas prone reservoirs. Some examples of type II kerogens are sporinite, cutinite, resinite, and liptinite, each classified according to the precursor organic material of which they are formed.

4.2.3 Type III

Humic Kerogens

This type of kerogen is characterized by a relatively low HI of less than 1, and a high OI index between 0.2-0.3. It is principally produced by coastal organic material (such as terrestrial plants) containing lignin and cellulose. Type III kerogens have a low potential of producing oil, since the H/C ratio values are small. However, oil reserves born of this type of kerogen can be economically attractive, since large quantities of methane can be produced.

4.3 Vitrinite

Vitrinite is one type of macerals, mainly found in coals and in source rocks. Vitrinite is a shiny mineral formed by components from the wooden part of higher plants like cellulose and lignin.

Vitrinite's concentration in rock samples has been studied thoroughly because of its reflectance property is a reliable thermal maturation parameter in characterizing the degree of heating in sedimentary rocks *Burrus,J.(1985)*[41] Vitrinite reflectance is a measure of the percentage of incident light reflected from the surface of vitrinite particles in a sedimentary rock (%Ro). Vitrinite reflectance is a very difficult parameter to evaluate since many parameters need to be studied simultaneously – such as oxidation conditions, type of kerogen, and oil-gas zones. Vitrinite's data are usually examined with a histogram of multiple measurements, but most of the time it is difficult to

determine a specific value with high confidence.

The reason that the reflectance of vitrinite is mentioned is because many researchers have tried to correlate some polyaromatic hydrocarbon distributions and relative quantities between the components, using vitrinite reflectance index, in order to find out parameters and ratios between the components that reflect the maturation conditions of the oil.

4.4 Normal Alkanes as Biomarkers

Normal alkanes are linear hydrocarbon chains with a chemical formula of C_nH_{2n+2}. Every carbon atom shares a sp3 hybrid bond (sigma bond) with another carbon atom. Cyclic alkanes are called naphthenes, and in petroleum chemistry, alkanes are usually correspond to the majority of the total compounds in the oil mass.

Branched alkanes have the same molecular formula with n-alkanes, but they also have additional methyl-, ethyl-, and other alkyl groups as branches in the skeleton of the compound.

The study of normal alkanes/saturates in petroleum as biomarkers was one of the first studies ever conducted, because these compounds are easily separated and extracted from the rest oil mass with a relatively high efficiency and quantity. On the other hand, these compounds appear to present a challenge for oil evaluation, because of the fact that these compounds have a very simple chemical form. Thus, there are dozens of different ways for nature to produce them.

In geochemical studies, alkanes play a significant role when very specific mathematical methods are applied. Many studies have shown that oil with a relatively larger value of C25-C35 H/Cs come from terrestrial organic matter such as higher plants, due to the fact that waxes and heavy H/C chains are used by plants for mechanical stability and protection from other organisms. H/Cs with a majority of <C25 compounds mainly come from aquatic plants and organisms and provide them with their own physical characteristics.

From the gas chromatography analysis, it is apparent that some oils have a preference in odd or even numbered carbons in their hydrocarbon chains. Biosynthesis of the molecules produced by bacteria appears to have a normal distribution for odd and even numbered carbons in the molecule structures, while the herbal material from plants tends to favor odd numbered hydrocarbons. The ratio ODD (H/C)/EVEN (H/C) is used to compare these figures.

The Terrigenous/Aquatic Ratio (TAR) gives information about the nature and

type of the precursor organic matter.

$$TAR = \frac{nC_{27} + nC_{29} + nC_{31}}{nC_{15} + nC_{17} + nC_{19}}.$$

. *Bourbonniere,R.A. and Meyers,P.A.(1996)* [44]

The nC17/nC29 Index is a ratio that is also used for the evaluation of the type of organic material, and for characterizing an oil as paraffinic or waxy – similar to the CPI index and OEP (Odd to Even Predominance). The CPI and OEP can be used to measure the level of maturation of oil and the biodegradation of organic matter.

$$CPI_{C_{24}-C_{34}} = \Big[\frac{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}{nC_{24} + nC_{26} + nC_{28} + nC_{30} + nC_{32}} + \frac{nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}}{nC_{26} + nC_{28} + nC_{30} + nC_{32} + nC_{34}}\Big] \times \frac{1}{2}$$

Bray,E.E. and Evans, E.D. (1961) [45]

$$OEP = \Big[\frac{C_i + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}}\Big]^{(-1)^{i+1}}$$

Scalan, R.S.and Smith, J.E. (1970)[46]

4.5 Isoprene, Isoprenoids and Terpenoids

Isoprene, known as 2-methyl-1,3-butadiene is an organic compound that can be created in all organisms. In plants, a special procedure called the Non-mevalonate pathway (MEP) that occurs in the chloroplasts of plant cells can produce isoprene in significant quantities.

The shape and the chemistry of the isoprene molecule makes this small – 5 carbon molecule chemically and thermally stable and can thus survive the conditions that take place during the catagenesis and diagenesis of kerogen. Isoprene is perhaps the most significant substance in petroleum geochemistry because it can very easily polymerize into other larger molecules, producing terpenoids (i.e. terpenes, diterpanes, triterpanes, etc.).

The ratios and consistency of these terpenoids provide a significant amount of information regarding the geochemical characteristics of the depositional environment of the organic matter, and the chemical conditions, such as whether or not it is a reducing or oxic environment. Geochemists can reveal these conditions by identifying certain compounds. For example, in chlorophyll, hydrolysis separates the phytol molecule from the porphyrin molecule. Phytol in a reductive environment transforms to phytane (C20), but in an oxidizing environment a (COOH) group is released and

pristane (C19) is produced. Geochemists can identify these compounds and so evaluate the conditions of the environment.

Cyclic triterpenoids such as hopanes and steranes also have a huge impact on the evaluation of petroleum geochemistry. They provide information about the precursor organic matter, the level of biodegradation and maturation of the oil, and the depositional environment of basins. Studies of triterpenoids are related to their isomerization, stereochemistry, and chemistry.

4.5.1 Cyclic Terpenoids - Hopanes

In geochemistry, pentacyclic compounds (triterpanes) are known as hopanes. These compounds include between (27-35) carbon numbers in their molecules and are formed by four exacyclic and one pentacyclic ring, followed by a hydrocarbon chain. Most abundant compounds are C29-C30 hopanes. Hopanes were one of the first categories of biomarkers used for the evaluation of the depositional environment, and the maturation of the oil and oil-source correlations.

4.5.2 Cyclic Terpenoids - Steranes

Steranes are compounds that can be created during the reduction of sterols. These biomarkers are constructed by three exacyclic and one pentacyclic ring, followed by a variety of hydrocarbon chains. Sterols are associated with eukaryotic and prokaryotic organisms, and are used mainly as constructive material of cell membranes, due to their mechanical properties and stability. The different organisms that are responsible for the creation of sterols are produced as precursors, such as cholesterol, sitosterol, sigmasterol, and ergosterol. The chemical study of steranes as biomarkers, together with stereochemistry can, like in hopanes, provide a great deal of information.

4.6 Geochemical Evaluation of Oils Using Saturated Biomarkers

Saturated hydrocarbons have been used as biomarkers to describe the conditions of the depositional environment, the kind of the organic matter and other processes like biodegradation. The presence of these molecules and their distribution in the oil mass originate from specific biological precursors. These hydrocarbon molecules show a great similarity with their relative organic molecules, and any possible distortion of the organic precursor molecules is due to specific geochemical conditions.

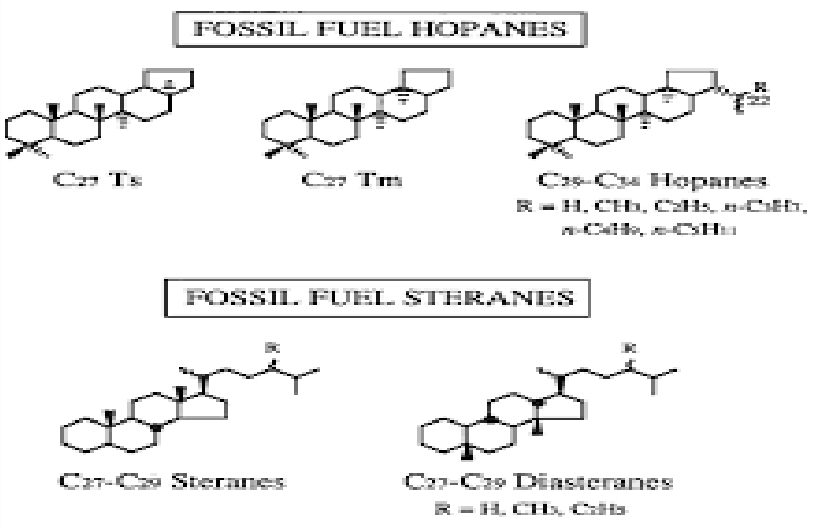


Figure 4.2: Hopane and Sterane [56]
Picture from [Fossil fuel biomarkers in plant waxes as pollution parameters Carine Bryselbout, Pascale Henner, Eric Lichtfouse (1998)]

This section will briefly describe some of the most important geochemical indices for organic precursors, environmental conditions, and maturation using saturated biomarkers.

4.6.1 Steranes / 17a-Hopanes

Steranes can be observed with the chromatographic ion m/z = 217, while hopanes can be identified at m/z = 191. The C27, C28, C29 ααα(20S+20R) and αββ(20S+20R) steranes are used for this index. Similarly, only hopanes C29-C33 including S+R structures for C31-C33 are used. This ratio is calculated using absolute concentrations. If this ratio is higher than 1, organisms such as planktons and seaweeds are major contributors; but if the ratio is low, terrestrial organic matter dominates. *Moldowan,J. M., Seifert, W. K. and Gallegos, E. J. (1985)*[42]

4.6.2 Distribution of C27-C28-C29 Steranes and Diasteranes

C27-C28-C29 of the steranes and diasteranes distributions, can predict the precursor organic matter. Diasteranes are used in highly biodegraded oil. These compounds are calculated from the m/z=217 ion chromatogram. These data are plotted in a ternary diagram with C27, C28 C29 at each axis. The area inside the triangle is separated into sections, each of which corresponds to a specific origin of organic matter - marine, lacustrine, and terrestrial. *K.E. Peters, J.M. (1986)*[43]

4.6.3 Distribution and C35-Index of Homohopanes

Bacteriohopanotetrol is the precursor organic component of homohopanes. Like hopanes, homohopanes can be observed with m/z=191 ion. Homohopanes are sensitive to oxidizing and reducing environments, and so are used to identify environmental conditions and thermal maturation. The C35-Index is calculated as $C35/(C31 - C35)$, including 22S and 22R structures of the molecules in high values indicate anoxic conditions. *Ourisson, G. and Nakatani, Y. (1994)*[47]

4.6.4 C29-Nor-Hopane / C30-Hopane

Anoxic conditions of carbonates are identified with a $C29 - Nor - hopane/C30 - Hopane$ index greater than 1. Norhopane is more thermally stable than hopane, which means that this ratio increases during the thermal maturation process. *Seifert, W. K. (1973)*[48]

4.6.5 Oleane Index

The oleane index is calculated as the ratio of oleane over the C30-Hopane. This index provides information about the precursor organic matter and the age of geological structures. The main source of oleane is most likely angiosperms which were the first flowers on Earth. A high value of this oleane index ratio indicates that terrestrial organic matter is the main contributor to basin area. *Ekweozor, C. M. and Telnaes, N. (1990)*[49]

4.6.6 Gammacerane

Since salinity of the environment can affect the chemistry of the final product, it is important to determine the level of salinity. One method of determining salinity level is by using the gammacerane index, which is the ratio of gammacerane over the C30-Hopane. Gammacerane is an organic molecule produced by Tetrahymanol. Gammacerane is abundant in marine sediments, and its presence is an indicator of hypersaline environments *Ten Haven,H. L., Rohmer, M.,Rullk otter, J. and Bisseret, P. (1989)*[2]. Gammacerane can identify depositional environment and oxic conditions – lower quantities of gammacerane could suggest shallow water environments or more oxic conditions*L. Mattavelli L. Novelli;(1987)* [3].

4.6.7 Index of Homohopane's Isomers

During maturation the temperature endured by organic matter increases. This forces the molecules to form more stable isomers. In the case of homohopanes the 22R structure transforms to 22R and 22S and they can be analyzed by m/z=191 ion chromatogram. The value of the homohopanes Index is $22S/(22S + 22R)$ and can vary between 0 and 0.6. *Ensminger, A., Albrecht, P. and Oursson, G. (1972)* [50]

4.6.8 Moretane / Hopane Index

The 17β,21α(H)-Moretanes are less stable in temperature changes, compare to 17α,21β(H)-Hopanes. The ratio, can be calculated from the m/z=191 ion of the saturated extract of the oil. The values can be between less than 0.15 for mature source rock extracts up to 0.8 to the immature rocks. The relative value for oil in particular is less than 0.05. *Seifert, W. K. (1973)* [48]

4.6.9 Ts/(Ts+Tm) Index

A significant index for the identification and evaluation of thermal conditions that occur during catagenesis can be used quite effectively for the correlation of different oils or oil-sources, is Ts/(Ts+Tm) Index. The 17α(H),22,29,30-trisnorhopane (Ts) molecule is chemically less stable during catagenesis than the 18α(H) 22,29,30-trisnorhopane (Tm). *Seifert, W. K. (1973)*[48]

4.6.10 20S/(20S+20R) and ββ/(ββ+αα) of Sterane isomers

Isomerization of the 5α,14α,17α–steranes takes place during thermal maturation. The R form of steranes changes to S, and the values are approximately 0.5 at equilibrium conditions. These steranes can also be found in the m/z=217.

The ααα(R&S) form of Steranes converts to αββ(R&S) during thermal maturation. Using m/z=217 and C29 14β(H),17β(H) & C29 14α(H),17α(H) Steranes, the ratio (ββ/αα+ββ) can vary up to 0.7 at equilibrium. This ratio increases during thermal maturation, similar to 20S/(20S+20R) . *Seifert, W. K. (1973)*[48]

4.6.11 Diasteranes Over Normal Steranes Index

Diasteranes are a group of isomers of steranes formed during diagenesis. Thermal maturation is the contributing factor for the conversion of the normal-steranes into diasteranes, but environmental conditions and lithology can significantly affect this process. *Rubinstein, I. and Albrecht, P. (1975)* [51]

Chapter 5

Aromatic Biomarkers in Oils

5.1 Introduction to Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments (Origin)

THIS thesis focuses on the identification and quantification of aromatic polyaromatic hydrocarbons in oil that can be used as biomarkers.

Polyaromatic hydrocarbons can often be found in ancient sediments. They are complicated molecules with a relatively high molecular weight. They include aromatic and naphthenic rings, other hydrocarbon chains, other elements like sulfur, oxygen, nitrogen and many alkyl- groups as well as their isomers. Thus the total number of different aromatic molecules that can be found in petroleum is extremely high.

The chemical stability of these compounds is relatively higher than the other hydrocarbons because of the strong aromatic bonds between the carbons of the molecules. The lipophilic characterization of these compounds has shown the tendency of these molecules to rest on sediments rather in the aquatic phase. Bertilsson, S. Widenfalk, A. Hydrobiologia (2002) [37] According to *Chunqing Jiang., et al (1998)* [4], PAHs can be classified into two main categories: combustion-derived or Pyrolytic PAHs and PAHs born from natural biological precursors.

5.2 Combustion-Derived PAHs

Combustion derived PAHs produce pyrogenic substances which are actually created by the incomplete reaction of plants and fossil fuels with oxygen (in ancient fires produced by volcanism or lighting). Alkyl derivatives of these PAHs are usually in low ratios

because the extreme temperature conditions that this organic matter had suffered. The chemical procedure of this phenomenon includes not only combustion but also pyrolysis, cracking, and destructive distillation. *Saber et al. (2006)* [5]. Combustion-derived PAHs are significant in this study, because in the Prinos area, fires and volcanic activity played an important role, as can be assumed from the appearance of volcanic rocks at Rhodope mountains. This volcanic activity is related with tensile forces and with the basin formations of the Upper Eocene-Oligocene from 37-27 Ma *P. Kiomourtzi et. al.(2016)*[6]

Combustion-derived PAHs include Fluoranthrane (Flu), Pyrene (Pyr),benzo-[a]anthracene (BaAn), benzo[b]fluoranthene (B[b]Fla), benzo[k]fluoranthene (B[k]Fla), benzo[e]pyrene (B[e]Pyr), benzo[a]pyrene (B[a]Pyr), benzo[ghi]perylene (B[ghi]Pery), and coronene (Cor). These aromatic hydrocarbons are typically in higher concentrations than their alkylated counterparts especially in younger rock formations. Phenanthrene (P) in particular can also occur in recent sediments due to combustion or diagenetic processes *Wakeham et al., (1980b)* [7] .

All of the above Polyaromatic hydrocarbons can be found in sediments in a variety of different distributions, depending on the age of the formation, the organic matter, and the chemical conditions of the area of deposition. The Cretaceous–Paleogene (K–T) boundary delineates the end of the Cretaceous age and the beginning of the Cenozoic era (66 Ma). *Venkatesan and Dahl (1989)*[8] performed a study that showed that the distribution of the PAHs and unsubstituted PAHs inside and outside of the K-T boundary is different. The PAHs are prominent inside the K-T boundary (during the period of huge 'wild fires'). Above and below the boundary, PAHs such as phenanthrene, anthracene, pyrene and fluoranthene appear in reduced concentrations. This investigation revealed the tendency of the PAHs to be produced during strong fire events throughout the history of Earth.

Other investigations, such as *Killops and Massoud (1992)* [9] , (which studied the upper Jurassic formations), showed that the substituted and un-substituted PAHs distributions can provide information about vegetation fires if high concentrations of perylene components exist.

The Pyrogenic Index, (PI) can be used to differentiate Pyrogenic vs Petrogenic PAHs *Wang et al., (1999)* [10] . The five alkylated PAHs are : C1-C4 Naphthalene, Dibenzothiophene, Phenanthrene, Fluorene, and Chrysene. According to *Wang et al., (2008)* [11], the Pyrogenic Index is very effective at separating Pyrogenic Petrogenic-PAHs but without taking into account the effects of biodegradation and weathering. This is due to the fact that this ratio uses many different PAHs and thus, possible uncertainties can be small and unproblematic.

$$PI = \frac{\sum(3-6ring-PAHs)}{\sum(5-Alkylated-PAHs)}$$

5.3 PAHs From Natural Biological Precursors

During the Cretaceous Period, 160 million years ago, the first flowering plants appeared on Earth. During the Devonian Period, 320 million years ago, these plants evolved to produce wood matter- and PAHs. PAHs, from natural biological precursors according to *Chuqing Jiang (1998)* [4] can be sub-divided into three main groups.

1) Cadalene: Gymnosperms also known as Acrogymnospermae, are a group of seed-producing plants, and they are the main higher plant precursors of cadalene/4-Isopropyl-1,6-dimethylnaphthalene. This compound is derived from generic sesquiterpenes (a class of terpenes that consist of three isoprene units), and is abundant in conifer trees such as cedars, firs, hemlocks, larches, pines, and spruces.

2) Retene, or 1-methyl-7-isopropyl phenanthrene, can be found mainly in coals and indicates the presence of resinous plants. Retene has a high boiling point, which makes this compound relatively stable during catagenesis and diagenesis. Retene is derived from the degradation of specific diterpenoids, which are biologically produced mainly by conifer trees.

3) Simonellite (known as 1,1-dimethyl-1,2,3,4-tetrahydro-7-isopropyl phenanthrene) has very similar properties to retene, and is derived from diterpanes and produced by conifer trees. According to *Ramdahl, (1983)* [12], Retene and Simonelite, are produced during low-temperature combustion phenomena of coniferous plants with decarboxylation, aromatization and rearranging chemical procedures *Grimalt et al., (1988)*[13].

Perylene is a polycyclic aromatic hydrocarbon with the chemical formula C20H12 and is usually found in marine sediments. Perylene is produced by its precursors during diagenesis, and is actually formed after deposition. Perylene is also a compound that thermally unstable, as its concentration increase along with the increasing depth. The precursor molecule of Perylene is likely perylenequinone which is a compound derived mainly from plants. Quantities of perylene greater than trace amounts indicate the chemical state of depositional environment (i.e. acidic vs. reducing). Perylene is better conserved in reducingt environments *Chuqing Jiang (1998)*[4].

5.4 Compound Classes

As previously discussed, organic matter that originated from higher plants and other microorganisms under varying geological conditions can be transported and accumulated into geological formations that have a low gravitational potential energy-such as basins. Some of the basins that play an important role in the formation of petroleum are Lacustrine, Marine and Terrestrial.

These environments have the ability to preserve and transform the organic matter various ways due to differences in oxidation levels, biological effects, pH levels, rate of sedimentation, lithology, geology, temperature and pressure. The type of precursors of organic matter is one of the major factors that a Petroleum geoscientist needs to take into consideration for geochemical interpretations.

Variations in the distributions and ratios among Naphthalenes (N) Phenylnaphthalenes (PN), Fluoranthanes (Fla), Dibenzobiphenyls (DBF) and Naphthobenzothiophenes (NBT), can actually be used to classify the different oils and study the parameters about their origin, organic matter, and depositional environment. *Fan Pu et al., (1990)*[14] .

Petroleum consists of thousands of different components, each of which can have similar or completely different chemical characteristics. Therefore it is important, to divide the components into groups or even sub-groups, in order to better visualize the chemistry of the black gold.

The next few sections will describe and analyze the main groups of aromatic-polyaromatic hydrocarbons, and discuss the geochemical significance of these compounds in oil exploration.

5.4.1 Naphthalenes

Methylnaphthalenes have a large variety of different isomers. A molecule of Naphthalene can have up to six boned methyl-groups. The different distributions of the methylated groups are a function of the varying chemical conditions of the depositional environment, the organic matter as a precursor, the catagenesis – diagenesis effects, and the thermal stress. *Bastow et al,., (1998)* [15] . The source of these methylated Naphthalenes, according to studies done by *Puttman and Villar et . al (1987)* [16] , are commonly hydrocarbons derived from land plants and microbial life.

Other studies by these researchers indicated sesquiterpanes and triterpanes have an association with the production of alkylnaphthalenes *Mark Obermajer et al (2002)* [17] .

The chemical procedures that take place for the transformation of methylnaphthalenes are mainly transalkylation and disproportionation, according to *Radke et al., (1982a); Alexander et al., (1985); Strachan et al., (1988)*[35]. Later on *Bastow, et al., (1999)* [18] also referred methylation and demethylation processes via electrophilic substitution.

5.4.1.1 Naphthalene

Naphthalene (N) is the first component that detected by the FID and can be observed in the m/z=128 scan. In this study, Naphthalene travels rapidly inside the column and is not always observed, because it is detected before the time of data collection begins. Naphthalene and 1-Fluoronaphthalene – which is used as Internal Standard (IS) and is a compound used to quantify Methyl-Naphthalenes – have very close retention times, so that they usually appear as one peak.

5.4.1.2 Methylnaphthalenes

Methylnaphthalenes (MN) consist of two aromatic rings and one methyl group with the chemical formula $C_{10}H_8$ and a molecular weight of 142. The main components are 1-MN and 2-MN, which can be identified in the m/z =142 ion of GC-MS data. These are the second and third compounds that are identified by the FID.

Naphthalenes have a relatively low molecular weight compared other PAHs, which makes Methyl-Naphthalenes more soluble in water. Studies have shown that Methyl- Naphthalenes have higher biodegradation rates than those of other groups. Adding Methyl components with a low molecular weight, increases their chemical stability and reduces the rate of biodegradation.

One parameter that is used to determine the biodegradation level is the ratio of Methylnaphthalenes to Naphthalene. If this ratio is closer to 0, then the biodegradation level is high on the other hand, if this ratio is closer to 1, the biodegradation level is low *Zhendi and Carl, (2008)* [19]. The methylnaphthalene ratio MNR=2-MN/1-MN is also a useful indicator of maturation level. *Radke et al., (1982b)* [20]. The value of 2-MN is much higher in relation to 1-MN in extended maturation (>0.9 Rm).

5.4.1.3 Ethylnaphthalenes

Ethylnaphtaneles (ENs) can be identified in the chromatographic spectrum of m/z=156. The two main ethylnaphthalenes studied in this section are 1-EN and 2-EN. Like Methylnaphthalenes, the ratio ENR = 2-EN/1-EN is used as an indicator for thermal maturation.

5.4.1.4 Dimethylnaphthalenes

Six peaks of nine different dimethylnaphthalenes (DMNs) are observed in oil samples, since some components elude simultaneously from the column so that they appear

to have the same retention times. The components are 2,6-2,7 DMN, 1,3-1,7 DMN, 1,6 DMN, 1,4-2,3 DMN, 1,5 DMN and finally 1,2 DMN. The compound 1,8-DMN is absent from these samples.

The value of the Extracted Ion Chromatogram (EIC) which is m/z=156, is required to identify these compounds.

A study of 1,8-DMN done by *Robert Alexander; (1984)* [21] was related to the maturation of oil associated with the abundance of 1,8-DMN in the sediments. Their results showed that the relative amount of 1,8-DMN is depended to the degree of burial of the sediments and temperature. The negative algorithm value of (1,8-DMN/total DMNs) has been used to assess samples associated with high-maturity condensate zones. *Robert Alexander et al (1984)* [21], plotted the depth in y axes and -log(1,8-DMN/total DMNs) in x axes and where able to separate the different maturation zones from Immature to mature gas zones. Further studies done by the same researchers showed that 1,8-DMN cannot provide any information about the source of organic matter.

Dimethylnaphthalenes in general are effective when they are used as maturation indicators. In addition, studies showed that DMNs are proportional to the maturation of an oil, especially when mean Vitrinite reflectance Ro>0.9% *Radke et al., (1982b); (1984)* [22] .

A paper that was published in 1994 by *M.Radke , et al (1994)* [23] showed, using PCA analysis with DMNs concentrations that 1,6 DMN is the main DMN component and is related to the original source kerogen. Also 1,6 DMN is the main precursor of the other DMNs that are produced by a first order reaction due to thermal effects. 1,6 DMN is relatively higher in terrestrial than in marine organic matter.

The precursor of 1,6 DMN is believed to indicate the presence of degraded resins from Araucariaceae conifer remains in source rocks from the Jurassic-Lower Cretaceous (146 Ma to 100Ma) *K.E.Peters,C.C.Walters,J.M. Moldowan, (2007)* [24]. Also studies showed that and 1,6-DMN is increasing with depth in post-Triassic (50.6 Ma) sediments. *Alexander et al. (1994)* [25]

- DNR-1 = (2,6-DMN + 2,7-DMN)/1,5-DMN *Radke et al. (1982b)*
- DNR-2 = 2,7-DMN/1,8-DMN *Alexander et al. (1985)*
- DNR-3 = 2,6-DMN/1,8-DMN *Alexander et al. (1985)*
- DNR-4 = 1,7-DMN/1,8-DMN *Alexander et al. (1985)*
- DNR-5 = 1,6-DMN/1,8-DMN *Alexander et al. (1985)*

- 1,8-DMN = 1,8-DMN/total DMNs *Alexander et al. (1984)*

5.4.1.5 Trimethylnaphthalenes

Trimethylnaphthalenes (TMNs) are chemical components with a main naphthenic group and additional three methyl groups. The molecular ion that makes TMNs observable in a chromatogram is the m/z=170. This thesis focuses on eleven isomers of TMNs that can be observed in ten different peaks.

These isomers are: 1,3,7-TMN, 1,3,6-TMN, 1,4,61,3,5-TMN, 2,3,6-TMN, 1,2,7-TMN, 1,6,7-TMN, 1,2,6-TMN, 1,2,4-TMN, 1,2,5-TMN and 1,4,5-TMN.

TMNs -especially 1,2,6-TMN are indicators of the presence of angiosperms. *K.E.Peters,C.C.Walters,J.M. Moldowan,(2007)*[24]. Torbanite is a shale formation that is usually found in the Permian Age (298-251 Ma), and may contain coal matter. Torbanites usually include chemical substances named drimanes, which are bicyclic sesquiterpenes. With δ13C experiments *Grice et al. (2001)* [26] suggested that 125-TMN and drimanes have a common cyanobacterial hopanoid precursor. Generally, trimethylated Naphthalenes have a higher tendency to form in terrestrial environments. Triterpenoids -more specifically, the Olean-type according to *Chaffee and Johns, (1983); Chaffee et al., (1984)* [27] , can produce 1,2,5 and 1,2,7-TMNs. 1,2,5-TMN together with 1,2,7-TMN, can provide information regarding the presence of angiosperm precursor organic matter. A study done by *Strachen et al. (1988)* [28], discovered that the concentration of 127-TMN was much higher in younger formations than in old formations. With experiments that use the relative concentrations of 127-TMN and 137-TMN, it is possible to identify terrigenous plant input, higher plant material, and marine source oils.

The ratios that can be used are

- TDE-1 = 1,2,5-TMN/1,2,4-TMN • TDE-2 = 1,2,7-TMN/1,2,6-TMN

If the ratio of 125-TMN/137-TMN is low it is not possible to make conclusions about the precursors, because other unknown factors appear to interact with the concentrations of these TMNs. *Strachen et al. (1988)* [28] Also proposed that other TMNs can be rearranged into more stable chemical compounds and be transformed to 125 127-TMN. TMNs are significant components used to find information about maturation in a high thermal maturity range.

- TNR-1 = 2,3,6-TMN/(1,4,6-TMN + 1,3,5-TMN) *Alexander et al., (1985)*:

- TNR-2 =[1,3,7-TMN]+[2,3,6-TMN] / [1,3,5-TMN]+[1,3,6-TMN]+[1,4,6-TMN]

Rcb(%)=0.4-0.6 *Radke et al., (1986)*

• TNR-2 increases with maturity with simultaneous reduce of [1,3,5 + 1,4,6-TMN] parameter.

• TNRs= [1,3,7-TMN]+[2,3,6-TMN]/[1,3,6-TMN]

• The range of TNR-2 is [1,3,5-TMN]+[1,4,6-TMN]/[1,3,6-TMN] >= 0.6 *cf. WEISS,(1985)*

When 125-TMN and 137-TMN are present in an oil sample, a reliable method to measure the maturation effect on the sample is to find the inclination between the peaks of these two components. This ratio is called TMNr = [1,3,7-TMN]/[1,2,5-TMN + 1,3,7-TMN]. Low maturity oils have a value of less than one, medium maturity oils have a value of one, and high maturated oils have value greater than one. *Ben G.K. van Aarssen.,et al (1999)* [15]

5.4.1.6 Tetramethylnaphthalenes

TeMNs are Naphthalenes with three additional methyl groups. They can be observed when m/z=184. In the present paper, seven peaks of TeMNs are identified, including eight components in total.

These Tetramethylnaphthalenes are: 1,2,4,7-TeMN, 1,2,5,7-TeMN, 2,3,6,7-TeMN, 1,2,6,7-TeMN, 1,2,3,7-TeMN, 1,2,3,6-TeMN, 1,2,5,6-1,2,3,5-TeMN

Tetramethylnaphthalenes (TeMNs) like TMNs are subjected to alterations of their chemical structure. In general, β-substituted methylnaphthalenes are thermally more stable than α-substituted. This was used to create Maturity Index ratios and measure the thermal stresses that the organic matter experienced *Radke, M., Garrigues, P. and Willsch, H. (1990).* [29] TeMNs also vary in distributions in chromatograms according to their maturation.

The low maturated oils appear to have lower quantities of 1,3,6,7-TeMN and higher quantities of 1,2,5,6-TeMN + 1,2,3,5-TeMN, since these compounds are not as thermally stable as 1,3,6,7-TeMN. The ratio that is used for these compounds is called TeMNr, and is equal to 1,3,6,7-TeMN/(1,3,6,7-TeMN+(1,2,5,6-TeMN + 1,2,3,5-TeMN)) *Ben G.K. et al,., (1999)*[15]

5.4.2 Cadalene-Isocadalene – Retene and Simonellite

Cadalene is a polycyclic aromatic hydrocarbon with a chemical formula of C15H18. As was previously discussed [PAHs From Natural Biological Precursors] section, this compound comes from higher plants, and have sesquiterpanes precursor molecules

Simoneit, (1986); Puttman and Villar, (1987). [30] Retene is also a higher plant product that originates mainly from conifer trees.

The Higher-plant index HPI= (retene + cadalene + iHMN)/1,3,6,7-TeMN, is where iHMN is 1-isohexyl-2-methyl-6-isopropylnaphthalene. A study done by *Ben G.K. et al., (1999)*[15] characterized the relative input of higher plants to source rocks and crude oils. This ratio can indicate the main contributors of this organic matter.

1,3,6,7-TeMN comes from bacteria, while the components of the HPI index numerator comes from plants. Simonelite mainly comes from conifer trees like retene *Simoneit,B.R.T. ,Grimalt,J.G.,Wang,T.G.,et al. (1986)* . [31]

5.4.3 Dibenzothiophene, Phenanthrene Anthracene

5.4.3.1 Dibenzothiophene

Dibenzothiophene (DBT) is a compound that consists of two benzene rings bonded with a thiophene molecule. With a molecular weight of 184.6 g/mol, this compound and its methyl- versions, comprise significant thio-compound categories used in the study of the organic geochemistry of Aromatic compounds. Later sections will discuss the geochemical significance of Dibenzothiophene and its methylated versions in greater detail.

The main ion that DBT can observe using MS spectroscopy is m/z=184. For the purpose of this study, three methylated DBT compounds are investigated 3-MDBT, 4-MDBT, and 1-MDBT. These MDBTs belong to m/z=198 ion.

DBT can accumulate into sediments in a relatively reducing environment since thiophene is formed mainly by H2S that is created by microorganisms. A study done by *Fan Pu et al., (1990)* [14] , showed that DBT among other compounds such as Fluorenes and Dibenzofurans, can be used as indicators of environmental conditions and differentiate between marine and terrestrial oils.

In terrestrial oils the concentration of DBT increases in the order of freshwater saline, and hypersaline facies, whereas the concentrations of Fluorene and Dibenzofurans in such environments are decreasing. According to studies done by *Ten Haven,H.L.,de Leeuw,J.W., Sinninghe Damst e, J S.(1988)* ,[32] , DBT is an indicator of reducing hypersaline environments and can be used alone as it is. Its methylated versions can be used according to *Hughes.,et all, (1995)*,[54] for the classification of various sedimentary environments.

The results of *Fan Pu et al., (1990)* [14] also showed that the methylated DBTs (C2- and C3- versions) change their relative concentration distributions with respect

to DBT, according to certain environmental conditions - more specifically C2- and C3 – DBTs appear to have lower concentrations in respect to the samples from hypersaline environments.

Marine sediments appear to have a higher ratio of DBTs and MDBTs. Lower ratios of these methyl- compounds imply the terrestrial source rocks according to the research done by *M.M EL NADY et all. (2009)*[33]. According to the study 4-MDBT, 1-MDBT, 2-MDBT, 3-MDBT can be used to characterize the maturation of the oils. MDR=4-MDBT/1-MDBT is a ratio that increases as the oil is extracted at a deeper level *Santamaria-Orozco et al, (1998).* [34] Since isomer 4-MDBT is thermally more stable than 1-MDBT this ratio can then be used as a reliable indicator of the maturation level of the oil. Another useful maturity indicator is the ratio MDR-23=2+3-MDBT/1-MDBT *Santamaria-Orozco., et al (1998)*[34]

5.4.3.2 Phenanthrene

Phenanthrene (P) is an aromatic hydrocarbon composed of three fused benzene rings. phenanthrenoids are chemical components that include a phenanthrene skeleton, and originate from organic precursors like plants. This paper studies the two main sub-groups of phenanthrenes - the Methyl- and Ethyl- phenanthrenes. 1-MP, 3-MP and 2-MP can be observed in the mass spectroscopy for ion m/z=192, 9-EP/2-EP and 1-EP can be observed at the ion m/z=206. Ion chromatogram for phenanthrene is m/z=178.

Dimethylphenanthrenes and more specifically, the degraded aromatic compounds 1,7-DMP and 1-MP may originate from pentacyclic terpenoids. These dimethylphenanthrenes could come from diterpanes if the relative concentrations of other compounds such as 136-TMN and 9-MP are high. According to *Radke.,et al., (1982b)* [32] , the thermal maturity of the area affects the distributions of phenanthrene methylhomologs in the window between 0.6-1.7 % mean Ro.

Phenanthrene is used as an indicator of thermal maturation usually among other categories like naphthalenes and dibenzothiophenes, because some compounds are thermally more stable than others *Radke et al., (1982a); Radke et al., (1986); Radke et al., (1990); Radke and Welte, (1983); Radke, (1987).* [35]

A study by *Fan Pu., et al (1990)* [14], has proved that the relative abundance of Phenanthrenes is lower in Marine source rocks than in terrestrial rocks.

Some of the ratios that can be used to identify the maturation level and other parameters are:

- MPI-1 = 1.5*[2-MP+3-MP]/[P+1-MP+9-MP] *Radke and Welte, (1983)*

This ratio determines very good specified response factors, otherwise Cassani et al.(1988) modified version of MPI-1 can be used.

The phenanthrene index MPI-1 appears to have a linear correlation with Vitrinite reflectance, especially in the 0.65–1.35% Ro window, which is positive, but in the 1.35–2.00% Ro window the correlation is negative. *Radke andWelte, (1983); Boreham et al., (1988).* [35]

• MPI-1 = 1.89(2-MP + 3-MP)/[P + 1.26(1-MP + 9-MP)] Cassani et al.(1988) modified version of MPI

• MPI-2 = 3*2MP/(PHEN+9MP+1MP) *Radke and Welte, (1983)*

• MPI-3=[2-MP + 3-MP]/[1-MP+9MP]

• [DBT]/[P] (This ratio is thought to be an indicator of source rock lithology with carbonates having ratios greater than 1 and shales having less than 1) *Radke et al., 1986;Hughes et al., 1995*

• 0.6*(1.5*(2MP+3MP))/(PHEN+9MP+1MP))+0.37)Re(a) if Ro<1.3 *Radke and Welte, (1983)*

• -0.6*(1.5*(2MP+3MP))/(PHEN+9MP+1MP))+2.3) Re(a) if Ro>1.3 *Radke and Welte, (1983)*

• MPR=[2-MP]/[1-MP]

• MPR2=[2-MP]/[9-MP]

• DPR=[3,5-DMP]+[2,6-DMP]+[2,7-DMP]/[1,3+3,9+2,10+3,10+1,6+2,9+2,5DMP]

A study done by *Fan Pu,R.P.Philp,Li Zhenxi and Ying Guangguo, (1990)* [14] says that information about the oil source can be extracted from the statistical mean value of the total naphthalene/phenanthrene ratio $\sum(N)/\sum(P)$.

5.4.3.3 Anthracene

Anthracene (An) is an isomer of phenanthrene. It consists of three fused benzene rings and is quite common in coal tars (about 1.5%).

The methyl-compounds of anthracene that are studied in this paper are 2-MAn, 9-MAn and 1-MAn. The mass-to-charge ratio of anthracene is m/z=178 and its methylhomologs have a value of m/z=192. The 1-MAn compound appears to co-elute

with 9-MP in the same peak area.

These various methyl homologues can be used in ratios to identify the maturation level.

5.4.4 Other Aromatic Parent Compounds

The oils analyzed in this thesis have been studied to obtain information about the distribution of the following components Benzofurans, Fluorene, Fluoranthanes, Pyrene, Chrysene Benzo[b]Fluoranthane, Benzo[e,j,k]Fluoranthrane, Benzo[k]Fluoranthrane, Benzo [e]Pyrene, Benzo[a]Pyrene, Perylene/Methylperylene, Indeno[1,2,3-cd]Pyrene, Dibenz[a,h]Anthracene and Benzo[ghi]Perylene. Benzo[a]Anthracene, is also observed but it cannot be quantified. The relative concentrations of these molecules can be used mainly to study the precursor organic matter and the chemical conditions of the environment.

Methyl-Benzofurans, Fluorenes, and Dibenzofurans are components that can be used to identify the sedimentary environment of crude oils and source rocks if the relative concentrations of those are plotted in a ternary plot.

Benzo[e]Pyrene and benzo[a]Pyrene are pyrosynthetic PAH compounds that are usually located in Quaternary period rock formations. They are produced by organic matter in the presence of hydrothermal activity, and they usually indicate high maturation levels. *K.E.Peters,C.C. Walters,J.M.Moldowan,(2007).* [24] Benzo[e]Pyrene can be used as an index for the classification of pyrogenic or natural biological precursor PAHs. When this index is relatively high, the pyrogenic processes prevail.[4]

Methylfluoranthrenes and Methylpyrenes in high concentrations are an indicator of combustion derived PAHs.[4]

According to *Wang and Stout, (2006)* [36] Fluoranthane, Pyrene and C4-Phenanthrene can be found in contaminated with oil soils after high biodegradation has occured. The Pyrogenic Index includes C1-C4 Naphthalene, Dibenzothiophene, Phenanthrene, Fluorene, and Chrysene.

The ratios that are used for the purpose of this thesis are presented below in the tables 5.1 and 5.2

Ratio	Parameter	Ro %
MNR	MATURATION	>0.9
ENR	MATURATION	-
DNR-1	MATURATION	Rca%= 0.49+0.09 (DNR)
TDE-1	ORG. MATTER	-
TDE-2	ORG. MATTER	-
TNR-1	MATURATION	-
TNR-2	MATURATION	Rcb(%)=0.4-0.6 (TNR-2)
TNRs	MATURATION	-
TNR-2	MATURATION	Ro(%) >= 0.6
MDR	MATURATION	-
MPI-3	MATURATION	-
P/DBT	ROCK TYPE	-
MPR	MATURATION	1.0 to 1.7 %Ro
DPR	MATURATION	1.0 to 1.7 %Ro.
[1,2,5-TMN]/[1,3,6-TMN]	ORG. MATTER	-
[1,2,7-TMN]/[1,3,7-TMN]	ORG. MATTER/ MATURATION	-
TMNr	MATURATION	-
TeMNR-1	MATURATION	-
DPR2	MATURATION	
DBT/P	SOURCE TYPE	-

Table 5.1: Ratios

Ratio	Equation
MNR	2-MN/1-MN
ENR	2-EN/1-EN
DNR-1	(2,6-DMN + 2,7-DMN)/1,5-DMN
TDE-1	1,2,5-TMN/1,2,4-TMN
TDE-2	1,2,7-TMN/1,2,6-TMN
TNR-1	= 2,3,6-TMN/(1,4,6-TMN + 1,3,5-TMN)
TNR-2	[1,3,7-TMN]+[2,3,6-TMN] / [1,3,5-TMN]+[1,3,6-TMN]+[1,4,6-TMN]
TNRs	[1,3,7-TMN]+[2,3,6-TMN]/[1,3,6-TMN]
TNR-2	[1,3,5-TMN]+[1,4,6-TMN]/[1,3,6-TMN]
MDR	4-MDBT/1-MDBT
MPI-3	[2-MP + 3-MP]/[1-MP+9MP]
MPR	[2-MP]/[1-MP]
DPR	[3-DMP]+[4-DMP]/[5-DMP]+[6-DMP]
[1,2,5-TMN]/[1,3,6-TMN]	[1,2,5-TMN]/[1,3,6-TMN]
[1,2,7-TMN]/[1,3,7-TMN]	[1,2,7-TMN]/[137-TMN]
TMNr	[1,3,7-TMN]/[1,2,5-TMN+ 1,3,7-TMN]
TeMNR-1	(2,3,6,7-TeMN/1,2,3,6-TeMN)
DPR 2	[2,7-DP]/[1,7-DP]
DBT/P	DBT/P

Table 5.2: Ratios and Equations

Chapter 6

Analytical Determination of Compounds

MANY different techniques have been developed in order to identify different components. These techniques are based on the various characteristics of these components, which include discrepancies in molecular weight, polarization, structure of the molecule, chemical bonds between the atoms, and chemical properties such as hydrophilicity or absorption. All those parameters and more are what make a molecule unique.

Identification of compounds can be (sub)divided in two main categories; the Modern Chromatographic methods (which use Chromatographic analyzers), and traditional analytical Chromatographic techniques. Analytical methods are more rigorous and are more sensitive to human errors. The analyst must set up a chromatographic column and all of the necessary equipment and gauges in order to separate the different components. These techniques appear to be a challenge for the separation and identification of the components, especially if they are in very small proportions in the sample. Also the quantity of the sample and the concentration of the analytes must be relatively large – something that is not always achievable in the laboratory conditions. In 1903 Mikhail Semyonovich Tswett, was a botanist and was the first to develop the chromatographic separation techniques, using calcium carbonate as adsorbent and petrol ether/ethanol mixtures as eluent to separate chlorophylls and carotenoids.

Modern Chromatographic techniques use chromatographic equipment, so the analyst has to carefully prepare a sample, set the correct parameters in the program, and insert the prepared sample into the device. The signal will then return as an output on the computer screen; at this point, the data of the sample are ready to be edited.

In this thesis, the different aromatic components are separated from the orig-

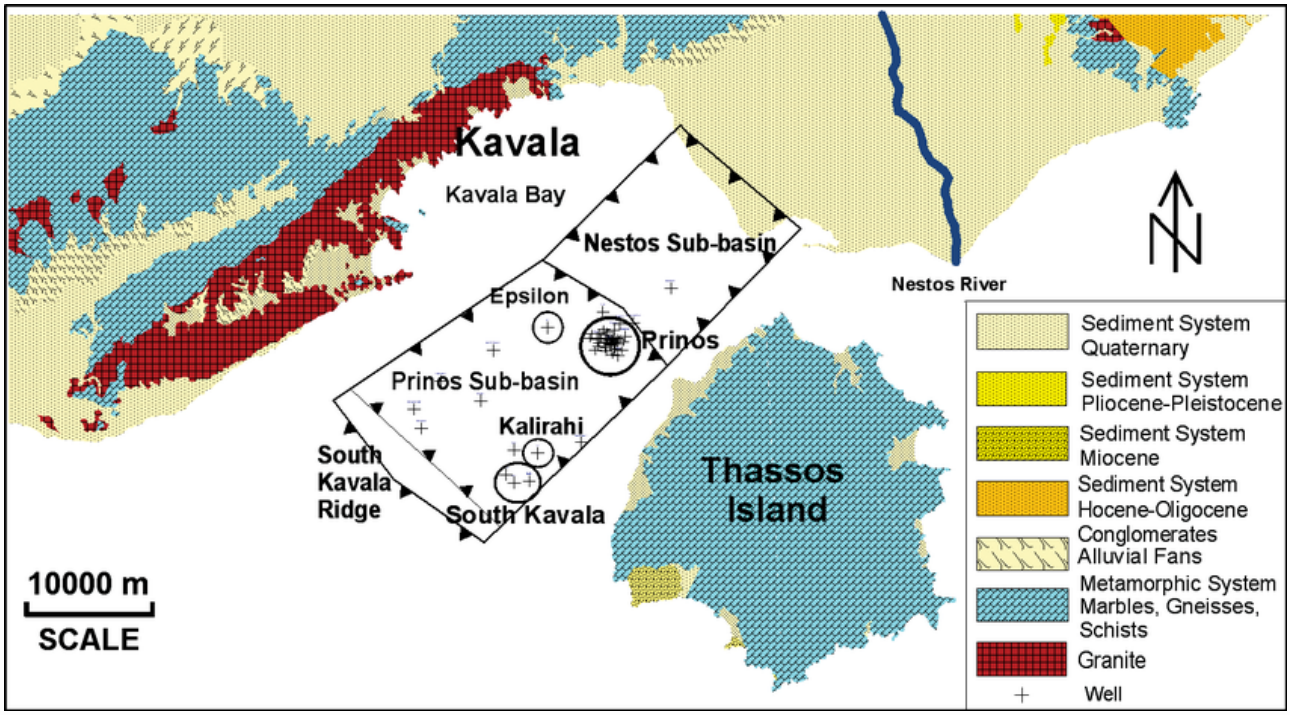


Figure 6.1: Prinos – Kavala Basin (improved version published after Kiomourtzi et al., (2007) [6]

inal samples and are analyzed using a Gas-Chromatography device. The components at the end of the GC column travel into the Mass Spectroscopy device and the data from the fractured molecules are then gathered in to a data base.

6.1 Samples and Experimental Procedures

6.1.1 Sample Pre-Treatment Procedures

THIS section discusses how the samples were selected, and describes the techniques that there used to prepare the samples for GC-MS analysis.

6.1.1.1 Sample Selection

After many years of petroleum exploitation and research, numerous boreholes have been (drilled) in the Prinos-South Kavala area. In order to have a full understanding of the geochemical parameters of this Prinos Basin, the samples that where studied in this thesis where not randomly selected, but cover many different boreholes from various locations, depths, and rock layers.

The selected samples of this report cover 5 different areas of the Prinos basin: Prinos, Northen Prinos, Epsilon, Kalirachi, and Southern Kavala. These samples are coming from 6 different boreholes. Prinos area consists of 3 main stromatographic series.

The shallower is the Post-Evaporitic which consists of marine sediments with fossils. Deeper sequence is the Evaporitic and it consists of two phases consisting of layers of anhydrite and limestone in alternations with sand, clays and marls, while the second phase concerns the SW part of the basin and consists of 7-8 layers of salt. Finally the deepest sequence is called Pre-Evaporitic and it consists of metamorphic rocks, such as gneiss, quartz and dolomite marbles. *P.Kiomourtzi (2016)* [6]

The samples from Prinos Oil deposit (PB-26), are coming from the Pre-Evaporitic series and more specifically from the depth of the reservoir. The samples from Epsilon field (E1) and (E1AS), are coming from the Pre-Evaporitic series and from the level of the reservoir. The North Prinos (PN2) samples are subject to the reservoir level from the Pre-Evaporitic series, and these are possible source rocks. The (K1) samples coming from Kalirachi area, and these are also coming from the Pre-Evaporitic series from the reservoir level. From the gas-reservoir of South Kavala, the samples (SK4), are also belong to Pre-Evaporitic sequence in a location subjected from the reservoir.*P.Kiomourtzi (2016)* [6]

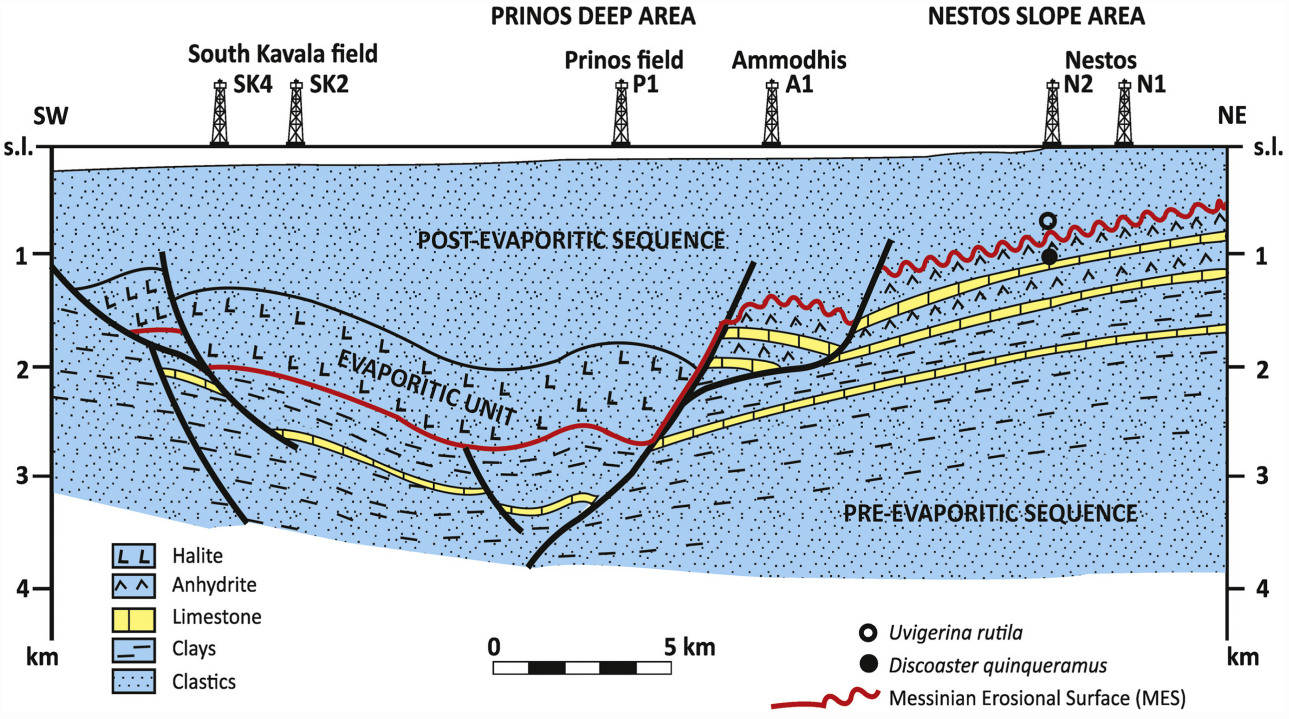


Figure 6.2: Evaporitic Sequences of Prinos Basin [55]
Picture from [Messinian salinity crisis record under strong freshwater input in marginal, intermediate, and deep environments: The case of the North Aegean (2017) - Volume 485, (1 November 2017), Pages 316-335]

6.1.1.2 Sample preparation

The organic materials from the ten samples studied in this thesis come from the extraction of the rock samples, and the total mass of Maltenes and the mg/g TOC is calculated. Other separation techniques where used to distinguish the Saturates, Aromatic NSO+ASHP compound groups. *P. Kiomourtzi (2016).* [6]

The following data is given by the geochemical analysis of the PhD thesis of *P. Kiomourtzi (2016)*[6], These dilution parameters will be used later in the Evaluation Section of this paper to estimate the real concentrations of the PAHs, given the concentrations of the quantitative analysis output.

	SK4	K1		E1			PN2		PB26	
	SK4-6670	K1_16	K1-19	E1As 42	E1As 36	E1 14	PN2-22	PN2 1	1B	1A2
Depth m	2032.92	2369.17	2292.35	3009.91	3008.32	2852.00	2709.63	2655.00	2620.71	2620.85
TOC	0.25	6.30	2.17	0.50	0.45	0.98	1.19	2.00	0.81	0.96
mg/g sed	0.60	11.99	10.09	4.46	2.79	4.72	1.90	4.00	11.09	11.91
m_arom (g)	0.0011	0.0151	0.0127	0.0097	0.0041	0.0065	0.0033	0.0055	0.0369	0.0097
V_CHCl3 (ml)	1.70	0.50	0.50	0.50	100.00	0.50	100.00	100.00	4.00	0.50
Saturates %	71.30	9.68	27.38	44.44	54.47	56.24	33.64	36.30	34.77	21.84
Aromatics %	28.70	13.96	11.99	26.71	22.80	10.75	22.43	16.46	30.48	35.98
NSO %	0.00	2.18	5.72	10.10	10.77	9.10	42.93	44.43	8.84	4.24
Asphalt %	0.00	74.18	54.90	18.75	11.96	23.91	1.00	2.80	25.92	37.95

Table 6.1: Chemical Analysis of Samples

The concentrations of the components of each sample are multiplied by the volume of the solvent divided by 1000 $(V\_CHCl_3)/1000$ in order to calculate the quantity of aromatics (g) of the original sample. Then the result is further multyplied by $1000/m\_arom(g)$ in order to calculate the aromatics exist in the aromatic phase solution. In order to calculate the percentage of the aromatics in the source rock extract, theese results are multiplied by the percentage of aromatic fraction $Aromatics\%/100$).

$$Original\_Concentration = \frac{[Comp] \times V\_CHCl_3(ml)}{1000} \times \frac{1000}{m\_arom(g)} \times \frac{Aromatics\%}{100}$$

The aromatic fraction samples where initially dissolved with chloroform in order to prepare the aromatic solutions. The concentration of these samples can be easily calculated since the mass of the aromatic fraction and the volume of the solvent is measurable. For quantitative reasons, an Internal Standard (IS) mixture of special aromatic components needs to be injected into the solutions. The concentration and the quantity of the injected components are known. Each one of these aromatic components describes and quantifies a unique aromatic compound group in which the compounds have similar chemical properties.

The IS solution that was used for the quantitation purpose of this thesis is the I.S. Chiron AS, Product Number S-4121-AS-IO; which contains n-Dodecane-d26, 5β(H)-Cholane, 1-Fluoronaphthalene, 4-Fluorobiphenyl, n-Hexadecane-d34, 3-Fluorophenanthrene and 2-Fluorochrysene. Also for the quantification process; the

standard that was used is the Oil Analysis Standard Part Number 90311 including 44 components, Solvent (in hexane : dichloromethane [9:1]), Concentration (100 ug/mL) by ABSOLUTE STANDARDS INC Company.

Since the IS compounds have similar properties compared to the analytes and have known concentration, the quantitative analysis method is able to adjust to the relative concentrations of the analytes to match the true concentrations, this is because the method correlates with the known responses of the analytes and the responses of the IS components.

The Internal Standard Concentrations are: 1-Fluoronaphthalene - 0.7 ppm , nC16-d34 - 58 ppm , 2-Fluorochrysene 0.7 ppm , nC12-d26 58.4 ppm , and 3-Fluorophenanthrane 0.7 ppm.

1-MN, 2-EN and 1,6-DMN solutions are analyzed with IS in order to construct the Calibration Curve and find the relative responses of MNs, ENs and DMNs. When calibration curves are found, the concentrations can be calculated with high accuracy. For the other Alkyl-Naphthalenes, it is not achieved this high accuracy because no calibration curves currently exist for these groups. In organic geochemistry, this procedure is rigorous and expensive, and so many geochemists assume that all the alkylated compounds have similar responses. In addition, instead using the concentration of the component, most geochemists use the areas of the peaks, an assumption that may cause small miss-calculations.

The table (4.2) shows the Parent PAHs, Saturates,and Alkylated PAHs in which the Calibration curve exist thus; the concentrations can be accurately estimated. This table also shows the IS compound that is used for each of the component.

When IS are added to the samples, they pass through a procedure of stirring and heating to detach the heavy components that are caught on the walls of the sample container.

Approximately 1 µl of the solution is injected into the injector of GC, using a specific type of syringe.

6.1.1.3 GC-MS Conditions for Sample Analysis

The parameters that are needed to adjust for the GC-MS instrument must be very accurate, so that any small change will be visible in the chromatographic results. All of samples must be studied under the same conditions and parameters.

The instrument that used for the purpose of this thesis is the GC-MS (Agilent 7890A/5975C); the column was a HP-5 MS UI (60m x 0,25mm x 0.25µm).

nC12-d26	**nC16-d34**	**1-fluoronaphthalene**	**2-Fluorochrysene**	**3-Fluorophenanthrane**
nC15	nC16	2-MN	Fluoranthrane	Fluorene
nC14	nC17	1-MN	Pyrene	Dibenzothiophene
nC13	nC18	2-EN	Chrysene	Phenanthrene
nC12	nC19	1-EN	Benzo[b]fluoranthrane	Anthracene
nC11	nC20	26,27-DMN	Benzo[k]fluoranthrane	
nC10	nC21	13,17-DMN	Benzo[e]pyrene	
	nC22	16-DMN	Benzo[a]pyrene	
	nC23	14,23-DMN	Perylene	
	nC24	15-DMN	Indeno[1,2,3-cd]pyrene	
	nC25	12-DMN	Dibenz[a,h]anthracene	
	nC26		Benzo[ghi]perylene	
	nC27		Benzo[a]anthracene	
	nC28			
	nC29			
	nC30			
	nC31			
	nC32			
	nC33			
	nC34			
	nC35			

Table 6.2: Internal Standard table

The temperature conditions of the column were initially at 40°C for two minutes from the time of sample injection. The temperature was then increased at a rate of 20°C per minute up until the temperature reached 200°C. Immediately afterwards , the temperature was increased at a rate of 2°C per minute until conditions reached 300°C – at this point, the column was stabilized for another 20 minutes. The total time for this procedure was 80 minutes.

The sample injection method is Split/Splitless with an injector temperature of 280°C. The injected volume of the sample was 1µl. The MS-TIC m/z values was set from 50-850 mass to charge ratio.

6.1.2 Prinos Sample Data Set

The following sections provide information about how the data was extracted from GC-MS, and how they were analyzed and treated.

6.1.2.1 GC-MS Data Processing

Ten samples from Prinos oil were analyzed in qualitative and quantitative analysis. The selected samples, alphabetically named are: 1_A2, 1_B, E1_14, E1AS_36, E1AS_42, K1_16, PN2_1, PN2_22, SK4_6670 and K1_19.

Samples PN2_1, E1_14 K1_19, were used for compound identification and creation of the CEF files for the quantitate method. In total, 54 Alkyl-compounds and 15 Parent PAH were identified. The reason that not only one sample was used to identify all of the components was that not all samples displayed clear peaks. Only the clearest peaks with the smallest noise level were used for method development. *(Chunqing Jiang's PhD (1998)* [4], was used as a guide for the selection of the peaks.

The chromatograms (m/z) that the developed method extracts from each sample are: N=128, MNs=142, DMNs=156, TMNs=170, TeMNs=184, DBTs=184, MDTs=198, Cadalene=198, DBF=168, MDBF=182, Flu=166, P=178, An=178, MPs=192, MAn=192, EPs=206, DMPs=206, Retene=234, Simonelite=252,Fla=202, Pyr=202, Mfla=216, B[a]An=228, B[e]Py, B[a]Py, B[k]Fla,B[k]Fla Pery=252, Ipyr=276, B[g,h,i]Pery=276, according to *Chunqing Jiang et all.,(1998).* [4]

6.2 Analytical Procedures

6.2.1 Gas Chromatography - Mass Spectroscopy

6.2.1.1 Gas Chromatography-GC

Gas chromatography techniques can be Gas-Solid, Gas-Liquid or Liquid-Liquid. In the case of Gas-Liquid chromatography (which has been applied for the purpose of this thesis), the stationary liquid phase coating the interior of the column is a function of the GC column which with its unique properties, can absorb each analyte differently, and cause their separation.

The first step in Gas chromatography is the injection of the sample into the device. The temperature of the injector is high enough to cause the vaporization of the compounds. In the next step the gaseous phase of the mobile phase is applied for the separation of sample components, and transfers the analytes through the GC column. The oven is a significant function of the GC because it regulates the temperature conditions of the column with great precision. After the end of the GC column, the analytes pass into the MS analyzer.

GC device allows for the selection of several different options, during the sample injection. One significant option is to use the Split, Splitless, or On Column injection method. For this analysis the Splitless injection method was selected. The carrier gas is a major parameter for correct operation procedure, since this gas provides the force for the analytes to flow though the column. The carrier gas must not interact with the other functions inside the column and must be chemically inactive; otherwise chemical reactions would occur inside the GC column. Both helium and nitrogen can be used

Figure 6.3: GC-MS by Agilent Technologies

as carrier gases.

The sample injected into the GC device will go through a sudden thermal shock with temperatures reaching 280 degrees Celsius. This rapid temperature change will evaporate the sample instantly, and the gaseous phase will go into the GC column. The temperature conditions of the GC column, the injector, and the rate that the temperature changes must be very carefully controlled, since chromatography is very sensitive to temperature conditions.

6.2.1.2 Mass Spectrometry-MS

Mass Spectrometers are devices that are used immediately following the GC column. After separation, the analytes are pass inside the Spectrometer. An electron beam bombards the analytes with electrons and breaks them into ion fragments. These fragments can be furthered fractured into even smaller molecule fragments.

A strong magnet is used to change the path that the ions travel. Instead of traveling in a straight path, the ions are forced to travel at an angle. In addition these ions are deflected according to their mass-to-charge ratio m/z. Ions then pass through a slit to the detector which produces a tiny electrical signal for each ion.

The Mass spectrum is essentially a chemical fingerprint of each compound. A mass spectrum is a histogram of the ion signal as a function of the mass-to-charge ratio. The various mass to charge ratios m/z and the ratios between those, comprise the Mass Spectrum, and this is used along with other parameters, for the purpose of identifying compounds.

The GC-MS data are 3-Dimensional; consisting of the mass to charge ratio, the time, and the response of the signal. The next 3D picture corresponds to the sample PN2_1. The m/z values used in this plot are the ones that are used to identify the components for this report.

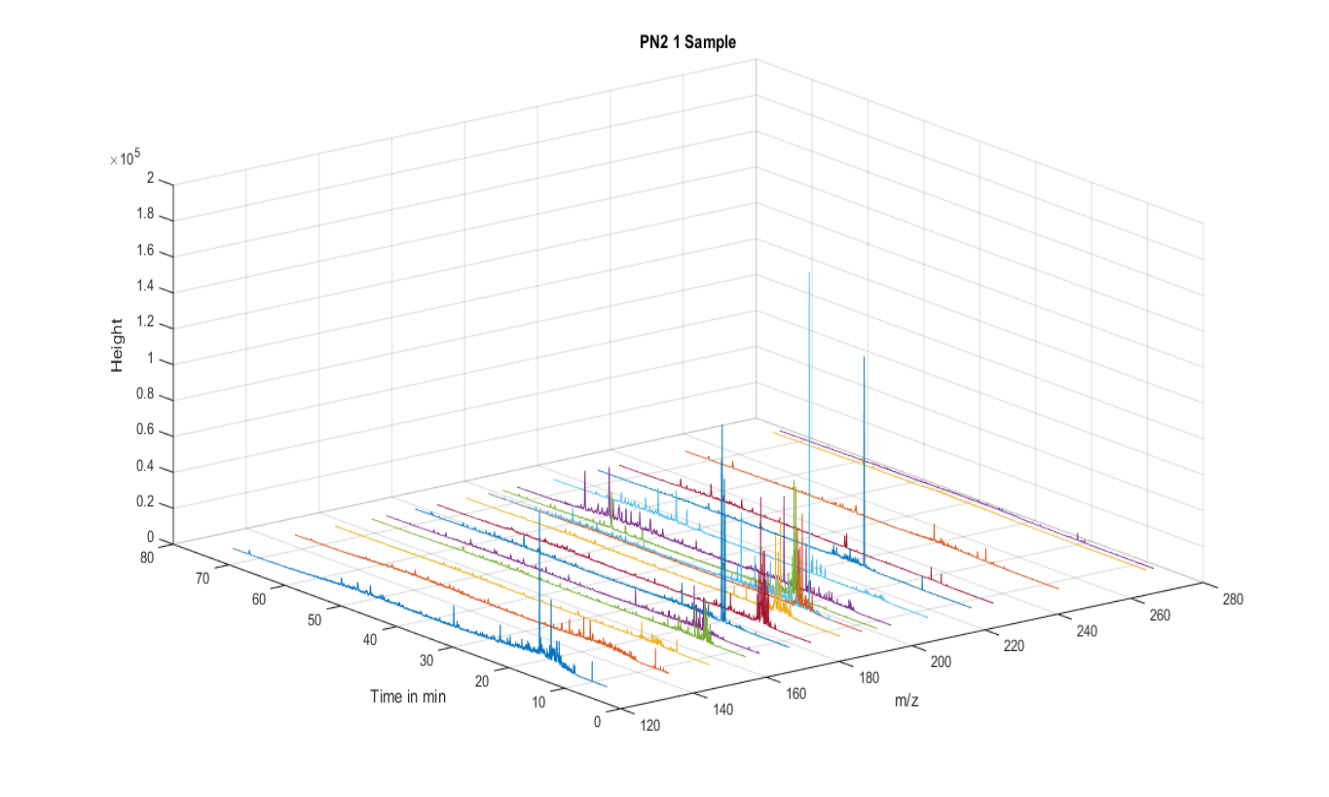


Figure 6.4: GC-MS 3D Plot

6.2.2 Identification of PAHs

6.2.2.1 Retention Time

As previously mentioned each compound has a special relationship with the chromatographic column that depends on several parameters. One of these parameters is the total residence time, or retention time, This is the duration that the compound stays at the stationary phase, plus the amount of time that it stay sat the mobile phase.

This time comes from the fact that the probabilities of these compounds for staying at the stationary or mobile phase are: $n_s/(n_m + n_s)$ and $n_m/(n_m + n_s)$. So that :

$$n_m/n_s = t_m/t'_R$$

Thus, the retention time is given by

$$t_R = t_m + t'_R$$

.

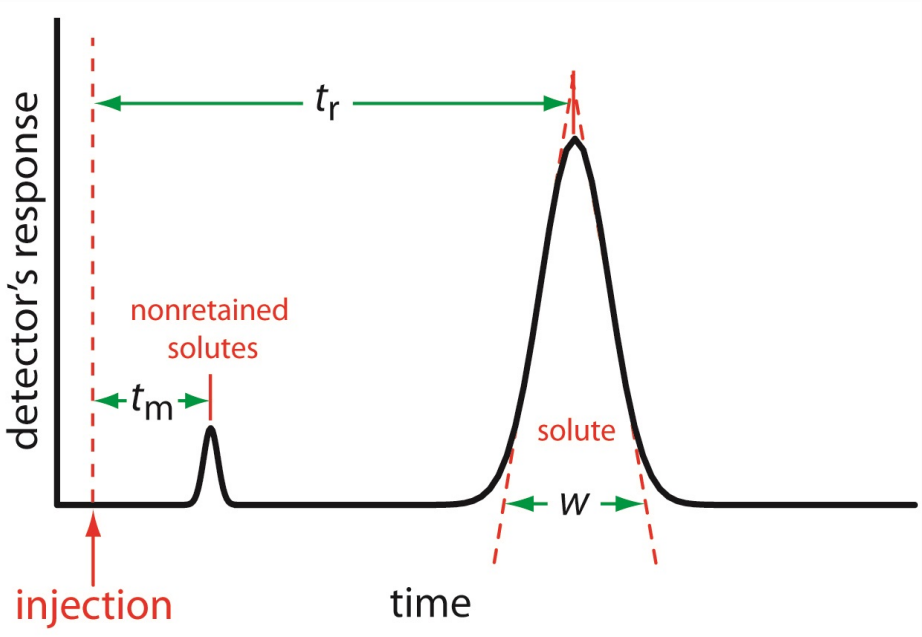


Figure 6.5: Retention Time

The partition coefficient is a ratio that is affected by the stationary phase and the analyte. The higher the partition coefficient, the higher the total retardation of the analyte inside the stationary phase mass. In addition, the separation of the components depends on their volatility. The more volatile the components are, the faster they will travel through the GC column. Partition Coefficient $K = C_a/C_b$, $Ca = SoluteA$ and $Cb = SoluteB$. It is established that $K = m_s V_m/m_m V_s$ If Vm is the volume of the mobile phase and Vs is the volume of the stable phase : $m_s/(m_s + m_m) = 1/(1 + V_m/K * V_s)$ Where ms is equal to the mass of the stationary phase and mm is equal to the mass of mobile phase.

($t_m = t_R$*fraction of time the analyte spent in the mobile phase)

$$t_m = t_R * m_a/m_{tot}$$

With all of the above considerations, becomes the equation:

$$T_m = t_R * (1/1 + KV_s/V_m)$$

Or

$$t_R = T_m/(1/1 + KV_s/V_m)$$

Schomburg, Gerhard, (1929)[39]

Retention times may vary for different GC columns, temperatures, etc., but the basic principle of chromatography demands that the order of elution from the GC column is stable. The only case in which some differences in the order of elution can be

observed is due to the polarity of the column. Columns with the same polarity have a common order of eluded components; however, columns with different polarities may appear to have enormous differences in the retention times of the analytes.

6.2.2.2 Retention Index

Retention indices are used for the identification and location of different compounds on a chromatogram. There are many different methods of calculation retention indices for every type of compound group. The theory behind this is to create a series of referenced compounds as a guide to identify and locate other compounds by their retention index. The retention index is a number that is calculated for a component (X) by the retention time t(X) of the same component, and two relative retention times of the two compounds that enclose this t(N) t(N+1).

The most common method was developed by Kovatz, using unbranched alkanes. Retention index (RI) of each alkane is calculated as the number of carbon atoms multiplied by 100. The retention time of an enclosed substance by two close branched Alkenes with n and N lower and higher number of carbons respectively), is given by the Kovatz formula.

$$RI = 100 \times \left[n + (N + n) \times \frac{\log_{t'_{r(unknown)}} - \log_{t'_{r(n)}}}{\log_{t'_{r(N)}} - \log_{t'_{r(n)}}} \right]$$

Kováts, E. (1958)[52]

Another way to calculate the Retention Index especially for aromatic hydrocarbons is the equation formulated by Lee's and his co-workers equation . This equation takes into account the number of the carbon rings of the molecules and their retention times; which may make this index useful when only polyaromatic hydrocarbons are analyzed. According to Lee, Benzene (assigned index 100), Naphthalene (200), Phenanthrene (300), Chrysene (400) and Picene (500).

$$RI = 100n + \frac{100 \times (t_x - t_n)}{t_{n+1} - t_n}$$

M.L. Lee,. et all (1979)[53]

6.2.3 MassHunter Software

MassHunter is commercial Software developed by Agilent.

For the purpose of this thesis two interdependent softwares will be used in order to study the GC-MS data of the chromatograms, identify and list the new found

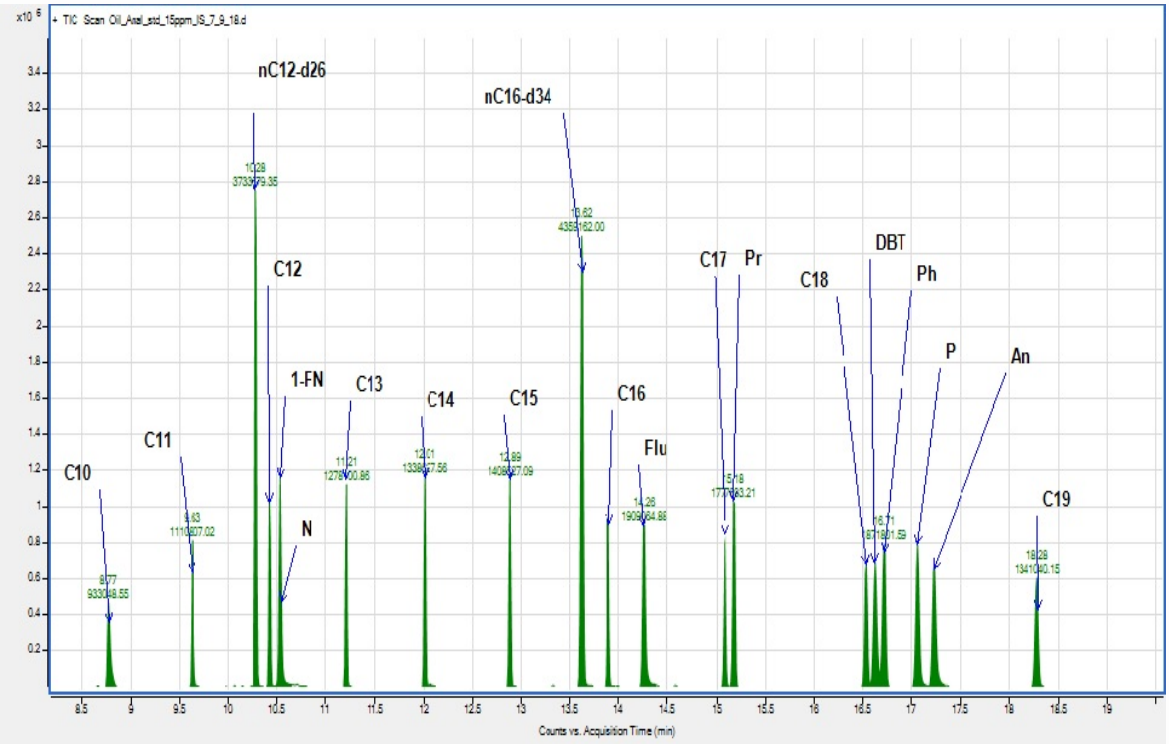


Figure 6.6: Retention Times of Saturated H/Cs used for Retention Indexes

compounds, find the peak areas and quantity the components using special features provided by the software. The softwares used are Qualitative Analysis B.07.00 & MS Quantitative Analysis B.07.00.

6.2.3.1 Qualitative Analysis

When a data set of a sample is added, initially the analyst can request the software to provide the Total Ion Chromatogram (TIC), which is a summation of all of the ions that where recorded at a specific time.

The integration of these curves is a function that is used to separate and calculate the areas of each individual peak. The integration method is selectable, but for the purpose of this thesis, Agile_2 was used. The analyst is always able to manipulate the integrated chromatogram and change possible miscalculations related to the starting and ending point of the peaks.

The analyst must search in a specific ION chromatogram (m/z) in order to find the different components. Each peak corresponds to a component (with some exceptions for co-eluding compounds), and when the peak is selected, its MS histogram will appear on the screen.

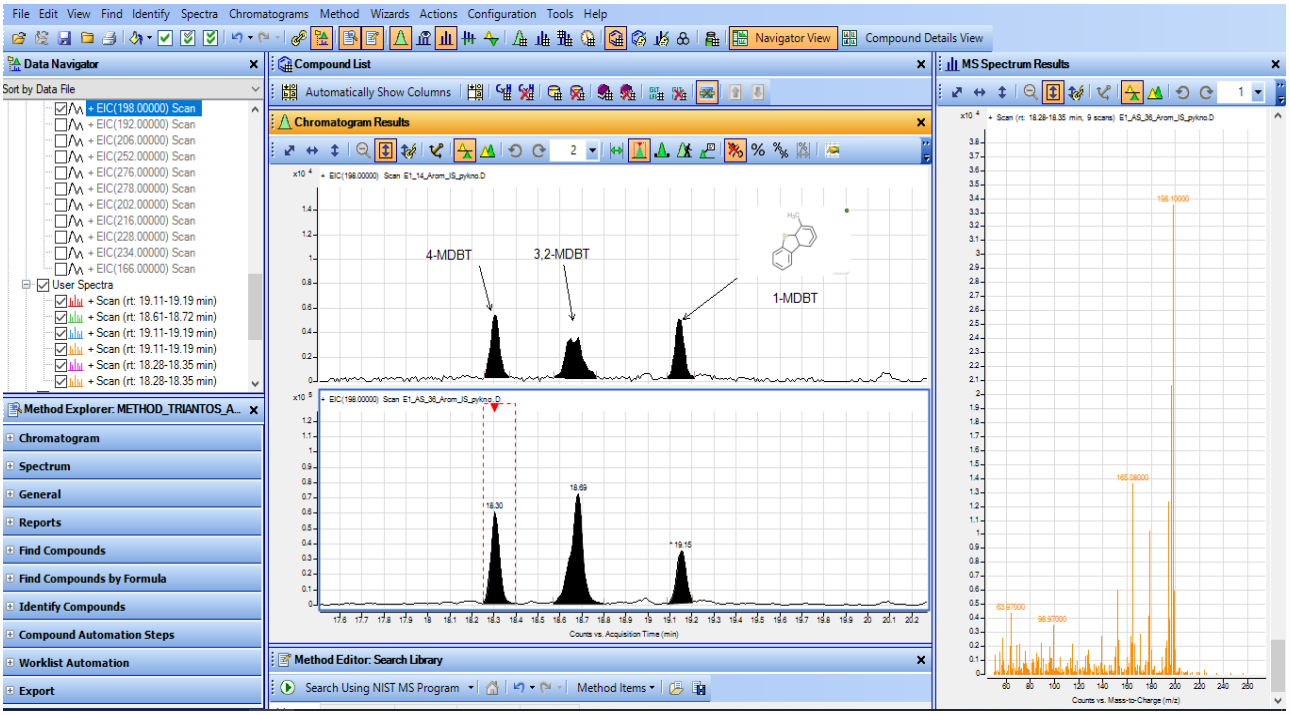


Figure 6.7: Qualitative Analysis Software

By studying this MS signal (usually for the average responses of the total Δt of the peak), the analyst is able to identify the specific components since every MS spectra and their relative responses are unique to each single compound.

When needed, special compound libraries are used for the identification of the components. Each library contains MS data from each individual compound. For the purpose of this thesis NIST Library was used. Every library has a data base of compound-MS spectrums, and when the analyst asks for compound identification of a particular peak, the algorithm in the program correlates the MS spectrum of the peak with the other MS spectra of the compounds from the library. The compound from the data base with the lowest geometrical multidimensional distance of its ions from the ions of the unknown peak is the most likely compound to correspond to this unknown peak. The analyst must then take into consideration similarities of components, such as isomers, noise level, and retention indices.

After the compound identification procedure, the compound data set includes the name, the start-end time of the peaks, the m/z ion that is extracted, the MS spectrum data for the responses and relative responses of the ions, and many other parameters. All of these data can be saved as a CEF file in order to prosed to use another software for quantitation, the data can also be exported as an excel/PDF file.

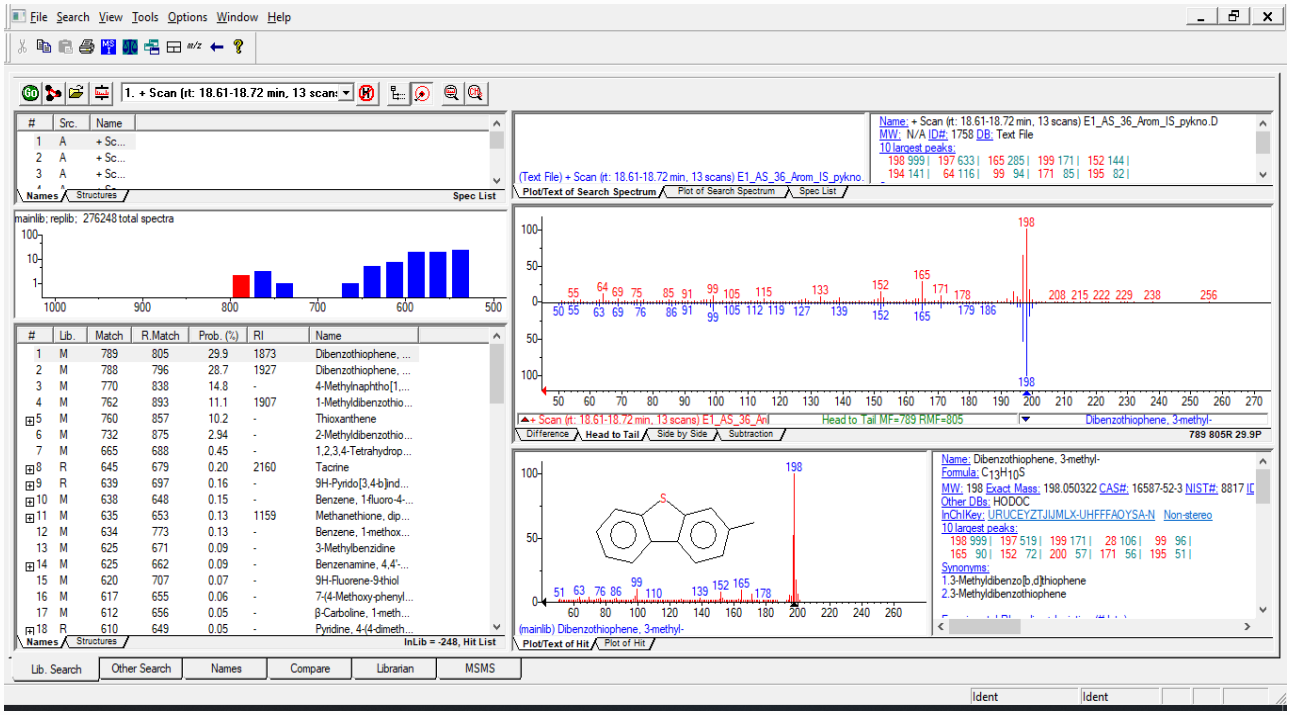


Figure 6.8: NIST Library - Qualitative Analysis

6.2.3.2 Quantitative Analysis

The quantitative process is complete with the use of MS Quantitative Analysis, which is a program with many special features specifically for peak selection, calculation of the area, and concentration of a compound.

It is proved that the instantaneous concentration of the analyte ($\bar{q}_i$), in the column effluent is a function of time, and is given; according to the mean-value theorem by the equation:

$$\bar{q}_i = \frac{1}{\Delta t} \times \int_{t1}^{t2} q_i \times dt$$

.

Since the instantaneous mean mass concentration of the analyte $q_{i,z}^{-}$ is given by the ratio $m_{iM}/\Delta V_{M,z}$, and $\bar{q}_i = \frac{m_i}{F_{\Delta t}}$, were m_i is the mass concentration of the analyte, and the product $F\Delta t$ is the volume of the effluent that exits from the column within the time interval of the elution of the respective zone. *Josef Novak (1987 pp.10)*[38].

the following equation arises: $m_i = F \times \int_{t1}^{t2} q_i(t)dt$,

where the t_1,t_2 are the starting and ending points of elution time of the effluent from the column. The above equation plays a significant role becuse it determines the amount of the analyte to be detected by the chromatographic detector*Josef Novak (1987 pp.11)*[38].

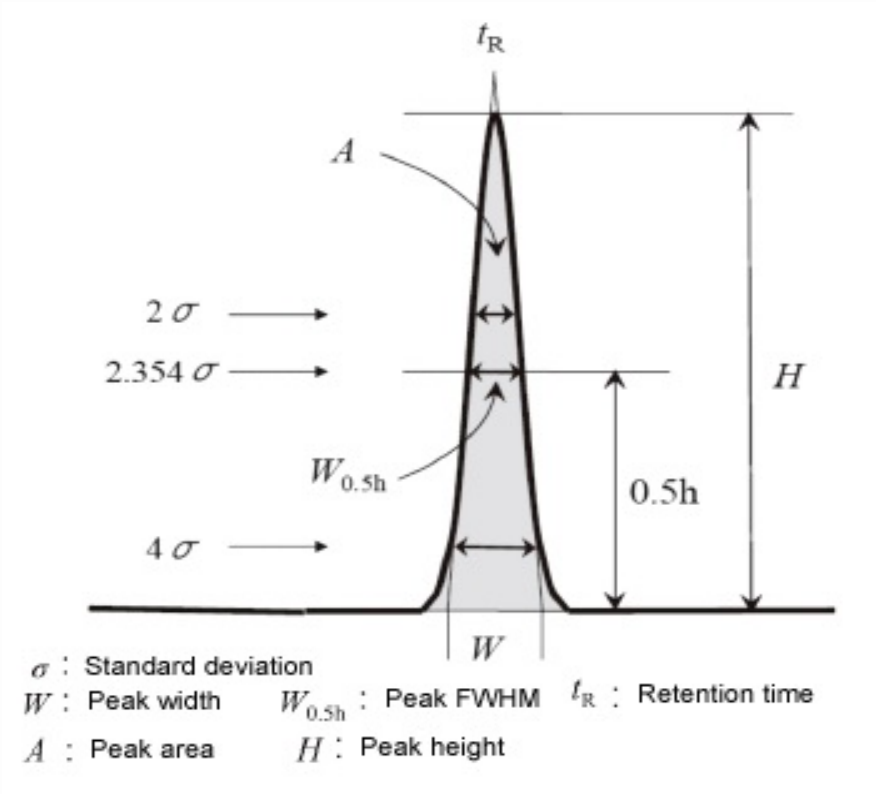


Figure 6.9: Parameters of a Peak

Also, the calculation of the area of a peak is given by a Gaussian distribution with the form of

$$A = \int_{x1}^{x2} y(x)dx = h \times \sigma_x \times \sqrt{(2\pi)}$$

Josef Novak (1987 pp.12)[38].

in which σ_x is the longitudinal standard deviation of the curve and h is the peak height. This mathematical form describes only the best shaped peaks, with no elongated tails, noise, and disturbances. This case is not practically applicable, and other analytical mathematical methods need to be used in order to calculate the area of the peak, such as the integration method Agile_2 used in Qualitative analysis.

In order to find the concentration of a compound the analyst must develop a method that takes into consideration parameters such as the Internal Standards, calibration curves, response factors, and the different main ions of the compounds.

The Quantitative analysis B.07.00 software initially auto-selects the peaks according to the m/z and the retention times, but also includes a mode for manual correction of the areas of the peak "compound at a glance mode". The unknown concentration of each compound is calculated using the calibration curve, which is the trend line of the known concentrations in respect to their responses of each individual compound. The unknown concentration of the compound in the sample uses a linear

equation in the form of $Concentration = a \times Response + b$ inorder to calculate the relative concentration with the peak area data.

The data for calibration curves and Internal Standards (IS) – used for the quantitative method-was obtained from the same data base used by GC-MS chromatographic equipment. This equipment is located in the Hydrocarbons Chemistry and technology laboratory of the school of Mineral Resources Engineering at the technical University of Crete.

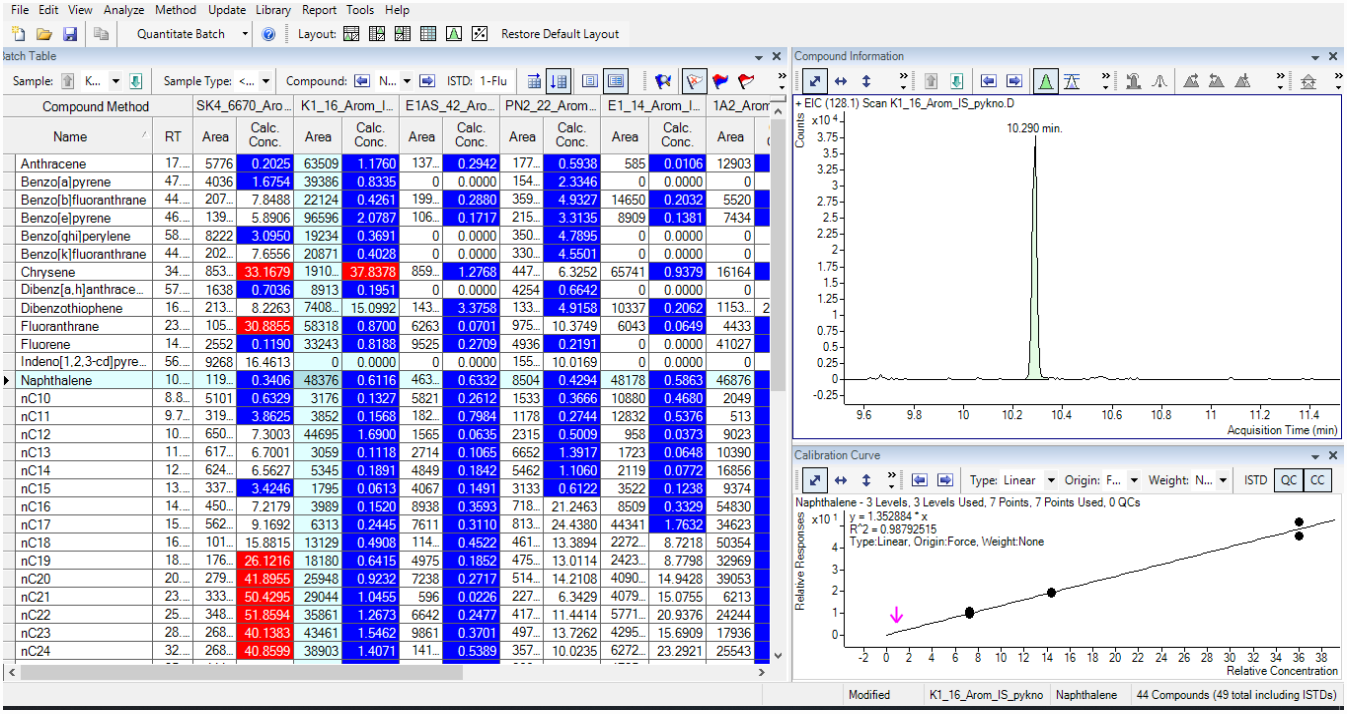


Figure 6.10: Quantitative Analysis Software

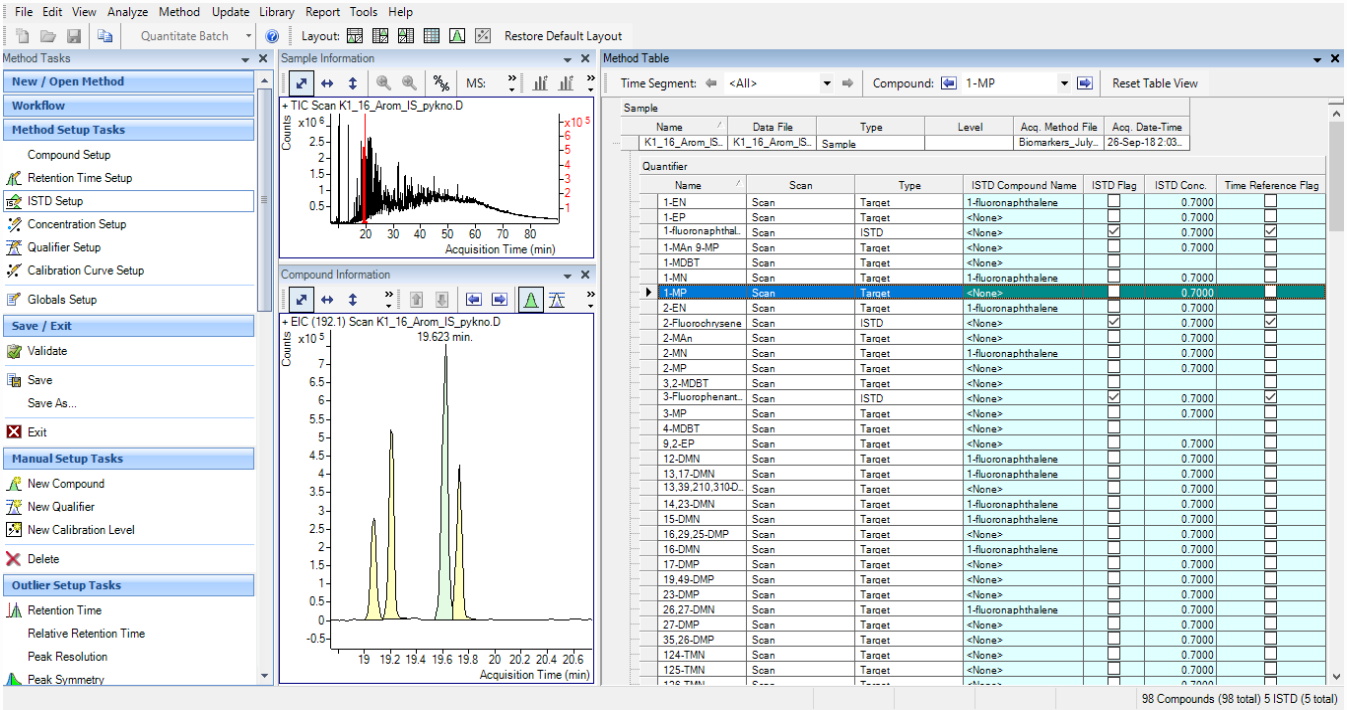


Figure 6.11: Method Developing - Quantitative Analysis

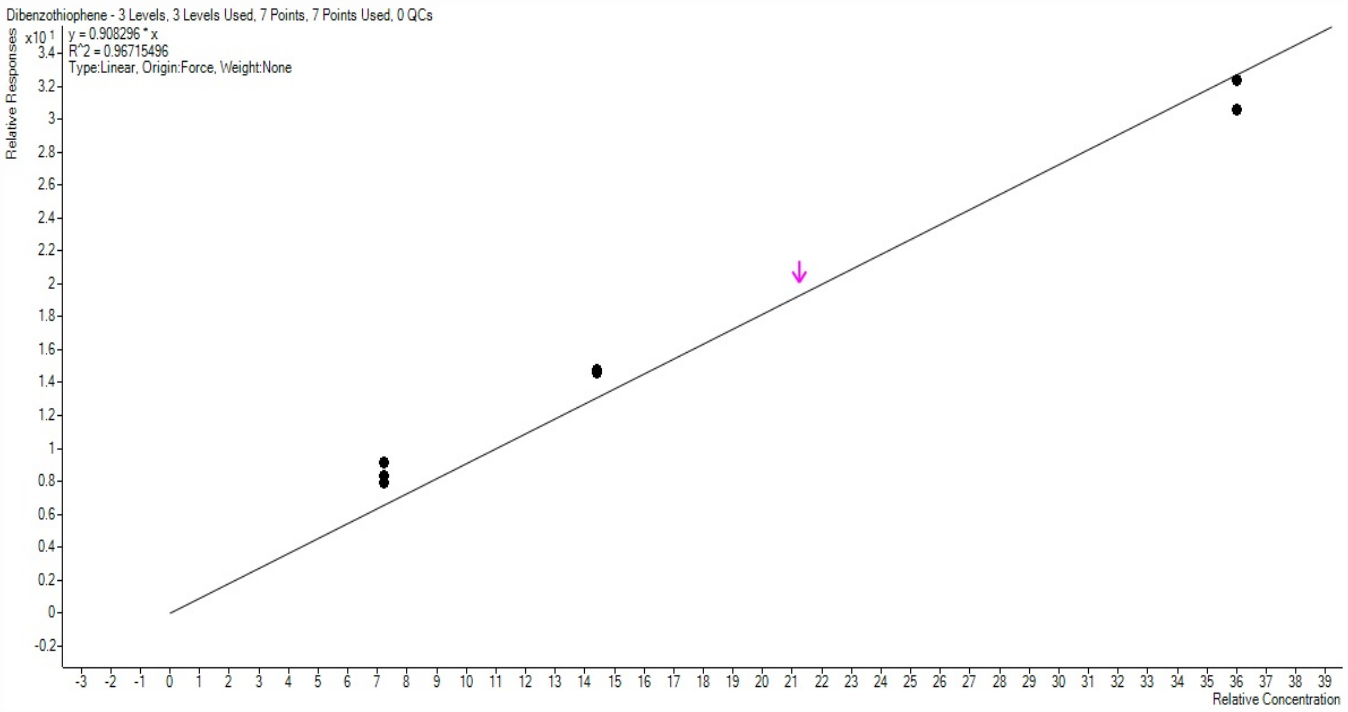


Figure 6.12: Calibration Curve - Quantitative Analysis

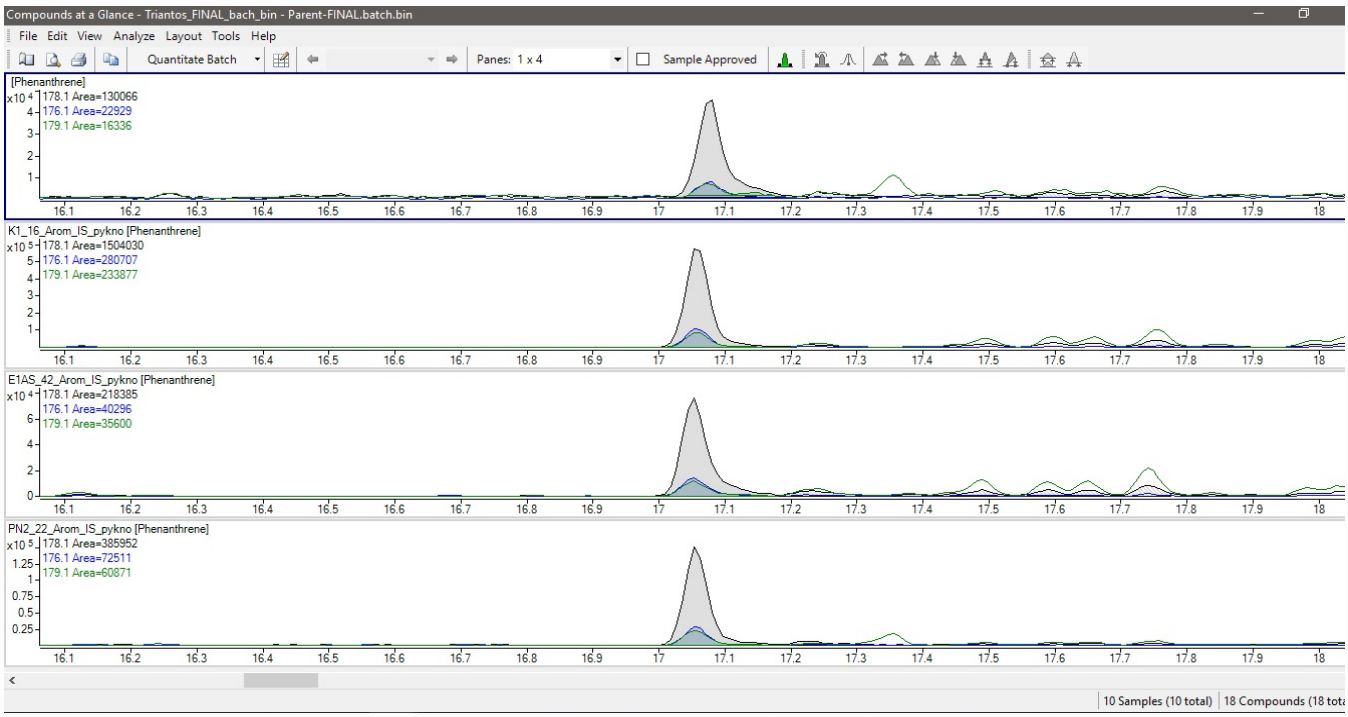


Figure 6.13: Compounds at a Glance - Quantitative Analysis

Chapter 7

Experimental Results

In this chapter the experimental results from the quantitative analysis for parent PAHs and semi-quantitative analysis for the alkylated PAHs are presented. In addition, the retention indices of the components are calculated according to the Kovatz formula (see section 6.2.2.2). Finally the geochemical ratios refereed in (section 5.4) are also calculated.

7.1 Quantitative Results of PAHs

The table below (7.1) correlates the parent and alkylated PAHs,with a relative number. This numbers are observed at the bar-charts of the components 7.1 & 7.2 representing them.

Parent PAHs on Bar-Charts							
1	Fluorene	**5**	Fluoranthrane	**9**	Benzo[k]fluoranthrane	**13**	Indeno[1,2,3-cd]pyrene
2	Dibenzothiophene	**6**	Pyrene	**10**	Benzo[e]pyrene	**14**	Dibenz[a,h]anthracene
3	Phenanthrene	**7**	Chrysene	**11**	Benzo[a]pyrene	**15**	Benzo[ghi]perylene
4	Anthracene	**8**	Benzo[b]fluoranthrane	**12**	Perylene		

Alkylated PAHs on Bar-Charts							
1	N	**15**	2,3,6-TMN	**29**	1,2,5,6 & 1,2,3,5-TeMN	**43**	1,6&2,9&2,5-DMP
2	2-MN	**16**	1,2,7-TMN	**30**	4-MDBT	**44**	1,7-DMP
3	1-MN	**17**	1,6,7-TMN	**31**	3,2-MDBT	**45**	2,3-DMP
4	2-EN	**18**	1,2,6-TMN	**32**	3-MP	**46**	1,9 & 4,9-DMP
5	1-EN	**19**	1,2,4-TMN	**33**	1-MDBT	**47**	Mfla
6	2,6 & 2,7-DMN	**20**	1,2,5-TMN	**34**	2-MP	**48**	Mfla
7	1,3 & 1,7-DMN	**21**	1,4,5-TMN	**35**	2-MAn	**49**	Mfla
8	1,6-DMN	**22**	Cad	**36**	1-MAn 9-MP	**50**	Mfla
9	1,4 & 2,3-DMN	**23**	1,2,4,7-TeMN	**37**	1-MP	**51**	Mpyr
10	1,5-DMN	**24**	1,2,5,7-TeMN	**38**	9,2-EP	**52**	Mpyr
11	1,2-DMN	**25**	2,3,6,7-TeMN	**39**	1-EP	**53**	Mpyr
12	137-TMN	**26**	1,2,6,7-TeMN	**40**	3,5 & 2,6-DMP	**54**	Ret
13	1,3,6-TMN	**27**	1,2,3,7-TeMN	**41**	2,7-DMP		
14	1,4,6 & 1,3,5-TMN	**28**	12,3,6-TeMN	**42**	1,3 & 3,9& 2,10& 3,10-DMP		

Table 7.1: Numbered PAHs on Bar-Charts

7.1.1 Quantitative Results of Parent PAHs

	SK4	K1		E1			PN2		PB-26	
CONCENTRATION IN EXTRACT (ppm)	SK4 6670	K1-16	K1-19	E1As-42	E1As-36	E1-14	PN2-22	PN2-1	1-B	1-A2
Fluorene	0.00	3.78	2.20	3.73	0.00	0.00	1.49	0.29	3.07	17.57
Dibenzothiophene	564.65	68.71	120.78	44.02	9.91	1.71	32.91	14.94	283.14	408.57
Phenanthrene	340.96	128.92	50.29	62.91	29.81	1.39	87.08	30.86	38.16	43.46
Anthracene	15.37	5.44	1.61	4.05	1.83	0.13	4.04	0.92	5.39	3.67
Fluoranthrane	200.89	4.02	1.24	0.97	1.86	0.54	42.40	8.28	1.80	1.10
Pyrene	75.91	17.21	3.78	5.04	10.11	1.33	41.29	7.60	3.91	3.49
Chrysene	215.73	174.90	70.43	17.58	36.22	7.76	25.85	4.57	6.95	5.34
Benzo[b]fluoranthrane	51.05	3.83	0.98	3.97	3.70	1.68	20.16	3.04	2.02	1.54
Benzo[k]fluoranthrane	25.16	0.00	0.00	0.00	0.00	0.00	18.63	0.00	0.00	0.00
Benzo[e]pyrene	38.31	9.61	3.09	2.36	1.25	1.14	13.54	2.12	2.15	2.67
Benzo[a]pyrene	10.90	3.85	0.00	0.00	0.00	0.00	9.54	1.54	0.00	0.00
Perylene	0.00	0.00	0.00	0.00	0.00	0.00	3.28	1.13	0.00	0.00
Indeno[1,2,3-cd]pyrene	107.06	0.00	0.00	0.00	0.00	0.00	40.94	5.40	0.00	0.00
Dibenz[a,h]anthracene	0.00	0.78	0.00	0.00	0.00	0.00	2.71	0.00	0.00	0.00
Benzo[ghi]perylene	20.13	1.71	0.61	0.00	0.85	0.00	19.57	2.57	0.00	0.00

Table 7.2: Concentration of the Parent PAHs of the Samples

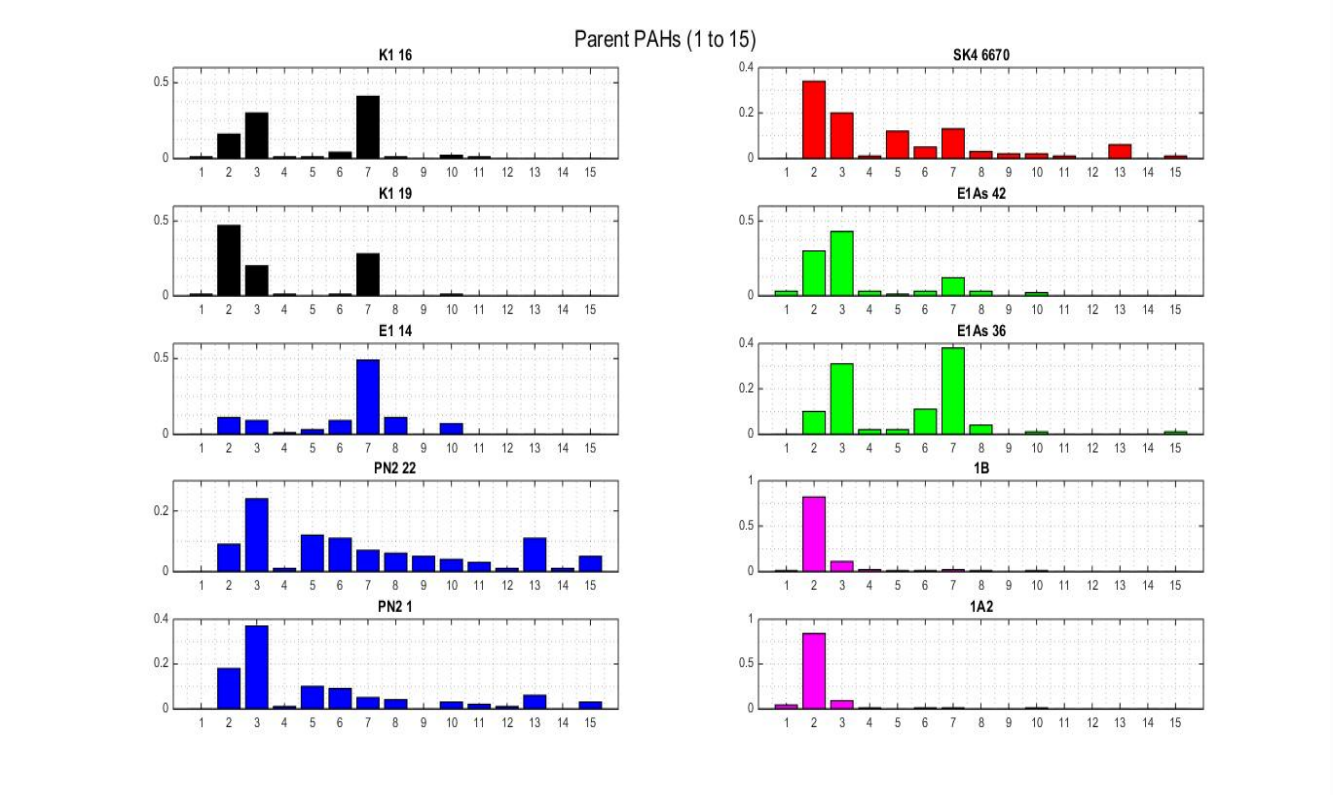


Figure 7.1: Graphical representation of the Parent PAH Compounds - Bar Charts

7.1.2 Quantitative/Semi-quantitative Results of Alkylated PAHs

	SK4	K1		E1			PN2		PB-26	
CONCENTRATION IN EXTRACT (ppm)	SK4 6670	K1-16	K1-19	E1As-42	E1As-36	E1-14	PN2-22	PN2-1	1-B	1-A2
2-MN	26.59	0.00	0.32	0.00	0.33	0.00	0.00	0.00	1.54	2.79
1-MN	31.93	0.00	0.35	0.00	0.33	0.00	0.00	0.00	1.45	3.98
2-EN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.48
1-EN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.31
2,6 & 2,7-DMN	21.29	0.00	0.67	0.00	0.46	0.00	0.00	0.26	2.79	19.64
1,3 & 1,7-DMN	33.25	0.00	1.13	0.00	0.45	0.00	0.00	0.00	3.06	46.07
1,6-DMN	40.56	0.00	1.11	0.00	0.43	0.00	0.00	0.00	3.19	41.00
1,4 & 2,3-DMN	13.88	0.00	0.85	0.00	0.30	0.00	0.00	0.00	1.69	47.02
1,5-DMN	14.33	0.00	0.99	0.00	0.22	0.00	0.00	0.00	1.25	36.83
1,2-DMN	11.98	0.00	0.85	0.00	0.18	0.00	0.00	0.00	0.92	25.19

Table 7.3: Concentration of Alkylated Compounds (Quantitative)

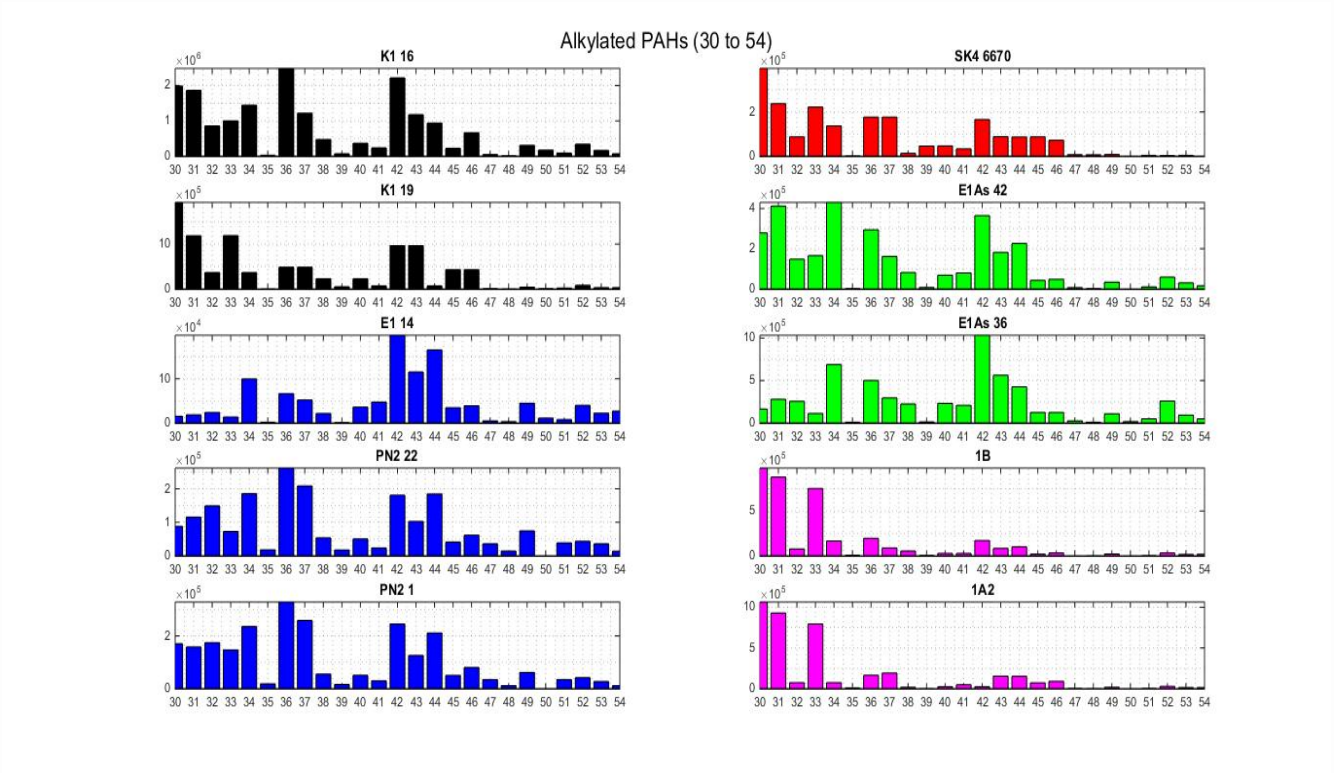


Figure 7.2: Alkylated Compounds of Samples Bar-Chart

	SK4	K1		E1			PN2		PB-26	
	SK4_6670	K_16	K1_19	E1AS_42	E1_AS_36	E1_14	PN2_22	PN2_1	1B	1-A2
N	7729	0	0	0	1724	0	0	0	0	2024
2-MN	7642	0	2228	0	1376	0	0	0	3459	5532
1-MN	9174	0	2428	0	1384	0	0	0	3258	7878
2-EN	0	0	0	0	0	0	0	0	0	9072
1-EN	0	0	0	0	0	0	0	0	0	4119
2,6 & 2,7-DMN	4678	0	3515	0	1463	0	0	1045	4791	29735
1,3 & 1,7-DMN	7304	0	5936	0	1443	0	0	0	5249	69741
1,6-DMN	8912	0	5848	0	1372	0	0	0	5463	62063
1,4 & 2,3-DMN	3049	0	4457	0	950	0	0	0	2890	71165
1,5-DMN	3149	0	5181	0	698	0	0	0	2143	55743
1,2-DMN	2632	0	4444	0	587	0	0	0	1585	38125
1,3,7-TMN	8158	817	89866	0	761	0	0	0	14078	202577
1,3,6-TMN	3463	0	29380	0	0	0	0	0	10214	70709
1,4,6 & 1,3,5-TMN	7315	1622	60761	1687	0	0	0	0	15694	133343
2,3,6-TMN	4675	0	43512	0	0	0	0	0	12202	96930
1,2,7-TMN	0	0	0	2716	0	0	3574	0	0	0
1,6,7-TMN	0	0	30142	2716	0	0	0	0	1764	15703
1,2,6-TMN	0	0	0	0	0	0	0	0	0	0
1,2,4-TMN	0	0	0	0	0	0	0	0	0	0
1,2,5-TMN	4161	0	76654	0	0	0	23951	11935	17244	97972
1,4,5-TMN	0	0	0	0	0	0	0	0	0	0
Cad	5250	0	27527	0	0	0	0	0	5013	25039
1,2,4,7-TeMN	5352	0	95925	0	0	0	91713	49547	10813	25712
1,2,5,7-TeMN	4836	0	99169	0	0	0	47511	30677	10521	51889
2,3,6,7-TeMN	4813	0	3341	0	5887		9132	49547	6894	9662
1,2,6,7-TeMN	11731	0	53129	0	5841	0	42533	11612	22154	35728
1,2,3,7-TeMN	4002	0	25192	0	5841	0	25080	51395	7810	14788
12,3,6-TeMN	10632	0	116656	0	5844	0	86378	51395	23620	42653
1,2,5,6 & 1,2,3,5-TeMN	19154	0	148263	0	2678	0	119278	12176	26090	33429
4-MDBT	396484	1987219	1928927	278219	164151	15021	87946	170551	980018	1064118
3,2-MDBT	237200	1864707	1186290	411418	279131	18497	115719	157873	879283	929701
3-MP	86883	855170	366861	147803	254090	23795	149174	174586	76498	73222
1-MDBT	221827	998533	1189968	165876	111319	13318	72565	146998	751962	793988
2-MP	136711	1445325	366899	430022	686829	99746	185421	235591	165244	72787
2-MAn	1287	26680	2827	2462	9141	1763	17494	18014	7309	8267
1-MAn 9-MP	176132	2485021	485531	293957	501526	66417	262089	328552	195837	163686
1-MP	176039	1216983	486596	161029	295472	52124	208648	258959	87373	190384
9,2-EP	12523	471426	227358	81411	223774	21576	53741	54881	53285	15504
1-EP	45751	66854	49844	7174	12607	1131	17454	15958	4578	1670
3,5 & 2,6-DMP	46036	363233	226497	68237	230130	35928	50675	50404	26049	23502
2,7-DMP	32898	236916	70316	79385	207962	47295	23431	29911	25995	47457
1,3 & 3,9& 2,10& 3,10-DMP	165243	2216219	964028	364591	1032844	198885	181111	245449	171189	24107
1,6&2,9&2,5-DMP	87747	1176819	963221	181881	560897	115591	102679	126102	81980	152926
1,7-DMP	86521	936104	69705	225710	425267	165776	184814	211047	101420	150517
2,3-DMP	87285	220637	429631	42570	123005	34707	41090	49883	18552	71407
1,9 & 4,9-DMP	71881	664941	429941	48218	124634	38902	61495	80491	31022	90122
Mfla	6655	46409	9283	6298	23601	4620	35833	34254	0	4030
Mfla	6129	13074	3959	2313	8149	2902	14070	11226	1558	1006
Mfla	7645	306457	38234	33784	107576	44513	74204	61142	19856	15879
Mfla	0	171643	8587	0	16201	10930	0	0	0	0
Mpyr	3276	89454	20311	10468	48198	7827	38527	34190	3899	4250
Mpyr	2938	341490	81718	59221	257866	39928	43284	41628	30807	26572
Mpyr	3085	162416	29542	29863	93103	22013	35906	27234	15433	12639
Ret	0	66970	29338	15965	48393	27020	13776	11228	16203	12804

Table 7.4: Areas of Alkylated Compounds (Semi-Quantitative)

7.2 Calculation of Retention Indices

The next tables 7.5 & 7.6 are made by the RT of the components identified by qualitative analysis, using the Kovatz formula 6.2.2.2

Name	RT	KOVATS RI			
nC10	8.81	1000.0	2,3,6-TMN	14.00	1609.3
nC11	9.66	1100.0	Fluorene	14.28	1633.0
nC12	10.44	1200.0	1,2,4-TMN	14.28	1633.0
N	10.56	1215.4	1,2,5-TMN	14.28	1633.0
nC13	11.22	1300.0	1,4,5-TMN	14.82	1678.4
2-MN	11.45	1429.9	nC17	15.09	1700.0
1-MN	11.60	1449.2	Cad	15.17	1605.9
nC14	12.01	1400.0	Pr	15.18	1606.5
2-EN	12.28	1431.4	1,2,4,7-TeMN	15.46	1626.2
1-EN	12.39	1443.7	1,2,5,7-TeMN	15.46	1726.2
2,6 & 2,7-DMN	12.39	1443.7	2,3,6,7-TeMN	15.46	1726.2
1,3 & 1,7-DMN	12.52	1459.0	1,2,6,7-TeMN	15.80	1749.9
1,6-DMN	12.57	1464.0	1,2,3,7-TeMN	15.88	1755.4
1,4 & 2,3-DMN	12.73	1482.1	1,2,3,6-TeMN	15.95	1760.4
1,5-DMN	12.76	1486.1	1,2,5,6 & 1,2,3,5-TeMN	16.21	1778.5
nC15	12.89	1500.0	nC18	16.54	1800.0
1,2-DMN	12.89	1500.0	DBT	16.63	1805.9
1,3,7-TMN	13.77	1588.0	Ph	16.72	1811.2
1,3,6-TMN	13.81	1592.2	P	17.08	1832.2
nC16	13.90	1600.0	An	17.24	1841.5
1,2,6-TMN	13.98	1607.0	nC19	18.28	1900.0
1,2,7-TMN	13.98	1607.0	4-MDBT	18.33	1902.3
1,4,6 &1,3,5-TMN	13.98	1607.0	3 & 2 -MDBT	18.70	1921.0
1,6,7-TMN	13.98	1607.0	3-MP	19.08	1939.3

Table 7.5: Retention Indices

Name	RT	KOVATS RI			
1-MDBT	19.17	1943.7	Mpyr	28.41	2299.1
2-MP	19.21	1945.8	Mpyr	28.41	2299.1
2-MAn	19.39	1954.4	nC23	28.44	2300.0
1-MAn & 9-MP	19.61	1964.5	Ret	29.35	2330.2
1-MP	19.61	1964.5	nC24	31.56	2400.0
nC20	20.37	2000.0	Chry	34.19	2499.7
9-EP & 2-EP	20.99	2026.5	nC25	34.20	2500.0
1-EP	21.39	2043.3	nC26	38.05	2600.0
3,5 & 2,6-DMP	21.39	2043.3	nC27	41.33	2700.0
2,7-DMP	21.75	2058.0	B[b]Fla	43.86	2778.3
1,3 & 3,9 & 2,10 & 3,10 -DMP	22.07	2071.0	B[k]Fla	43.96	2781.2
1,6&2,9&2,5-DMP	22.25	2078.2	nC28	44.60	2800.0
1,7-DMP	22.25	2078.2	B[e]Py	46.24	2851.8
2,3-DMP	22.25	2078.2	B[a]Py	46.73	2867.0
1,9&4,9-DMP	22.39	2083.8	Pery	47.44	2888.7
nC21	22.80	2100.0	nC29	47.82	2900.0
Flu	22.84	2101.7	nC30	50.95	3000.0
Pyr	24.22	2154.0	nC31	54.03	3100.0
nC22	25.49	2200.0	InPy	56.40	3179.4
Mfla	25.98	2217.1	DB[a,h]An	56.71	3189.6
Mfla	26.64	2240.1	nC32	57.03	3200.0
Mfla	26.74	2243.8	B[g,h,i]Pery	58.26	3244.7
Mfla	27.48	2268.8	nC33	59.83	3300.0
Mpyr	27.48	2268.8	nC34	63.06	3400.0

Table 7.6: Retention Indices 2

Chapter 8

Interpretation of Experimental Data

In this chapter the aromatic compounds of the samples will be evaluated based on the analysis data. In addition graphical representations of these data are presented. These kind of representations helps to group the Prinos samples according to their geochemical information, and thus one has a better view of these samples and Prinos basin.

8.1 Comparative Evaluation of PAH compounds

8.1.1 Parent PAH Compounds

Studding the parent PAH compound bar-charts 7.1 one can observe that the samples derived from the same wells are similar. Also the wells appear to have differences in between. Sample E1-14 is slightly different especially for P, DBT, and An from the other E1As samples; as it is derived from the same well but from a different geological layer.

Samples K1 are also very similar in between with E1 according to parent PAH bar-charts.

The parent PAH hierarchical clustering plot 8.1 agrees with all of the above since samples PB appear to be in an isolated area on the graph from the other samples. PN2 samples are also classified as a common data gather.

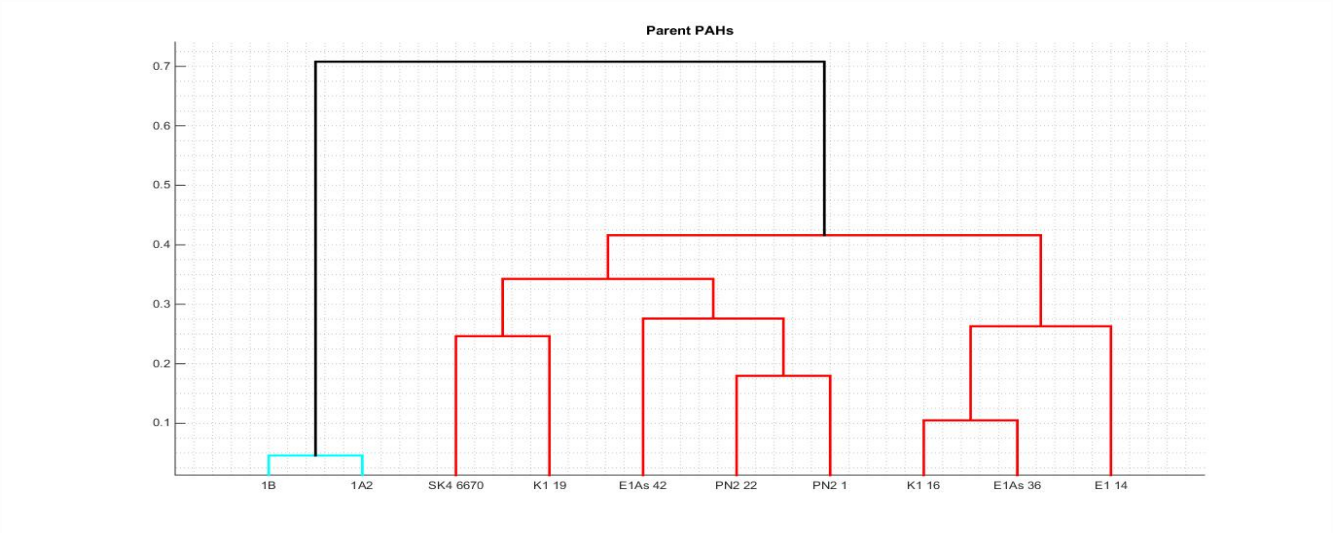


Figure 8.1: Hierarchical Clustering of Parent PAHs

PCA analysis 8.2 classifies the samples according to parent PAH components in 4 clusters the first cluster includes PN2 samples the second E1-14, E1As-36, and K1-16, the third cluster includes E1As-42, Sk4-6670, and K1-19 and the fourth cluster the samples from the well PB-26. This PCA plot gives very similar information with the relative hierarchical clustering plot for the comparative evaluation of the samples using parent PAH compounds.

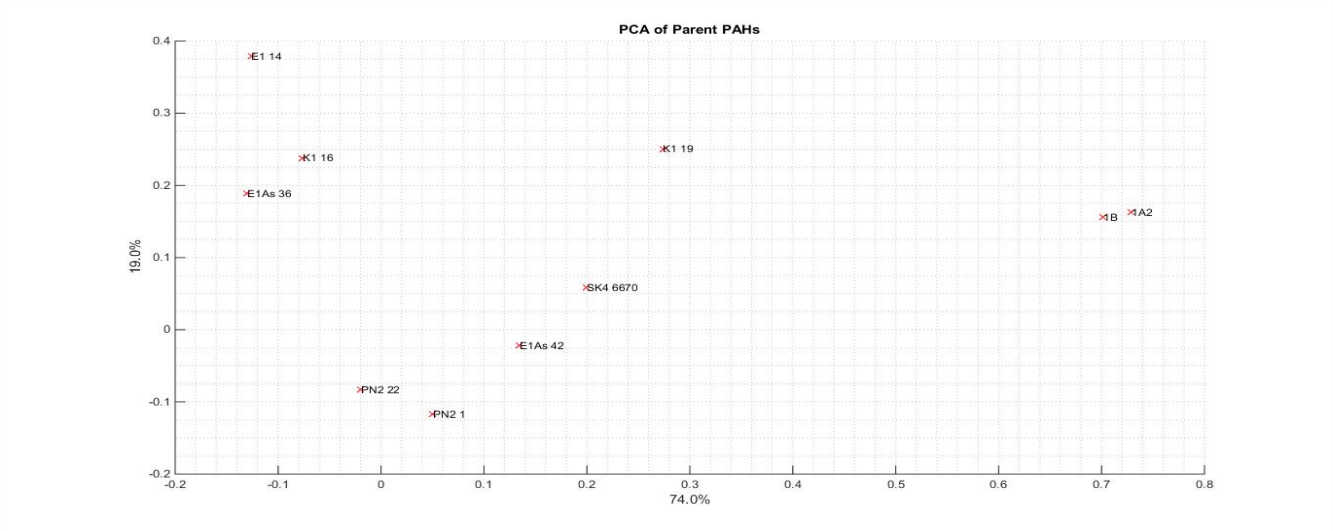


Figure 8.2: PCA plot of Parent PAHs

8.1.2 Alkylated PAH Compounds

The bar-charts between the samples of the alkylated components 7.2 look very similar for PB26 and PN2 samples. Distribution of alkylated naphthalenes for samples E1As-36 and E1-14 is slightly different from sample E1As-42. K1 oil samples have different component distribution in between. A comment for sample SK4-6670 distribution is that it looks very similar with the distribution of the sample K1-19.

The Hierarchical clustering plot of alkylated components 8.3 can provide us with the information; again for the homogeneity between the PB26 and PN2 samples. In addition this diagram categories the oils in common concentration groups K1-16 with E1As-42, E1-14 with E1As-36, and SK4-6670 with K1-19. The PCA **??** method fully agrees with all of the above, since the samples are categorized in five groups like in the Hierarchical clustering plot.

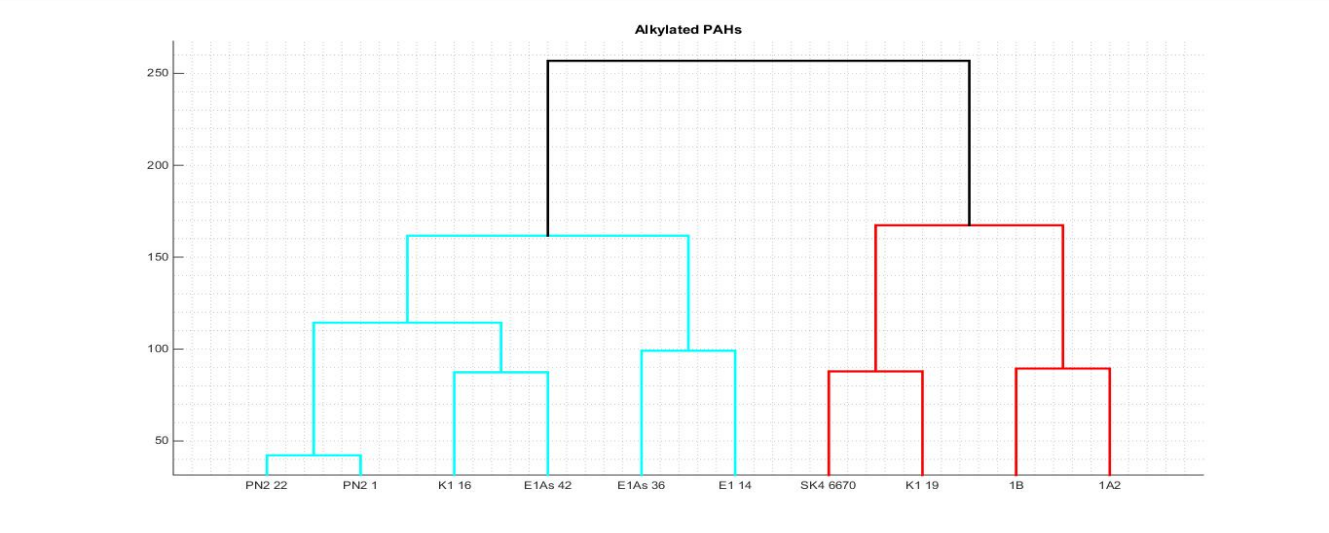


Figure 8.3: Hierarchical Clustering of Alkylated PAHs

From all of the above considerations; one can assume that Prinos oil field is separated in 2 main groups. in the first group, the samples of the PB26 well are included. The second group consists of all the other wells in Prinos basin. The oils of SK4-6670 and K1-19 samples are very similar in between. Also PN2-1 and PN2 22 samples have identical properties and distributions of alkylated and parent PAHs concentrations. Samples E1As-36 and E1-14 appears to have similar properties and distributions. Finally samples K1-16 and E1As-42 also seems to have common properties relative to the distributions of PAHs.

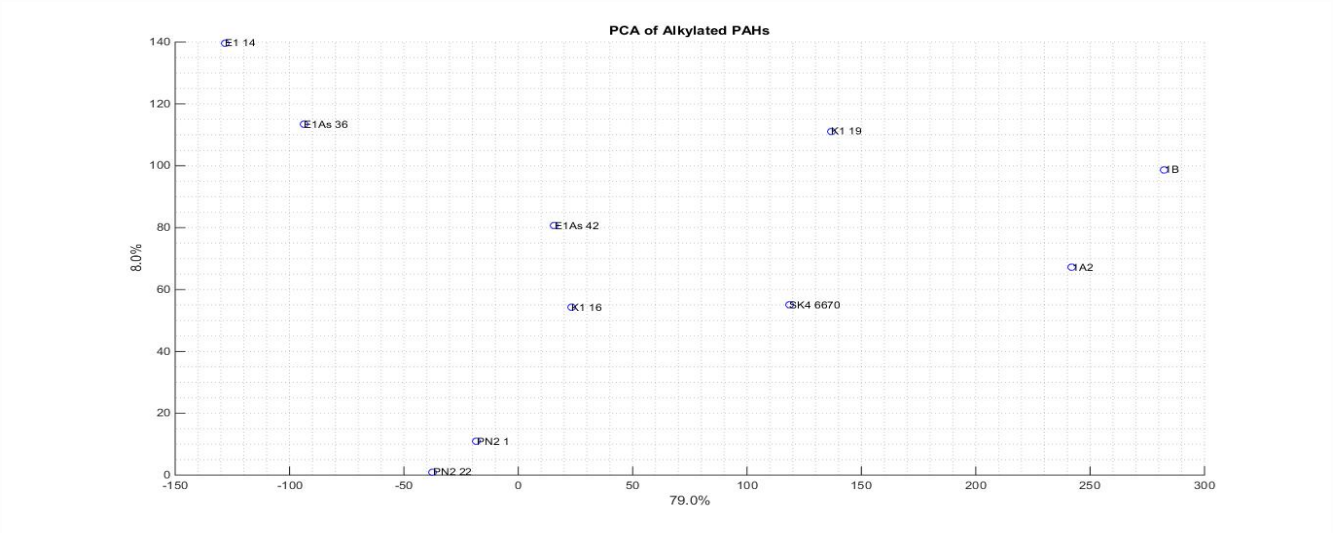


Figure 8.4: PCA of Alkylated PAHs

8.2 Geochemical Interpretation of Prinos Oils

	SK4	K1		E1			PN2		PB-26	
	SK4-6670	K1-16	K1-19	E1As-42	E1As-36	E1-14	PN2-22	PN2-1	1-B	1-A2
MNR	0.83		0.92		0.99				1.06	0.70
ENR										2.20
DNR-1	1.49		0.68		2.09				2.24	0.53
TDE-1										
TDE-2										
TNR-1	0.64	0.00	0.72	0.00					0.78	0.73
TNR-2	1.19	0.50	1.48	0.00					1.01	1.47
TNRs	3.71		4.54						2.57	4.24
TNR-2	2.11		2.07						1.54	1.89
MDR	1.79	1.99	1.62	1.68	1.47	1.13	1.21	1.16	1.30	1.34
MPI-3	0.63	0.62	0.75	1.27	1.18	1.04	0.71	0.70	0.85	0.41
MPR	0.78	1.19	0.75	2.67	2.32	1.91	0.89	0.91	1.89	0.38
DPR	0.31	0.18	0.15	0.27	0.27	0.26	0.26	0.22	0.21	0.40
[1,2,5-TMN]/[1,3,6-TMN]	1.20		2.61						1.69	1.39
[1,2,7-TMN]/[137-TMN]	0.00	0.00	0.00		0.00				0.00	0.00
TMNr	0.66	1.00	0.54		1.00		0.00	0.00	0.45	0.67
TeMNR-1	0.45		0.03		1.01		0.11	0.96	0.29	0.23
DPR 2	0.38	0.25	1.01	0.35	0.49	0.29	0.13	0.14	0.26	0.32
DBT/P	1.66	0.53	2.40	0.70	0.33	1.23	0.38	0.48	7.42	9.40

Table 8.1: Values of Ratios of The Samples

The hierarchical clustering and PCA plot using this time, the ratios of the alkylated components, 8.6 was able to identify the common well between the E1 samples and the different geological layers between E1 and E1 As samples, the different and unique properties of PB26 well samples, the homogeneity of PN2 samples and the simmilarities between SK4 and K1 samples.

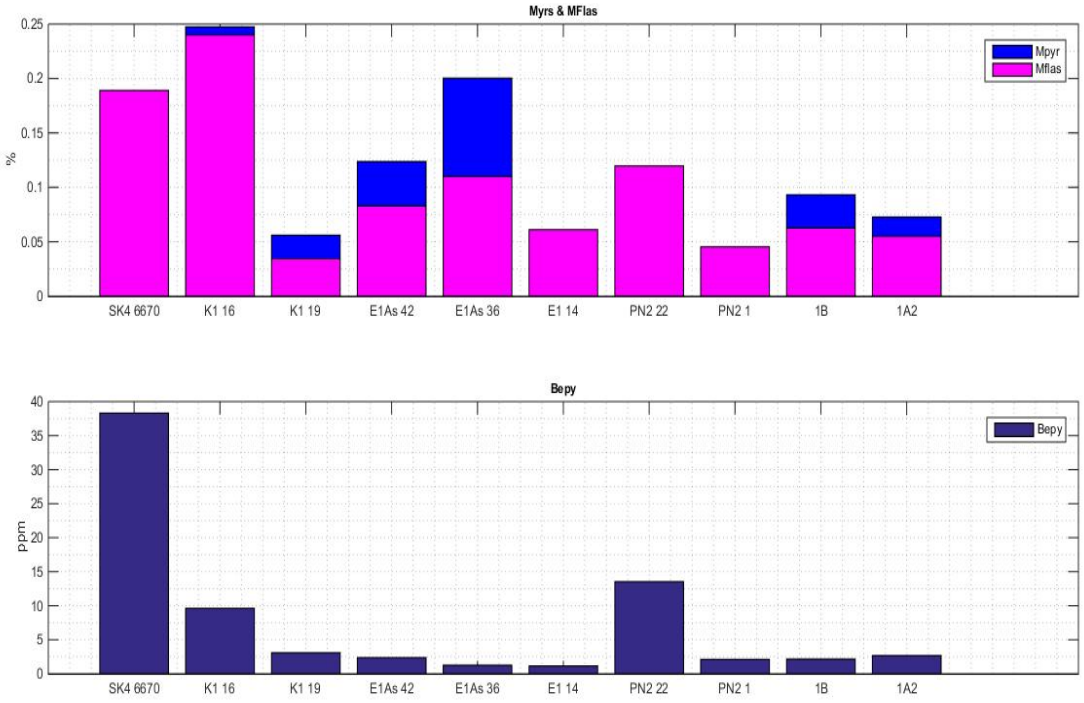


Figure 8.5: MFlas-Mpyrs and B[e]Py Bar Chart

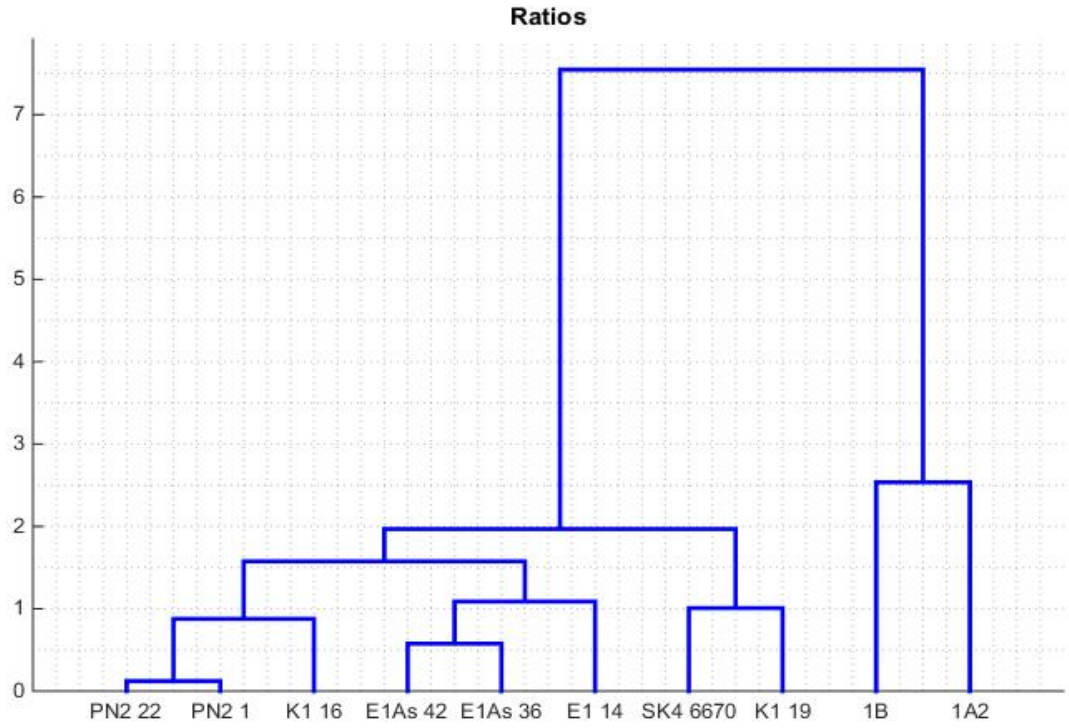


Figure 8.6: Hierarchical Clustering of the Ratios of the Samples

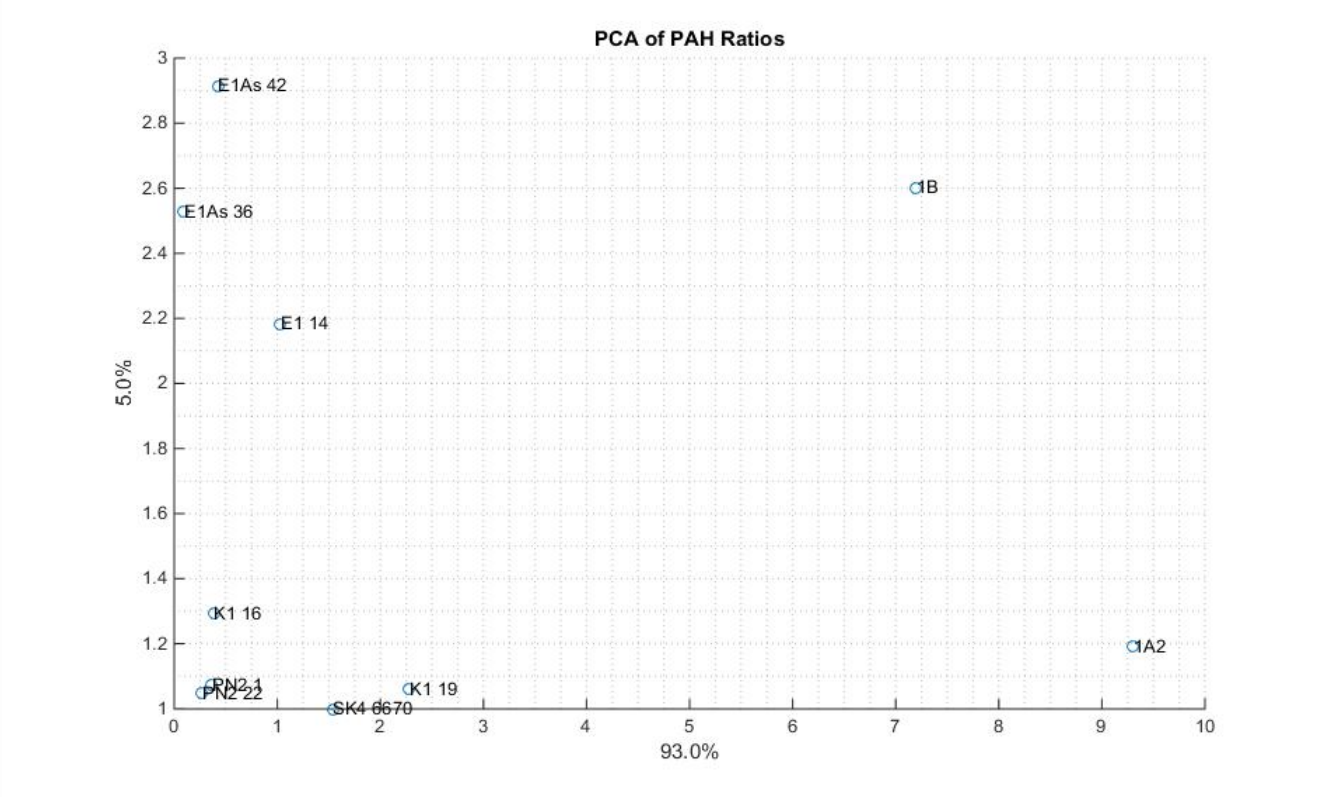


Figure 8.7: PCA of PAHs Ratios of the Samples

8.2.1 Samples K1

For the sample K1-16 the alkyl-naphthalene compounds are almost absent, while for sample K1-19 the concentrationns are slightly higher. It is noted that alkylated components such as MDBTs, MPs, DMPs, Mflas, and Mpyrs have relatively high peaks for the sample K1-16.

For sample K1-16, the concentration of parent PAHs are high enough for An, B[a]Pyr, B[b]Fla, B[e]Pyr, B[g,h,i]Pery, Chry, DB[a,h]An, DBT, Fla, Flu, P and Pyr. However no B[k]Fla, Ipyr and Pery were found in sample K1-16.

For sample K1-19, The concentration of parent PAHs are high enough for An, B[b]Fla, B[e]Pyr, B[g,h,i]Pery, Chry, DBT, Fla, Flu, P and Pyr. No B[a]Pyr, DB[a,h]An ,Ipyr and Pery were found in sample K1-19.

The concentrations of sample K1-16 are higher for Chry, DBT and P. This same phenomenon occurs in sample K1-19.

Samples K1-19 and K1-16 belong to the fine grained sediments of Kalirahi. According to the ratio DBT/P mostly originate from **carbonates and shale source rock** formations respectively. These results appear to agree with *Kiomourtzi et.,al*

(2016)[6], since shales and dark gray clay rocks exists at the depth of 2329.60-2331.20m . In lower depths of 2266.05-2266.75m the rock appears to have a slightly higher concentration of carbonates.

P mainly comes from phenanthrenoids, which in turn originate from terrestrial organic material. Similarly, Chry which occurs in a high abundance, suggests that woody plants are the precursor organic matter. Thus the K1 samples mainly include terrestrial organic precursors. According to *M.Radke., et all (1994)* [23], the [125-TMN] / [136-TMN] ratio for the sample K1-19, has a relatively high value of 2.61, which indicates that the source organic material is terrestrial, since 1,2,5-TMN usually originates from resinous organic matter. Lastly according to the B[e]Pyr plot, the incoming **terrestrial organic matter** of the K1 samples display intermediate values compared to the rest of the data for sample K1-16 and low values for sample K1-19 which corresponds to **marine organic matter**. In addition, the relatively high values of DBT correspond to a marine environment, and therefore corresponds **planktonic organic material**.

K1 samples are characterized as low to **very low biodegraded** oils since Fla, Pyr and MPs appear in very low concentrations.

The maturation effect is similar for both samples K1-16 and K1-19 according to the ratios: MDR, MPI-3, MPR, DPR, TMNr. These ratios show that K1-16 is slightly more mature that K1-19, but they are all still characterized as **very-immature to immature**, as the ratios for both samples range between the values of 0.15 to 1.99 with an average of 0.88. The higher the ratios, the higher the effect of maturation. The immaturity of these samples can also be viewed by the very low concentrations or absence of B[a]Pyr and B[e]Pyr.

Since the relative concentrations of Flu and DBFs are very low while the concentrations ofDBT are comparatively higher, the environment can be characterized as **Saline- Hypersaline – Reducing**. Also, samples K1-16 and K1-19 are extracted at deep depths; thus, changes appear in their relative concentrations of DBT, Chrys, and Ps. These changes may be able to determine whether or not there were certain environmental conditions during the time of deposition.

The concentration of MFlas and MPyrs is relatively high for sample K1-16. According to *Jiang Chunqing (1998) PHD* [4] the concentrations of the alkylated versions of Fla and Pyrs increase during burial procedures. This also means that the origin of these unsubstituted PAHs is mainly due to **combustion processes** of the organic material. The shallower sample K1-19 has concentrations of MFlas and MPyrs that are lower-probably mostly**biological precursors**. B[e]Pery concentration shows mostly **higher pyrogenic effect for K1-16** and lower level of **pyrogenic processes for K1-19**.

8.2.2 Samples PN2

Samples PN2 22 and PN2-1 are the two samples that come from the PN2 borehole. The PN2 samples appear to have relatively higher concentrations of Aromatic Hydrocarbons than the other samples, and thus the peaks are higer and cleaner. The absence of all alkylated Naphthalenes is observed except for TMNs which are present. All other alkyl- Compounds are present, including MDBTs, MPs, DMPs, Mflas, and MPyrs.

Slightly higher values of DBT and P are observed in sample PN2-1 as compared to PN2 22, which in turn has relatively higher values for all the other components.

These samples belong to the northern regions of the basin and are characterized by a medium grained rock matrix formation. PN2-1 was collected at a depth of 2655.00m and PN2 22 was collected 2709.63m.

Since DBT/P ratio of samples PN2-1 and PN2 22 have values 0.38 and 0.51 respectively, it can be inferred that these two samples are produced by **shale source rocks**.

The maturation ratios MDR, MPI-3, MPR, and DPR indicate that the PN2 samples are **very immature** oils. PN2 22 has maturity ratios with values between 0.26 and 1.21, and PN2-1 has maturity ratios with values between 0.22 and 1.16. They have similar maturation effects, since the average values are these ratios of 0.77 and 0.75 respectively.

The presence of B[e]Pyr, B[a]Pyr, Chry, and P can be justified by the **very high rates of incoming terrigenous higher plant material**. Results of the concentrations of B[e]Pyr indicate that the relatively high terrestrial organic matter was deposited in the basin. Cadalene – which is a component that comes from conifer trees – as well as retene, are present in higher quantities in PN2 samples. This is another index that identifies the high rates of incoming higher plant organic matter. The DBT in PN2 samples have lower values than P, this likely indicates that **marine organisms** contributed to its creation.

DBT and Ps in PN2 samples correspond to high values in respect to the very low abundance of Flu this may imply a **Saline – Hypersaline Reductant** environment with organic material coming mainly from **terrestrial organisms** like higher plants and resinous conifer trees.

The **biodegradation** of PN2 samples is **relatively higher** than the other samples, because Fla, Pyr, and C4-Ps are observed in higher concentrations in comparison with the other samples.

The B[e]Pyr plot shows that samples PN2 22 and PN2-1, has low values and

thus **low pyrogenic procedures**. MFlas and MPyrs in PN2 samples occur in very high relative concentration, which indicates the **combustion derived PAHs**.

8.2.3 Samples E1AS and E1

The absence of alkylated-naphthalenes is apparent for the sample E1As-42. Only MNs, DMNs, and some TeMNs are observed in sample E1As-36. All of the other alkyl-compounds are observed in relatively high concentrations. In addition absence of alkylated-naphthalenes is observed in sample E1-14.

The relative concentrations of Chry, DBT, and P in these samples appear to have some differences.

Some PAHs are missing from samples E1As-42 and E1-14 such as B[a]Pyr, B[e]Pyr, Ipyr, DB[a,h]An, and B[g,h,i]Pery however sample E1As-36 does includes DB[a,h]An and B[g,h,i]Pery.

In general, these samples do not contain significant amounts of alkylated-Naphthalenes for quantitation. Only some TMNs are observed in Sample E1As-36. The Areas of the rest of the compounds are normally quantified.

Samples E1As-36 and E1-14 have higher concentrations of Chry than sample E1As-42. Also E1As-36 and E1-14 have approximately same concentrations of DBT, although they are lower than the concentration of E1As-42. Concentrations of P in E1As-42 and E1As-36 are relatively higher than in E1-14. These three samples appear to have relatively similar amounts of Pyr. B[b]Fla and B[e]Pyr are slightly higher in value for the sample E1-14.

Oil sample E1As-42 (collected at 3009.91m) comes from a **shale** formation and is geologically older than E1As-36 (collected at 3008.32m), which also comes from shale formations according to the Ratio of DBT/P (which is less than 1 in both of E1AS samples, 0.74 for E1As-42 and 0.38 for E1As-36). Sample E1-14 is shallower than the E1AS samples, at a depth of (2852.00m), and originates in **carbonate rock formations** (DBT/P=1.25)

From the parent PAHs Plot and the relative concentrations of Chry, P, and DBT we can assume the geological conditions and changes that took place in that era can be assumed. Chry is formed in small amounts during the burning or distillation of coal, crude oil, and plant material. The **reducing environmental conditions** during this period of formation of the oil of sample E1As-42 were relatively stronger than those for the sample E1As-36. (More **oxic** conditions appear later on for the formation of oil sample E1As-36, since the relative concentrations of DBT are reducing between the two). These conditions affect the concentration of P in the samples as well the higher

the (relative) concentration of DBT, the higher the concentration of P.

The change in the **environmental oxic conditions** or in the rate of incoming organic material may have an effect on the concentration of Chry. Studies have shown that switching anoxic and oxic conditions for Chrys and Flas do not have a significant effect on their process of biodegradation. *Vitte, I., et all (2011)*[40]. Therefore the concentration of Chry is likely not affected by oxic conditions; in addition, the difference in the oxic conditions seems to not interfere with the concentration of P. According to this information, it can be assumed that since there is a difference in the concentration of Chry it must be caused by differences of the lithology of the E1AS samples, (E1As-36 sandstone type is arkose, and E1As-42 type is greywacke) these two types of sandstones correspond to different oryctology and geochemistry). The increased concentration of Chry could be explained if the rate of organic matter was increasing, but this is unlikely since other compounds such as B[e]Pyr, retene, and cadalene should also show increased values.

The precursor organic material of these two groups of samples seems to be the same, as both samples include information about **terrestrial higher plant organic matter with the participation of planktonic life-forms**, since DBT, P, and Chry are present in all of the samples.

The Maturation effect is the same for the samples E1As-42 and E1As-36 with an average value for the ratios MDR, MPI-3, MPR, DPR and DPR 2 of 0.99 and 0.93 respectively. Maturation of sample E1-14 is less than that of the E1AS samples, with an average value of 0.85. This is probably because sample E1-14 is younger and is located in shallower and cooler environments. The Maturation level of samples E1AS and E1 is higher than the other sample groups, but this oil is still characterized as **immature**.

The relative concentration of Fla, Pyr, and MPs are relatively lower in sample E1-14, which means that the biodegradation level of this sample is lower compared to the E1AS samples. In general, the oil in the area of the E1AS and E1 samples is characterized as **low-biodegraded oil**.

The concentrations of Mpyr and Mflas are relatively high for sample E1-14. The combustion processes for this sample is probably higher than for the E1As samples. Combustion derived PAHs of the E1 sample is relativelly **higher** than those of the E1As samples PAHs. B[e]Pyr's concentration levels show **low pyrogenic effect** for E1As samples and higher for E1-14.

8.2.4 Samples PB-26

The PB-26 borehole includes samples 1-B and 1-A2, both of which come from **Carbonate rock formations**. The sample 1-A2 appears to have higher concentrations of alkylated-naphthalenes than 1-B. This is normal, due to the fact that sample 1-A2 is denser than 1-B.

Samples 1-B and 1-A2 lack many parent PAHs, but also appear to have a good correlation in the normalized values of concentrations in the parent PAH plot. These oils also have alkylated Naphthalenes from small amounts of MNs and ENs to Higher amounts of DMNs, TMNs, and TeMNs. They also include the rest of the alkylated components.

These Samples appear to have lower relative concentrations in heavier alkyl-components such as Mflas and DMPs.

Sample (group) PB-26 includes 1-B and 1-A2, which were collected at close depth of 2620.71m and 2620.85m respectively.

The parent PAHs and the alkylated-compounds plots are almost identical, which means that these samples come from the same petroleum and have undergone the same environmental conditions, maturation, and biodegradation processes.

The high abundance of DBT in these samples corresponds to high **reductant environment and Hypersaline source**. These samples also include naphthalene series in the aromatic fractions of samples 1-B and 1-A2, and correspond to **mainly marine oils**. Less organic matter may have been derived from **woody organisms**, since P is also observed in the PAHs plot. The ratios MNR, DNR-1, TNR-1, TNRs, TNR-2, MDR, MPI-3, MPR, DPR, TMNr, TeMNR-1 and DPR 2 for alkyl-naphthalenes and MPs have average values between 0.89 and 1.1 which corresponds to oils with low to **very low maturation levels**.

Fla, Pyr and MPs are very low in concentrations and sometimes even have a value of 0. This is an indication of **very low biodegraded** oil.

The intermediate relative concentrations of MFlas, MPyrs of PB26 samples,indicate mostly **Terrestrial organic matter** and B[e]Pyr concentration shows **low pyrogenic effect**.

8.2.5 Samples SK4

SK4 Oil samples originate from **carbonate source rocks**. SK4-6670 is the only Sample from the SK4 borehole that is investigated in this thesis.

Sample SK4-6670 comes from the sparse batch, since no sample is left for dense analysis.

All parent PAHs are observed in this Sample. MNs and DMNs are also observed in small but quantifiable amounts, but no other alkyl-Naphthalenes can be observed and determined with accuracy. Heavier alkylated PAHs can also be quantified.

SK4-6670 is a sample that was obtained at a depth of 2032.92m, and originates from Carbonate rocks. The relative abundance of DBT, Chry, and P are high in this sample. The relative concentration of DBT in sample SK4-6670 is lower than that of the other samples; this may correspond to an environment of deposition that is **low in salinity**. Ipyr is observed in relatively high quantities but lower concentrations, most notably with B[b]Fla, Pyr and B[e]Pyr. The ratios [125-TMN]/[136-TMN], TDE-1, and [127-TMN]/[137-TMN] are relatively high which is an indicator of **terrestrial organic material**.

The Maturation of SK4-6670 is the highest of all the samples. According to the maturation parameters MNR, ENR, DNR-1, TNR-1, TNRs, TNR-2, MDR, MPI-3, MPR, DPR, TMNr, TeMNR-1 and DPR 2 the average maturation value is 1.6. Thus the oil can be characterized as **immature to low mature**.

Fla, Pyr and MPs are calculated in not very small quantities, especially for Fla, these values of the components point to a relatively **medium biodegradation level**.

The concentrations of MFlas and MPyrs are very high for sample SK 6670, which means that **Terrestrial organic matter** is the main organic source for this area. Also, since B[e]Pyr occurs with the highest concentration comparing all the samples, **pyrogenic** procedures were the dominant process.

8.3 Interpretation of Prinos Oil

		Maturation	Biodegration	Type of Org. Matter	Pyrogenic effect	Combustion/Natural Biological Precursors	Saline-Hypersaline levels	Rock formation
SK4	SK4-6670	Immature	Medium levels	Terrestrial	Higher Levels	Mostly Combustion Derived Precursors	low salinity	Carbonates
K1	K1-16	Very- Immature to Immature	low to very low	Terrestrial & marine	Intermediate levels	Combustion Derived	Saline- Hypersaline	Shale
	K1-19	Very- Immature to Immature	low to very low	Terrestrial & marine	Lower Levels	Mostly Bilogical	Saline- Hypersaline	Carbonates
PN2	PN2-22	Very Immature	Higher Levels	terrestrial (high rates) & marine	Lower Levels	Mostly Combustion	low salinity	Shale
	PN2-1	Very Immature	Higher Levels	terrestrial (high rates) & marine	Lower Levels	Mostly Combustion	low salinity	Shale
E1	E1AS-42	Immature	Higher Levels	Terrestrial & marine	Lower Levels	Mostly Bilogical	low salinity	Shale
	E1-14	Immature	Higher Levels	Terrestrial & marine	Higher Levels	Combustion and Natural Biological	low salinity	Carbonates
	E1AS-36	Immature	Higher Levels	Terrestrial & marine	Lower Levels	Mostly Bilogical	low salinity	Shale
PB26	A2-1	Very- Immature to Immature	Very Low Biodegration Levels	Mainly marine organisms with small participation of terrestrial	Lower Levels	Combustion and Natural Biological	Saline- Hypersaline	Carbonates
	B1	Very- Immature to Immature	Very Low Biodegration Levels	Mainly marine organisms with small participation of terrestrial	Lower Levels	Combustion and Natural Biological	Hypersaline	Carbonates
		Data from previous investigations (P. Kiomourtzi (2016))						
		Maturation	Biodegration	Type of Org. Matter	Pyrogenic effect	Combustion/Natural Biological Precursors	Saline-Hypersaline levels	Rock formation
SK4-6670		-	No Biodegradation		-	-	-	Carbonates/Shales
K1		Less Immature	No Biodegradation	Low Participation of Terrestrial with some high values	-	-	Reducive/Hypersaline	Carbonates
PN2		Immature	No Biodegradation	High participation of Terrestrial	-	-	Reducive/Hypersaline	Non-Carbonates
E1AS		Less Immature	No Biodegradation	Intermediate Participation of Terrestrial	-	-	Reducive/Hypersaline	Carbonates
E1		Immature/Less Immature	No Biodegradation	Intermediate Participation of Terrestrial	-	-	Reducive/Hypersaline	Carbonates
PB26		Less Immature	No Biodegradation	Low Participation of Terrestrial	-	-	Reducive/Hypersaline	Carbonates

Chapter 9

CHROMATOGRAM APPENDIX

No	Name	RT	No	Name	RT
1	N	10.55	**36**	3-MP	19.1
2	2-MN	11.46	**37**	1-MDBT	19.19
3	1-MN	11.61	**38**	2-MP	19.23
4	2-EN	12.29	**39**	2-MAn	19.42
5	1-EN	12.34	**40**	1-MAn 9-MP	19.63
6	26,27-DMN	12.39	**41**	1-MP	19.75
7	13,17-DMN	12.52	**42**	9,2-EP	21.43
8	16-DMN	12.57	**43**	1-EP	21.54
9	14,23-DMN	12.73	**44**	35,26-DMP	21.66
10	15-DMN	12.76	**45**	27-DMP	21.76
11	12-DMN	12.89	**46**	13,39,210,310-DMP	22.09
12	137-TMN	13.54	**47**	16,29,25-DMP	22.27
13	136-TMN	13.6	**48**	17-DMP	22.42
14	146,135-TMN	13.78	**49**	23-DMP	22.56
15	236-TMN	13.83	**50**	19,49-DMP	22.68
16	127-TMN	13.96	**51**	Fluoranthrane	23.25
17	167-TMN	13.98	**52**	Pyrene	24.24
18	126-TMN	14.03	**53**	Mfla	25.97
19	124-TMN	14.2	**54**	Mfla	26.79
20	125-TMN	14.29	**55**	Mfla	27.26
21	Fluorene	14.46	**56**	Mfla	27.32
22	145-TMN	14.51	**57**	Mpyr	27.51
23	Cadalene	15.02	**58**	Mpyr	28.21
24	1247-TeMN	15.49	**59**	Mpyr	28.42
25	1257-TeMN	15.55	**60**	Retene	29.27
26	2367-TeMN	15.65	**61**	Benzo[a]anthracene	33.84
27	1267-TeMN	15.8	**62**	Chrysene	34.75
28	1237-TeMN	15.88	**63**	Benzo[b]fluoranthrane	44.49
29	1236-TeMN	15.97	**64**	Benzo[k]fluoranthrane	44.71
30	1256,1235-TeMN	16.23	**65**	Benzo[e]pyrene	46.87
31	Dibenzothiophene	16.9	**66**	Benzo[a]pyrene	47.3
32	Phenanthrene	17.35	**67**	Perylene	48.07
33	Anthracene	17.53	**68**	Indeno[1,2,3-cd]pyrene	56.99
34	4-MDBT	18.35	**69**	Dibenz[a,h]anthracene	57.32
35	3,2-MDBT	18.73	**70**	Benzo[ghi]perylene	58.9

Table 9.1: Numbering of Components in Chromatograms

9.1 N (m/z=128)

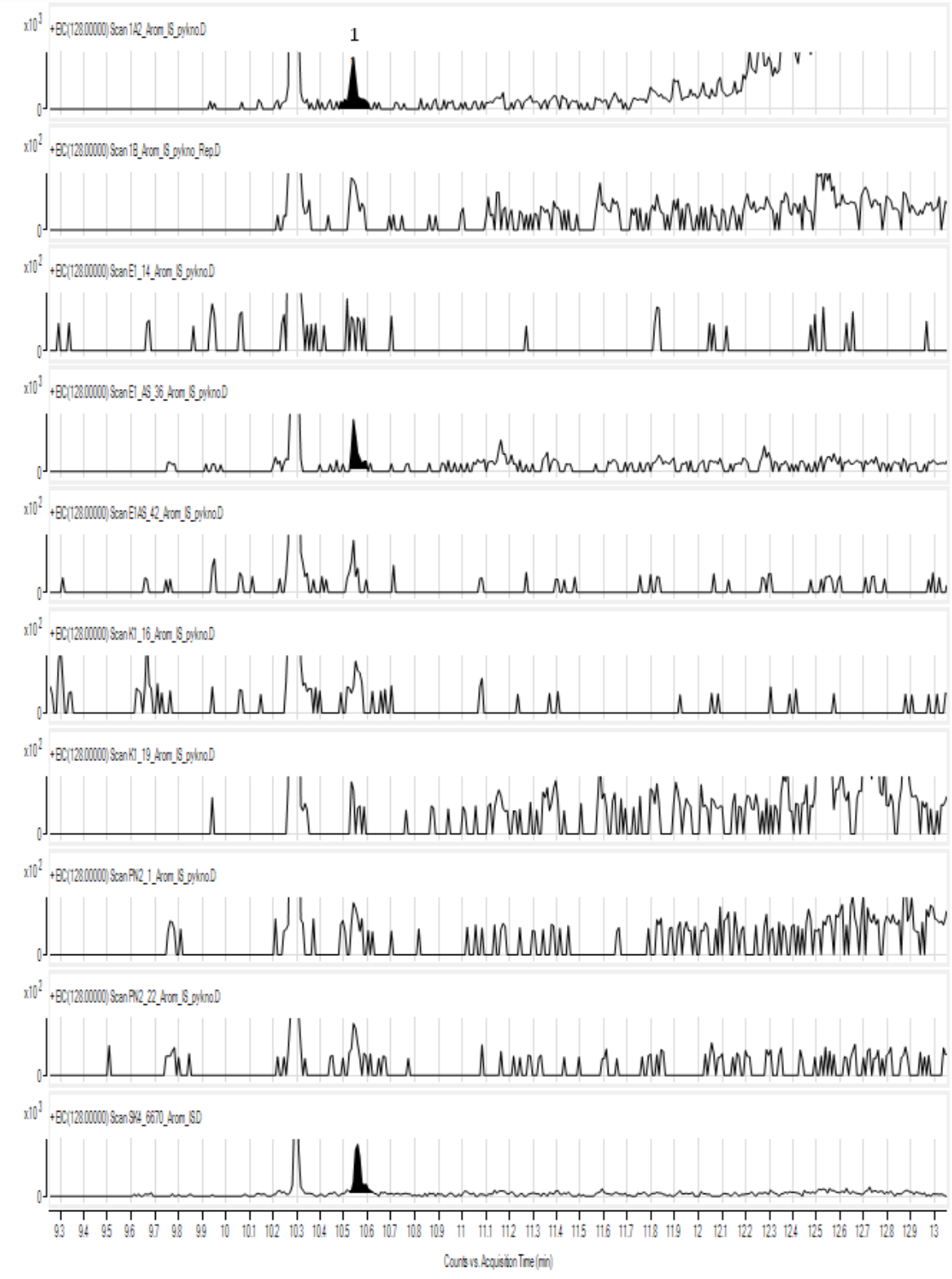


Figure 9.1: Naphthalenes (m/z=128)

9.2 MNs (m/z=145)

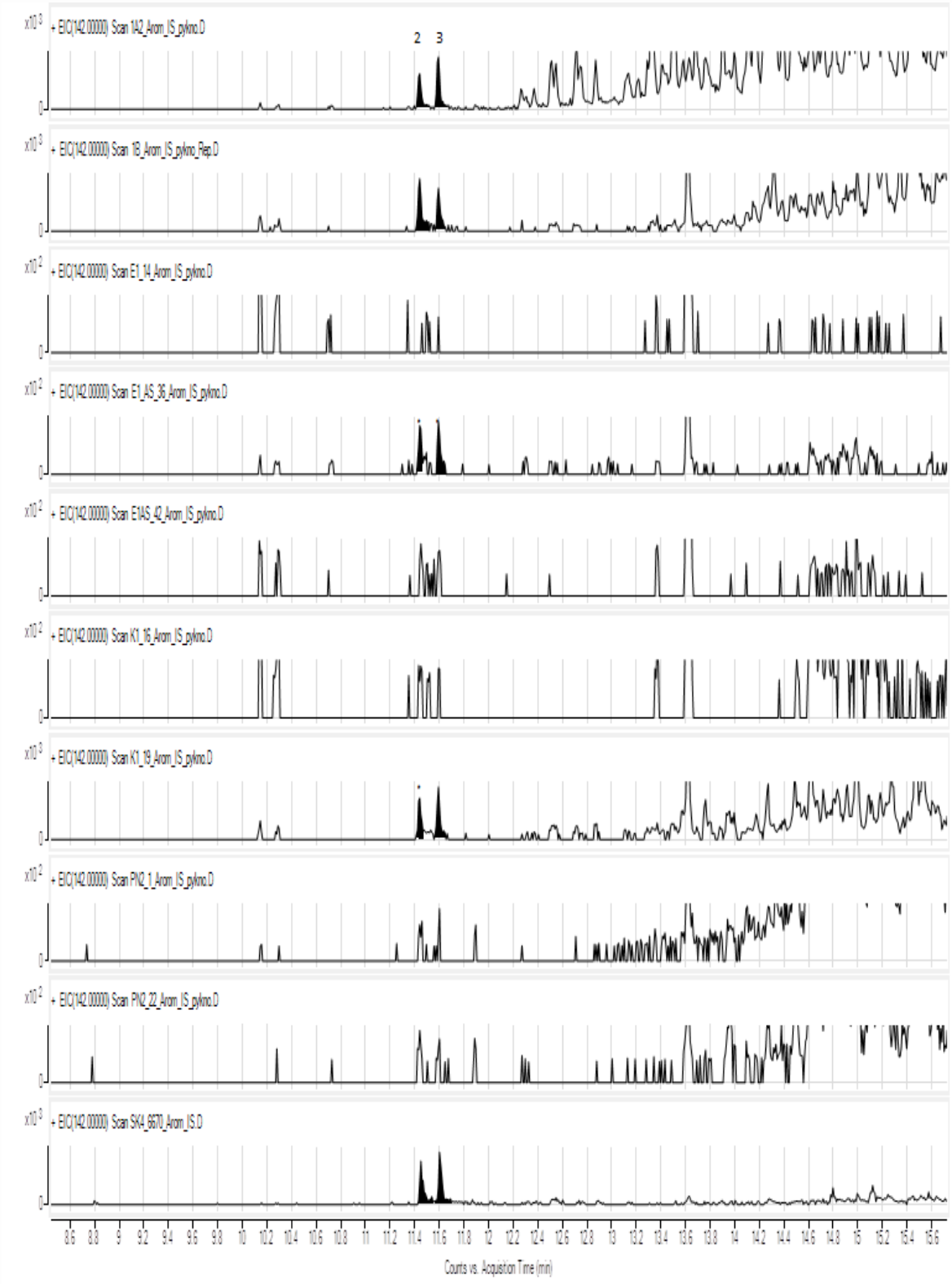


Figure 9.2: Methylnaphthalenes (m/z=145)

9.3 ENs & DMNs (m/z = 156)

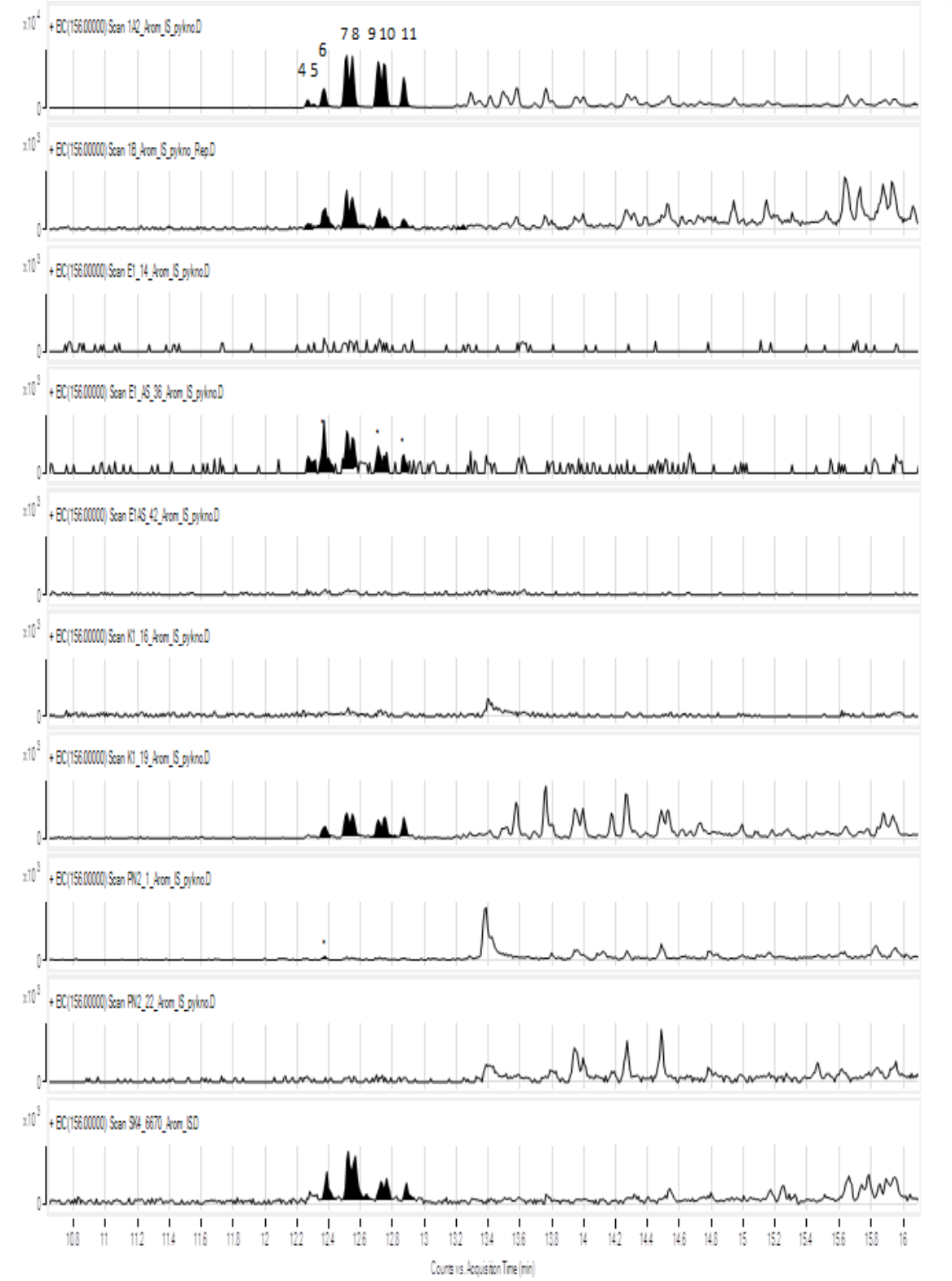


Figure 9.3: EthylNaphthalenes & Dimenthylnaphthalenes (m/z = 156)

9.4 TMNs (m/z 170)

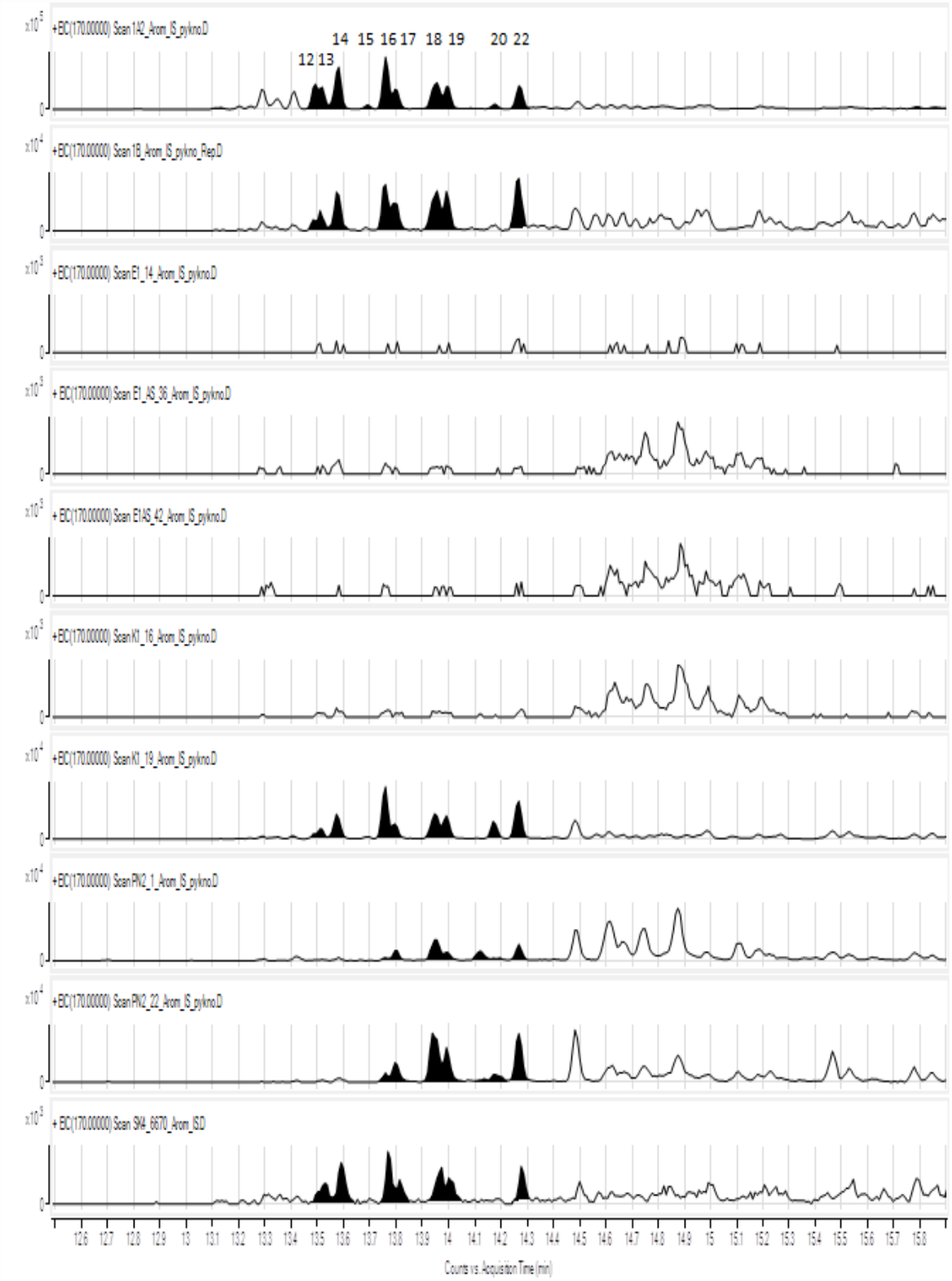


Figure 9.4: Trimethylnaphthalenes (m/z 170)

9.5 Flu (m/z = 166)

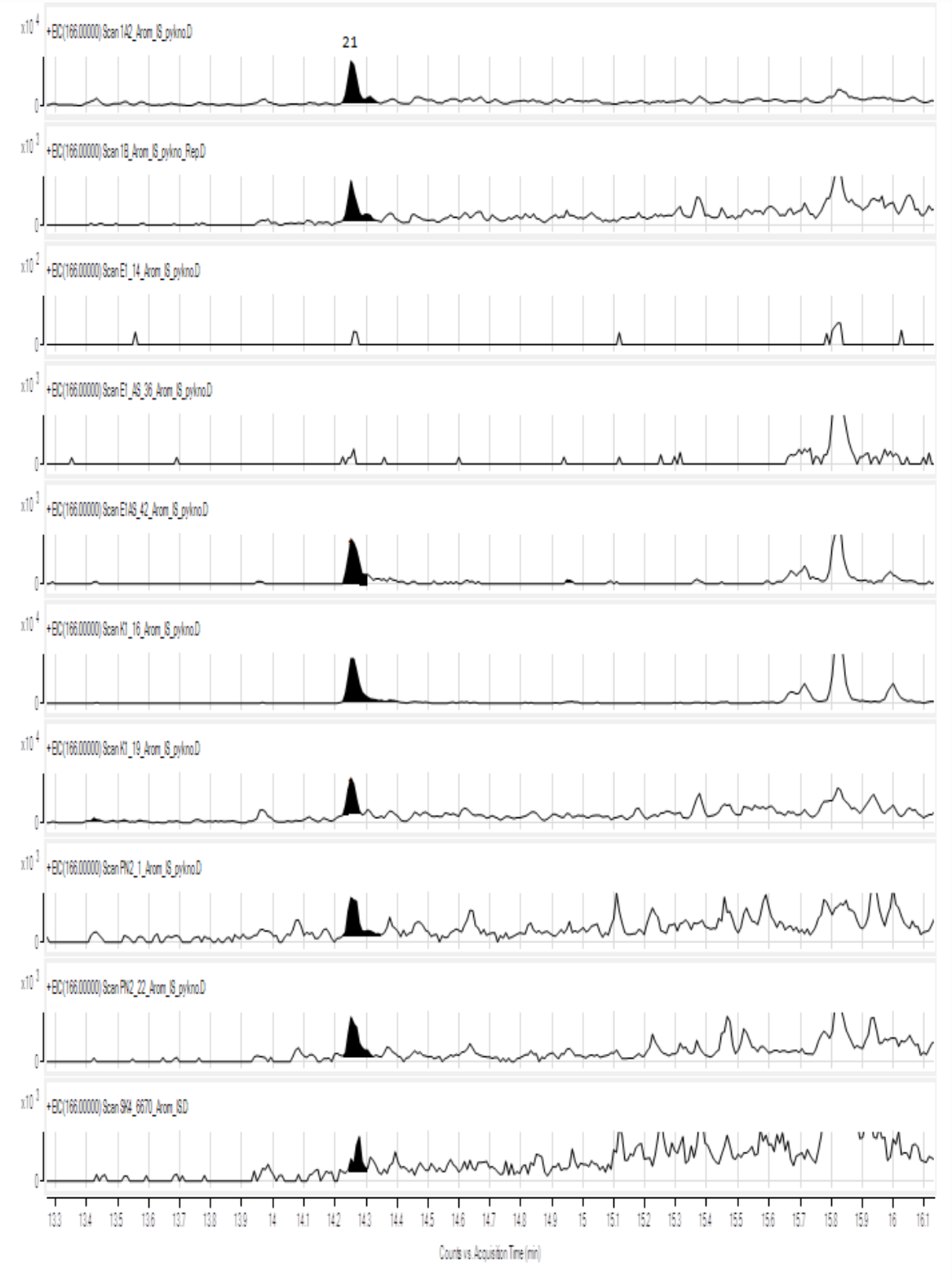


Figure 9.5: Fluorene (m/z = 166)

9.6 Cadalene (m/z = 198)

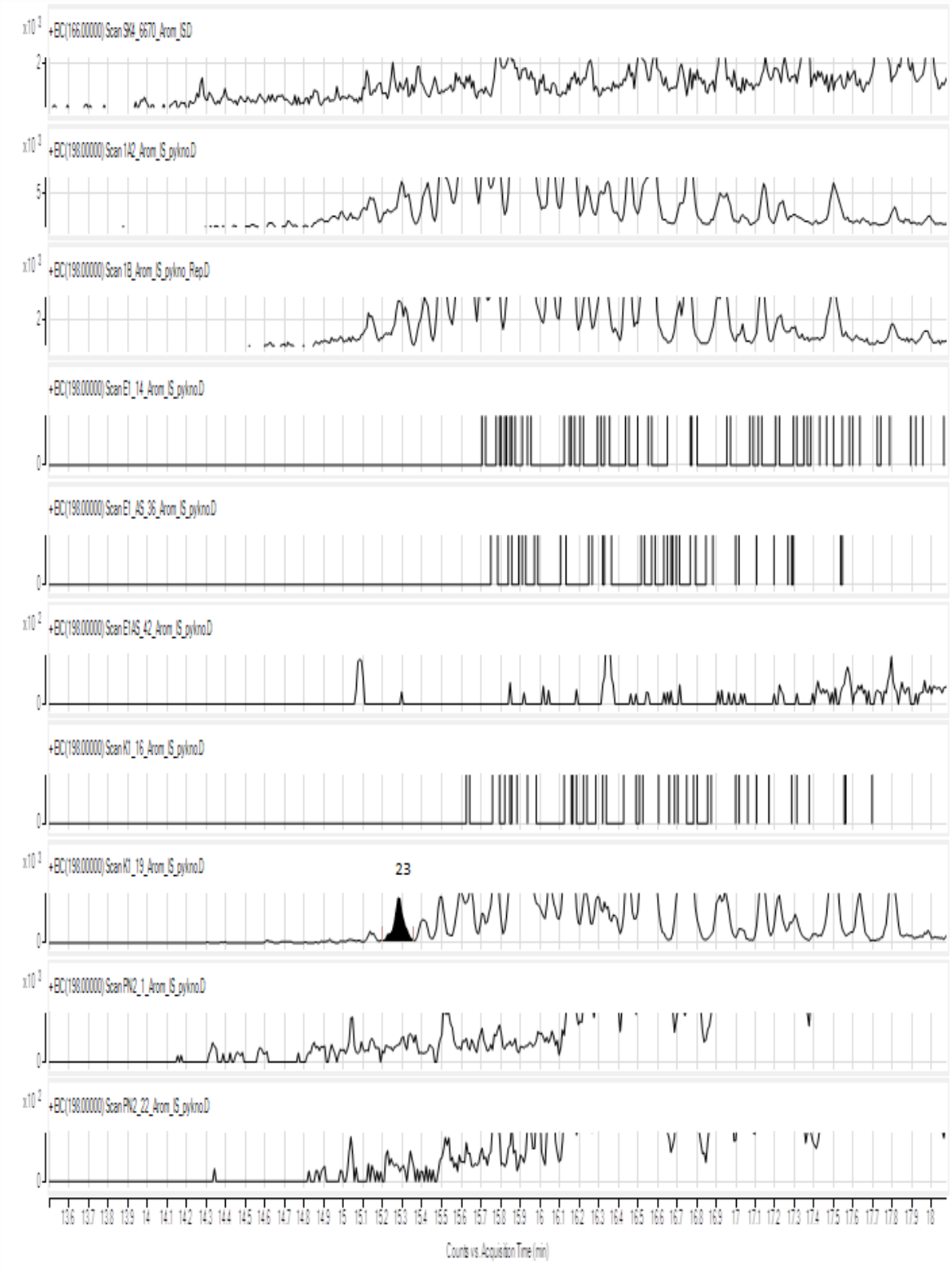


Figure 9.6: Cadalene (m/z = 198)

9.7 TeMN & DBT (m/z=184)

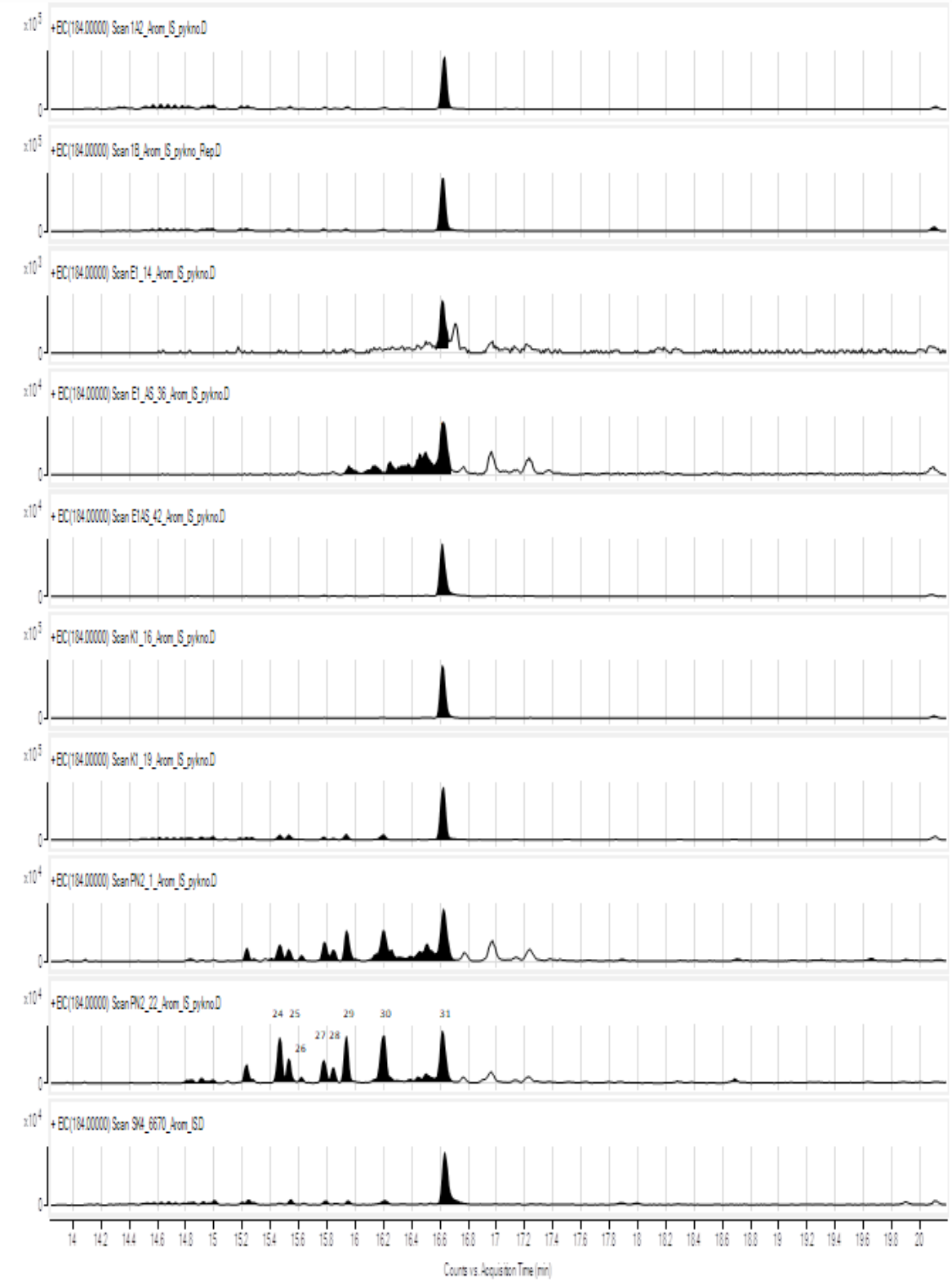


Figure 9.7: Tetramethylnaphthalenes & Dibenzothiophene (m/z = 184)

9.8 P & An (m/z = 178)

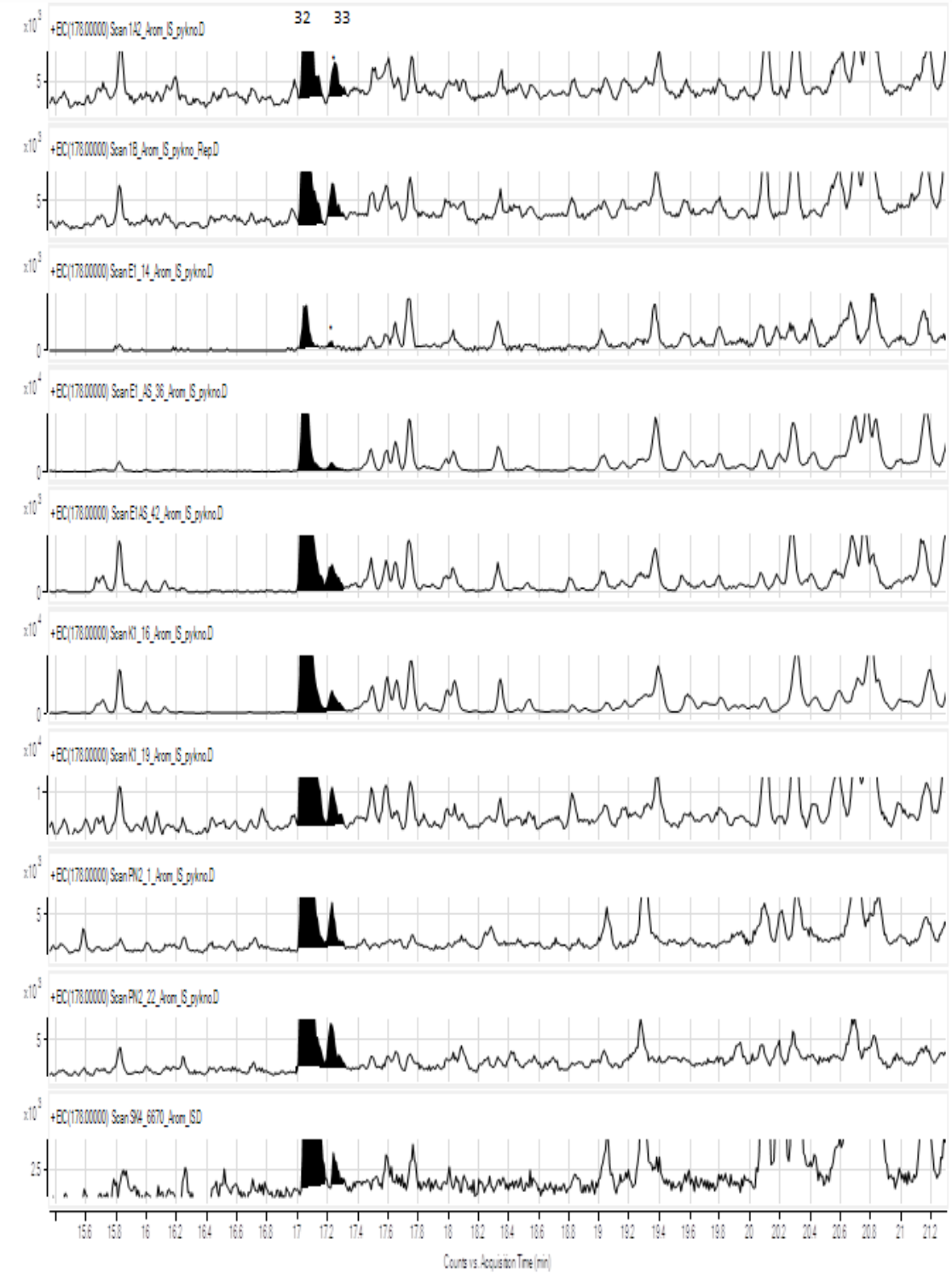


Figure 9.8: Phenanthrene & Anthracene (m/z = 178)

9.9 MDBTs (m/z = 198)

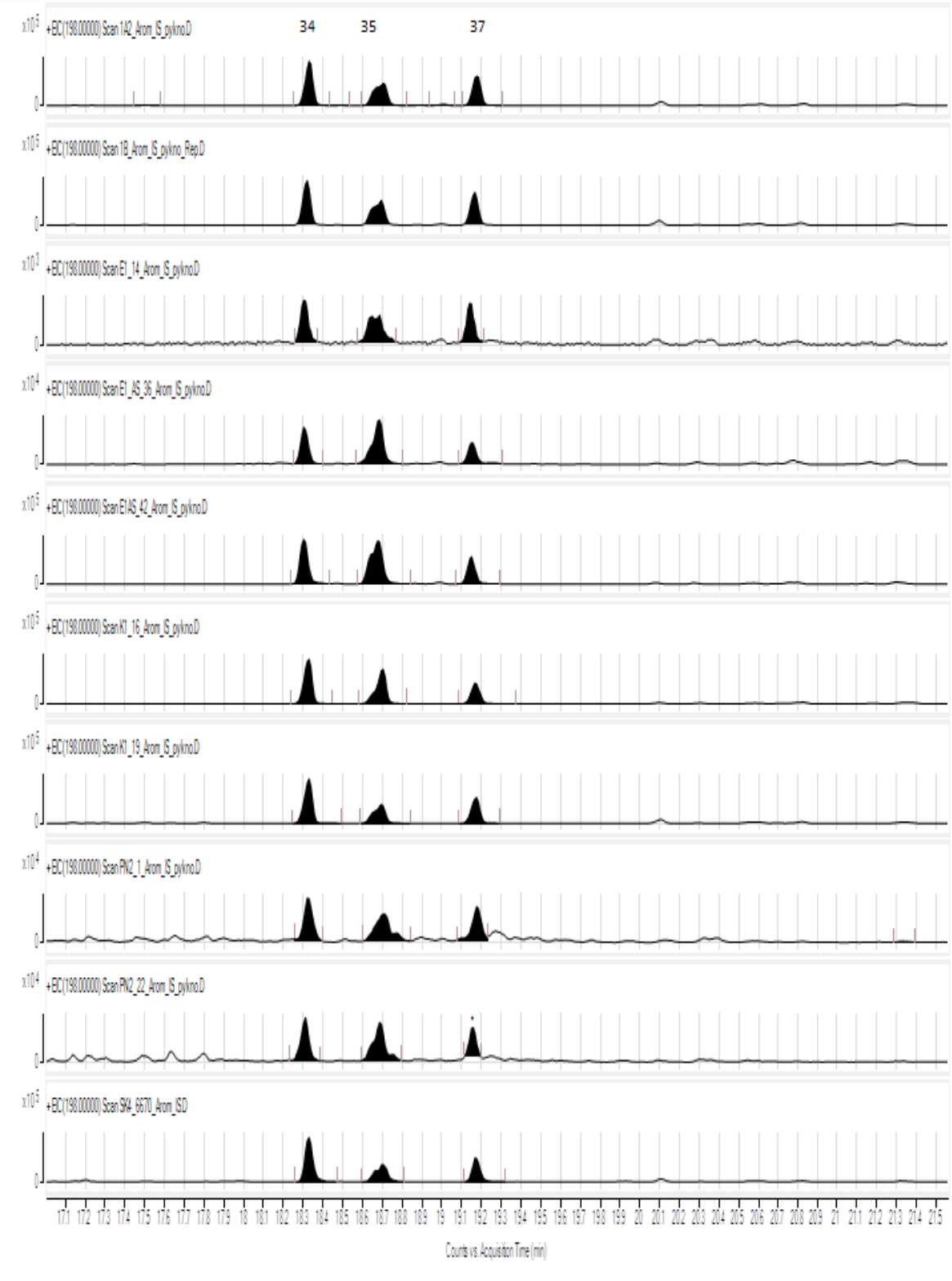


Figure 9.9: Methyldibenzothiophenes (m/z = 198)

9.10 MPs & MAns (m/z = 192)

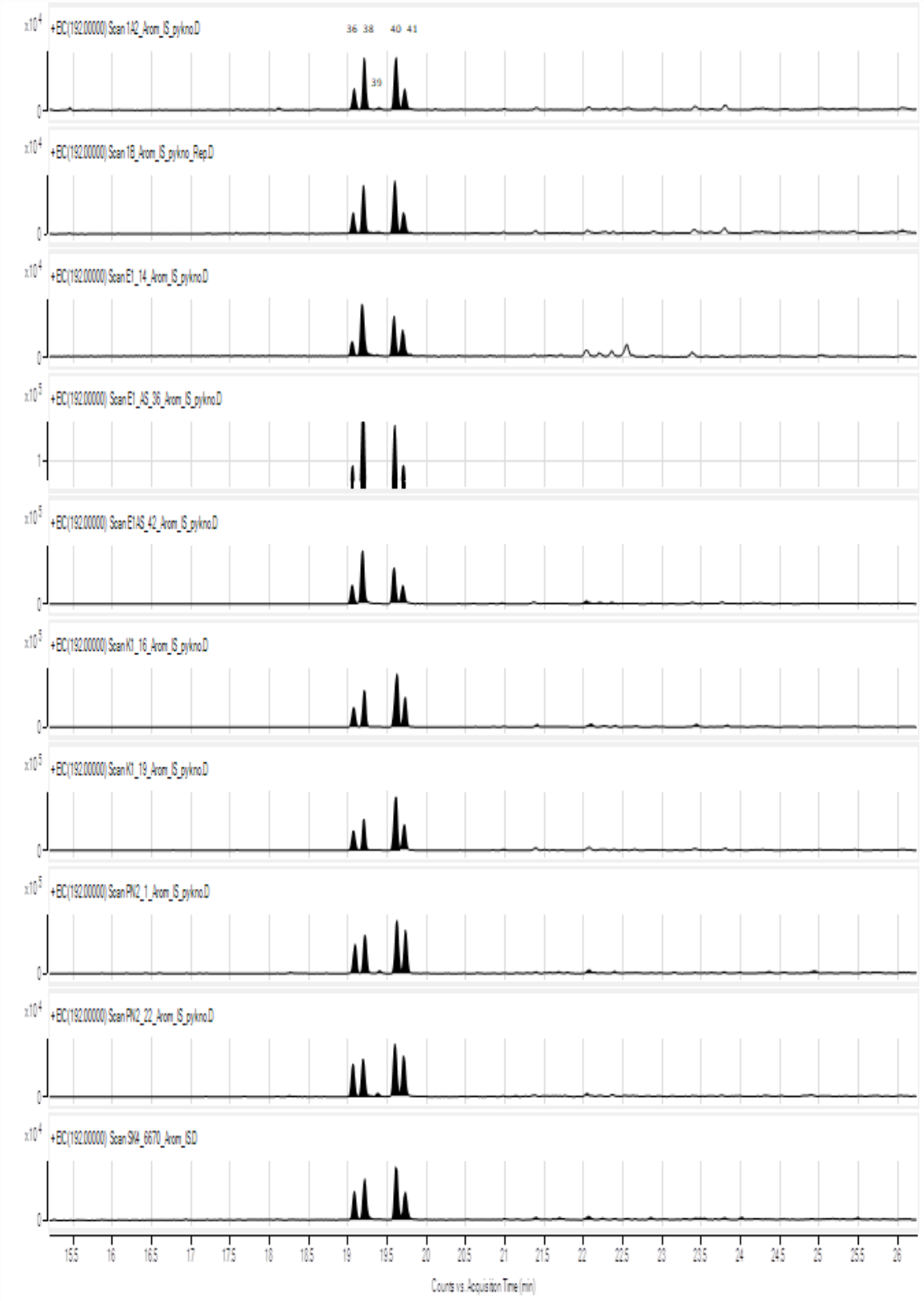


Figure 9.10: Mehylphenanthrenes & Methylanthracenes (m/z = 192)

9.11 EPs & DMPs (m/z = 206)

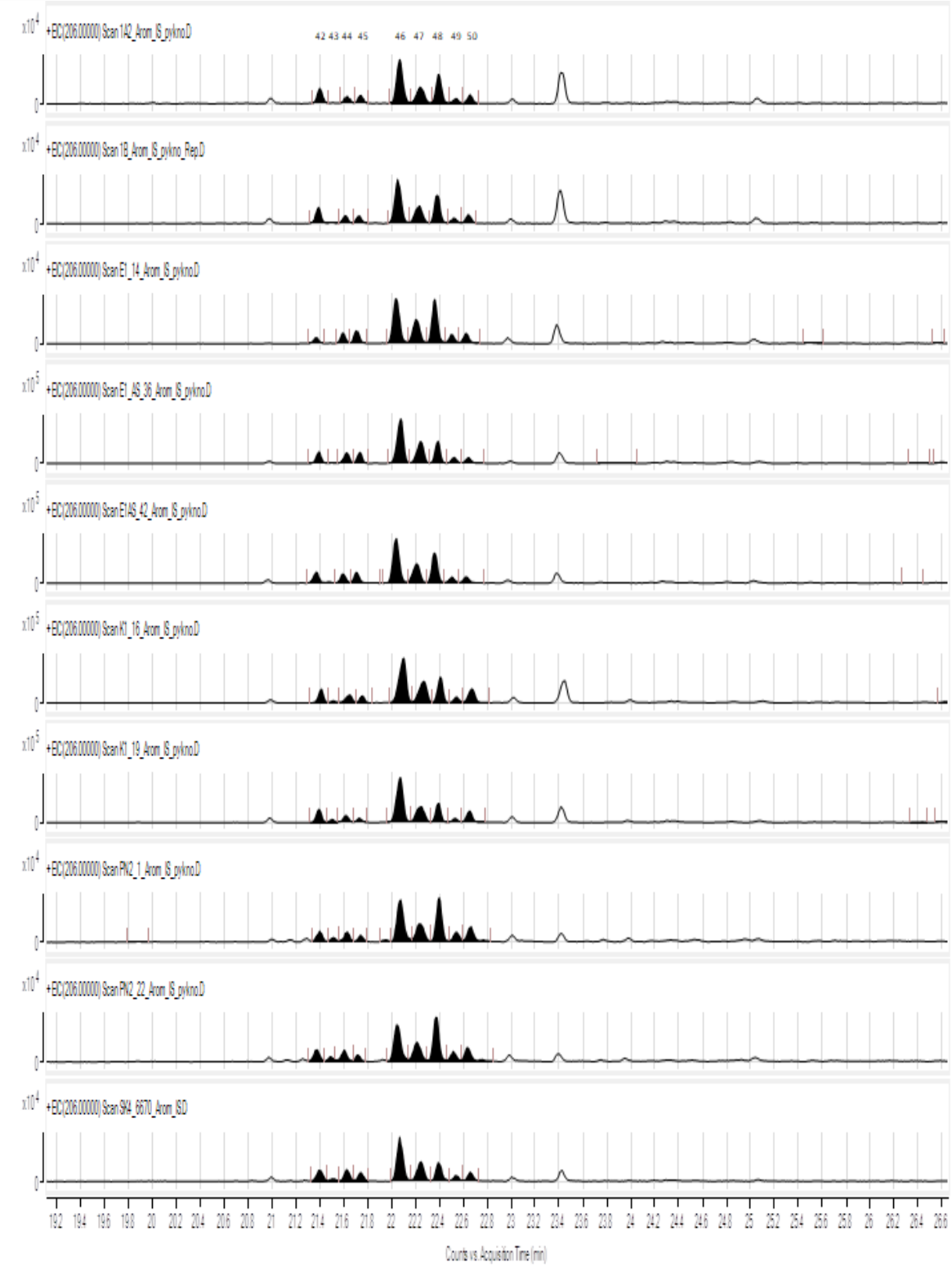


Figure 9.11: Ethylphenanthrenes & Dimethylphenanthrenes (m/z = 206)

9.12 Fla & Pyr (m/z = 202)

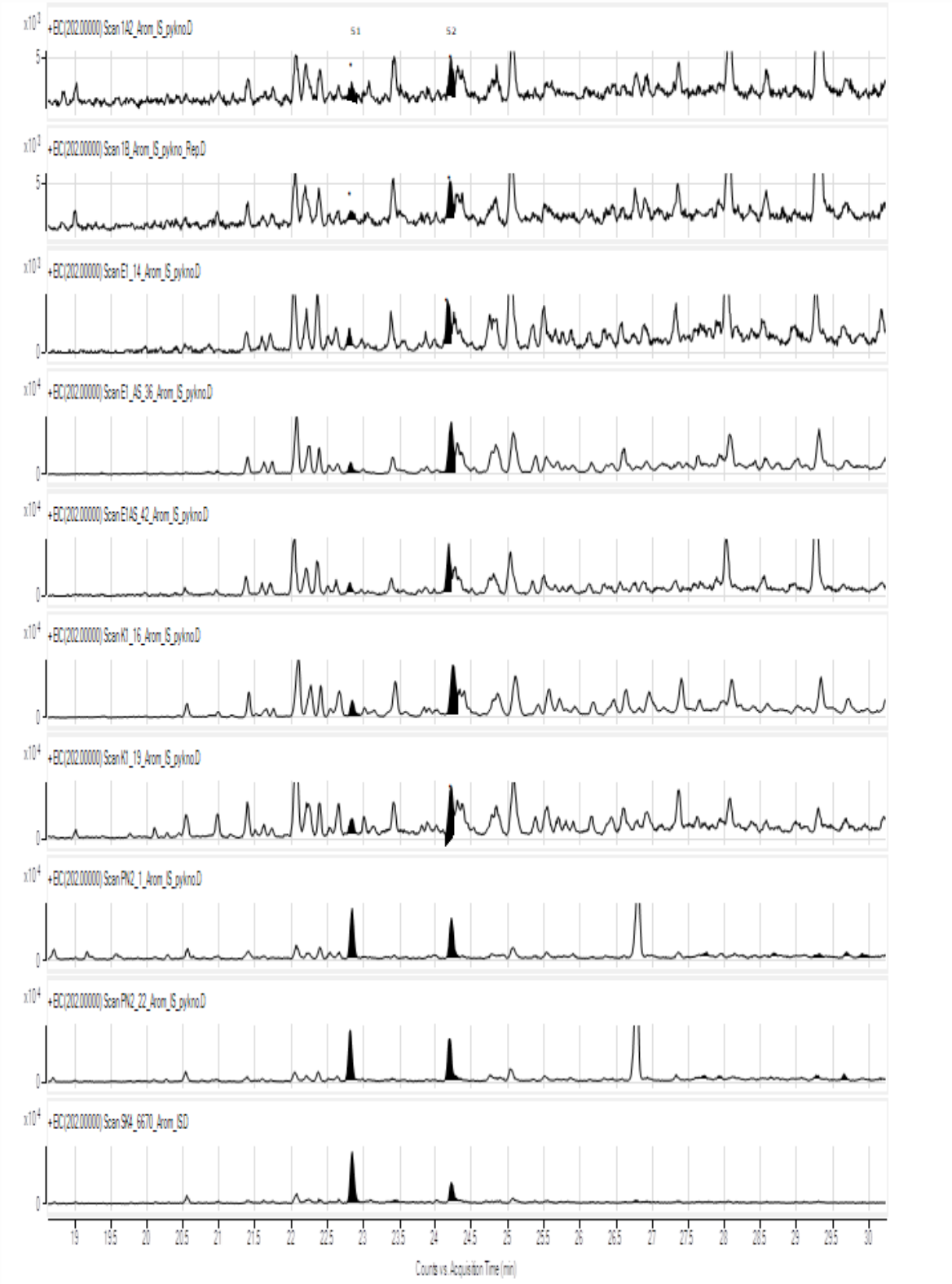


Figure 9.12: Fluoranthrene & Pyrene (m/z = 202)

9.13 MFlas & MPyrs (m/z = 216)

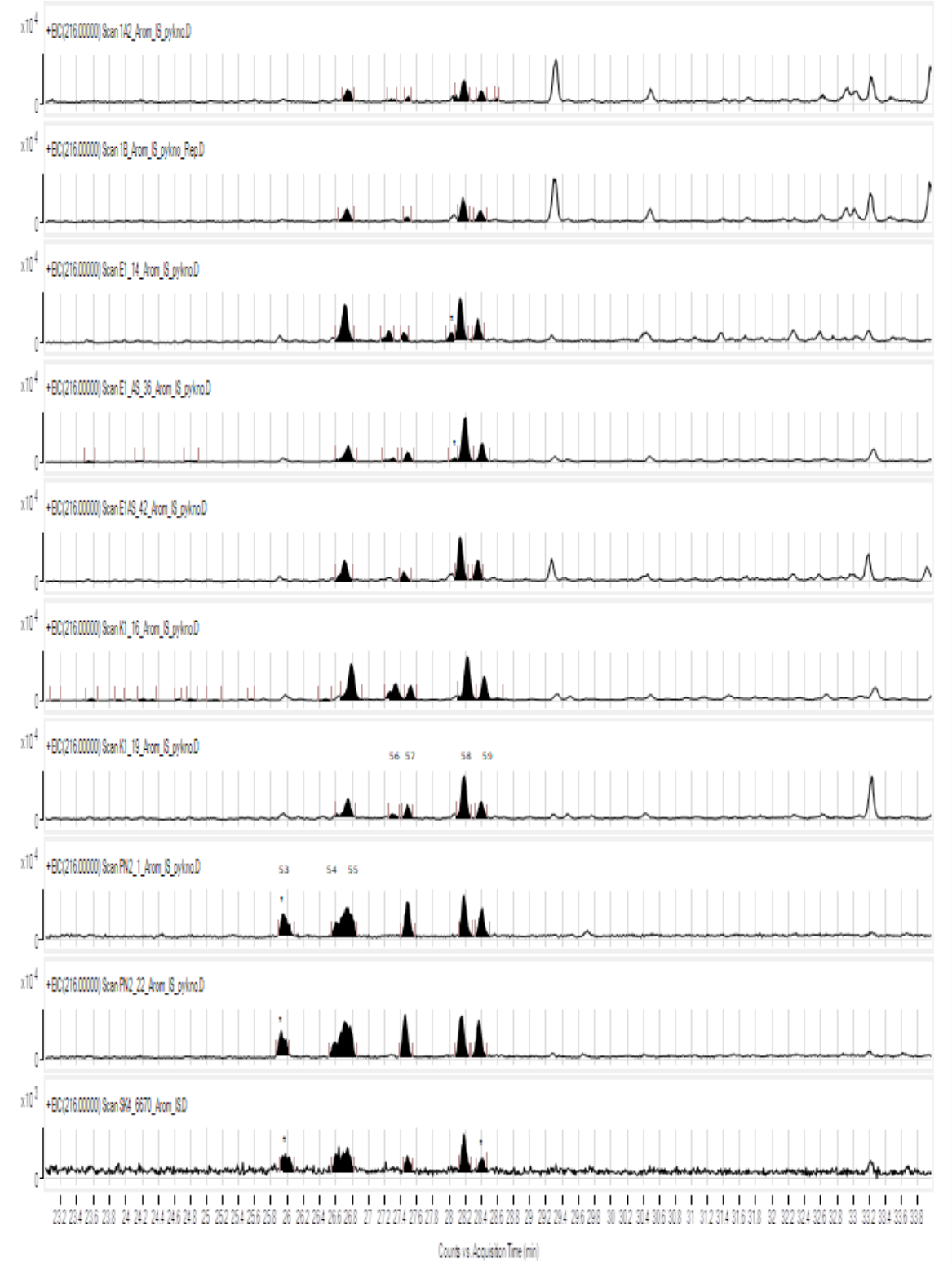


Figure 9.13: Methylfluoranthrenes & Methylpyrenes (m/z = 216)

9.14 Retene (m/z = 234)

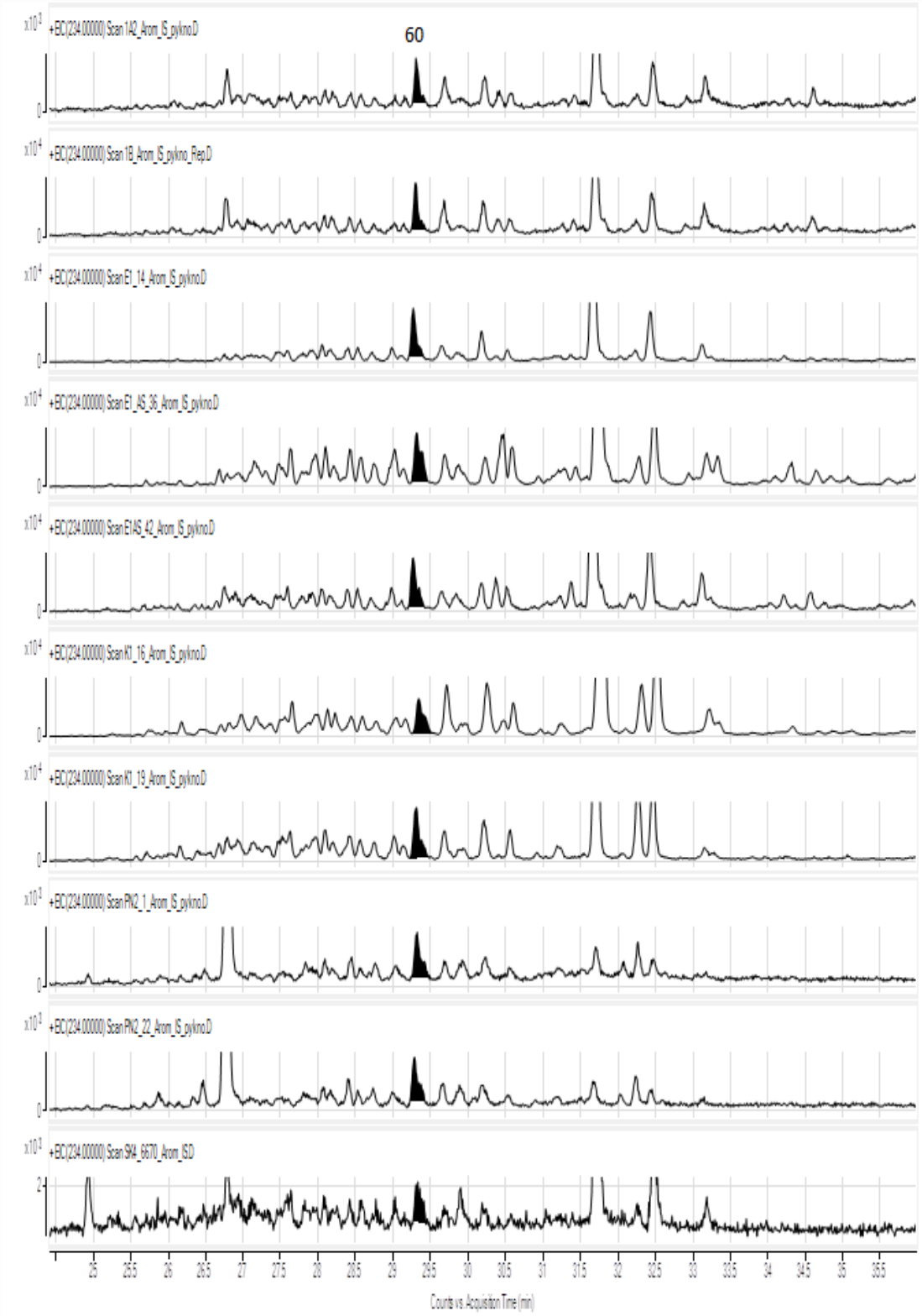


Figure 9.14: Retene (m/z = 234)

9.15 B[a]An & Chry (m/z = 228)

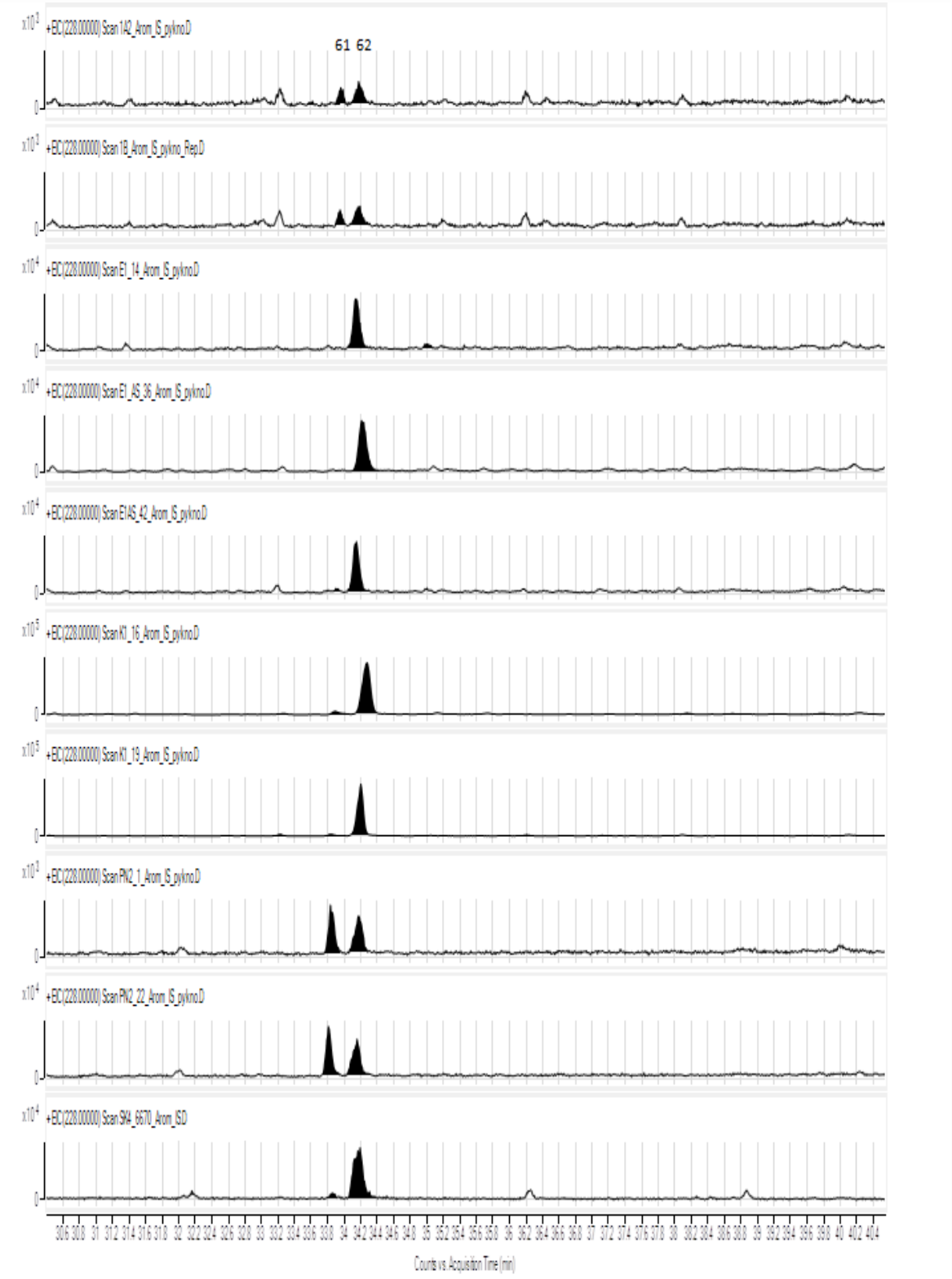


Figure 9.15: Benzo[a]anthracene & Chrysene (m/z = 228)

9.16 B[b]Fla/B[k]Fla/B[e]Py/B[a]Py(m/z=252)

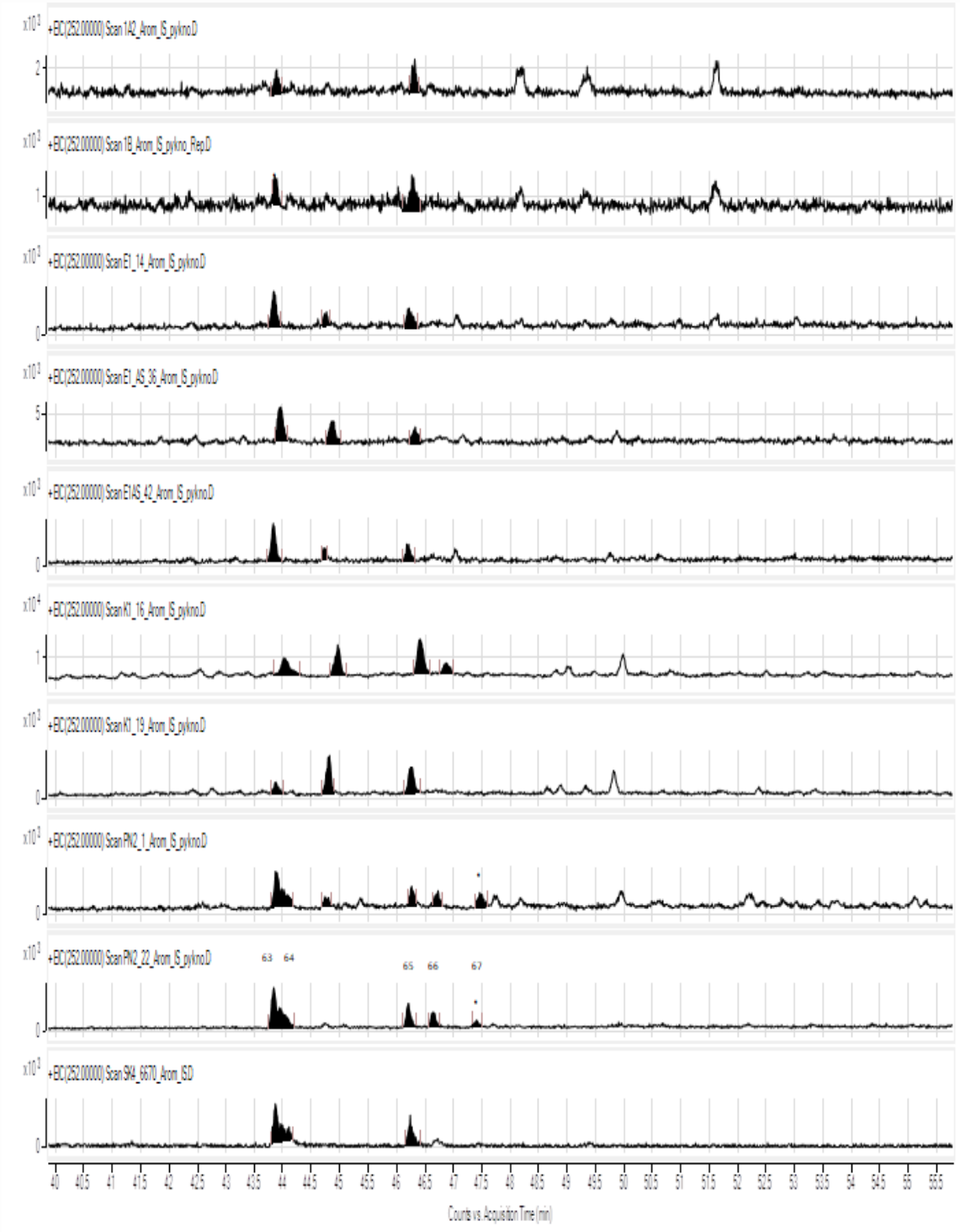


Figure 9.16: B[b]Fla / B[k]Fla / B[e]Py / B[a]Py & Perylene (m/z = 252)

9.17 Ipyr & B[g,h,i]Pyr(m/z = 276)

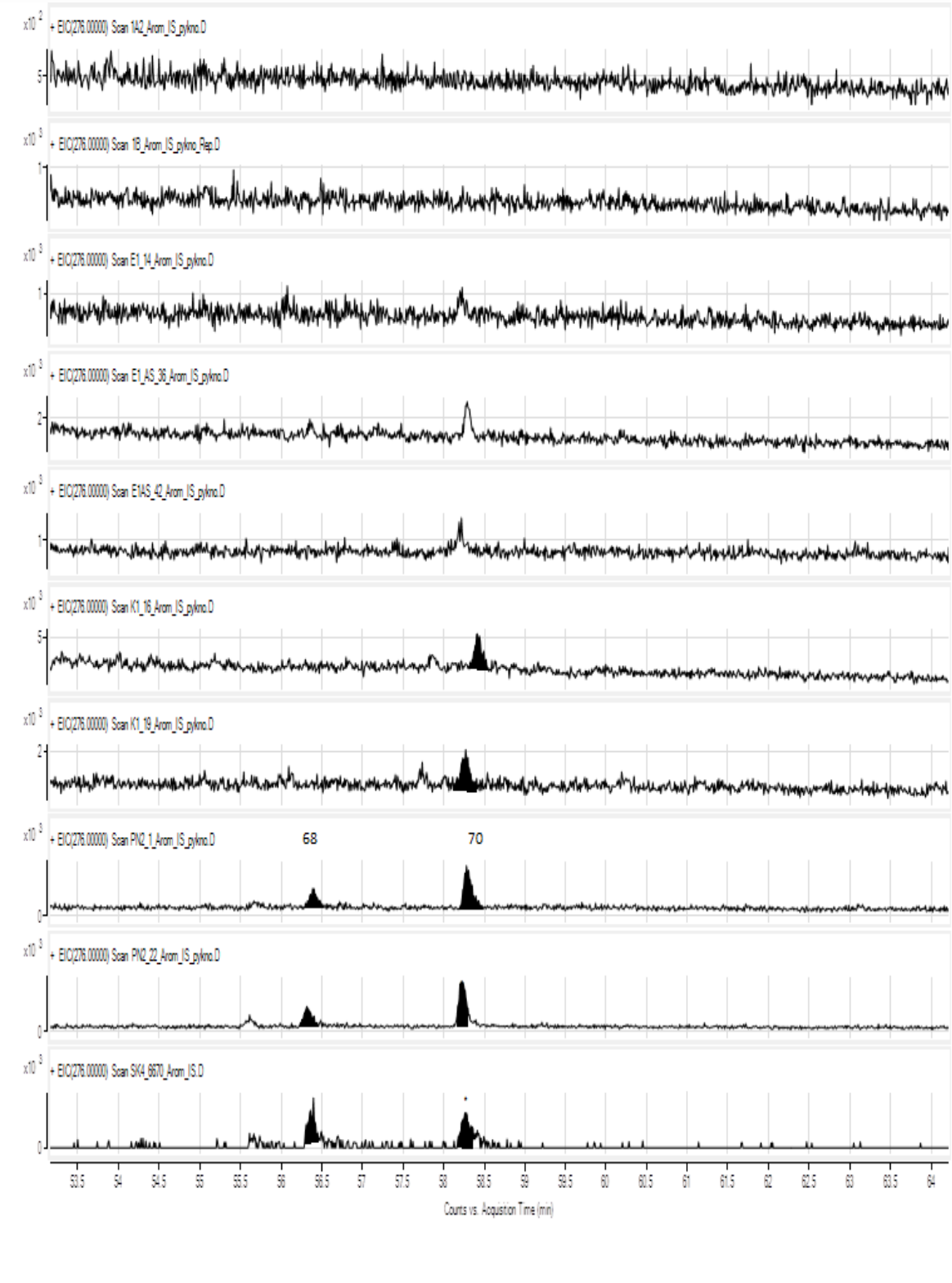


Figure 9.17: Indeno[1,2,3-cd]Pyrene & Benzo[g,h,i]pyrene (m/z = 276)

9.18 DB[a,h]An (m/z = 278)

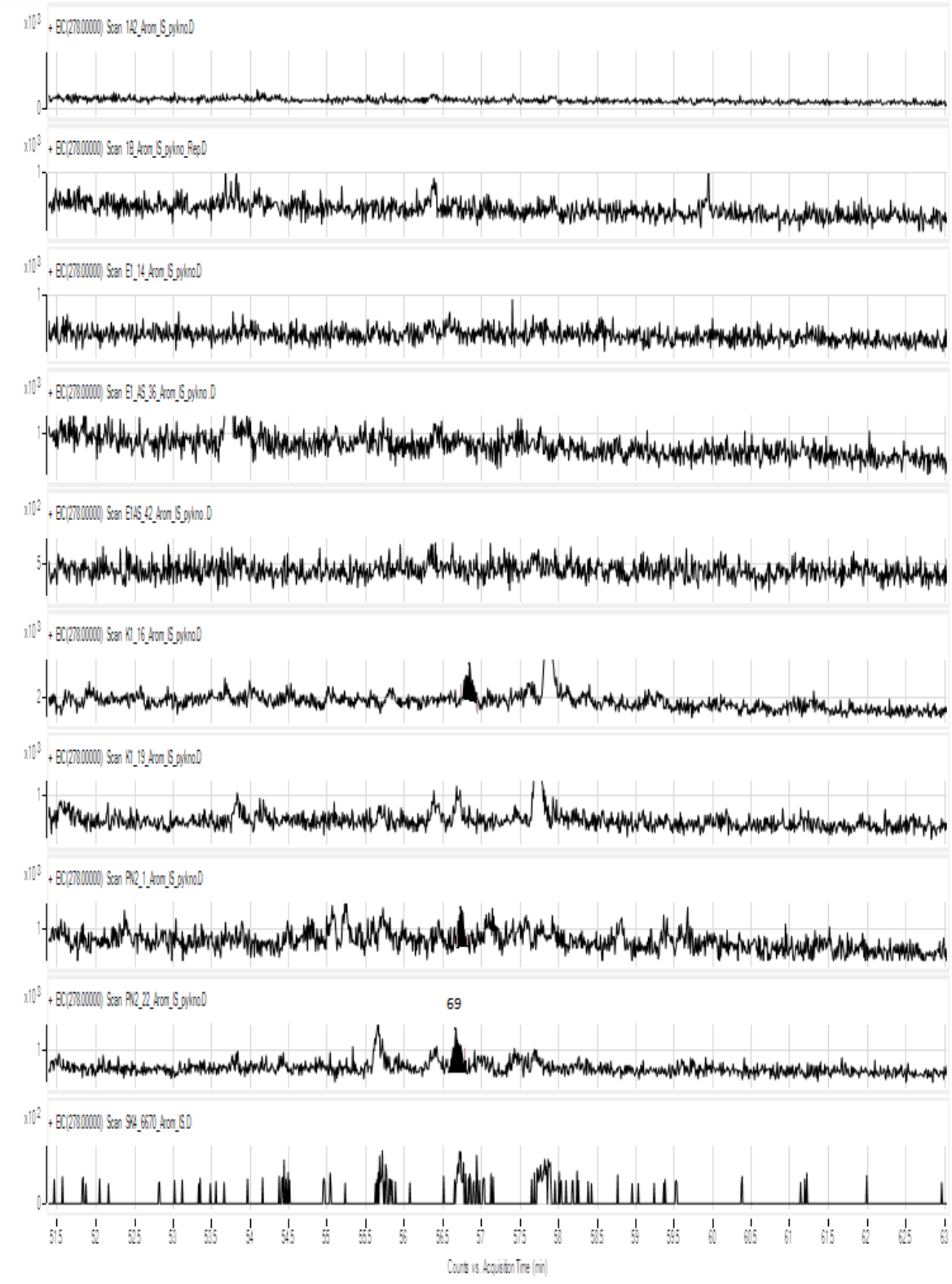
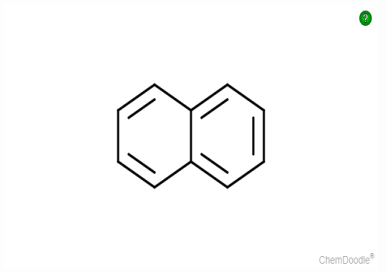


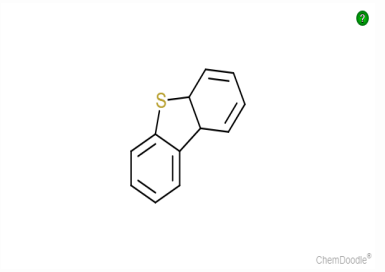
Figure 9.18: Dibenzo[a,h]Anthracene (m/z = 278)

Chapter 10

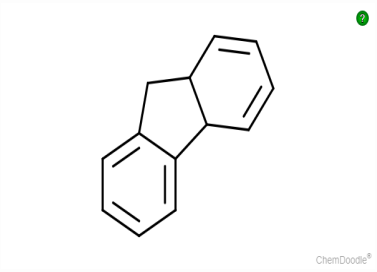
CHARACTERISTIC FORMS OF PAHs



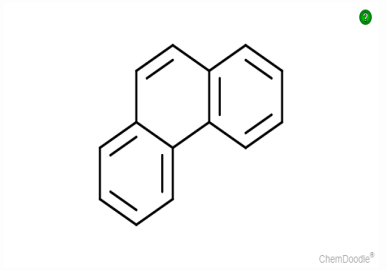
(a) Naphthalene



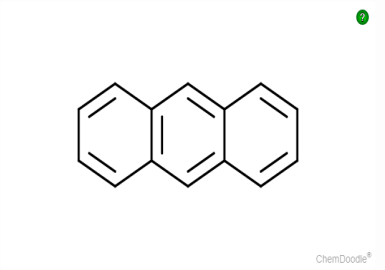
(b) Dibenzothiophene



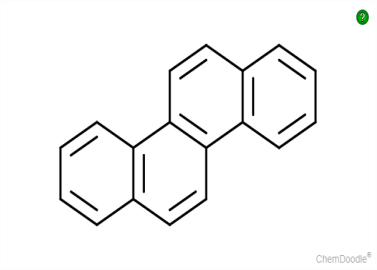
(c) Fluorene



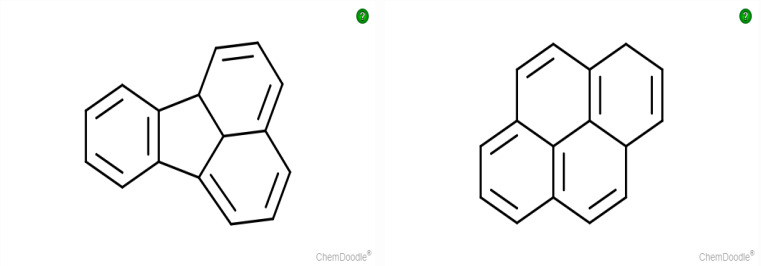
(a) Phenanthrene



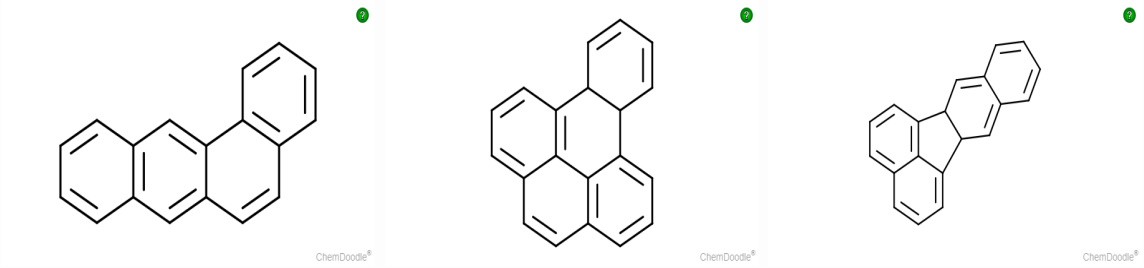
(b) Anthracene



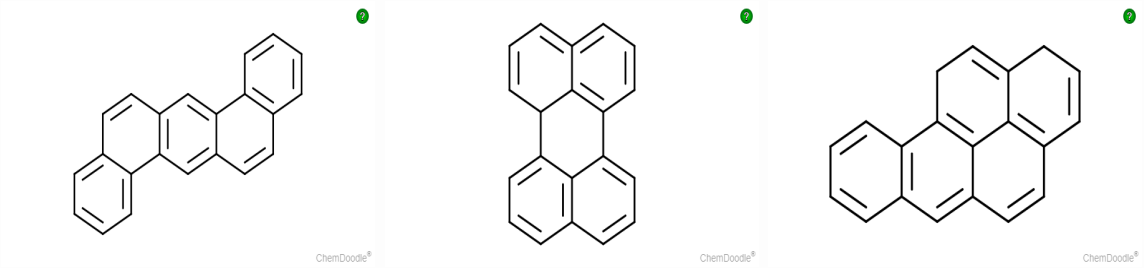
(c) Chrysene



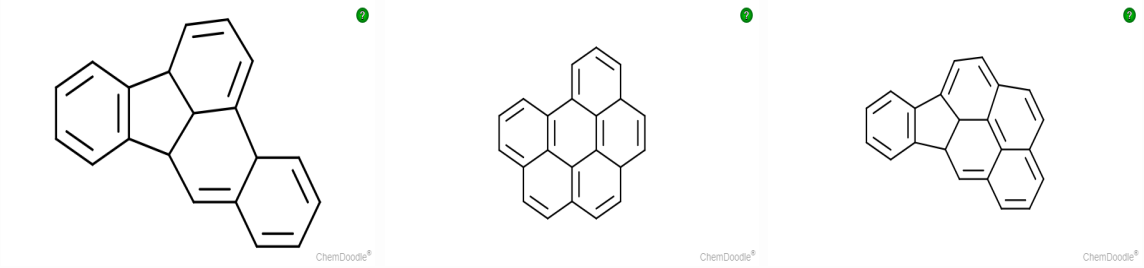
(a) Fluoranthrene (b) Pyrene



(a) Benzo[a]Anthracene (b) Benzo[e]Pyrene (c) Benzo[k]Fluoranthrene



(a) Dibenzo[a,h]Anthrecene (b) Perylene (c) Benzo[a]Pyrene



(a) Benzo[b]Fluoranthrene (b) Benzo[g,h,i]Perylene (c) Indeno[1,2,3-cd]Pyrene

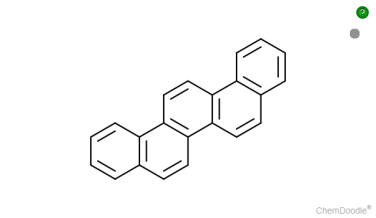
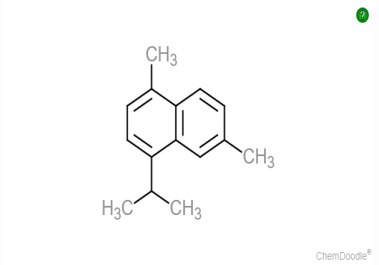
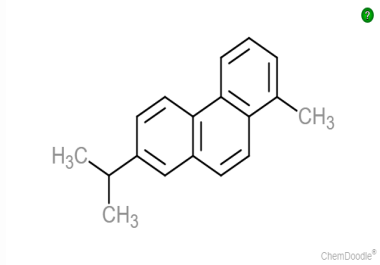


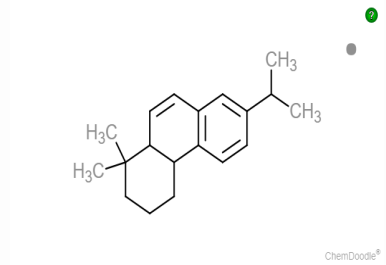
Figure 10.7: Picene



(a) Cadalene



(b) Retene



(c) Simonelite

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