IDENTIFICATION OF CRUDE OILS AND FUEL OILS AFTER WEATHERING USING BIOMARKERS, PYROGENIC INDEX AND ASPHALTENES CONTENTS

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A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2018

Thesis Title:	Identification of Crude Oils and Fuel Oils after Weathering Using Biomarkers, Pyrogenic Index and Asphaltenes Contents
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Program:	Petroleum Technology
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Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

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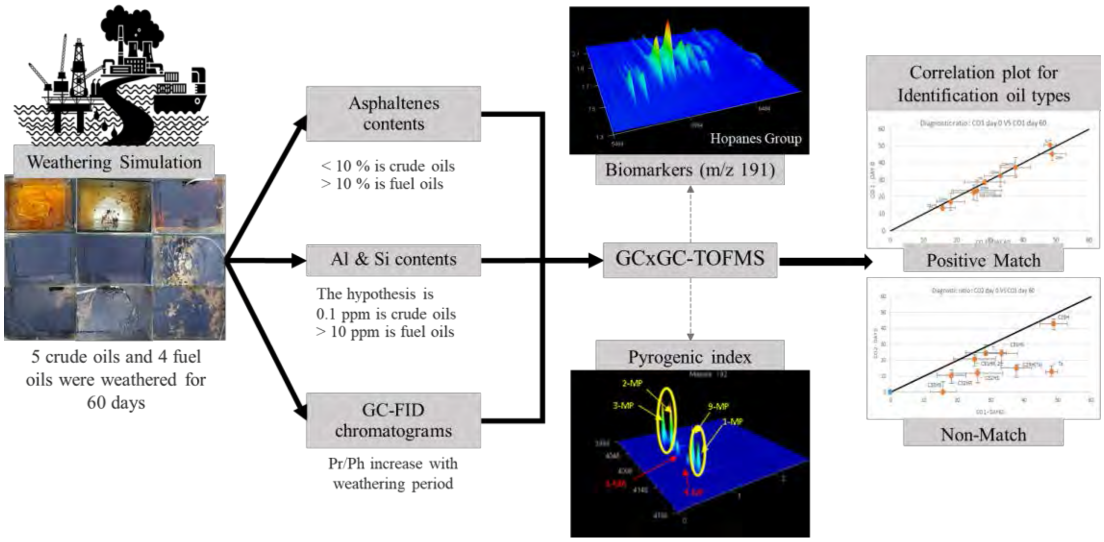
ABSTRACT

5973003063: Petroleum Technology Program
Hathairat Thongkorn: Identification of Crude Oils and Fuel Oils after Weathering Using Biomarkers, Pyrogenic Index and Asphaltenes Contents
Thesis Advisor: Assoc. Prof. Siriporn Jongpatiwut 100 pp.

Keywords: Biomarkers/ PAHs/ Oil spills/ Crude oil/ Fuel oil/ GCxGC-TOFMS

Oil spills have become a global problem. This is one of the serious problems in marine environment. The spills are generally from reservoir zipping, accident or unauthorized drainage. Typically, the spilled oils are fuel oils or crude oils which are difficult to differentiate. After oil spill incident, oils are undergone weathering processes such as evaporation, dissolution, and biodegradation etc., which are main factor of depleting hydrocarbon. This work focuses on the distribution of hydrocarbon and diagnostic ratio of polycyclic aromatic hydrocarbons such as pristane, phytane, phenanthrene, pyrene, chrysene and biomarker in hopane group after weathering processes. Moreover, measuring of Al, Si and asphaltenes contents also study in this research. Five crude oils and four fuel oils were weathered in the sea water for 60 days. All samples were characterized by GC-FID and GCxGC-TOFMS followed NORDTEST methodology. Moreover, all samples were measured for asphaltenes contents and Al, Si contents in order to differentiate the types of oil. The result from weathering simulation showed that weathering had significantly affected the distribution of *n*-alkanes and generally used diagnostic ratio (pristane/phytane) including Al and Si contents changed seriously. However, pyrogenic index and asphaltenes contents can be used as indicators to differentiate fuel oils and crude oils since both of them are strong anti-weathering.

GRAPHICAL ABSTRACT



บทคัดย่อ

หทัยรัตน์ ทองกร : การบ่งชี้น้ำมันดิบ และน้ำมันเตาที่ผ่านกระบวนการย่อยสลายทางธรรมชาติโดย ไบโอมาร์กเกอร์, ดัชนีบ่งชี้ไพโรเจนิกซ์ และ ปริมาณแอสฟัลต์ทีน (Identification of Crude Oils and Fuel Oils after Weathering Using Biomarkers, Pyrogenic Index and Asphaltenes Contents) อ. ที่ปรึกษา : รศ. ดร. ศิริพร จงผาติวุฒิ 100 หน้า

เหตุการณ์น้ำมันรั่วจัดเป็นหนึ่งในปัญหาสำคัญของระบบนิเวศทางทะเล การรั่วไหลของน้ำมันเกิดได้จากหลายสาเหตุไม่ว่าจะเป็น อุบัติเหตุทางท่อขนส่ง หรือการลักลอบทิ้งน้ำมันโดยไม่ได้รับอนุญาต ซึ่งน้ำมันส่วนใหญ่ที่รั่วไหลนั่นได้แก่ น้ำมันดิบ และน้ำมันเตา โดยเมื่อเกิดเหตุการณ์น้ำมันรั่ว น้ำมันเหล่านั้นจะถูกย่อยสลายด้วยกระบวนการทางธรรมชาติ เช่น การระเหย การกระจายตัวของน้ำมันในน้ำ และการย่อยสลายทางชีวภาพ เป็นต้น ซึ่งกระบวนการเหล่านี้ส่งผลให้องค์ประกอบของน้ำมันมีสัดส่วนลดลง และส่งผลให้ลักษณะการกระจายตัวขององค์ประกอบในน้ำมันดิบ และน้ำมันเตามีความคล้ายคลึงกัน ทำให้ยากต่อการระบุประเภทของน้ำมันที่รั่วไหล ดังนั้นในงานวิจัยนี้จึงมีจุดประสงค์ในการศึกษาการกระจายตัวของสารประกอบไฮโดรคาร์บอน และหาดัชนีของตัวบ่งชี้เอกลักษณ์น้ำมันจากกลุ่มสารประกอบโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอน และ ไบโอมาร์เกอร์กลุ่มโฮปเพน เพื่อทำการบ่งชี้ประเภทของน้ำมันที่รั่วไหล โดยงานวิจัยนี้ทำการทดสอบด้วยน้ำมันดิบ 5 ชนิด และน้ำมันเตา 4 ชนิดจากกระบวนการที่แตกต่างกัน โดยทำการจำลองเหตุการณ์น้ำมันรั่วลงในน้ำทะเลและเก็บตัวอย่างในวันที่ 0, วันที่ 7 และวันที่ 60 น้ำมันทุกตัวอย่างถูกวิเคราะห์โดยใช้เครื่องแก๊สโครมาโตกราฟฟี และวัดปริมาณโลหะอะลูมิเนียม และซิลิกอนด้วยเครื่องไอซีพี หรือเครื่องวัดเสปกตรัมแสงในช่วงความยาวคลื่นที่มองเห็น รวมทั้งวัดปริมาณแอสฟัลต์ทีนในน้ำมัน ผลที่ได้จากงานวิจัยพบว่าการวัดปริมาณโลหะอะลูมิเนียมยังมีความไม่เหมาะสมในการแยกประเภทน้ำมันเนื่องจากเมื่อผ่านกระบวนการสลายทางธรรมชาติแล้วจะส่งผลให้น้ำมันดิบมีปริมาณโลหะอะลูมิเนียมเข้มข้นขึ้นในระดับเดียวกับน้ำมันเตา จึงไม่สามารถบ่งชี้ประเภทของน้ำมันได้ แต่อย่างไรก็ตามจากงานวิจัยพบว่าไบโอมาร์กเกอร์ กลุ่มโฮปเพนมีความต้านทานต่อการสลายตัวทางธรรมชาติมากกว่าสารประกอบกลุ่มอื่นในน้ำมัน นอกจากนี้ดัชนีไพโรเจนิกซ์จากสารประกอบโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนและการวัดปริมาณแอสฟัลต์ทีนสามารถบ่งชี้ประเภทของน้ำมันที่รั่วไหลได้

ACKNOWLEDGEMENTS

This thesis could not be success without the kindness of advisor, committees, many people and organizations.

First of all, I am grateful for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College; and Center of Excellence on Petrochemicals, and Materials technology, Thailand.

I would like to express my gratitude to my advisor, Assoc. Prof. Siriporn Jongpatiwut for her advice, supervision and support in various ways from the very stage of this research.

I also gratefully thank to Dr. Ampira Charoensaeng and Dr. Pornsri Mingkwan for their kindness to be committees and important comments on this research.

In particular, I would like to express my special thanks to Mr. Pisut Eg-karntrong and entire staff in laboratory at PTT Global Chemical Public Company Limited for their helpful suggestion, advices and important support.

I would like to extend my sincere thanks to PTT Global Chemical Public Company Limited and Star Petroleum Refining Public Company Limited for providing all samples, supports and helpful suggestions.

Unforgettably, I am deeply grateful to my family and friends for their encouragement and greatest support.

Finally, I would like to thank all PPC staffs and those whose names are not mentioned here who made valuable contributions to this research.

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ABBREVIATION

A	Anthracene
Al	Aluminum
CL	confident limit
CO	crude oil
D	Dibenzothiophene
F	Fluorene
FCC	fluid catalytic cracking
FO	fuel oil
HFO	heavy fuel oil
HP	high purity
HVGO	heavy gas oil
IS	internal standard
m/z	mass to charge ratio
MA	methyl-anthracene
MP	methyl-phenanthrene
N	Naphthalene
Ni	Nickel
P	Phenanthrene
PAHs	polycyclic aromatic hydrocarbons
Ph	Phytane
PI	Pyrogenic index
Pr	Pristane
SIM	selected ion monitoring mode
TIC	total ion chromatogram
UCMs	unresolved complex mixtures
UHP	ultra-high purity
V	Vanadium

CHAPTER I
INTRODUCTION

The oil spill incident is one of the serious problems in marine environment. In worldwide scale, there are approximately 5.74 million tons of oil spill to marine and coastal area within fourth decades. Although, Thailand has not had large oil spill since 2013, oil spill incidents still were founded. These incidents have significant effect on marine and coastal environments (Riley *et al.*, 2016). Moreover, in environment forensic point of view, some cases of an oil spill were still unknown the origin or source of an oil spill. Thus, oil fingerprinting needs to be developed in order to identifying spilled source. Commonly, the relevant spilled oils are crude oil, fuel oil, used and waste lubricating oil, and diesel. After oil spill to marine environment, it has undergone weathering processes (evaporation, photo-oxidation, dispersion, dissolution and biodegradation) that have significant effect on the chemical fingerprints (Tarr *et al.*, 2016). Hence, determining potential sources of oil spill becomes a large challenge when the oil was weathered by environment.

Normally, the most widely used analytical methods for oil spill fingerprinting are gas chromatography-flame ionization detector (GC-FID) and gas chromatography-mass spectrometry (GC-MS). In this method, GC-MS is applied to determine spilled source. However, one dimension GC-MS has a limitation to identify and qualify many compounds in unresolved complex mixtures (UCMs) under the baseline. Hence, the complexity of oil, which is difficult to analyze could be resolved by using two-dimensional gas chromatography time of flight mass spectrometry (GCxGC-TOFMS). The GCxGC-TOFMS is a new technology for complex compound analysis. This instrument consists of two columns with a different separation mechanisms, which can provide an effective information for oil fingerprinting (Faksness *et al.*, 2002).

Moreover, there is optional technique such as finding metals in oil by inductively coupled plasma optical emission spectroscopy (ICP-OES) or Atomic Absorption Spectrophotometer (AAS) also be used for differentiation oil type. Normally, these techniques be used to measure vanadium and nickel ratio to identify oils from their original source rock, however, they also used for measuring aluminum and silicon concentration with the hypotheses that fuel oil will have aluminum higher than crude oil since catalyst loss from a fluid catalytic cracking unit. Thus, identifying oil spilled by these 2 methods will make the oil fingerprinting more robust and reliable.

Therefore, the objectives of my thesis are study the effect of weathering processes on the distribution of chemical fingerprints. Moreover, this research focuses on distinguishing between crude oil and processed oil (heavy fuel oil) after weathering by using the distribution of PAH and PI (pyrogenic index), and measuring the aluminum and silicon content. Furthermore, this research also investigated asphaltene contents, which are normally precipitated during oil extraction and has high concentration in fuel oil from visbreaking unit.

CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Crude Oil

Crude oil is a complex mixture of thousands of compounds. Most of the compounds in crude oil are hydrocarbons (carbon and hydrogen). Others compounds in crude oil contain not only hydrocarbon, but also small amount of other element such as sulfur, nitrogen and certain metals (e.g., nickel, vanadium and so on.) Crude oil is originated from plants and animals that died millions of years ago. It exists in liquid form in underground pools or reservoirs under temperature and pressure condition within sedimentary rocks and near the surface in tar (or oil) sands as illustrated in Figure 2.1 (EIA, 2017).

In general, crude oils have many types, which depend on the properties of crude oil. For example, sweet and sour crude oils, they are called according to their sulfur content, the term heavy and light crude oil are called according to API gravity etc. Moreover, abundantly source and formed condition of crude oil lead to variety types and different of component in crude oil. Hence, the different of composition in crude oil result in a distinction chemical that can be used for forensic spilled oil fingerprinting (Vermeire, 2012).

Figure 2.1 Crude oil formation diagram (EIA, 2017).

2.2 Processed Oil

Processed oils or refined products are products of crude oils that pass through processes such as distillation, cracking, treating and reforming. Processed oil normally have physical and chemical characteristic different from crude oil. The first step of refining is distillation unit and the major processed oil products are gasoline, kerosene, fuel oil and lubricating oil. This study will be focus only fuel oil. The Figure 2.2 is illustrated processed oil from distillation unit.

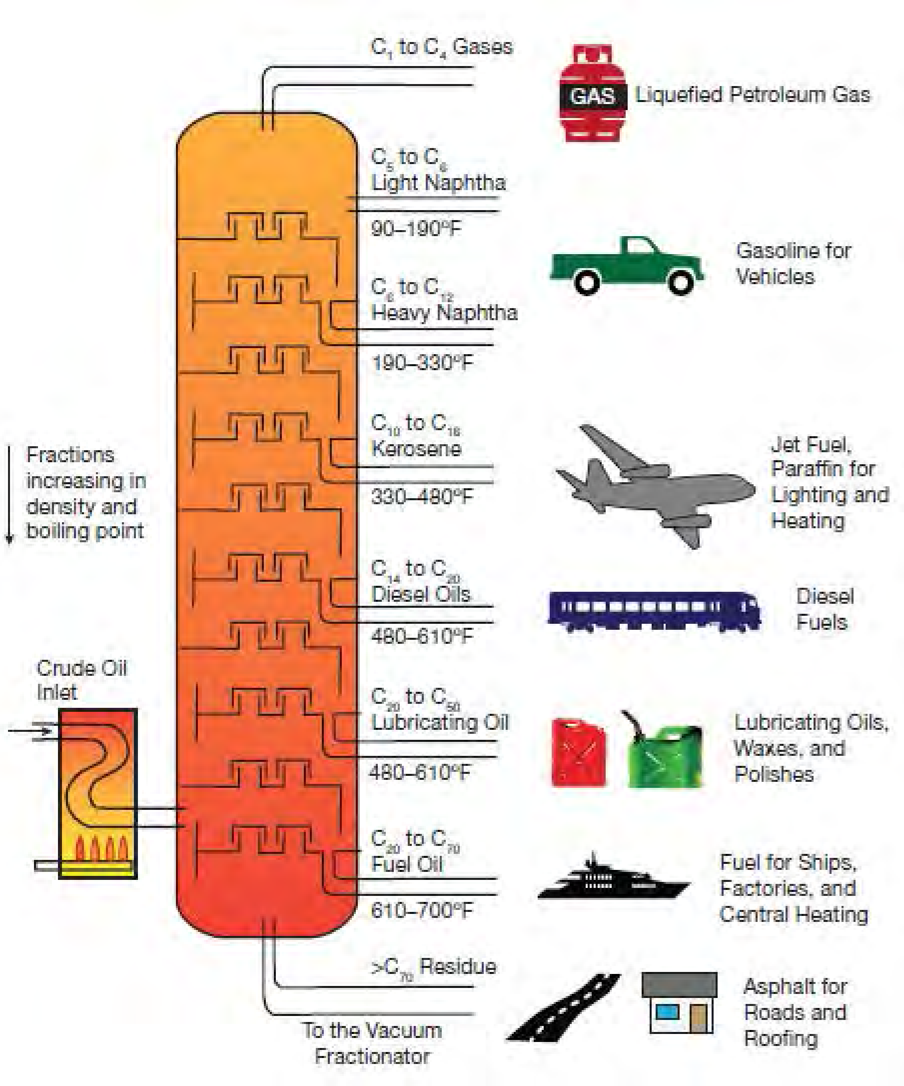


Figure 2.2 Processed oil from distillation unit (Mascone ,2014).

2.2.1 Fuel Oil or Residue Oil

Fuel oil is produced from petroleum distillation to meet the specification. Normally, the term “fuel oil” refer to the heaviest commercial fuel that can be obtained from crude oil and used as liquid fuel that is burned in furnace. Technically, fuel oil is classified into six classes from number 1 through 6. The number of fuel oil depend on the boiling point, carbon chain length and viscosity, which increase with fuel oil number. For the Price of fuel oil generally decrease as the number of fuel increases.

Number 1 fuel oil is a product of the straight run distillation. It is similar to kerosene that boil off after gasoline. Former names are coal oil, stove oil and range oil.

Number 2 fuel oil or Bunker A is a heating oil. Sometimes it is also known as “road diesel” that truck and some car use for drive engine. Both heating oil and diesel fuel are obtained from light gas oil cut or the blending of straight run and catalytic cracking.

Number 3 fuel oil is a distillate fuel oil for burner. In the mid20th century, this term has been rarely used and ASTM has merged this class into number 2 fuel oil specification.

Number 4 fuel oil or Bunker B is a commercial heating oil. It is typically a blend of distillate and residue fuel oil to meet specification of ASTM. Moreover, it is also obtained from the heavy gas oil cut.

Number 5 fuel oil or Bunker B is called residue fuel or an industrial heating oil that require preheating to 77-104°C. It is obtained from the heavy gas oil cut or a mixture of number 6 fuel oil and number 2 fuel oil to meet the specification of ASTM.

Number 6 fuel oil or Bunker C is called residue fuel oils (RFO) or heavy fuel oil (HFO). It is material that remain after the more valuable cuts of crude oil are extracted from distillate. This fuel is also known as “Navy special fuel oil” or just “Navy special” and it is the most common bunker fuel.

Each refinery operates individually therefore, fuel oil blending in any classes will not be the same. It is depend on its economic, current operating and demand from market, which are an advantage in tracking spilled fuel oil in the sea.

Figures 2.3 and 2.4 show simple straight run refinery and complex refinery with fluid catalytic cracking (FCC) and visbreaking.

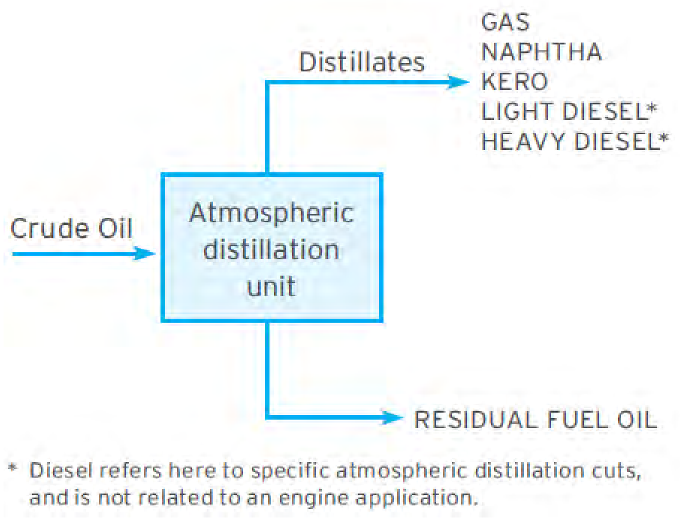


Figure 2.3 Simple straight run refinery (Vermeire, 2012).

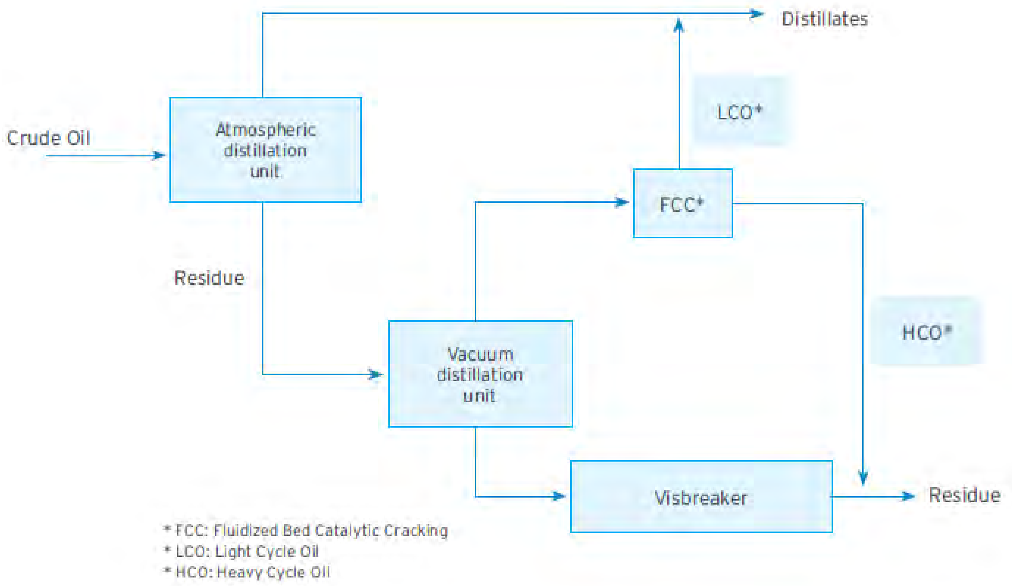


Figure 2.4 Complex refinery with fluid catalytic cracking (FCC) and visbreaking (Vermeire, 2012).

2.3 Petroleum Chemical Fingerprint

2.3.1 Chemical Composition of Oil

Crude oils consist of complex mixtures of hydrocarbons and non-hydrocarbons that range from small volatile compounds to large non-volatile ones. In general, petroleum components are classified into 4 groups called SARA analysis ,namely saturates, olefins, aromatics, resin (wide variety of compounds containing sulfur, oxygen, and nitrogen), and asphaltene (Wang *et al.*, 2006).

Saturated is the predominant class of hydrocarbons in most crude oil that composed of only carbon and hydrogen with no carbon–carbon double bonds. Saturated include straight chain and branched chain (also called paraffins) and cycloalkanes (also called naphthenes) and some biomarker (e.g. steranes and terpanes and so on). Olefins or Alkenes are partially unsaturated hydrocarbons that consist of one or multiple double carbon-carbon bonds. These compounds are rarely to find in crude oil but present in some petroleum products as there are formed during the refining process.

Aromatic hydrocarbons contain a benzene ring, which is unsaturated but very stable and frequently behaves as a saturated compound. Aromatic in petroleum include the mono- aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (also called BTEX), other alkyl substituted benzene compounds (C_n-benzenes) and polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, phenanthrene, dibenzothiophene etc.

Resins are the smaller polar compounds that are chemically similar to the asphaltenes. Polar compounds are those with distinct regions of positive or negative charge that bonding with atoms such as nitrogen, oxygen or sulfur. Generally, resins are concentrated in heaviest fraction of oils as heteroatom constituent that consist of N-S-O or metal.

Asphaltenes are very large heteroatom-containing compounds, which are the highest molecular weight heaviest in crude oil. Normally, Asphaltenes are insoluble in liquefied petroleum gases such as methane, ethane and propane but disperse as colloids. The amount and the characteristics of the asphaltene in crude oil depend on a greater or lesser extent on the source of the crude oil. Table 2.1 shows the typical composition of some oils and petroleum products (Speight, 2006, Wang *et al.*, 2006).

Table 2.1 Typical composition of crude oils and petroleum products

Group	Compound Class	Gasoline	Diesel	Light crude	Heavy crude	IFO	Bunker C
Saturated		50-60	65-95	55-90	25-80	25-45	2040
	Alkanes	45-55	35-45				
	Cyclo-alkanes	~5	30-50				
	waxes		0-1	0-20	0-10	2-10	5-15
Olefins		5-10	0-10	-	-	-	-
Aromatics		25-40	5-25	10-35	15-40	40-60	30-50
	BTEX	15-35	0.5-2	0.1-2.5	0.01-2	0.05-1	0-1
	PAHs		0.5-5	0.5-3	1-4	1-10	1-10
Polar compounds		-	0-2	1-15	5-40	15-25	10-30
	Resins	-	0-2	0-10	2-25	10-15	10-20
	Asphaltenes	-	-	0-10	0-20	5-10	5-20
Sulphur		<0.05	0.05-0.5	0-2	0-5	0.5-2	2-4
Metals (PPM)				30-50	100 - 500	100 - 1000	100 - 2000

BTEX = benzene, toluene, ethylbenzene, and xylenes; PAHs = polycyclic aromatic hydrocarbons.

2.3.2 Petroleum Biomarkers

Biomarkers are complex molecules that derive from formerly living organism. In the past, biomarkers have been widely used by petroleum and reservoir geochemist for characterization the thermal maturity of the oil, determination of the deposition environment of the source rock, classification the type of source rock and degree of biodegradation of the oil ,etc. Nowadays, biomarkers play an important role in forensic investigations of oil spills because biomarkers can keep most of original carbon structure of oil and resist with weathering process than other hydrocarbon groups. Moreover, biomarkers are formed under various geological conditions and ages, which exhibit different biomarkers. Therefore, biomarker analysis of the oils provide essential information for determining the source of oil spill, differentiating and correlating oils, etc (Wang *et al.*, 2006).

In general, oil biomarkers can be classified into two classes that is acyclic or aliphatic biomarkers and cyclic biomarkers. The basic structure unit of biomarker is isoprene, which is a compound that composes of isoprene subunits are called terpenoids or isopenoids. Furthermore, the terpenoids have many categorizes based on approximately number of isoprene subunit as shown in the Table 2.2.

Table 2.2 Families of terpenoids (Wang *et al.*, 2006)

Hemiterpane (C_5)	Containing one isoprene subunit
Monoterpanes (C_{10})	Containing two isoprene subunit
Sesquiterpanes (C_{15})	Containing three isoprene subunit
Diterpanes (C_{20})	Containing four isoprene subunit
Sesterterpanes (C_{25})	Containing five isoprene subunit
Triterpanes and steranes (C_{30})	Containing six isoprene subunit
Tetraterpanes (C_{40})	Containing eight isoprene subunit
Polyterpanes ($C_{5n\,(n>8)}$)	Containing nine or more isoprene subunit

2.3.2.1 Acyclic or Aliphatic Biomarker

Acyclic or aliphatic biomarker has a large number in oils that have different linkage pattern between isoprene subunits. However, it can be categorized to two form linkage, namely regular (head to tail) and irregular (different order of head-to-head or tail-to-tail). The most common acyclic biomarker is pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$). Pristane and phytane, which are often used for estimate degree of oil weathering, are a typical example of acyclic biomarker that isoprene subunits link from head to tail (regular linkage). Other examples of acyclic biomarkers, which are also quite abundant in oils is shown in Figure 2.2, such as farnesane (C_{15}), trimethy-C_{13} (C_{16}) and norpristane (C_{18}) including pristine and phytane (Wang *et al.*, 2006).

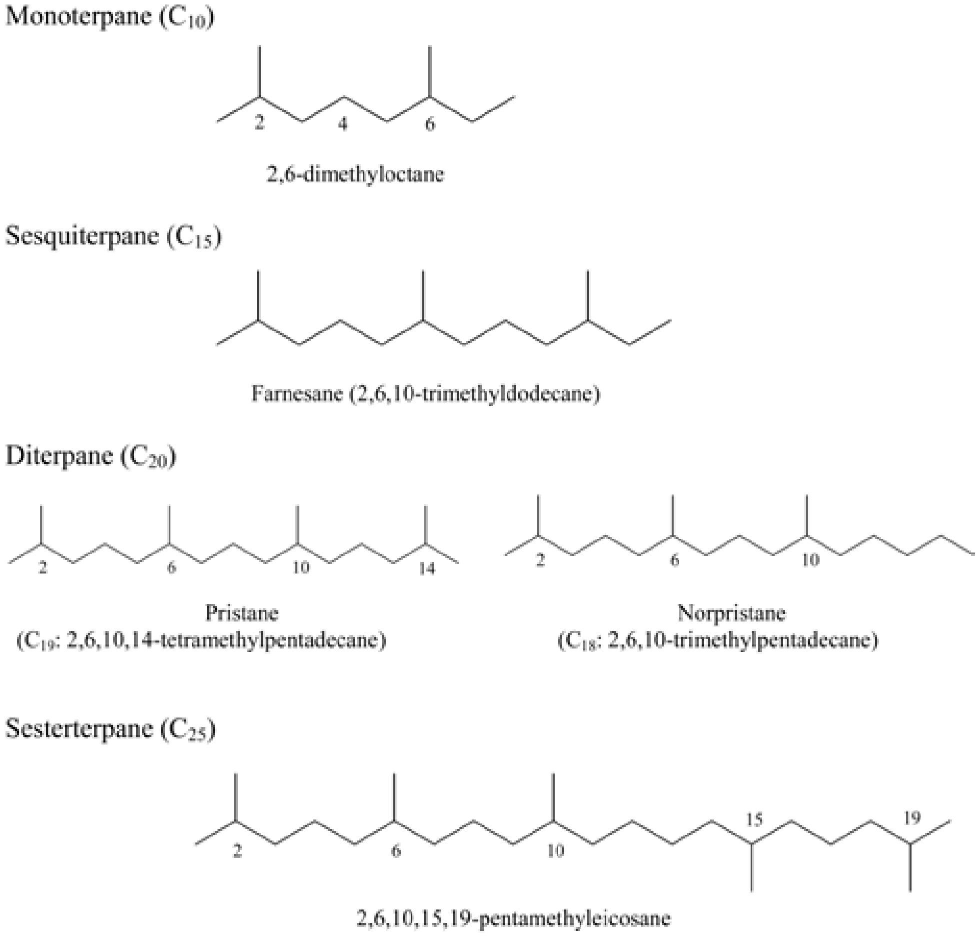


Figure 2.5 Structure of acyclic or aliphatic biomarkers (Wang *et al.*, 2006).

2.3.2.2 Cyclic Biomarker

The most common cyclic biomarkers are terpanes, steranes (irregular cyclic terpenoid compounds) and aromatic steranes. Terpanes in petroleum include sesquit- (C_{15}), di- (C_{20}), sester- (C_{25}) and triterpanes (C_{30}). They are found in almost all of the oils. The terpanes consist of several homologous series, including bicyclic, tricyclic and pentacyclic (e.g., hopanes) compounds. Hopane, which are pentacyclic triterpanes commonly have 27 to 35 carbon atom, are characteristic of petroleum especially hopane with 17 αβ-configuration in the range of C_{27} to C_{35} because of their large abundance and thermos dynamic stability compare to other epimeric (ββ and βα) series.

For steranes, they are a class of biomarkers that have carbon atoms in the range of 21 to 30, including regular steranes, mono- and tri aromatic steranes and rearrange diasteranes. The most common steranes are C_{27}- C_{28}-C_{29} (cholestane, ergostane, and stigmastane) which are very useful for oil fingerprinting because there are high source specificity. Example of structure of cyclic biomarkers and range of carbon atom of cyclic biomarker are shown in Figures 2.6 and 2.7, respectively. For the summary of biomarkers, they are listed in Table 2.3.

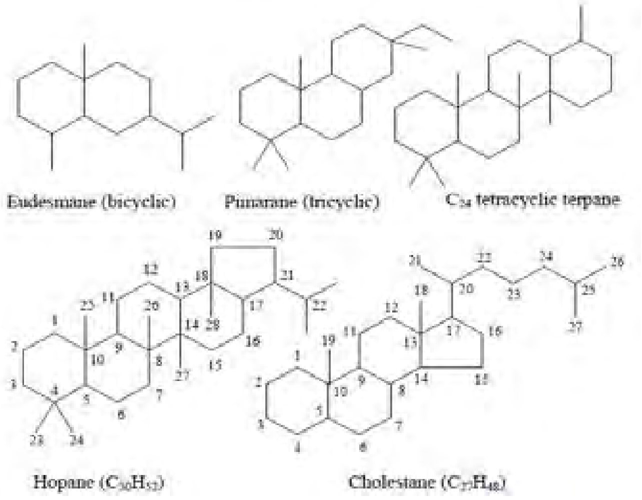


Figure 2.6 The structure of cyclic biomarkers (Wang *et al.*, 2004).

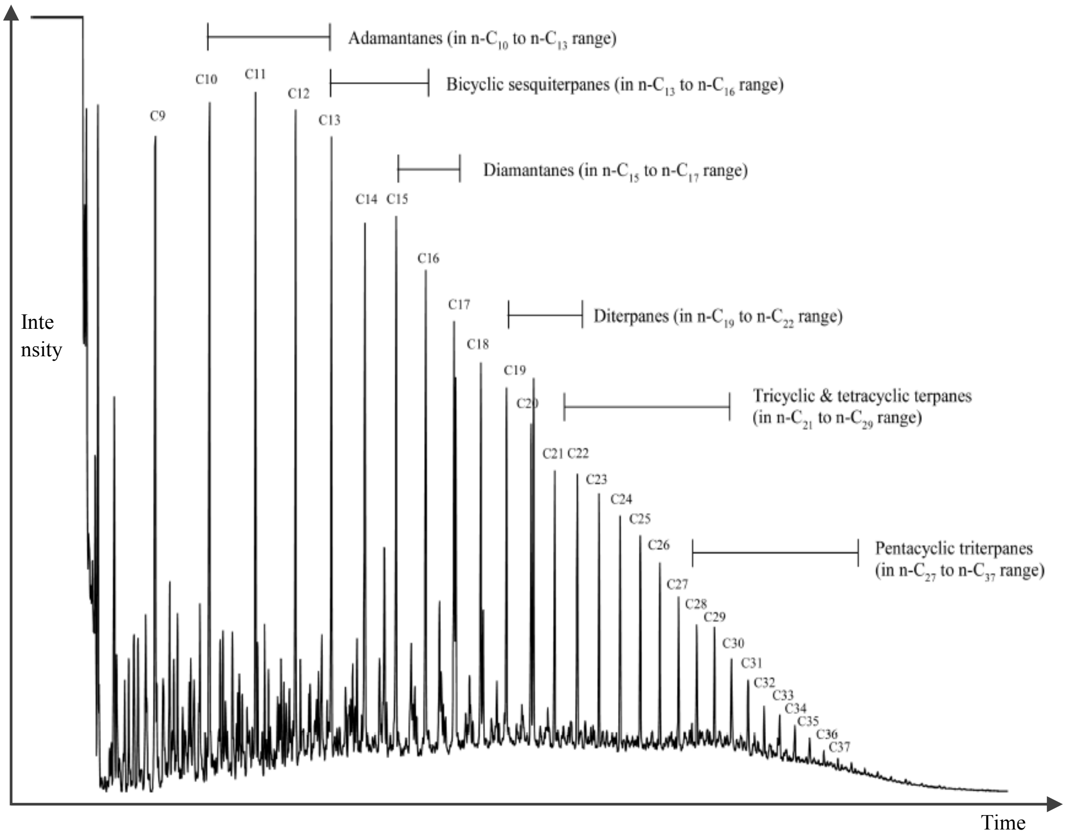


Figure 2.7 Range of carbon atom of cyclic biomarkers in crude oils and processed oils (Wang *et al*., 2004).

Table 2.3 Summary of petroleum biomarkers regularly used for forensic oil spill investigations (Wang *et al.*, 2006)

Compound	Empirical formula	Target ions
Acyclic or Aliphatic biomarker		
pristane	C17	
phytane	C18	
Sesquiterpane (bicyclic terpanes)		
Drimanes	$C_{14}H_{26}$, $C_{15}H_{28}$, $C_{16}H_{30}$,	123
Diamondoids		
Adamantanes	$C_{10}H_{16}$, alkyl-$C_{10}H_{15}$	136, 135, 149, 163, 177
Diamantanes	$C_{14}H_{20}$, alkyl-$C_{14}H_{19}$	188, 187, 201, 215, 229

Compound	**Empirical formula**	**Target ions**
Terpanes		
C_{19} tricyclic terpane	$C_{19}H_{34}$	191
C_{20} tricyclic terpane	$C_{20}H_{36}$	191
C_{21} tricyclic terpane	$C_{21}H_{38}$	191
C_{22} tricyclic terpane	$C_{22}H_{40}$	191
C_{23} tricyclic terpane	$C_{23}H_{42}$	
C_{24} tricyclic terpane (a)	$C_{24}H_{44}$	191
C_{25} tricyclic terpane (b)	$C_{25}H_{46}$	191
C_{26} (S+R)tricyclic terpane	$C_{24}H_{42}$ + $C_{26}H_{48}$	191
C_{28} tricyclic terpane (a)	$C_{28}H_{52}$	191
C_{28} tricyclic terpane (b)	$C_{28}H_{52}$	191
C_{29} tricyclic terpane (a)	$C_{29}H_{54}$	191
C_{29} tricyclic terpane (b)	$C_{29}H_{54}$	191
Ts: 18α(H),21β(H)-22,29,30-trisnorhopane	$C_{27}H_{46}$	191
17α(H),18α(H),21β(H)-25,28,30-trisnorhopane	$C_{27}H_{46}$	191, 177
Tm: 17α(H),21β(H)-22,29,30-trisnorhopane	$C_{27}H_{46}$	191
C30 tricyclic terpane 1	$C_{30}H_{52}$	191
C30 tricyclic terpane 2	$C_{30}H_{52}$	191
17α(H),18α(H),21β(H)-28,30-bisnorhopane	$C_{28}H_{48}$	191
17α(H),21β(H)-25-norhopane	$C_{29}H_{50}$	191,177
17α(H),21β(H)-30-norhopane	$C_{29}H_{50}$	191
17α(H),21β(H)-30-norneohopane (C_{29}Ts)	$C_{29}H_{50}$	191
17α(H)-diahopane	$C_{30}H_{52}$	191
17α(H),21β(H)-30-norhopane (normoretane)	$C_{29}H_{50}$	191
18α(H) and 18β(H)-oleanane	$C_{30}H_{52}$	191, 412
17α(H),21β(H)-hopane	$C_{30}H_{52}$	191
17α(H)-30-nor-29-homohopane	$C_{30}H_{52}$	191
17β(H),21α(H)-hopane (moretane)	$C_{30}H_{52}$	191
22*S*-17α(H),21β(H)-30-homohopane	$C_{31}H_{54}$	191
22*R*-17α(H),21β(H)-30-homohopane	$C_{31}H_{54}$	191
Gammacerane	$C_{30}H_{52}$	191, 412
17β(H),21β(H)-hopane	Internal standard	191
22*S*-17α(H),21β(H)-30,31-bishomohopane	$C_{19}H_{34}$	191
22*R*-17α(H),21β(H)-30,31-bishomohopane	$C_{19}H_{34}$	191
22*S*-17α(H),21β(H)-30,31,32-trishomohopane	$C_{19}H_{34}$	191
22*R*-17α(H),21β(H)-30,31,32-trishomohopane	$C_{19}H_{34}$	191
22*S*-17α(H),21β(H)-30,31,32,33-tetrakishomohopane	$C_{19}H_{34}$	191
22*R*-17α(H),21β(H)-30,31,32,33-tetrakishomohopane	$C_{19}H_{34}$	191
22S-17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	$C_{19}H_{34}$	191

Compound	**Empirical formula**	**Target ions**
22*R*-17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	$C_{19}H_{34}$	191
Stearanes		
C20 5α(H),14α(H),17α(H)-sterane	$C_{20}H_{34}$	217, 218
C21 5α(H),14β(H),17β(H)-sterane	$C_{21}H_{36}$	217, 218
C22 5α(H),14β(H),17β(H)-sterane	$C_{22}H_{38}$	217, 218
C27 20*S* − 13β(H),17α(H)-diasterane	$C_{27}H_{48}$	217, 218, 259
C27 20*R* − 13β(H),17α(H)-diasterane	$C_{27}H_{48}$	217, 218, 259
C27 20*S* − 13α(H),17β(H)-diasterane	$C_{27}H_{48}$	217, 218, 259
C28 20S − 13β(H),17α(H)-diasterane	$C_{28}H_{50}$	217, 218, 259
C28 20*R* − 13β(H),17α(H)-diasterane	$C_{28}H_{50}$	217, 218, 259
C29 20*S* − 13β(H),17α(H)-diasterane	$C_{29}H_{52}$	217, 218, 259
C29 20*R* − 13α(H),17β(H)-diasterane	$C_{29}H_{52}$	217, 218, 259
C27 20*S* − 5α(H),14α(H),17α(H)-cholestane	$C_{27}H_{48}$	217, 218
C27 20*R* − 5α(H),14β(H),17β(H)-cholestane	$C_{27}H_{48}$	217, 218
C27 20*S* − 5α(H),14β(H),17β(H)-cholestane	$C_{27}H_{48}$	217, 218
C27 20*R* − 5α(H),14α(H),17α(H)-cholestane	$C_{27}H_{48}$	217, 218
C28 20*S* − 5α(H),14α(H),17α(H)-ergostane	$C_{28}H_{50}$	217, 218
C28 20*R* − 5α(H),14β(H),17β(H)-ergostane	$C_{28}H_{50}$	217, 218
C28 20*S* − 5α(H),14β(H),17β(H)-ergostane	$C_{28}H_{50}$	217, 218
C28 20*R* − 5α(H),14α(H),17α(H)-ergostane	$C_{28}H_{50}$	217, 218
C29 20*S* − 5α(H),14α(H),17α(H)-stigmastane	$C_{29}H_{52}$	217, 218
C29 20*R* − 5α(H),14β(H),17β(H)-stigmastane	$C_{29}H_{52}$	217, 218
C29 20*S* − 5α(H),14β(H),17β(H)-stigmastane	$C_{29}H_{52}$	217, 218
C29 20*R* − 5α(H),14α(H),17α(H)-stigmastane	$C_{29}H_{52}$	217, 218
C30 steranes	$C_{30}H_{54}$	217, 218
Monoaromatic Steranes		253
Triaromatic Steranes		231

2.3.3 The Recommended Distribution of Biomarker

The distribution patterns of biomarkers are normally different from oil to oil or oil to processed oil. The distributions of hopanes and steranes are the most common of biomarkers that are observed in crude oils. In crude oils, the distribution of biomarker is quite wide range. While, the distribution of refined products are depended on their parent of crude oils and carbon range. As illustrated in Figure 2.8, processed oil present the concentration and variety of steranes lower than crude oil (Sockeye and Orimulsion) because processed oils are removed high molecular hydrocarbons (Wang *et al.*, 2004). Thus, this distribution will be are advantage for distinguish crude oil from processed oil. However, steranes and terpanes are not suitable for differentiate lighter petroleum product since all of them are almost removed from lighter petroleum products. The recommend biomarker for this case is sesquiterpanes and diamandoid, which are still present in petroleum products and most abundance after refining processes (Wang *et al.*, 2005).

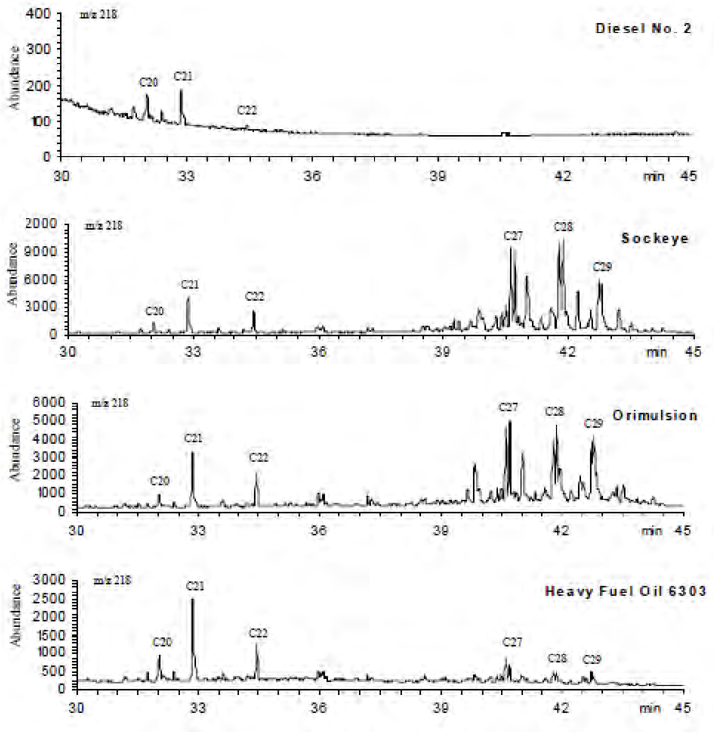


Figure 2.8 Distribution of biomarker steranes compounds (at m/z 218) of Diesel No. 2, Sockeye oil, Orimulsion, and HFO 6303. (Wang *et al.*, 2004)

2.3.4 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) are a type of chemicals that present naturally in crude oil, gasoline and coal. There are well known as carcinogen, mutagen and toxic, which may cause of health hazards. The structure of PAHs are two or more aromatic rings, which shared carbon atom between rings in their molecules and bond in linear cluster or angular arrangement (Emsbo-Mattingly *et al.*, 2016). Example of PAHs are illustrated in Figure 2.9. The common characteristic of PAHs are high melting and boiling point, low aqueous solubility and low partial pressure. Although, PAHs have low in solubility and partial pressure. It is resistance to weathering process such as oxidation and reduction. Moreover, PAHs also have very characteristic about UV absorbance spectra. It is particularly useful for identifying PAHs.

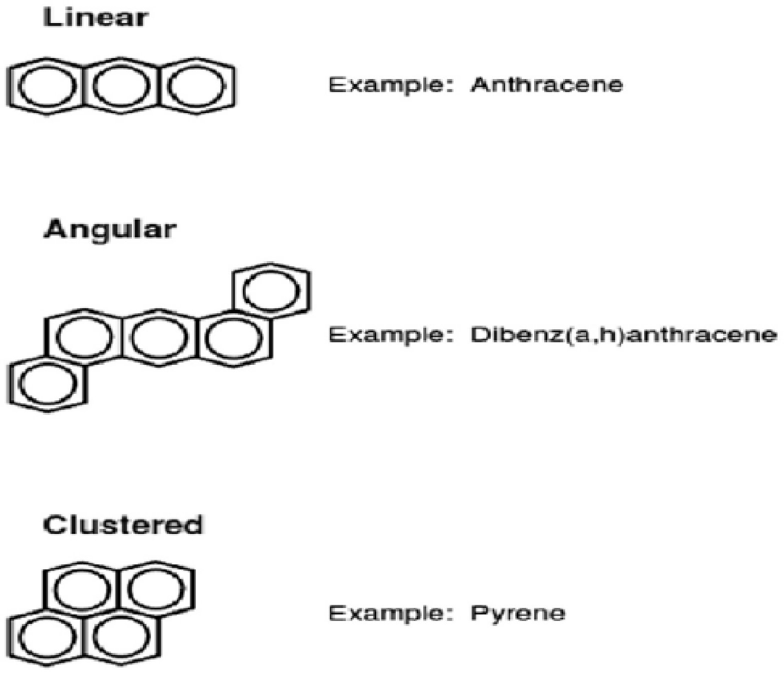


Figure 2.9 The structure arrangement of polycyclic aromatic hydrocarbon (PAHs) (Abdel-Shafy, 2016).

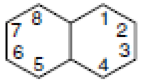
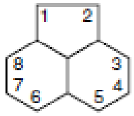
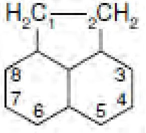
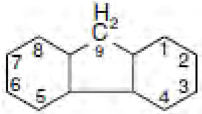
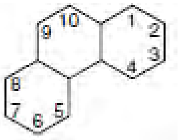
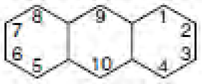
The major source of PAHs can be classified into three types, pyrogenic petrogenic and biological. PAHs, which are formed under high temperature and low oxygen, is called pyrogenic PAHs. Therefore, the example of pyrogenic process are the thermal cracking of crude oil or distillation of coal. The temperature that the pyrogenic PAHs occur are around 350 °C to more than 1200 °C. On the other hand, PAHs can be formed under low temperature, which are called petrogenic PAHs. These PAHs occur during crude oil maturation. Therefore, the most of petrogenic PAHs can be found in crude oil. In addition, PAHs can also be formed from certain plant or bacteria during degradation, which are called biologically PAHs (Abdel-Shafy, 2016).

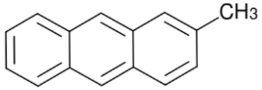
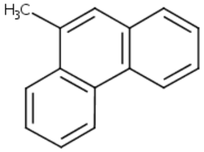
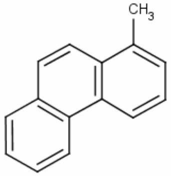
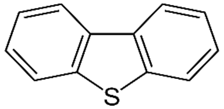
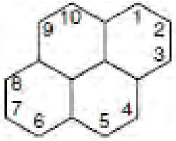
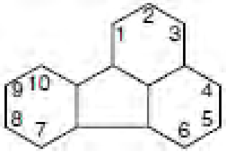
As previously mentioned, the condition of formation is one of the factors used for defining PAHs source because higher temperature condition tend to produce PAHs with fewer alkylate than low temperature condition. Therefore, it is very useful to oil spill investigation and others. Table 2.4 shows the common use of some PAHs. The properties and photograph of PAHs that use in oil spill investigation are described in Table 2.5.

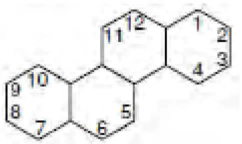
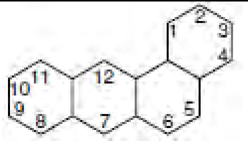
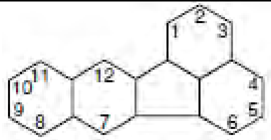
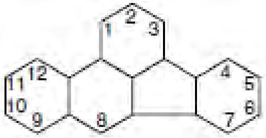
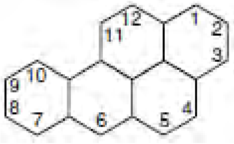
Table 2.4 The common use of some PAHs

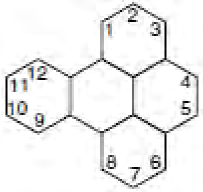
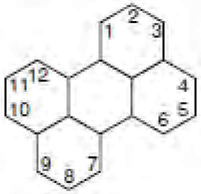
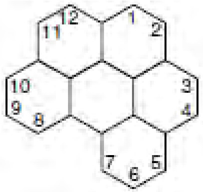
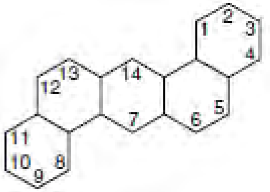
PAHs	Applications
Acenaphthene	Manufacture of pigments, dyes, plastics, pesticides and pharmaceuticals.
Anthracene	Diluent for wood preservatives and manufacture of dyes and pigments.
Fluoranthene	Manufacture of agrochemicals, dyes and pharmaceuticals.
Fluorene	Manufacture of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic.
Phenanthrene	Manufacture of resins and pesticides.
Pyrene	Manufacture of pigments.

Table 2.5 The properties and photograph of PAHs that use in oil spill investigation (Stogiannidis *et al.*, 2015)

PAH	structure	MW (g)	Benzene ring	S (mg/l)	P (Pa)	BP (°C)	Carcinogenicity[a]
Naphthalene		128.2	2	32	11	218	NC
Acenaphthylene		152.2	2	3.9	9.0×10^{-1}	280	NC
Acenaphthene		154.2	2	3.9	3.0×10^{-2}	279	NC
Fluorene		166.2	2	1.9	9.0×10^{-2}	295	NC
Phenanthrene		178.2	3	1.1	2.0×10^{-2}	340	NC
Anthracene		178.2	3	0.05	1.0×10^{-3}	342	NC

PAH	**structure**	**MW (g)**	**Benzene ring**	**S (mg/l)**	**P (Pa)**	**BP (°C)**	**Carcinogenicity** [a]
2-methylanthracene		192.3	3	0.21[a]		204	NC
9-methylphenanthrene		192.3	3	2.61[a]		197	NC
1-methylphenanthrene		192.3	3	2.69[a]		353	NC
Dibenzothiophene		184.0	2	1.0		333	NC
Pyrene		202.1	4	0.13	6.0×10^{-4}	393	NC
Fluoranthene		202.3	3	0.26	1.2×10^{-3}	375	NC

PAH	**structure**	**MW (g)**	**Benzene ring**	**S (mg/l)**	**P (Pa)**	**BP (°C)**	**Carcinogenicity** [a]
Chrysene		228.3	4	0.002	1.4×10^{-6}	448	WC
Benz[a]anthracene		228.3	4	0.011[a]	2.8×10^{-5}	400	C
Benzo[k]fluoranthene		252.3	4	0.0007	5.2×10^{-8}	480	C
Benzo[b]fluoranthene		252.3	4	0.0014	6.7×10^{-5}	481	C
Benzo[a]pyrene		252.3	5	0.003	7.0×10^{-7}	496	SC

PAH	structure	MW (g)	Benzene ring	S (mg/l)	P (Pa)	BP (°C)	Carcinogenicity [a]
Benzo[e]pyrene		252.3	5	0.005	7.3×10^{-6}	311	NC
Perylene		252.3	6	0.0004	1.8×10^{-8}	503	NC
Benzo[ghi]perylene		276.4	6	0.00026	1.4×10^{-8}	550	NC
Dibenz[ah]anthrancene		278.3	5	0.0005	3.7×10^{-8}	524	C

Note: MW = Molecular weight, S = Solubility at 25°C, P = Vapor pressure at 25°C, BP = boiling point, NC = Non-carcinogenic, WC = Weakly carcinogenic, C = Carcinogenic, SC = Strongly carcinogenic [a](Pampanin *et al.*, 2013)

2.3.5 Recommended Diagnostic Ratios of PAHs

From Faksness, *et al.* 2002 studied about characteristic of PAHs, it was described that the ratio of 2-methylnaphthalene to 1-methylnaphthalene can be used to distinguish spilled oil with light weathering because this ratio is unaffected by initial weathering stage. Moreover, the relative of naphthalene and methylnaphthalene ratio with dimethylnaphthalene can also be used for measuring the loss of PAHs from dissolution (Faksness *et al.*, 2002).

For differentiation crude oils from processed oil as studied in (reference) can be distinguish from methylphenanthrene. For example, in crude oils, the distribution of 3- and 2- methylphenanthrene is smaller than 9- ,4- and 1-methylphenanthrene and the methyl anthracene is very small as show in Figure 2.10. While, heavy fuel oil have 3- and 2- methylphenanthrene higher than 9- ,4- and 1-methylphenanthrene as shown in Figure 2.11 (Zhang *et al.*, 2016). Moreover, they reported that the presence/absence of chrysene can also be used for differentiate crude oils from processed oils. From Wang, et al. 2008, they recommend another ratio for distinguish crude oil and refined products which is called PI index (pyrogenic index). This index calculate from the sum of the concentration of three to six rings EPA priority PAH divide with the sum of five alkylated PAH. According from NORDTEST, They reported that the range of PI in crude should be lower than 0.01 and in heavy fuel oil should be lower than 0.05 (Stogiannidis *et al.*, 2015).

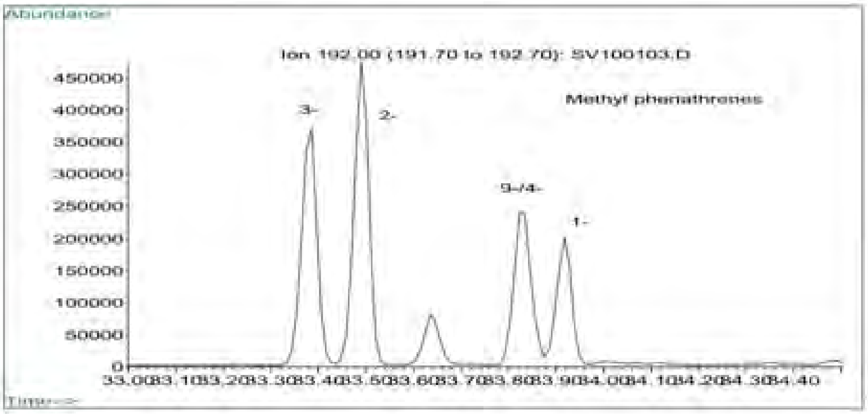


Figure 2.10 Differentiation of methylphenanthrene in heavy fuel oil (Faksness *et al.*, 2002).

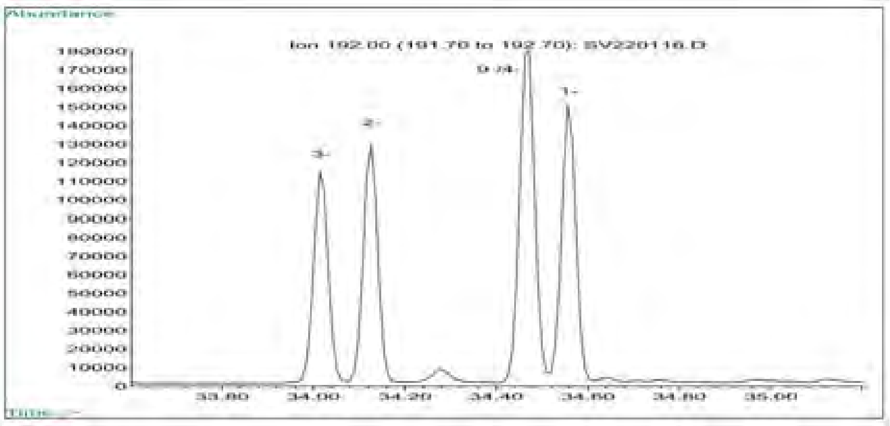


Figure 2.11 Differentiation of methylphenanthrene in crude oil (Faksness *et al.*, 2002).

Furthermore, for highly weathering, the ratio of retene to C4-phenanthrene can be used for distinguishing between similar oils since it resist with highly weathering process. Another ratio that used for highly weathering is C3-dibenzothioprene/C3-chrysene (Wang *et al.*, 2008).

2.3.6 Weathering Processes

The “weathering processes” are process that oil changes immediately after released to environments by physical, chemical and biological processes. The examples of oil weathering are spreading, evaporation, emulsification, dispersion, dissolution or photo-oxidation (as illustrated in Figure 2.12). These processes are affected by spill location, wind, waves and the exposure of oil to the sun. As oil weathered, initial oil losses some low molecular weight hydrocarbon so its density increases and some parts of the oil disperse into the seawater. While, the remaining oil on the surface is turn into emulsified oil with seawater and oxidized by the sunlight. Finally, oil residue can be subjected to the process sedimentation. The descriptions of weathering processes are described in following section. Figure 2.13 illustrate the estimation time of each weathering processes (ITOPF, 2014, Tarr *et al.*, 2016).

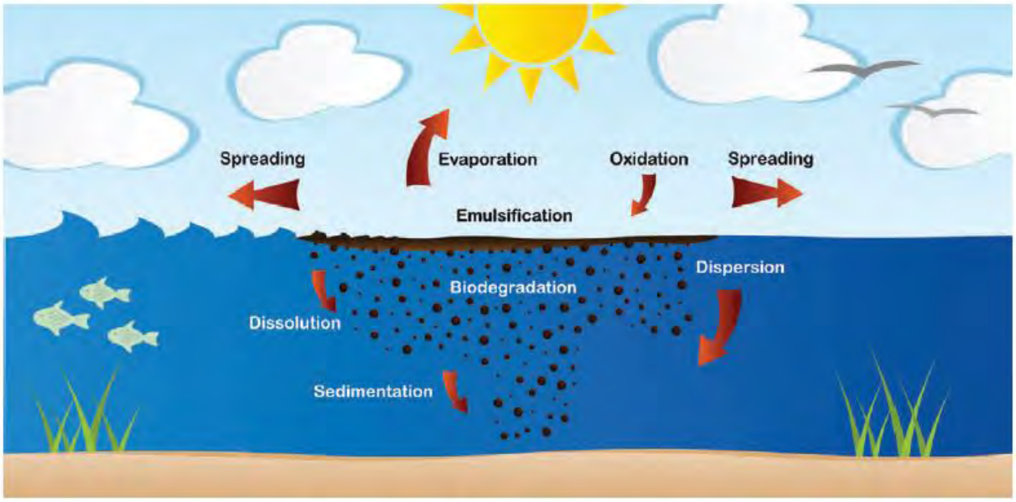


Figure 2.12 Overview of the major oil weathering processes (ITOPF, 2014).

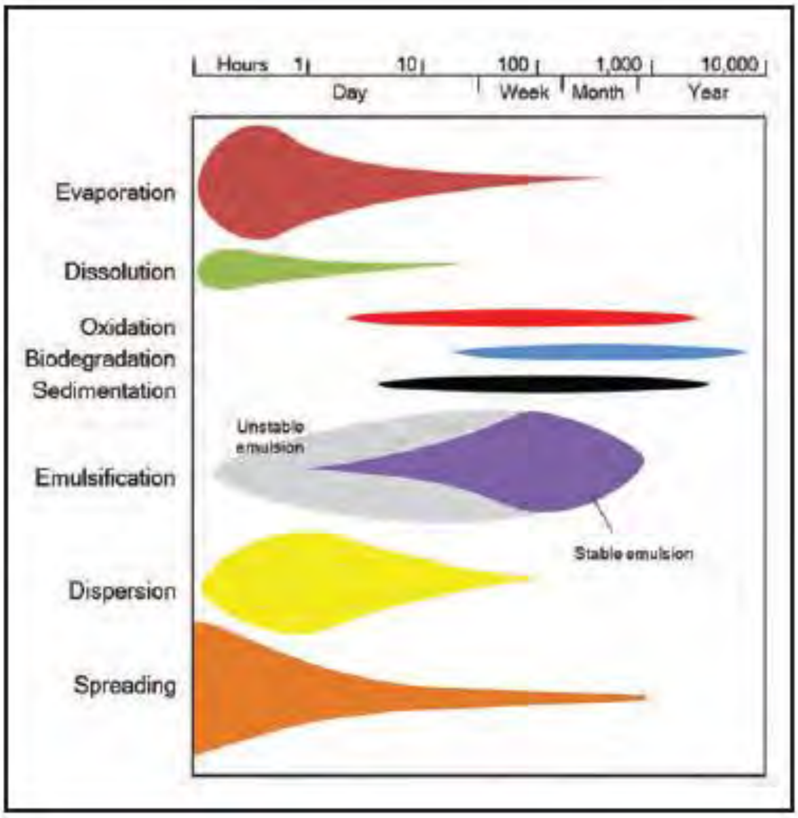


Figure 2.13 The estimation time of each weathering processes (ITOPF, 2014).

2.3.6.1 Spreading

After oil is spilled, it immediately starts to spread over the seawater. It depends on viscosity of the oil which effect on speed of spreading. Moreover, the temperature is one factor of spreading. It also spread in high temperature faster than low temperature. After oil spreading for few hours, the slick will normally begin to break up because of wave, wind activity and will often narrow bands.

2.3.6.2 Evaporation

Evaporation is loss of the lighter molecular weight. Generally, the rate of evaporation depend on the volatility of oil, ambient temperature, spreading area and wind speed. For example, oil with a large percentage of light compounds will evaporate more than oil with large percentage of heavier compound. Moreover, oil components with boiling point lower than 200 °C will evaporate within 24 hours. For spreading area, it also effects to evaporation rate since the larger surface area of oil, the faster light components will evaporate. Therefore, the light product such as gasoline, kerosene and diesel tend to evaporate almost completely within a few days.

2.3.6.3 Dispersion

Dispersion occurs when surface slick break into oil drops which mix and spread within the sea water by the wave action. The rate of dispersion is largely depending upon the characteristic of oil and sea state. Therefore, dispersion occurs very quickly if the oil is light and low viscosity and the sea is turbulence.

2.3.6.4 Emulsification

Emulsification of oil spill refers to the combine of water in oil which leading to thickening oil. The formation of water in oil cause of increasing the volume of pollutant by three to four times. However, emulsification can also reduce the other natural weathering processes, which cause of persistent light and medium crude oils.

2.3.6.5 Dissolution

Dissolution of oil occurs at the surface between oil and seawater. The rate of dissolution depends on oil composition, surface area of oil, spreading, the water temperature and degree of dispersion. Generally, most of oil components have low solubility in water while lighter components especially monoaromatic hydrocarbons such as benzene and toluene have great solubility. However, most of component in oil are not very soluble and most of small component in oil are lost by evaporation. Therefore, concentration of dissolve oil in sea water normally not more than 1 ppm.

2.3.6.6 Photo-oxidation

Photo-oxidation is the process promoted by sunlight, which oil react with oxygen. It leads to the formation of soluble products or persistent compounds called tars. This process occurs very slow even in strong sunlight. Generally, thin oil film breaks down less than 0.1% per day and tend to oxidize from thin layer to oil residue rather than degrade. Typical example of this process is tar balls, which outer thick layer are formed in order to protect softer part by oxidation. Therefore, it can be frequently found standing on shoreline.

2.3.6.7 Sedimentation and Sinking

Sedimentation is a process that oil droplets interact with solid particles suspended in the sea and oil droplets will dense then sink to the seabed. In general, most of oils have lower specific gravity than seawater. Thereby, they float even they interact with dense materials. However, some residue oils have more specific gravity than seawater, which they will sink immediately when oil spills. However, sinking is observed only in shallow water or the area close to the shore.

2.3.6.8 Biodegradation

Biodegradation is the process which microorganism consume oil as an energy source. Microorganism normally are found in water everywhere and there are many types of them. Thus, they will effect to oil spill since each types of them tend to degrade specific group of hydrocarbon. In ideal condition, most of oil generally follow a degradation pattern, which is n-alkanes, branched alkanes, low molecular weight aromatic then high molecular weight aromatic and cyclic alkanes. However, biodegradation process is a slow process. As a result, oil compound remain unchanged for a long time and it also show a trace of oil along a shoreline.

2.3.7 Weathering Effect on Chemical Fingerprinting

From Zhang *et al.* 2015, they studied on weathering characteristics of crude oils from Dalian oil spill by using GC-MS. In their studied, they simulated weathering under 95 days. The result of the distribution of aliphatic hydrocarbon showed that light molecular weight of normal alkane and isoalkane (< *n*-C13) are undergone with weathering process and the unresolved complex mixture arise. However, it still showed some aliphatic compounds such as pristine (Pr) and phytane (Ph). Pr and Ph show strong unweathern and become prominent peak. Therefore, the diagnostic ratio for biodegradation indicators are *n*-C17/pristine and *n*-C18/phytane. Furthermore, the diagnostic ratio like Pr/Ph also used since Ph presents more degradation-resistant compared to Pr. For polycyclic aromatic hydrocarbons (PAHs), the major change of alkyl PAH compound from weathering is decreasing of naphthalene and its alkyl homologues. Moreover, the losing homologous of PAHs will loss from low molecular weight to high molecular weight (C0>C1>C2>C3>C4). While chrysene was observed that their do not degrade from evaporation. Furthermore, Ho, Wang et al 2008. also observed five classes of PAHs, of naphthalenes (N), phenanthrenes (P), dibenzothiophenes (D), fluorens (F), chrysenes (C) and their alkylated homologues. The result show that naphthalene and its homologous be firstly degraded. While chrysene are the strongest, unweather among PAHs. For biomarker, hopanes and steranes are more resistant than other biomarkers. Therefore, they commonly used as a diagnostic ratio for weathering check (Ho *et al.*, 2015, Zhang *et al.*, 2015, Zhang *et al.*, 2016).

2.4 Oil Spill Identification Methodology and Oil Spill in Thailand

2.4.1 Chemical Fingerprinting Techniques

Oil fingerprinting is widely used for find the source of an oil spill by matching information between the potential source and the spilled oil. Nowadays, analytical fingerprinting of oil have many different techniques either the use of instrumental or non-instrumental for example, gas chromatography (GC), gas chromatography – mass spectrometry (GC-MS), high performance chromatography (HPLC), thin layer chromatography (TLC), ultra violet (UV) spectroscopy and spectroscopic method and so on (Oforka *et al.*, 2012). However, the most extensively technique is GC which is technique used following the CEN TR15522-2 and the ASTM5739-00 standard. For other methodologies, they are development techniques that assist GC techniques to get a clearly result.

Chromatography is the separation of a compound mixture into their individual components according to their volatility. There are many types of chromatography such as liquid chromatography (LG), gas chromatography (GC), ion-exchange chromatography, but all of these operate with same principles. The gas chromatography (GC) is the most important one for oil fingerprinting since it has a many advantages. For example, the results of GC show both qualitative (identify component) and quantitative (measuring amount of sample component).

The gas chromatography (GC) is one of chromatography techniques, in which the component of a sample is separated between two phases (the stationary phase and the mobile phase). Normally, GC has three main parts, which are injector, column and detector. The sample solution is injected into instrument by injector and volatilized into vapor phase. Then, the sample stream is carried to column by carrier gas such as Helium or Nitrogen in order to separate various components. After that, the separated components are detected and measured by detector (Moustafa *et al.*, 2012). Figure 2.14 shows a photograph of a typical GC.

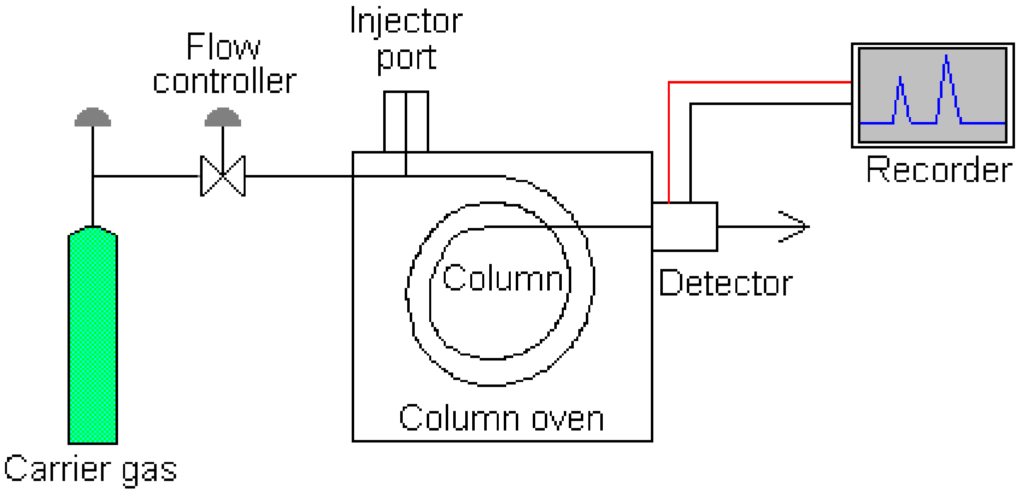


Figure 2.14 Typical Gas chromatography (GC) instrument (Moustafa *et al.*, 2012).

The heart of this system is column where the separation of various component take place. In column, there are stationary phase and packed material, which influence to the separation and affect the time of separation (retention time). Columns are classified as either capillary or packed columns. Generally, the capillary columns give better fine structure chromatographic fingerprinting and it is vastly used in environmental forensic than packed column. The column is placed in an oven where temperature can be controlled precisely over a wide range of temperature. The photograph of capillary and packed column are shown in Figures 2.15 and 2.16. For the detector of GC, there are many types of detector and the choice is bases on application. Most of detector that use in GC were especially invented for this technique. Mass spectroscopy (MS) is the one of detector, which is widely uses in GC technique. It provides the most information, both qualitative identification of various compound and quantitative analysis, with only few microgram of sample. When GC link with MS, Electron ionization (EI) or chemical ionization (CI) will ionizes the compounds that eluted from GC column into charge fragment. Then, charge fragments are accelerated into mass analyzer. The different of mass to charge ratio will generate different signals. Thus, the various compounds that produce ions within the range of mass analyzer will be detected. However, in complex sample sometimes their distribution pattern quite difficult to detect since co-eluted interfering of component could obstruct the accurate information from GC. Thus, there are many researches, which develop GC-MS. In this research will focus on GCxGC-TOFMS because it significantly reduce the interference of some component in same retention time (Piantanida *et al.*, 2014, Bayona *et al.*, 2015).

Figure 2.15 Capillary column of gas chromatography (Piantanida *et al.*, 2014).

Figure 2.16 Packed column of gas chromatography (Piantanida *et al.*, 2014).

2.4.1.1 GCxGC-TOFMS

In the past few years, two-dimensional gas chromatography (GCxGC) has been estimate for oil identification. The advantage of TOFs (time of flight) is the ability of confirmation of oil fingerprinting and resolving co-eluted PAHs and biomarkers in oil (Bayona *et al.*, 2015). Moreover, TOFMS detector will complementary to conventional GC-FID. GCxGC consists of two columns, which in the first column is a non-polar column, and the second one is a polar column. However, some researches are claimed that the opposite sequence allow a better result of non-polar component. The use of two columns of GCxGC expands the chromatogram distribution. The key of these is thermal modulator, which place between two columns. It is ensured that all of stream from the first column is properly reach to temperature before release into the second column. Figure 2.17 shows diagram of GCxGC-TOFMS. For the part of detector, analytical bands that eluted from the first column are significantly sharpen before it is released into the second column. The narrow peak require a detector that can collect data at rate 100 Hz. Hence, TOFMS is suitable since it provides mass spectral acquisition rate up to 500 Hz (LECO, 2014).

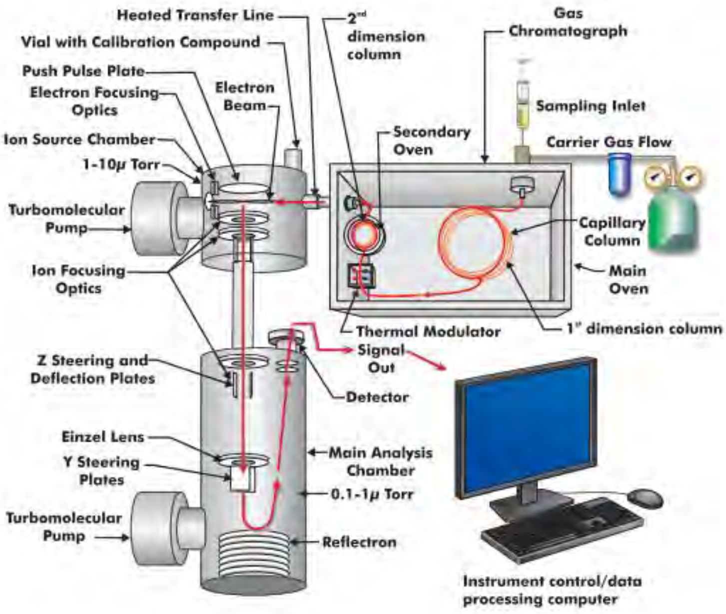


Figure 2.17 Diagram of GCxGC-TOFMS (LECO, 2014).

2.4.1.2 *Inductively Coupled Plasma Optical Emission Spectrometry*

Inductively Coupled Plasma Optical Emission Spectrometry or ICP-OES is one of the most powerful tool for the determination trace element. This technique can analyze multi-element in one time. Inductively coupled plasma or ICP is plasma, which is obtained the power from electromagnetic induction. This plasma provides a high energy, which have a temperature between 6000 K to 10000 K by emitting an argon gas through the torch, which have a copper coil surround the top of the torch as shown in Figure 2.18. This section is connected to a radio frequency (RF) generator providing an electromagnetic induction and spark with argon flow around the torch. This condition produces a high energy of argon electron and create the chain reaction, which is called plasma. This plasma is used for many applications, however, for the trace element the method that well known is optical emission spectrometer. This method based on measuring spectrums of changing state of electrons from ground state to excited state. While electrons change their state, they emit their spectrum, which present in an UV-visible and have a unique characteristic.

For analysis, the sample solution, which requires extraction or acid digestion, may be injected directly into the instrument. The sample is converted into an aerosol or very fine mist of liquid droplets by nebulizer. Then, the aerosol is carried into the center of plasma by the argon gas flow. After that, the droplet will undergo the three step. The first step is a removal of solvent from solution then it is vaporized to gaseous phase and the last step is atomization. This step is breaking gaseous molecules into atom and excitation atoms to an excited state. The excitation and ionization step occur in the initial radiation zone (IRZ) and normal analytical zone (NAZ) which analytical emission is collected at this zone. The picture of instrument shown in Figure 2.19

In oil fingerprinting field, ICP-OES is a very useful instrument for finding metal in oil such as V/Ni ratio. The main advantages of ICP-OES are efficient and reproducible vaporization, atomization, excitation, and ionization because the ICP can maintain high temperature at 6000 – 10000 K. This temperature makes it capable exciting element. Moreover, ICP is less noisy, better to operate with the liquid sample, inexpensive compared to another source of temperature, and lower detection limit than AAS. However, ICP-OES probably have a few interference from spectral interference since it able to excite almost every element that passes through plasma so the spectral are likely to be rich especially in concentrate sample.

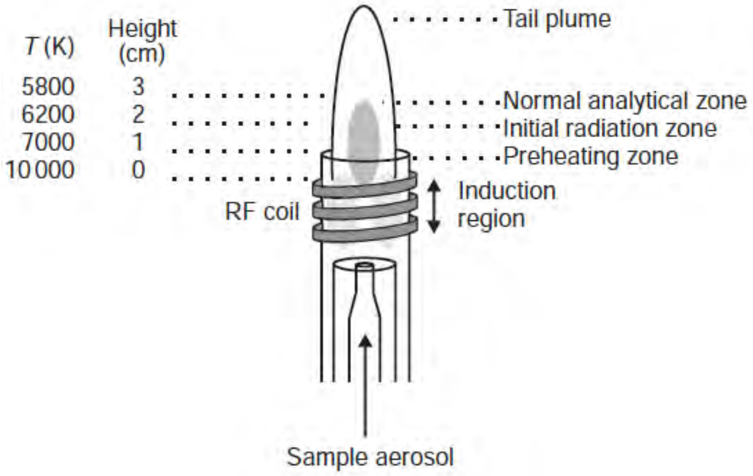


Figure 2.18 The schematic diagram of ICP torch and the RF coil.

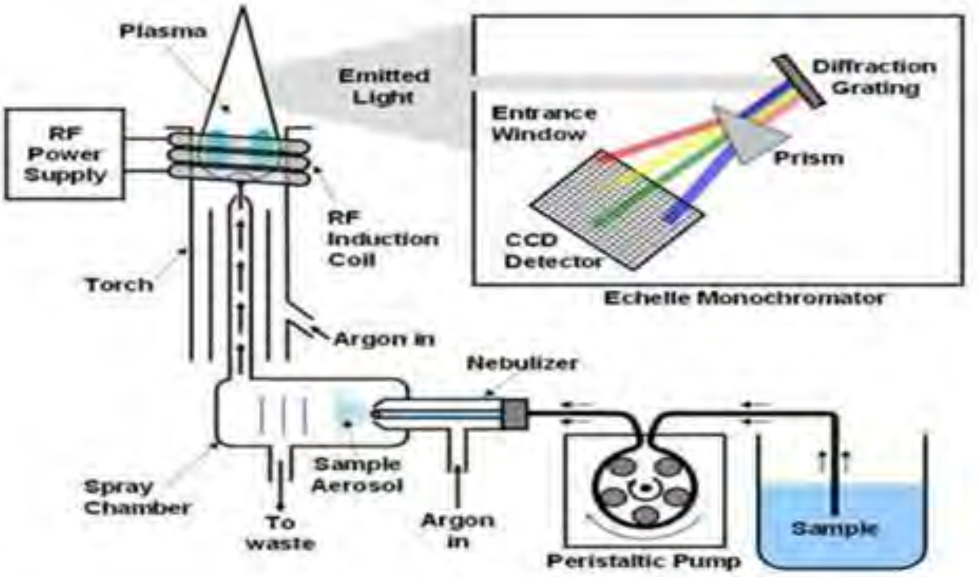


Figure 2.19 Diagram of ICP-OES instrument.

2.4.2 NORDTEST Methodology for Oil Spill Identification

The NORDTEST method for oil spill identification has formed since 1991. It is a principal for oil spill identification not only in Scandinavian counties, but also in other Europe countries. This method consists of three steps procedure. First step is screening of all sample characterization by GC/FID. Then, it is followed by GC/MS. After comparing the GC/MS, The final step is analysis to identify possible differences. The conclusion of these methods based on the chromatogram analysis, which would be either identity or non-identity (Hansen, 2002).

This methodology has been used for 10 to 15 years. However, it shows some need to be improved. For example, the weathering sample is not always easy to interpret. Thus in 2000, NORDTEST founded a "Revision of the NORDTEST Methodology for Oil Spill Identification" with other forensic oil spill laboratory in Denmark, Finland, Norway, Sweden, and researchers in United States. The objective for founding of that project is (1) review and assessment of public literature, and (2) an update of existing NORDTEST method into a technically more robust and legally defensible. The resulting of improvement NORDTEST methodology was still based on the same procedure; screening GC/FID, GC/MS fingerprinting and analytical data. The procedure chart for NORDTEST methodology is illustrated in Figure 2.20 and an analysis of oil spill identification will performed with this following step (Nordtest, 1991).

Level 1- GC/FID screening: After sample preparation, exacted sample is screened by GC/FID. If GC/FID is not available, GC/MS with full scan mode can be used. GC/FID chromatograms provide an information of the overall boiling range, dominance peak of n-alkanes and isoprenoid and weathering effect on oil spill. At this level, GC-FID provide information both qualitative and quantitative result. It can conclude to be "nonmatching" when the comparison of GC/FID chromatogram between oil spill sample and potential source are different in n-alkane distribution, the unresolved complex mixture (UCM) shapes or diagnostic ratios of n-alkane and isoprenoid without weathering effect. Thus, if there are still some doubt, it need to be considered in the next step.

Level 2- GC/MS fingerprinting: At this level, GC/MS in the selected ion-monitoring mode (GC/MS-SIM) is used for analyze potential source sample and spilled oil sample that has not been taken out from level 1. Moreover, the distribution of oils and diagnostic ratio of biomarker and PAHs are determined in this step.

Level 3- Evaluating data and weathering check: After sample analyzing in level 1 and 2, the result is evaluated diagnostic ratio and eliminated candidate source that show possible difference without weathering effect. Moreover, the result from two levels are used to calculate analytical relative standard deviation (RSD).Then, the diagnostic ratios that more robust (i.e., RSD>95%, precisely measurement and weathering resistant) are selected by using “Student’s t” statistic tool. After that, the results are shown in simple x-y plot and linear regression are performed. The conclusion based on the “fit” between spill and candidate source samples.

The overall conclusion can be classified into four categories, namely positive match, probable match, inconclusive and non-match. This category depends on degree of differences between spill and suspected sample. The analyses of two sample are according to the following criteria.

Positive match: The chromatographic pattern of the spill and suspected source samples are virtual identical. The only observed differences are caused by acceptable analytical variance and/or weathering.

Probable match: The chromatographic pattern of the spill and suspected source samples are similar except the difference, which cause from weathering processes (i.e. loss of lower molecular weight peaks, wax redistribution etc.) or contaminant.

Inconclusive: The chromatographic pattern of the spill and suspected source samples are quite similar, except the difference, which is impossible to ascertain. These different may be cause from heterogeneities of the oil quality either within the spill sample or the suspect source.

Non-match: The chromatographic pattern of the spill samples are unlike suspected source sample.

The conclusion categories that mentioned above should be used accompany with correlation plot analysis. For the correlation plot analysis, sample especially spilled sample need to be triplicate analyzed in order to calculate the analytical standard deviation of the diagnostic ratio.

Observation's diagnostic ratio can be calculated by equation (2.1)

$$Diagnostic\ ratio = \frac{100 \times A}{(A+B)} \tag{2.1}$$

A and B are concentrations generated from a multi-point calibration curve for biomarker compound with standard.

For biomarkers with no corresponding standard, the values for A and B were (area of analyst) / (area of internal standard).

The accuracy of correlation analysis (equation 2.2) and calculation of diagnostic ratio rely on the measurement of triplicate analyses. The result can be calculates as the relative variation 95% confidence interval or confident limit (CL) using the "Student's t" statistic tool.

Correlation analysis of Diagnostic ratio (2.2)

$$\mu = x \pm \frac{t \times s}{\sqrt{N}} \tag{2.2}$$

Where, x is mean value, the center of the distribution.

s is standard deviation.

t is student's t distribution.

N is number of observations.

T value is a relation between degree of freedom (N-1) and confident level, which can be found from Table 2.6.

Table 2.6 Values of Student's t (Harris, 1995)

Degree of freedom	**Confidence level (%)**		
(N-1)	95	98	99
1	12.706	31.821	63.657
2	4.303	6.965	9.925
3	3.182	4.541	5.841
∞	1.960	2.236	2.576

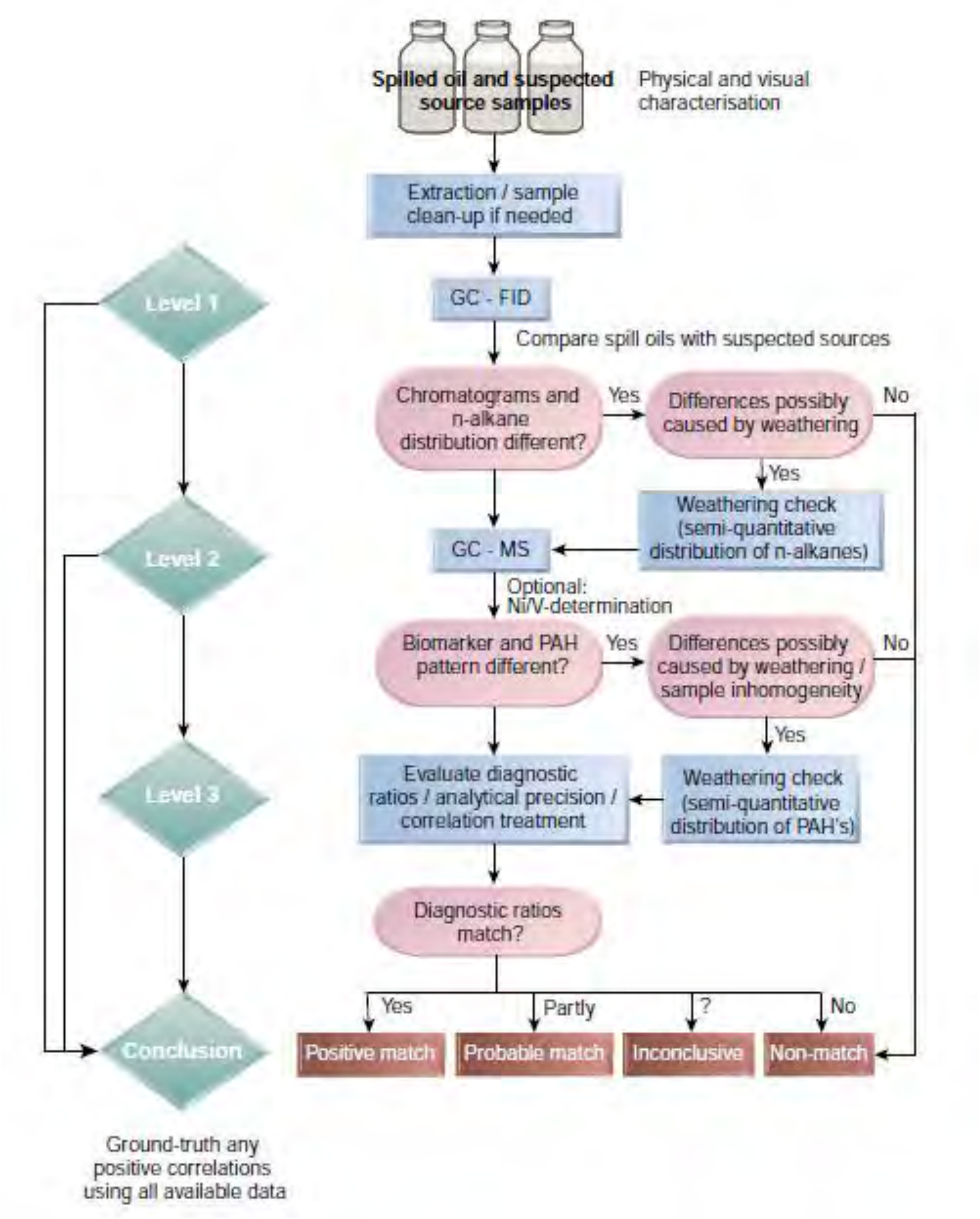


Figure 2.20 The procedure chart for NORDTEST methodology (Liv-Guri Faksness *et al*., 2002).

For confidence level, it is suggested a definition of positive match at a 95 % confidence interval as in examples from the Round Robin study (Round Robin study is participation of 12 different laboratories from 10 countries in order to analyses oil spill and demonstrate strong capability of NORDTEST method). These examples are shown in Figures 2.21 to 2.26. Furthermore, the recommend criteria for correlation analysis are followed by Round Robin study, which concludes in Table 2.7.

Table 2.7 Recommended criteria for correlation studies of diagnostic ratios (Liv-Guri Faksness *et al*., 2002)

Classification	**Definition**
Positive match	All DRs within the CL 95 %
Possible match	All DRs within the CL 98 % CL
No match	Any key DRs outside of CL 98 %

Note DRs = Diagnostic ratios, CL = Confidence limit

From the Round Robin study, the comparing result of the spill sample and suspected source(s) are presented in x-y plots, linear regressions are performed, and conclusion based on the "fit" between spill and source samples for the selected suite of diagnostic ratios can be made.

The straight line (x=y) is concluded the perfect match only when all DRs of the spill samples are the same as the suspected source oil. If the error bars of all DRs are overlapping the straight line, the spill sample is concluded positive match to the suspected source oil as shown in Figure 2.21 and 2.23. Unless one of the DRs is not overlapping the line x=y, it could be concluded no match to the source oil as illustrated in Figures 2.22 and 2.24.

The use of different confidence intervals such as 95 %, 98 %, and 99 % CL is shown in Figures 2.21, 2.25, and 2.26, respectively. It showed that some of the ratios are still outside the straight line although it was increased to 98 % or 99 % which gave the same conclusion: no match (Faksness *et al.*, 2002).

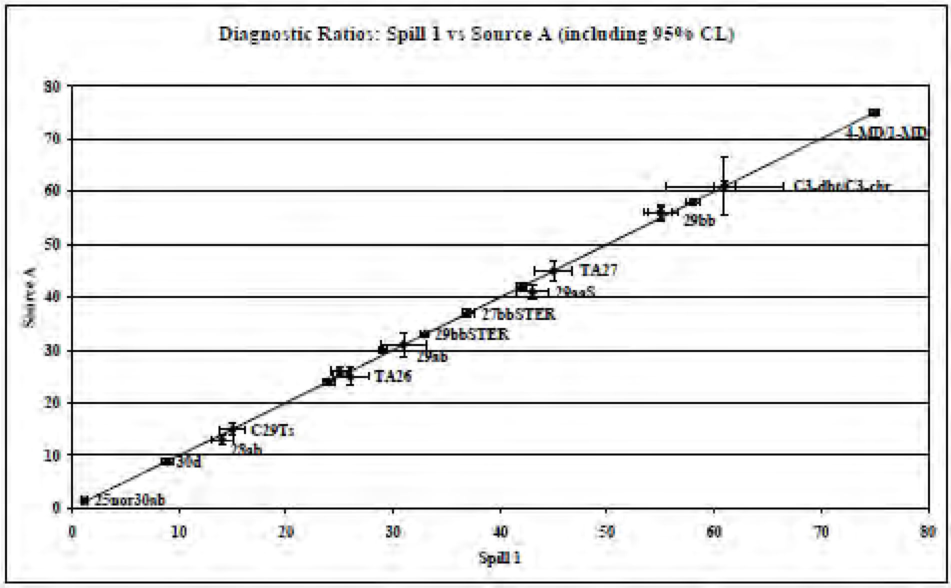


Figure 2.21 Correlation between spill 1 and source A, using a 95% confidence limit (positive match) (Faksness *et al.*, 2002).

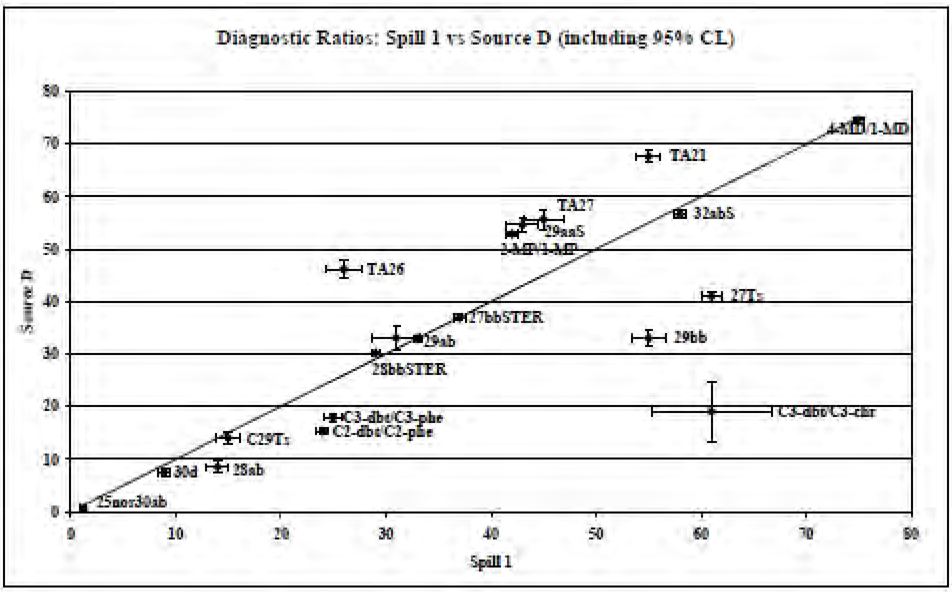


Figure 2.22 Correlation between spill 1 and source D, using a 95% confidence limit (Non-match) (Faksness *et al.*, 2002).

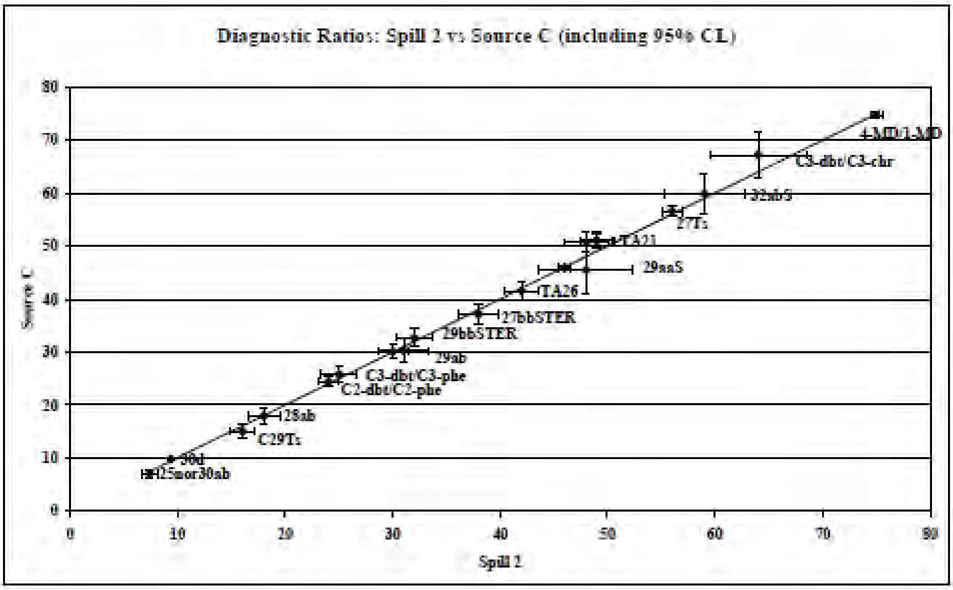


Figure 2.23 Correlation between spill 2 and source C, using a 95% confidence limit (Positive match) (Faksness *et al.*, 2002).

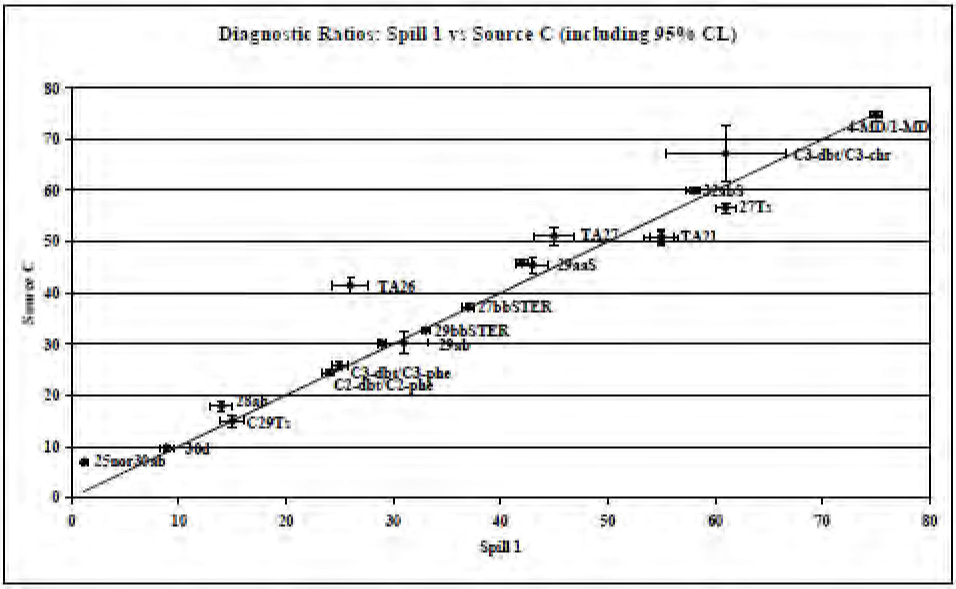


Figure 2.24 Correlation between spill 1 and source C, using a 95% confidence limit (Non-match) (Faksness *et al.*, 2002).

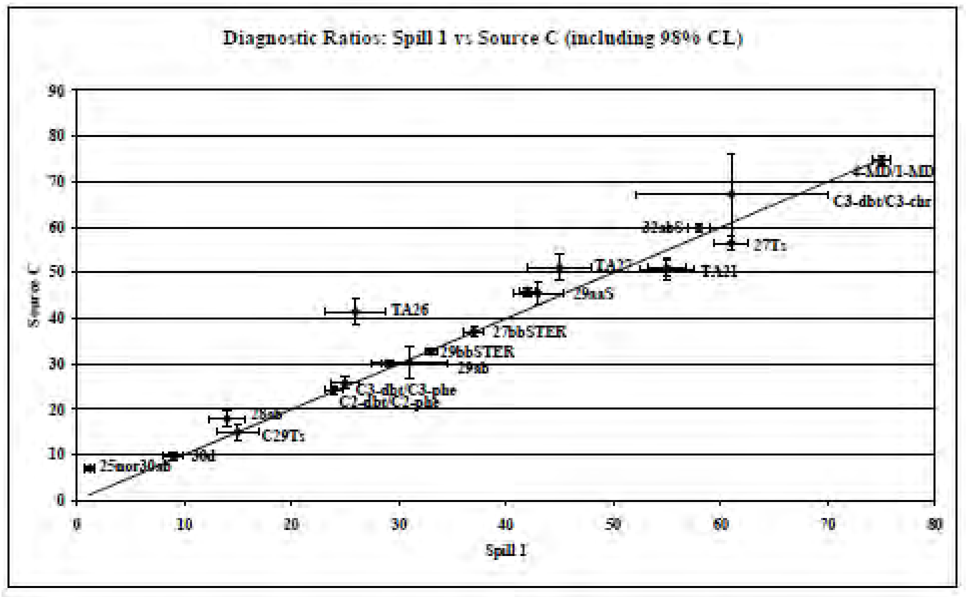


Figure 2.25 Correlation between spill 1 and source C, using a 98% confidence limit (Positive match) (Faksness *et al.*, 2002).

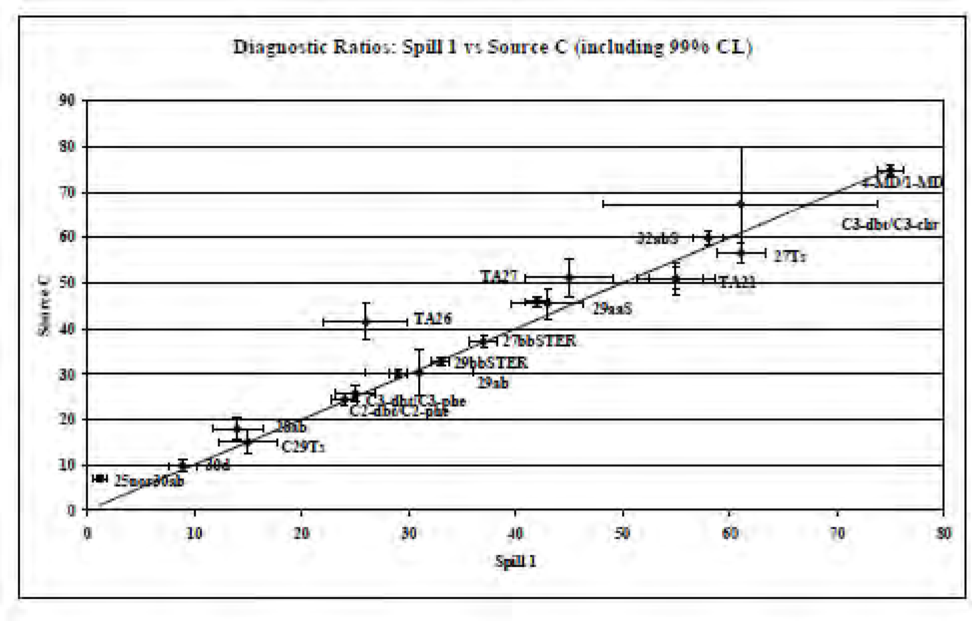


Figure 2.26 Correlation between spill 1 and source C, using a 99% confidence limit (Positive match) (Faksness *et al.*, 2002).

2.4.3 Measuring of Metal for Oil Spill Identification

The optional method for oil fingerprinting is measuring metal in oil such as vanadium (V) and nickel (Ni) metallo-porphyrins. These two element are well known in oil exploration since they present an important geochemical characteristic of oil source and origin (Khuhawar *et al.*, 2012). The metallo-porphyrins are high boiling biomarker derived from tetrapyrroles component of chlorophyll, which have Ni and V occur within their structure as shown in Figure 2.27 (Faksness *et al.*, 2002). The Ni and V in oil fingerprinting present in a ratio such as V/Ni or V/(V+Ni) ratio and so on. Normally, determining metal in oil is supporting method for a NORDTEST methodology when the compound of spilled oil is difficult to analyze since the concentration of V and Ni is very low. However, there are many researchers studying about determining of metals for oil fingerprinting such as (López *et al.*, 2017), (Vieira *et al.*, 2016). Their studies showed that V and Ni could be used to categorized crude oil samples with different origin such as lacustrine origin and marine origin.

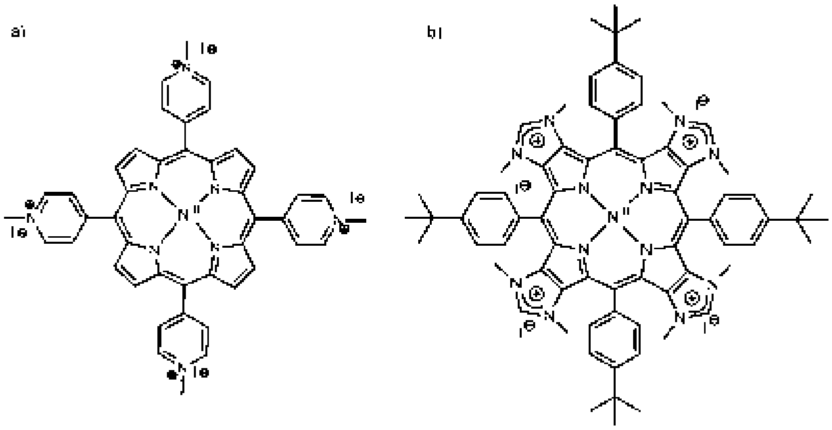


Figure 2.27 The schematic of metallo-porphyrins (Ni).

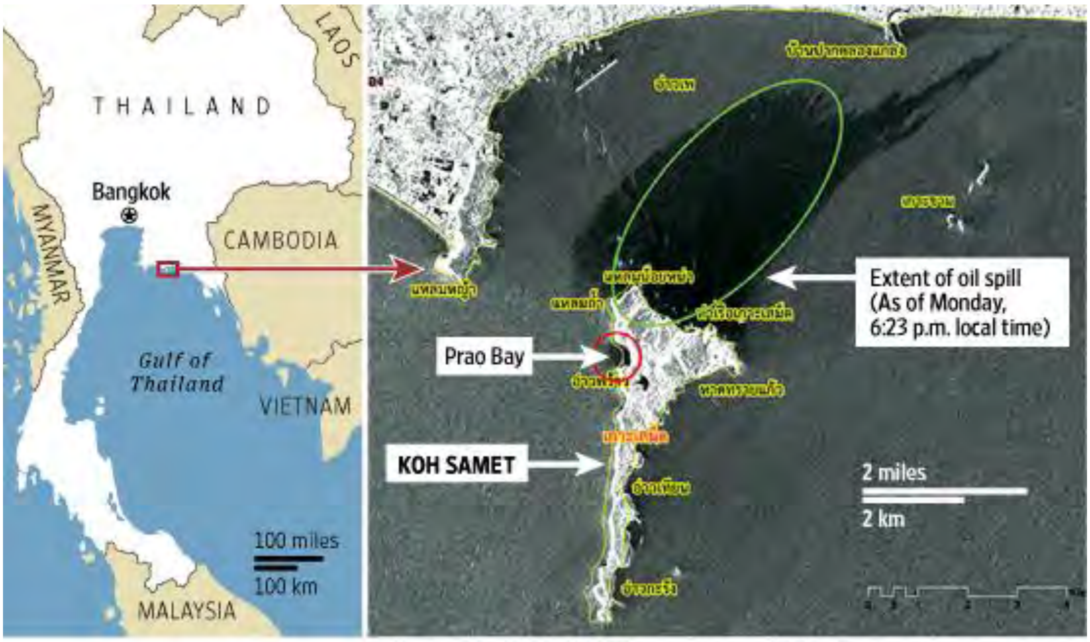
Moreover, the other interesting metals in oil are aluminum and silicon because of losing catalyst in cracking unit. This reason is hypotheses for discriminate crude oil from processed oil and help to identify spilled oil. From record data, their showed aluminum and silicon elements in processed oil between 1 to 100 ppm while crude oils should be lower than 1 ppm.

2.4.4 Example of Oil Spill in Thailand

On July 27, 2013, the Gulf of Thailand confronted with large oil spill problem in Rayong province. The oil spill happened because the pipeline owned by PTTGC plc, broke while a floating hose transferred oil from tanker to refinery. This cause resulted in 50,000 L (310 bbl) of crude oil spilled into the coastal where is far away from the beach at Ko Samet's Coconut Bay (Ao phrao) around 35 km. From this leakage lead to many effect for example, two beach were closed, the tourist evacuated and marine animal included coral reef obtained toxic. Figure 2.28 illustrates approximate location of oil spill in Gulf of Thailand and satellite picture of the extended area of oil spill (Maierbrugger, 2013).

Moreover, on Oct 27, 2015, In Prachuap Khiri Khan convince fled with the large quantity of oil, which coated garbage, leaves, wood and marine animal along the several kilometer of Hua Hin beach as show in Figures 2.29 and 2.30. The area that cover by the oil spill extended about 10 kilometers from Khao Takiap to Hua Hin fishing pier. However, the situation was improve in several day later since weathering process. For the cause of this situation, it was believed the oil spilled from a large vessel but authorities are still investigation. Thus, there was still unclear whether the oil came from a drilling plat form or from a commercial vessel (Fernquest *et al.*, 2015).

In addition, there are many situation of oil spill in Thailand as reported in statistic-spilled oil of marine department whether it is spilled oil from boat accident or smuggled discharge oil.



Satellite image: Geo-Informatics and Space Technology Development Agency, Thailand

Figure 2.28 Approximate location of oil spill in Rayong, 2013 (Maierbrugger, 2013).

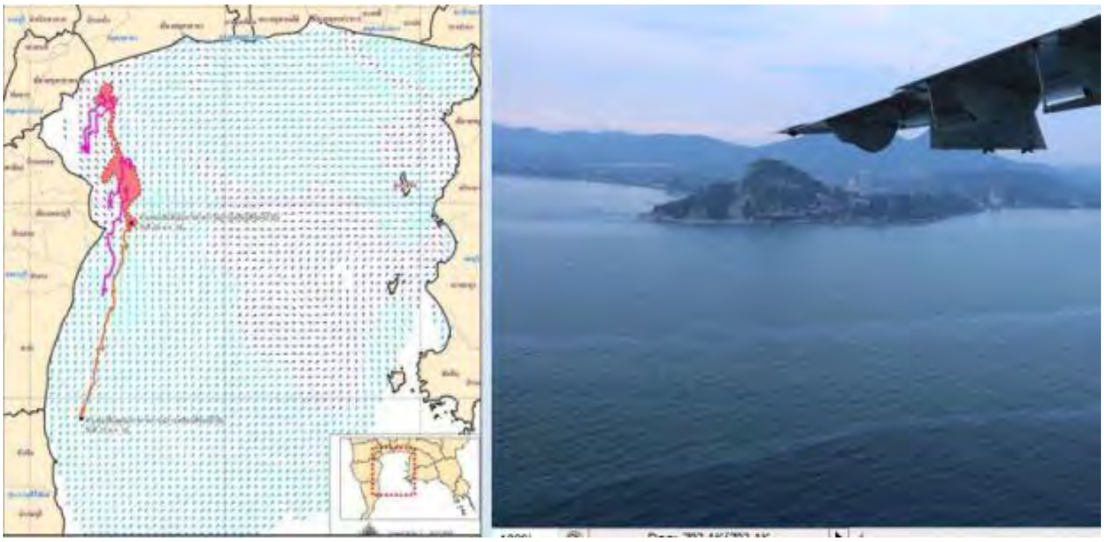


Figure 2.29 Approximate location of oil spill in Hua-Hin district, 2015 (Fernquest *et al.*, 2015).

Figure 2.30 Oil-coated garbage and animal pollute the water at Hua-Hin in Prachuap Khiri Khan province (Fernquest *et al.*, 2015).

CHAPTER III
EXPERIMENTAL

Part 1 Extraction and Analyses of Oils

3.1 Materials and Equipment

3.1.1 Sources of Oil Samples

In this research, there are nine crude oils and four fuel oils which were investigated as list in Table 3.1. Nine crude oils (CO1-CO9) and two fuel oils (FO3 and FO4) were obtained from PTTGC while another two fuel oils (FO1 and FO2) were obtained from Star Petroleum Refining Company Limited (SPRC). All of crude oil are typically used as a main feedstock for refining in Thailand refinery. FO1 and FO2 had Murban crude, Banang crude, Qatar Marine crude and Upper Zakum as the main feedstock. For FO3 and FO4, they had only Murban crude and Alshaheen crude as the main feedstock for producing fuel oil. Moreover, FO1 and FO2 from Star Petroleum Refining Company Limited (SPRC) were produced from the vacuum residue diluted with cutter from FCC while FO3 and FO4 from PTTGC were produced from visbreaking unit and diluted with kerosene and/or gas oil.

Table 3.1 Information of five crude oils and four fuel oils samples

No	Code	Sample Name	Description
1	CO1	Murban Crude	Crude Oil , Middle east
2	CO2	Banang Crude	Crude Oil , Malaysia
3	CO3	Qatar Marine Crude	Crude Oil, Middle east
4	CO4	Upper Zakum Crude	Crude Oil, Middle east
5	CO5	Al Shaheen Crude	Crude Oil, Middle east
6	CO6	Kikeh Crude	Crude Oil, Malaysia
7	CO7	Jasmine Crude	Crude Oil, Thailand
8	CO8	Pattani Crude	Crude oil, Thailand
9	CO9	Plazfior Crude	Crude oil, Brazil

Table 3.1 (Cont.) Information of five crude oils and four fuel oils samples

No	Code	Sample Name	Description
10	FO1	Residue Fuel Oil	Processed Oil, high Al, Si, high viscosity
11	FO2	Residue Fuel Oil	Processed Oil, high Al, Si, low viscosity
12	FO3	Visbreaking Fuel Oil	Processed Oil, low Al, Si, high viscosity
13	FO4	Visbreaking Fuel Oil	Processed Oil, low Al, Si, low viscosity

3.1.2 Gases

- The ultra-high purity (UHP) nitrogen for GC-TOFMS and GC-FID.
- The ultra-high purity (UHP) hydrogen is used for FID detector.
- The high purity (HP) helium 99.995 % for GC-TOFMS and GC-FID
- The zero grade air is used for FID detector.

3.1.3 Chemicals

- *n*-Hexane AR grade from RCI Labscan.
- *n*-Heptane AR grade from RCI Labscan.
- Toluene AR grade from RCI Labscan.
- Dichloromethane from Burdick Jackson.
- Silica gel is obtained from Merck, Germany.
- Anhydrous sodium is obtained from Merck, Germany.
- Sodium carbonate sulfate is obtained from Asia Pacific Specially Chemicals Limited, Australia.
- 17β (H), 21β (H)-hopane solution from Fluka.
- Tartaric acid and hydrochloric solution
- Flux (mixture of 90 % lithium tetraborate and 10 % lithium fluoride)

3.1.4 Equipment.

- Gas chromatography with flame ionization detector (GC-FID)
- Agilent© 7890 comprehensive two dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS)

- Inductively coupled plasma atomic emission spectroscopy (ICP-OES)
- Nylon syringe filter 0.45μm and 0.2μm
- Platinum dish 100 mL
- Electric muffle furnace, capable of being maintained at temperature 525 ± 25 °C and 925 ± 25 °C.
- Filter paper 0.8 μm and 5 μm
- Extraction thimble with pore size 20 to 30 μm
- Extraction apparatus and condenser

3.2 Methodology

3.2.1 Simulation of Seawater

The weathering simulated container which size was 1 m. long, 1 m. wide and 1.5 m. high was filled by 15 L seawater into each clean container. The sea water in this simulation is from Chonburi province with salinity 30 ppt. Then about 20 mL of oils were poured into seawater surface**.** To be noted that the seawater in this simulation was not passed the preparation process such as filtrate the sea water, etc. in order to preserve the microorganism of seawater that creates the biodegradation process. During weathering, the containers were placed outside the building to contact the sunlight for 60 days in order to create all weathering processes as shown in figure 2.13. Moreover, all weather oils were sampled at present intervals, namely day 0, day 7, day 30, day 45, and day 60.

3.2.2 Extraction of Oil Samples

The extraction of oil samples method was combined from two published articles which are Zhang *et al*., 2015 and Ho *et al*., 2015. First, 0.15 g of oil samples were accurately weighed and placed into clear vials. Then, the oil samples were extracted with 10 mL of high purity *n*-hexane/dichloromethane (1:1, v/v) and 0.5 g of anhydrous sodium sulfate to remove water. The mixture was vortexed for 5 min, and then the solutions were settled at the room temperature for 4 h. The supernatant in each vial was filtrated through 0.45 μm nylon syringe filter and transferred to a vial containing 0.25 g of silica gel and 0.25 g of anhydrous sodium sulfate. After that, the mixture was vortexed for 2 min and then settled for 2 min. Finally, the final sample was filtrated though 0.2 µm nylon syringe filter and transfer to a vial.

3.2.3 Analysis of Oil Sample Using GC-FID

The GC-FID conditions follow the NORDTEST oil spill identification (Faksness* *et al.*, 2002) and CEN methodology 2012. (Kienhuis *et al.*, 2016) The prepared samples are analyzed by capillary GC (equipped with Electron pressure control). GC-FID analyses were performed on Varian$^{©}$ CP-3800 gas chromatography fitted with high resolution HP-5 column (5% diphenyl and 95% dimethylpolysiloxane stationary phase, 30 m long × 0.25 mm internal diameter and 0.25 µm film thickness) in the splitless mode. The GC oven was held isothermally for 5 min at 40 °C, then programmed from 40 °C to 310 °C at 6 °C/min , and maintained at 310 °C for 10 min. Carrier gas is hydrogen (or Helium) with constant flowrates 2 mL/min, and detector gases are air and hydrogen. The temperature of injector and detector were 275 °C and 325 °C, respectively. Moreover, Alkane standard mixture was used as daily calibration.

3.2.4 Analysis of Oil Sample Using GC×GC-TOFMS

The extracted oil samples were analyzed by a LECO Pegasus 4D GC×GC-TOFMS. The capillary RTX-PAH column (60 m long × 0.25 mm internal diameter, and 0.25 µm film thickness) was used as the first dimension (1D) chromatographic column foe GCxGC – TOFMS analysis. For the second dimension (2D) column was performed by a capillary RTX-1HT column (1 m long × 0.25 mm internal diameter, and 0.25 µm film thickness). The 1D oven was held isothermally for 1 min at 40 °C, operated from 40 °C to 340 °C with ramped at 2.5 °C/min. For 2D ovens were operated with the same condition but the temperature offset of 5 °C higher than 1D oven. The samples were inject in the splitless mode with injection ratio equal 10:1 split. Helium was used as carrier gas with 1 mL/min constant flowrates. Moreover, The temperature of injector, transfer line and, MS source were 300 °C, 300 °C and 250 °C, respectively.

Qualitative analysis of extracted oil samples were performed in selection ion monitoring (SIM) mode.

3.2.5 Asphaltenes Precipitation

The hot oil sample was weight accurately 0.5, 1.5 and 10 g depending on the mass fraction of asphaltenes and added 200 mL of n-heptane. Then, the sample was shaken for 2 min and placed the flask in ultrasonic for 5 min. After that, the flask was shaken in a water bath at a temperature approximately 80 °C for 60 min. While the flask was shaken, the filter apparatus were prepared and the filter paper was weighed to the nearest 0.1 mg. Before weighing, a filter paper should be heated in an oven at 95 °C for 10 to 15 min and placed in desiccator for 30 min. After 60 min, the flask was removed from the water bath and poured into filter apparatus then using 100 mL of hot heptane rinse sample flask and poured into filter apparatus (rinse the sample flask at least 3 times). The filter cake was removed and placed in an oven at 95 °C for 10 to 15 min and placed in desiccator for 30 min. After that added filter cake in a thimble and prepared extraction apparatus by adding the thimble in extraction apparatus, place extraction apparatus on a hot plate then extract filter cake sample with 100 mL of hot toluene for 60 min or until dropping of toluene were clear. After 60 min, hot toluene was poured into evaporation dish which already weighed and was evaporated about 15 min then place the dish in an oven at 95 °C for 15 min and weighed to the nearest 0.1 mg.

3.2.6 Sample Preparation for Determination of Al and Si

A homogenized sample was weighted and heated in a clean platinum dish. Then, the combustible material was removed by burning with a Bunsen flame until remaining only carbon and ash. After that carbon was removed by heating in muffle furnace at a temperature of 550 ± 25 °C about 12 h. After 12 h, 0.4 g of flux (lithium tetraborate/lithium fluoride flux) was added to the residue and heated in a muffle furnace at a temperature of 925 ± 25 °C for 15 min. Then, the fusion was cooled at room temperature and added 50 mL of tartaric acid/hydrochloric acid solution. Then, the dish was placed on the hot plate at the temperature approximately 80 °C until the melt was dissolved. Allow the solution was cooled at room temperature and diluted to 100 mL with water. Finally, the resulting solution was measured aluminum and silicon content by inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Part 2 Collect and Analysis Data

3.3 Software

3.3.1 ChromaTOF Software

Data is acquired and processed using Leco ChromaTOF software. Both PAHs and hopane groups were set up to resample with a mass range 45 to 550 atomic mass units with an acquisition rate of 200 spectra/sec.

Diagnostic ratios were calculated using this equation,
Ratio = 100*A/(A+B), where the value for A and B were calculated by (area of analyte)/(area of internal standard).

3.3.2 Microsoft Excel

Microsoft Excel will provide the calculation of diagnostic ratios using the statistical theory that concerns about the confidence interval relatives to the student’s constant value which depend on number of the observation.

CHEAPTER IV
RESULTS AND DISCUSSION

This Chapter illustrates the results of 5 crude oils (CO1-CO5) and 4 fuel oils (FO1-FO4) before and after weathering processes in seawater for 60 days. The result shows physical appearance, distribution of aliphatic hydrocarbon, biomarker and PAH (Pyrogenic index) by using GC-FID and GCxGC-TOFMS. In addition, the determination of Al, Si and asphaltene contents between crude oils and fuel oils will be also discussed in this Chapter.

4.1 Effect of Weathering Processes

4.1.1 Physical Appearance of Oil from Day 0 to Day 60

The physical appearance of spill oil on day 0 shows that only Murban crude oil (CO1) spread over seawater immediately while the other oils spread over seawater after 3 days of spill. It happened because CO1 has high light hydrocarbon content as compared to other oils so it quickly dispersed to seawater. After 7 days of spill, all of the crude oils spread over seawater and some part of oil loss by evaporation process which observed from fading of oil over the surface. For the fuel oils (FO1-FO4), all of them spread over and formed a bunch sheet on the surface of seawater. In addition, in the middle phase of weathering (days 30-45), the seawater was evaporated by the sunlight so a salt crystal over the oil sheet was observed. Thus, some of the fuel oil sheets sink to the bottom as shown in Figures 4.1(f) and 4.1(h). In the last period of weathering, they had a sign of biodegradation since there were moss and algae grew up in all container. Thus, crude oils dramatically loss component especially in Murban and Banang crude oil as presented in Figures 4.1(a) and 4.1(b). For fuel oils on day 60, they were encompassed by algae and also made the oil sheet smaller. However, the quantity of fuel oil still almost the same as what observed on day 7. Thus, it could be concluded that crude oils was hard to collect after 2 months since it dispersed with seawater and expanded as a thin film especially CO1 and CO2 while fuel oils tended to merge and sink to the bottom. The physical appearance of oil samples on day 0, 7 and 60 are shown in Figures 4.1(a)-4.1(i).

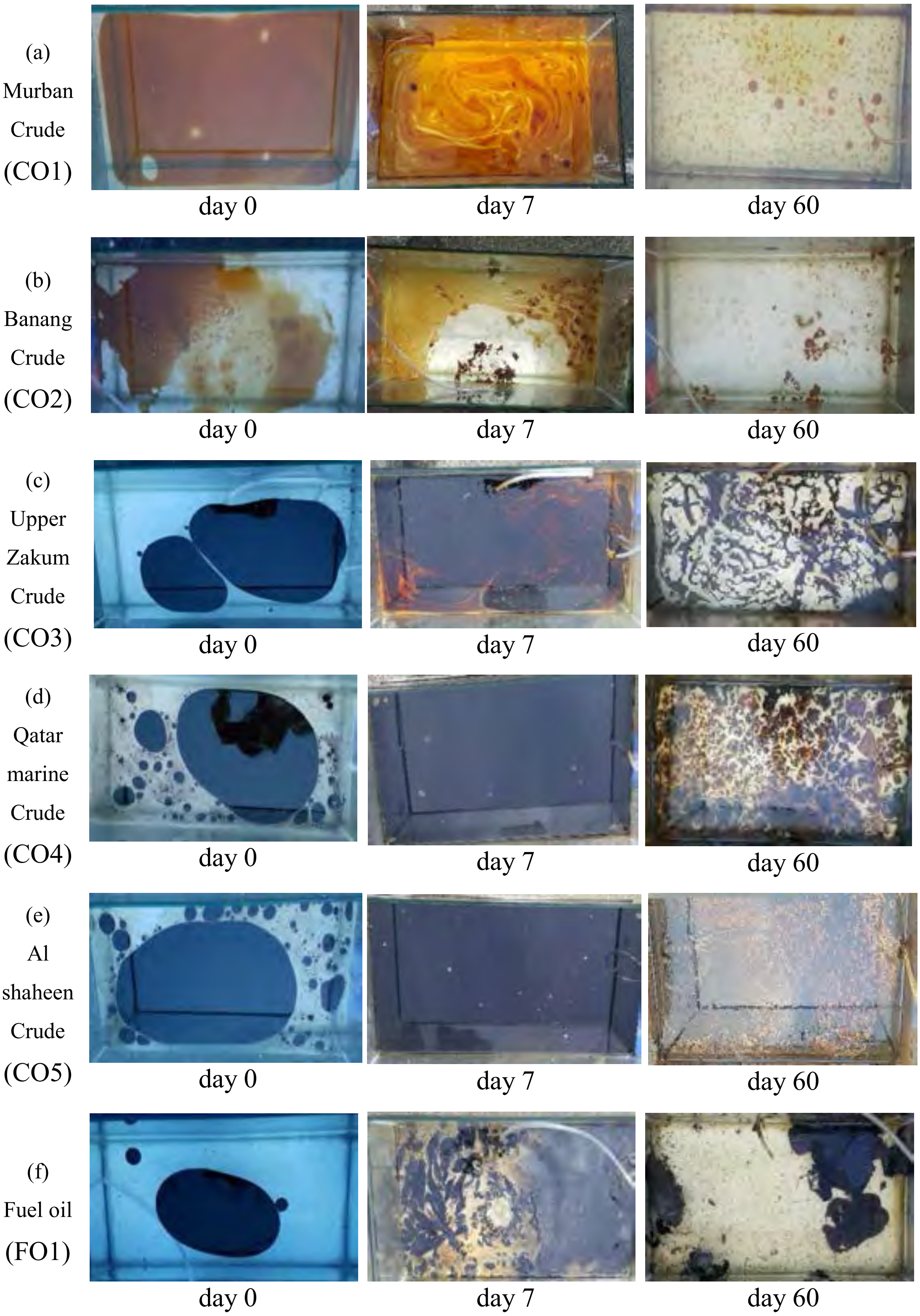


Figure 4.1 Physical appearance of all fresh samples (D0) comparing with their spilled on day 7 (D7), and day 60 (D60).

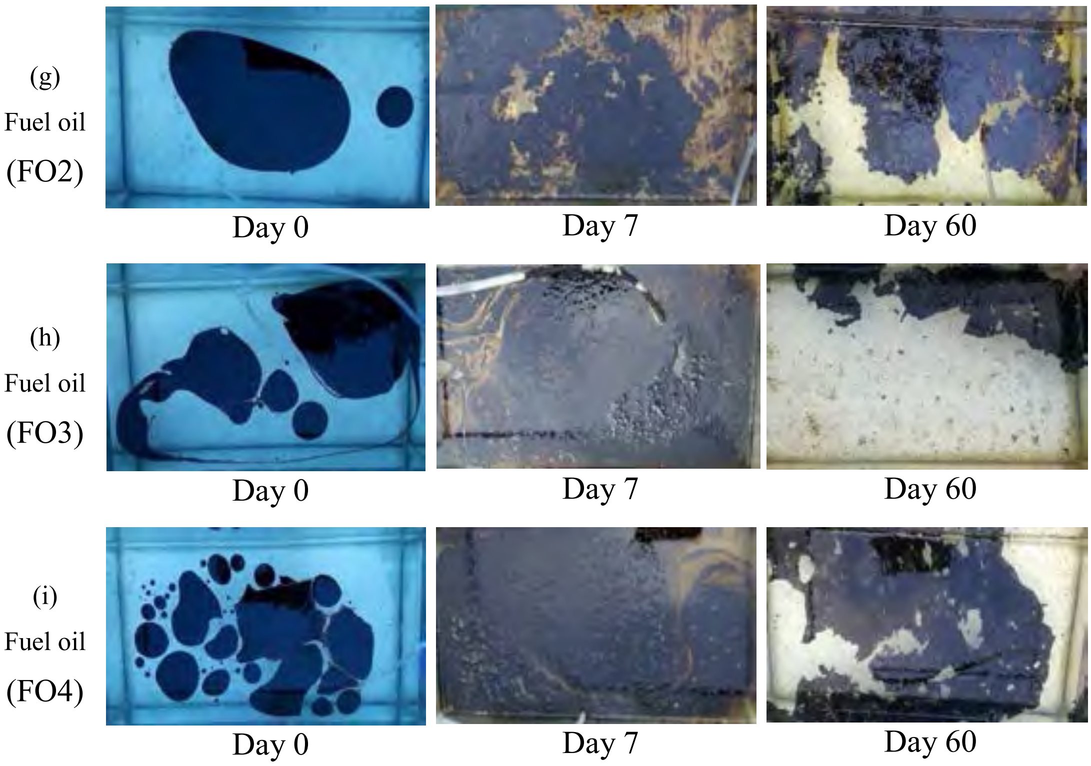


Figure 4.1 (cont.) Physical appearance of all fresh samples (D0) comparing with their spilled on day 7 (D7), and day 60 (D60).

4.1.2 Characterization of Aliphatic Hydrocarbon

The chromatograms of crude oil and fuel oil samples on day 0, 7 and 60 are shown in Figures 4.2(a)-(h). Once spilled, the oil was undergone weathering via evaporation and dispersion as indicated in chromatogram of day 7. The chromatogram shows the loss of light hydrocarbon (C8-C14). On day 60, CO1 and FO2 were observed the hump between *n*-C17 to *n*-C25. The hump in chromatogram can be referred to unresolved complex mixture or UCM component. It results from high biodegradation removing some components in oil and created new components which cannot be separated by GC. Typically, the depletion of *n*-alkanes is positively correlated with molecular mass as shown in chromatogram of GC-FID. However, the chromatograms demonstrated the peaks after *n*-C17, are less affected by weathering and *n*-C20 can be regarded as difficult to weathering. It can be concluded that all of oil samples on day 7 and 60 were highly degraded by evaporation and biodegradation process. Therefore, it cannot be identified by screening the chromatogram of GC-FID.

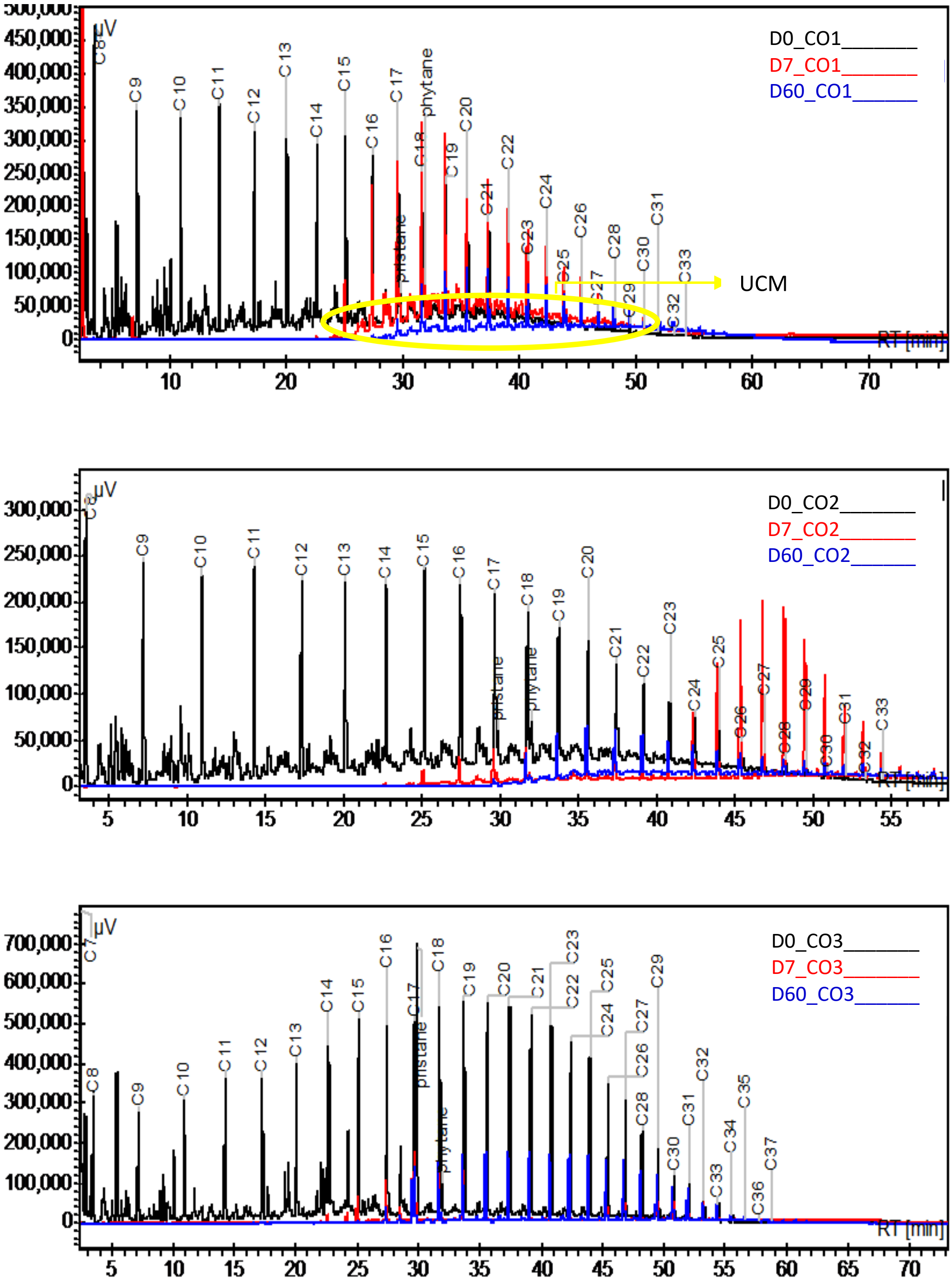


Figure 4.2 The FID chromatogram of crude oil and fuel oil sample on day 0, day7 and day 60.

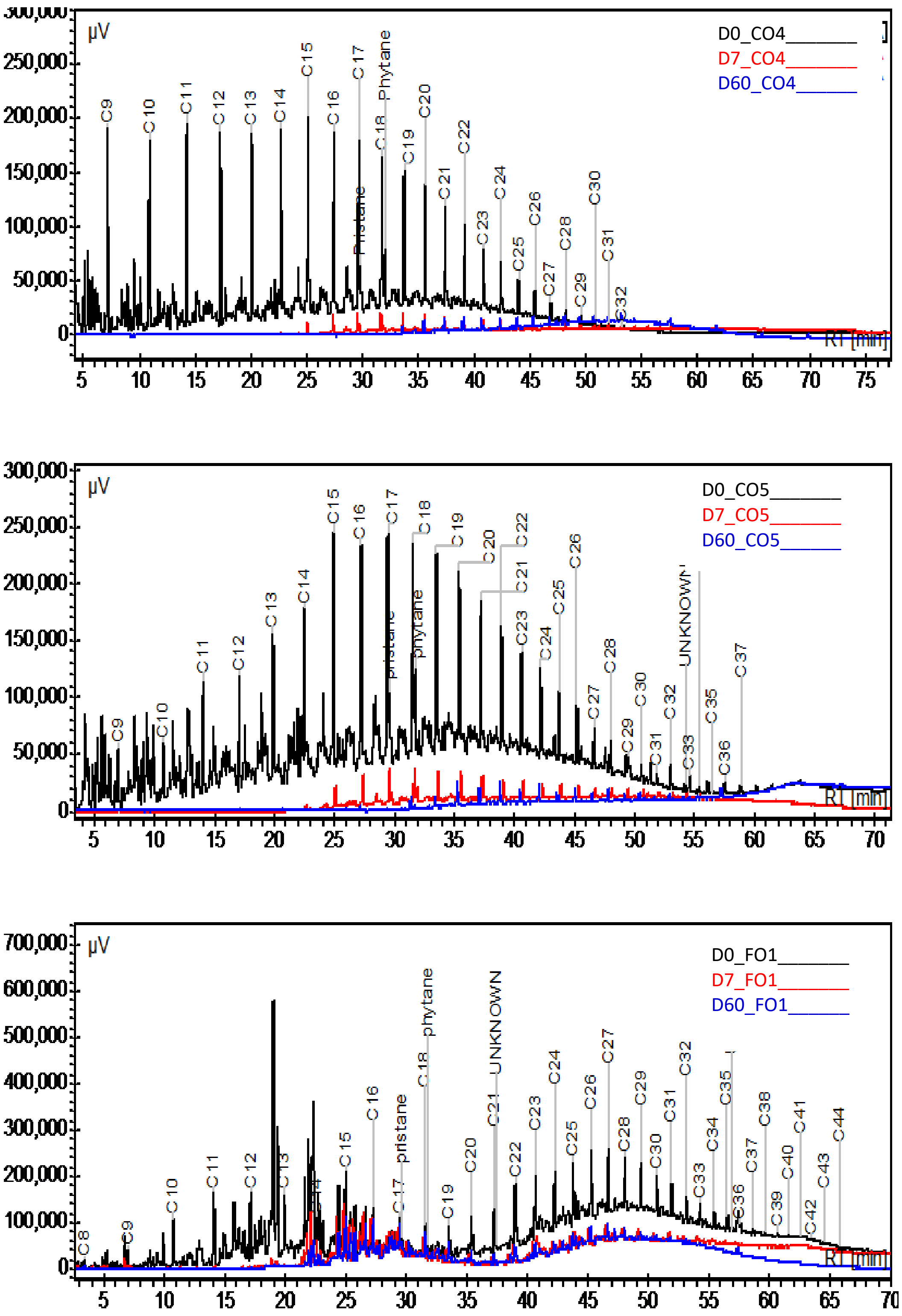


Figure 4.2 (cont.) The FID chromatogram of crude oil and fuel oil samples on day 0, day 7 and day 60.

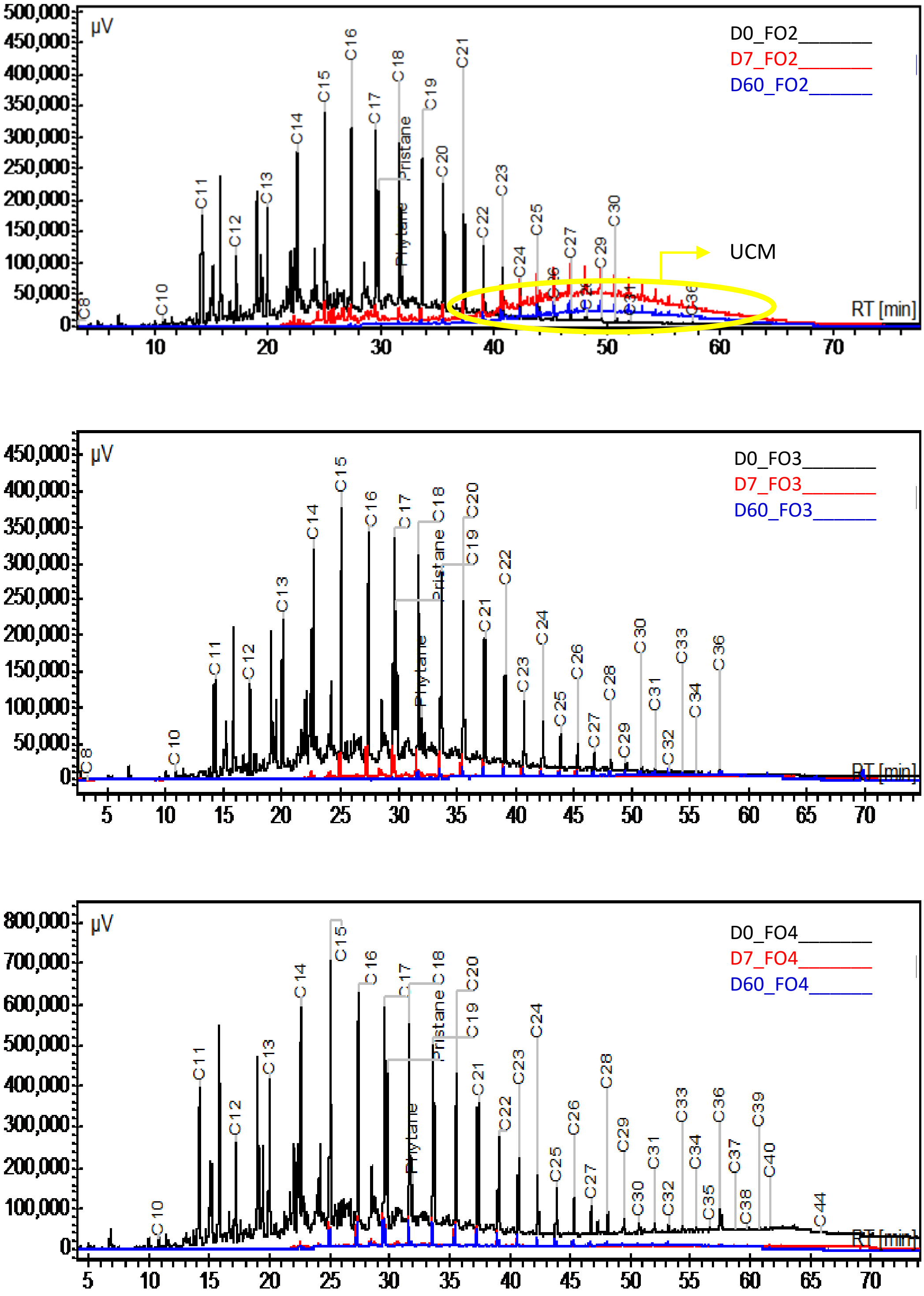


Figure 4.2 (cont.) The FID chromatogram of crude oil and fuel oil samples on day 0, day 7 and day 60.

However, the ratios of pristane and phytane are still different between crude oils and fuel oils. Crude oils generally have the ratio of pristane to phytane less than 1 except CO2 while all of fuel oils have a ratio higher than 1 as shown in Table 4.1. The ratio of pristane to phytane could be used to distinguish crude oil and processed oil in case crude oil is not from Far East crude. Likewise, *n*-C17/pristane and *n*-C18/phytane can also be used to discriminate the group of crude oils from fuel oils. Moreover, these ratios also show the sign of their main feedstock for example, FO3 and FO4 show the trend of ratios similar to CO2 which have higher ratios in *n*-C18/phytane and pristane/phytane than in *n*-C17/pristane. In addition, these ratios are widely used as indicators of weathering degree. The results demonstrate that the ratio of *n*-C17/pristane and *n*-C18/phytane decreased with increasing days of weathering. For example in CO1 the values of *n*-C17/pristane on days 0, 7 and 60 are 3.72 2.56 and 2.10, respectively. Since straight chain hydrocarbon (*n*-C8 to *n*-C25) are easier degradation than isopenoid group (pristane and phytane) thus, the ratio decreased as mentioned.

Table 4.1 Biodegradation ratio of fresh and weathered samples

Oil samples	**weathering period**	**Biodegradation Ratios**		
		$\frac{n\text{C-17}}{\text{pristane}}$	$\frac{n\text{C-18}}{\text{phytane}}$	$\frac{\text{pristane}}{\text{phytane}}$
CO1	Day 0	3.72	2.92	0.86
	Day 7	2.56	2.05	0.77
	Day 60	2.10	1.64	0.27
CO2	Day 0	0.72	6.15	8.36
	Day 7	0.66	5.61	8.01
	Day 60	0.44	3.72	5.93
CO3	Day 0	3.73	2.47	0.76
	Day 7	3.37	2.23	0.65
	Day 60	1.87	1.23	0.08
CO4	Day 0	2.88	1.93	0.77
	Day 7	2.64	1.77	0.68
	Day 60	1.44	0.97	0.28
CO5	Day 0	2.46	1.66	0.81
	Day 7	2.47	1.67	0.68
	Day 60	1.23	0.83	0.28

Oil samples	**weathering period**	**Biodegradation Ratios**		
		***n*C-17**	***n*C-18**	**pristane**
		pristane	**phytane**	**phytane**
FO1	Day 0	2.21	2.42	2.34
	Day 7	3.08	3.38	0.86
	Day 60	2.37	2.58	1.31
FO2	Day 0	2.67	1.85	1.25
	Day 7	3.01	2.11	0.83
	Day 60	1.34	0.93	0.35
FO3	Day 0	1.37	4.27	3.50
	Day 7	1.33	4.14	3.40
	Day 60	0.68	2.13	0.82
FO4	Day 0	1.33	3.41	3.17
	Day 7	1.25	1.71	1.51
	Day 60	1.24	1.73	1.56

*FO1, FO2 have CO1 and CO5 as a main feedstock *FO3, FO4 have CO1, CO2, CO3, and CO4 as a main feedstock

4.2 The Differentiation of Crude Oils and Processed Oils

Figure 4.3 shows the diagram of fuel oil processing. In petroleum refinery, fuel oil is produced from residue of vacuum distillation unit mixed with product from visbreaking and FCC unit (HVGO or heavy gas oil). The residue fuel is blended in order to improve their properties to meet the specification and reduce the viscosity of fuel oil. Thus, fuel oils have different characteristics from crude oil and themselves. It is significant for oil fingerprinting to identify the spilled oil. Analysis of fresh and weathered samples were analyzed by GCxGC-TOFMS and ICP-OES.

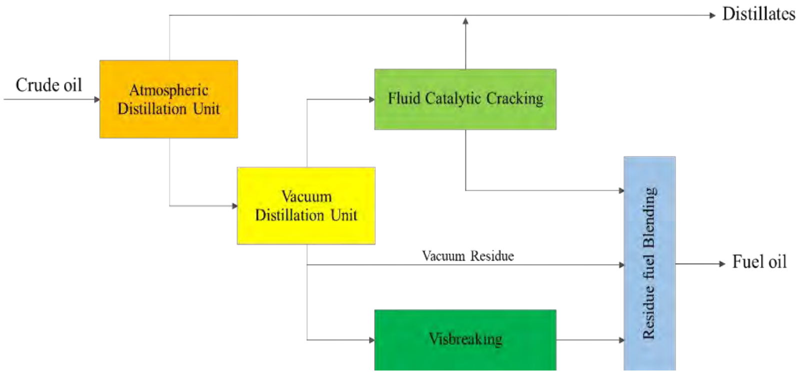


Figure 4.3 The diagram of fuel oil processing.

4.2.1 Standard Analysis

All of oil samples analyzed by GCxGC-TOFMS were added with 1 μL of internal standard (IS) in order to confirm the retention time. The chromatogram of internal standard with selected ion mass 191 (m/z 191) is indicated in Figure 4.4. The retention time of IS appears at 6351 s.

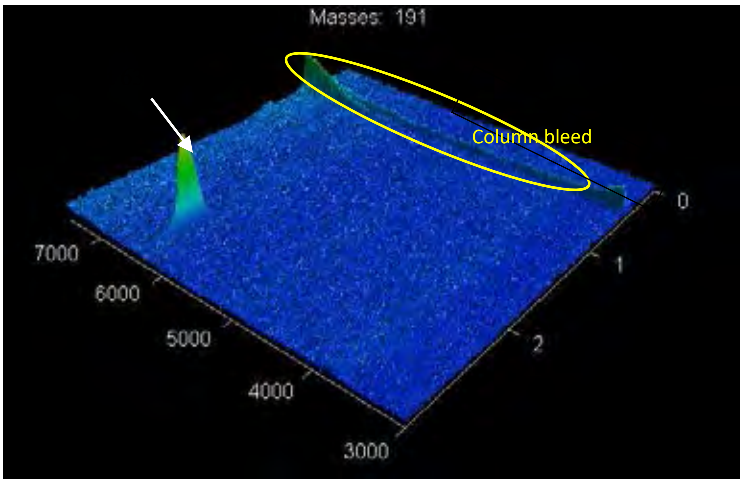


Figure 4.4 The surface chromatogram of IS 17β(H), 21β(H) - hopane solution.

4.2.2 General Total Ion Chromatograms of Oil Samples

The total ion chromatograms (TIC) of Murban crude oil sample is shown in Figure 4.5. The oil samples were analyzed by GCxGC-TOFMS using reverse phase column with delays times 3000 sec. The chromatogram shows that the hydrocarbon in crude oil sample can be divided into *n*-alkanes, cycloalkanes, polycyclic aromatic hydrocarbons hopane groups and other series. According to general principal of GCxGC, The first column provide a high resolution for polar compounds as shown in Figure 4.5. The second column is short non-polar column which provides a good resolution of co-elution compounds of first dimensional column including, aromatics, cycloalkanes and branch alkanes. However, the regions of monocyclic aromatic still have overlap which can be distinguished by selected mass ions as demonstrated in Figure 4.6. The two chromatograms in Figure 4.6 show that co-eluting of pentacyclic terpanes (hopane group) in GC-1D are resolved by GCxGC-TOFMS 2D. As mentioned, it can be concluded that GCxGC-TOFMS is suitable for identification of biomarker and be a useful instrument for oil fingerprinting.

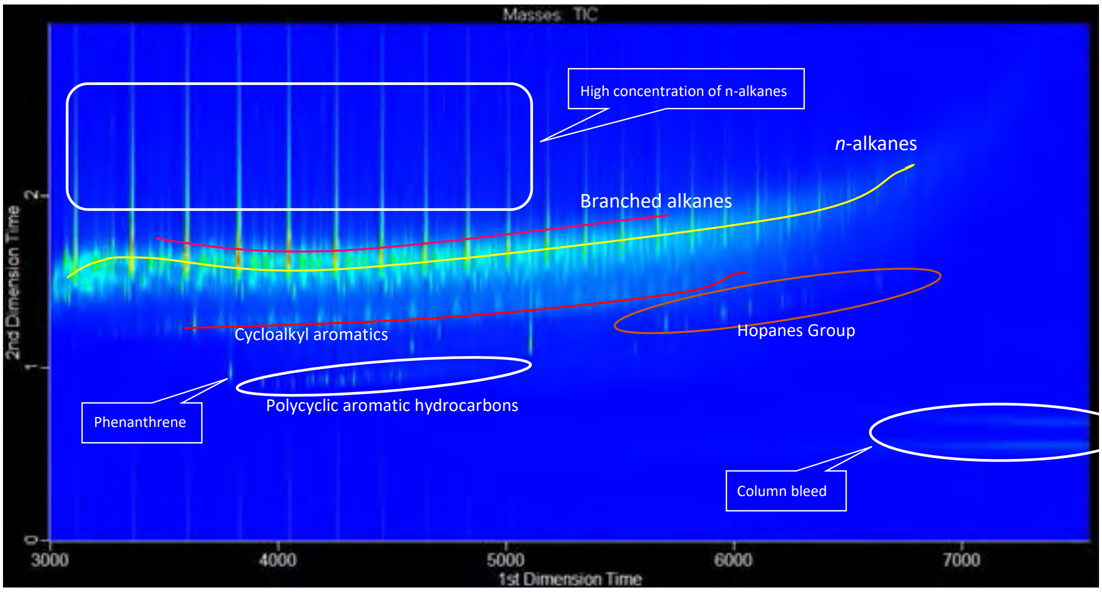


Figure 4.5 Total ion chromatogram (TIC) of hydrocarbon in fresh marine crude oil sample using GCxGC-TOFMS with reversed-phase column.

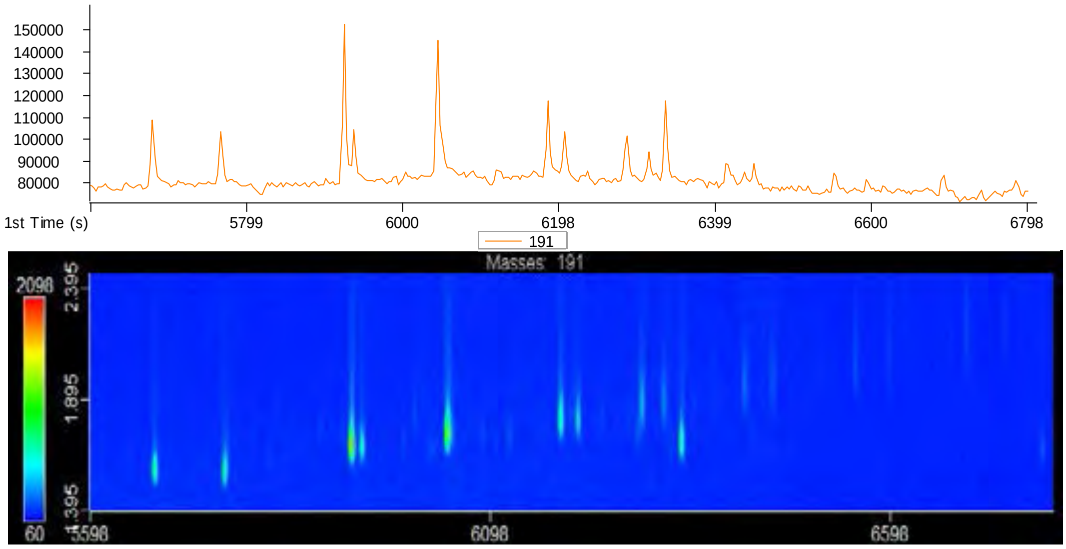


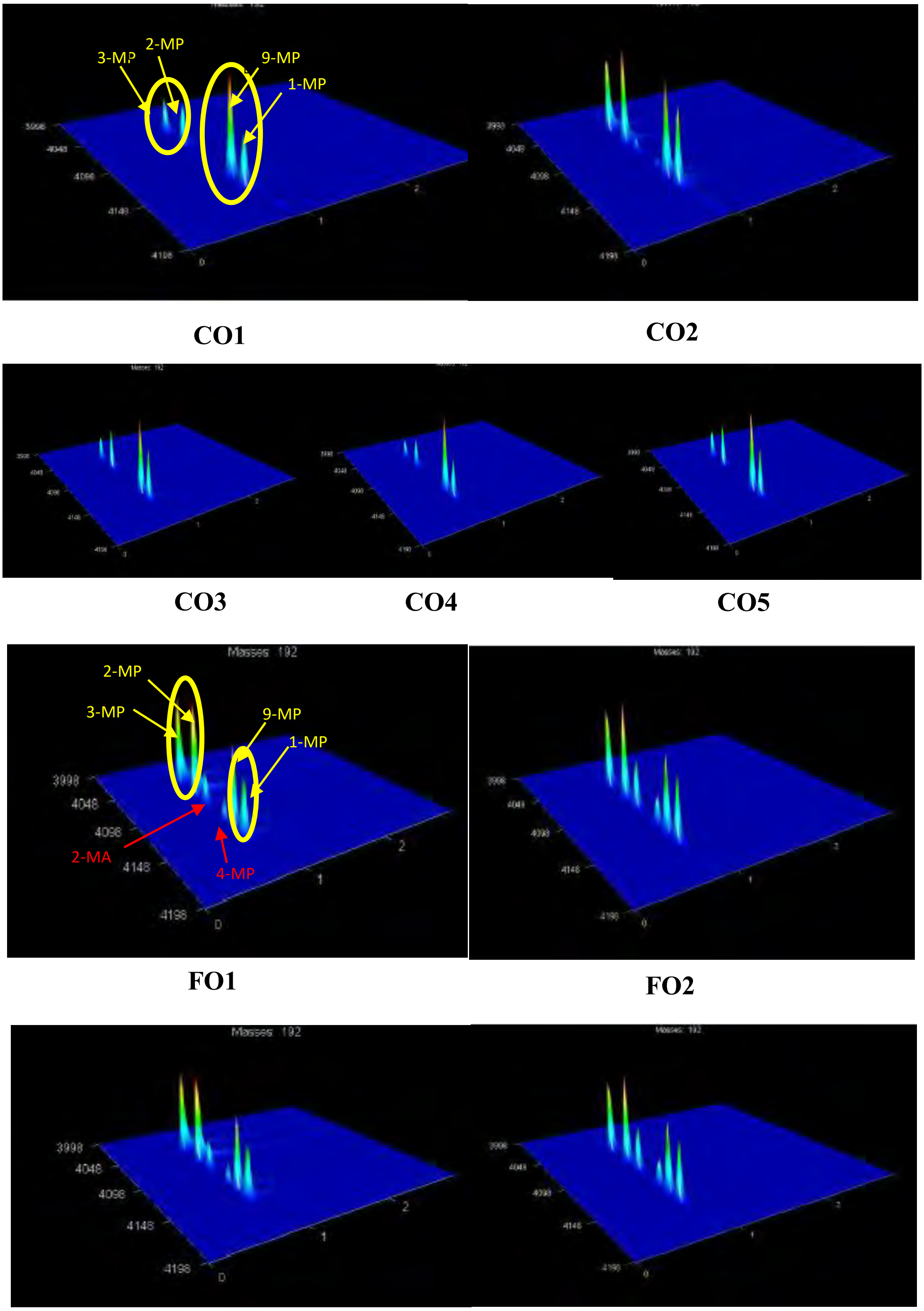
Figure 4.6 Selected ion chromatogram (m/z 191) of murban crude oil on day 0 (a) 1D chromatogram (GC-MS) (b) 2D chromatogram (GCxGC-TOFMS).

4.2.3 Differentiation of Crude Oils and Processed Oils by PAH

To differentiate crude oils and processed oils by GCxGC-TOFMS, the mass ion 192 (m/z 192) was selected to analyzed the component of alkylate anthracene and phenanthrene. The results of analyzed samples on GCxGC-TOFMS are reported in Table 4.2. The results show the difference between crude oils and fuel oils which 2-methylanthracene (2-MA) and 4-methylphenanthrene (4-MP) were not found in crude oils except CO2 (Banang crude oil). However, both 2-MA and 4-MP were observed in fuel oil samples. In day 7 of weathering period, 4-MP was disappeared from CO2 (Banang crude oil). Thus, it can be considered that 4-MP is not anti-weathering and alkylate PAHs can be used for distinguishing between crude oils and fuel oils in short term weathering. In addition, the surface plot in Figure 4.7 shows the different pattern of alkylated PAHs between crude oils and fuel oils. In crude oils, the chromatogram of the first 2 peaks, which are 3-methylphenanthrene (3-MP) and 2-methylphenanthrene (2-MP), have lower intensity than the last 2 peaks which are 9-methylphenanthrene (9-MP) and 1-methylphenanthrene (1-MP). On the other hand, fuel oils show the pattern of the first 2 peaks which have higher intensity than the last 2 peaks. All of crude oil results have same pattern except CO2. Thus, the alkylate PAHs can be used only for distinguishing between Middle East crude oil and fuel oil.

Table 4.2 Alkyl-phenanthrenes (MP) and alkyl-anthracenes (MA) presented in fresh and weathered samples

Weathering period	PAHs	3-MP	2-MP	2-MA	4-MP	9-MP	1-MP
Day 0	C1	✓	✓			✓	✓
	C2	✓	✓	✓	✓	✓	✓
	C3	✓	✓			✓	✓
	C4	✓	✓			✓	✓
	C5	✓	✓			✓	✓
	FO1	✓	✓	✓	✓	✓	✓
	FO2	✓	✓	✓	✓	✓	✓
	FO3	✓	✓	✓	✓	✓	✓
	FO4	✓	✓	✓	✓	✓	✓
Day 7	C1-D7	✓	✓			✓	✓
	C2-D7	✓	✓	✓		✓	✓
	C3-D7	✓	✓			✓	✓
	C4-D7	✓	✓			✓	✓
	C5-D7	✓	✓			✓	✓
	FO1-D7	✓	✓	✓	✓	✓	✓
	FO2-D7	✓	✓	✓	✓	✓	✓
	FO3-D7	✓	✓	✓	✓	✓	✓
	FO4-D7	✓	✓	✓	✓	✓	✓
Day 60	C1-D60	✓	✓			✓	✓
	C2-D60	✓	✓			✓	✓
	C3-D60	✓	✓			✓	✓
	C4-D60	✓	✓			✓	✓
	C5-D60	✓	✓			✓	✓
	FO1-D60	✓	✓			✓	✓
	FO2-D60	✓	✓			✓	✓
	FO3-D60	✓	✓			✓	✓
	FO4-D60	✓	✓			✓	✓



CO1 **CO2**

CO3 **CO4** **CO5**

FO1 **FO2**

FO3 **FO4**

Figure 4.7 The surface plot of selected ion m/z 192 of all samples.

4.2.4 Differentiation of Crude Oils and Processed Oils by Pyrogenic Index

Polycyclic aromatic hydrocarbons or PAHs are organic compounds in oils which consist of aromatic rings without heteroatom. PAHs can be classified to three types which are petrogenic, pyrogenic and biogenic PAHs. Each types of PAHs have their own characteristic. The petrogenic PAHs are defined as the substance from petroleum, including crude oil, fuel oil, and their refined product. Petrogenic PAHs are found in the aquatic environment through oil spill, unauthorized discharge or oil zipping. This PAHs are characterized by the dominance of C_1-C_4 alkylated homologues of PAHs which are naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene Generally, crude oil have low abundant of four to six ring PAHs than fuel oil (Abdel-Shafy, 2016). Therefore, it is useful to study petrogenic PAHs in order to differentiate fuel oil and crude oil in terms of the pyrogenic index (PI). PI is calculated from pyrogenic polycyclic aromatic hydrocarbon, which significantly increase after combustion processing, divided by five alkylated PAHs including naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene. The results of pyrogenic index (PI) in fresh oil and weathered oil demonstrated in Table 4.3. The result shows that all crude oil samples have PI less than 0.01 while all of fuel oils have PI higher than 0.1. Thus, the PI ratio is appropriate for distinguishing between crude oils and fuel oils since this index is reliable and can differentiate both Far East crudes and Middle East crudes from fuel oils. Moreover, the PI ratio on day 0 and day 60 demonstrated small difference value which indicates that PAHs used in this index are strong anti-weathering and can be applied in long term weathering processes. Moreover, this index also shows better accuracy with less inconsistency than the ratio of individual PAH compounds.

Table 4.3 Pyrogenic index of fresh and weathered samples

Oils	Pyrogenic index (PI)		
	Day 0	Day 7	Day 60
CO1	0.004	0.004	0.001
CO2	0.019	0.018	0.001
CO3	0.001	0.003	0.001
CO4	0.006	0.004	0.001
CO5	0.004	0.003	0.010
FO1	0.129	0.146	0.143
FO2	0.166	0.177	0.178
FO3	0.124	0.130	0.125
FO4	0.137	0.161	0.083

4.2.5 Differentiation of Crude Oils and Processed Oils by Determining Al and Si Contents

The determination of aluminum (Al) and silicon (Si) was performed using ICP-OES. All samples were collected and determined quantity of metals before weathering and after weathering for 45 days. The quantities of Al and Si are summarized in Table 4.4. The concentrations of Al and Si in fresh crude oil (day 0) are less than 1 ppm while the concentrations of Al and Si in fuel oils are higher than 1 ppm. The result follows the hypotheses that fuel oils have Al and Si from mixing with FCC product or kerosene. Because of catalyst contamination in FCC unit, the concentration of Al and Si increased as shown in FO1 and FO2. Moreover, FO3 and FO4 show lower Al concentration than FO1 and FO2 since FO3 and FO4 were mixed with product from visbreaking unit. This unit can be also called thermal cracking which operates without using catalyst. However, after oils were undergone weathering processes, they showed a negative result from fresh crude oil. The result indicated that the weathered crudes have higher concentration of Al and Si than weathered fuel oils. When crude oil spilled, the light hydrocarbons are evaporated which concentrate the Al content. On the contrary, fuel oils have lower light hydrocarbon than crude oils. Thus, evaporation of Al content in fuel oils are not concentrated as much as in weathered crude samples. Moreover, it has an effect of seawater that oil absorbed into their molecules causing an interference in ICP-OES and different value of Al to Si ratio between day 0 and day 60. Thus, it could be concluded that determination of Al and Si in the oil is not appropriate for oil fingerprinting since it is difficult to estimate degree of evaporated light hydrocarbon. Moreover, this technique needs to be treated a salt crystal because it can damaged the torch of ICP-OES.

Table 4.4 Metal concentration (Al and Si) of fresh and weathered samples

Oils	Al (ppm)		Si (ppm)		Al/Si (ppm)	
	Day 0	Day 45	Day 0	Day 45	Day 0	Day 45
CO1	0.32	124	0.37	372	0.85	0.33
CO2	0.05	34.6	0.16	134	0.29	0.26
CO3	0.65	110	2.56	440	0.26	0.25
CO4	0.97	32.4	2.08	165	0.47	0.20
CO5	0.11	192	0.40	643	0.28	0.30
FO1	9.21	17.7	13.4	70.2	0.68	0.25
FO2	9.15	83.4	12.0	45.1	0.76	1.85
FO3	2.60	23.3	6.23	58.6	0.42	0.40
FO4	3.15	83.4	7.55	75.9	0.42	1.10

4.2.6 Differentiation of Crude Oils and Processed Oils by Determining Asphaltene Contents

It well known that asphaltenes are the most refractory component in crude oils. Normally, asphaltene contents in heavy fuel oil are higher than those in crude oils. Moreover, the content of polynuclear aromatic compounds in heavy fuel oil also obstruct asphaltenes to convert and their thermal stability prevents thermal decomposition which results in large yields of asphaltene constituent. Therefore, these hypotheses were used to differentiate fuel oils from crude oils. The results of asphaltenes contents of fresh and weathered oil samples are shown in Table 4.5. The results show that the asphaltene contents increased in all samples after weathering (day 45). Fresh crude oil (day 0) had asphaltene contents between 0.20 to 3.40 while fresh fuel oils had high asphaltene contents between 5.25 to 10.66. After 45 days of weathering for CO1 (Murban Crude), almost all of hydrocarbons disappeared as a only thin film was observed. Thus, no enough sample is available for asphaltene analysis. However, other weathered oils still demonstrated significant result for differentiating fuel oils from crude oils. On day 45, the results show that crude oils (CO1, CO2, CO3 and CO5) have asphaltene contents lower than 10 % and fuel oil have asphaltene contents higher than 10 %. Although CO 4 have asphaltene contents of 13.66 which is higher than the range of asphaltene content in crude oils, the differentiation of crude oils and fuel oils still should be considered since asphaltenes are component resisting weathering and high stability.

Table 4.5 Asphaltenes contents of fresh and weathered oil samples

Oils	Asphaltenes content (%)	
	Day 0	Day 45
CO1	0.20	-
CO2	0.05	6.88
CO3	2.09	8.91
CO4	3.40	13.66
CO5	2.31	7.66
FO1	9.11	12.00
FO2	5.25	10.53
FO3	8.70	19.20
FO4	10.66	15.36

4.3 Identification of Oil Samples by Using Diagnostic Ratios of Biomarkers

Diagnostic ratios of biomarkers are widely used technique for oil correlation and environment forensic. This technique has many advantages, for example, it minimize effect of concentration and tend to induce a self-normalizing effect (Wang *et al.,* 2016). Diagnostic ratio of biomarker can be calculated both quantitative (compound concentration) and semiquantitative data (peak area or height). The reliable of diagnostic ratios depend on selection of biomarker and accuracy of instrument. In this research, it provides diagnostic ratio by calculating peak area from GCxGC-TOFMS. They were calculated from (biomarker1)/(biomarker1 +biomarker2). The frequently used diagnostic ratios are terpanes (m/z 191) and steranes (m/z 217), which are discussed in a topic of identification source of oil spill as follow.

Based on GCxGC-TOFMS analyses, the selected mass ion 191 was observed in order to calculate the diagnostic ratio. Figure 4.8 shows selected mass ion 191 chromatogram of fresh and weathered oil of Banang samples. The chromatogram of Banang crude oil was observed a dominant peak between C_{29} and C_{30} while the other chromatograms were not observed. Kiepper *et al.* (2014) reported that this peak was identified as 28-nor-spagulane or 21-methyl-28-nor-hopanes, which generally show in oil from Far East crude.

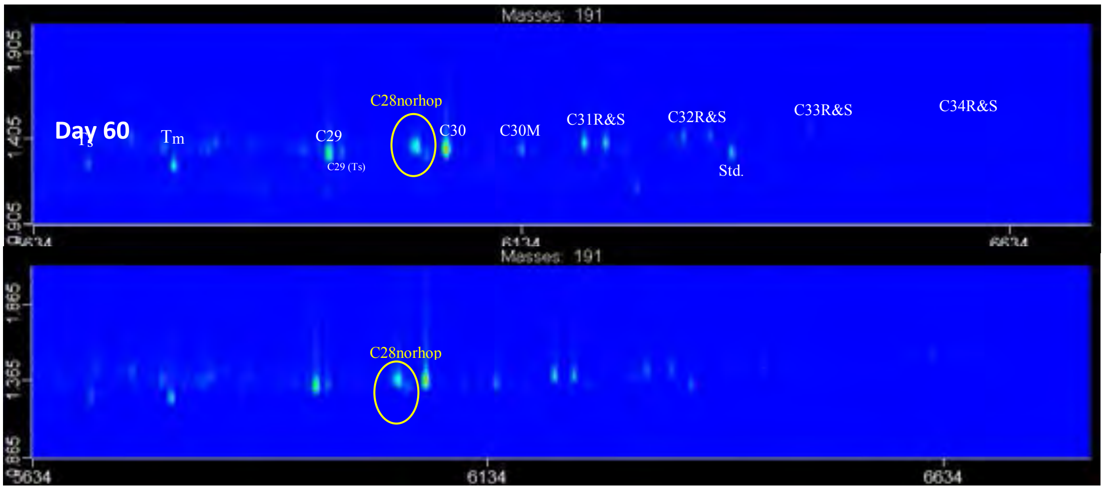


Figure 4.8 m/z 191 mass chromatograms of fresh and weathered Banang crude (CO2).

In order to confirm the peak of 28-nor-spagulane which was observed in Far East crude oil, this study analyzed five additional oil samples from Far East crude including Kikeh and Banang crude (from Malaysia offshore), Pattani and Jasmine crude (from Thailand offshore) and Plazfior crude (from Africa). The result demonstrated that Kikeh and Banang crudes show 28-nor-spagulane but Pattani, Jasmine and Plazfior did not observed this peak. However, both Pattani and Jasmine showed an important peak before the peak of C29 (retention time 6028 sec) as demonstrated in Figure 4.9. Therefore, it can be concluded that 28-nor-spagulane is useful to identify the source of oil from Malaysia Basin. Moreover, it should be noted that the oil from Thailand's offshore are observed the peak before C29.

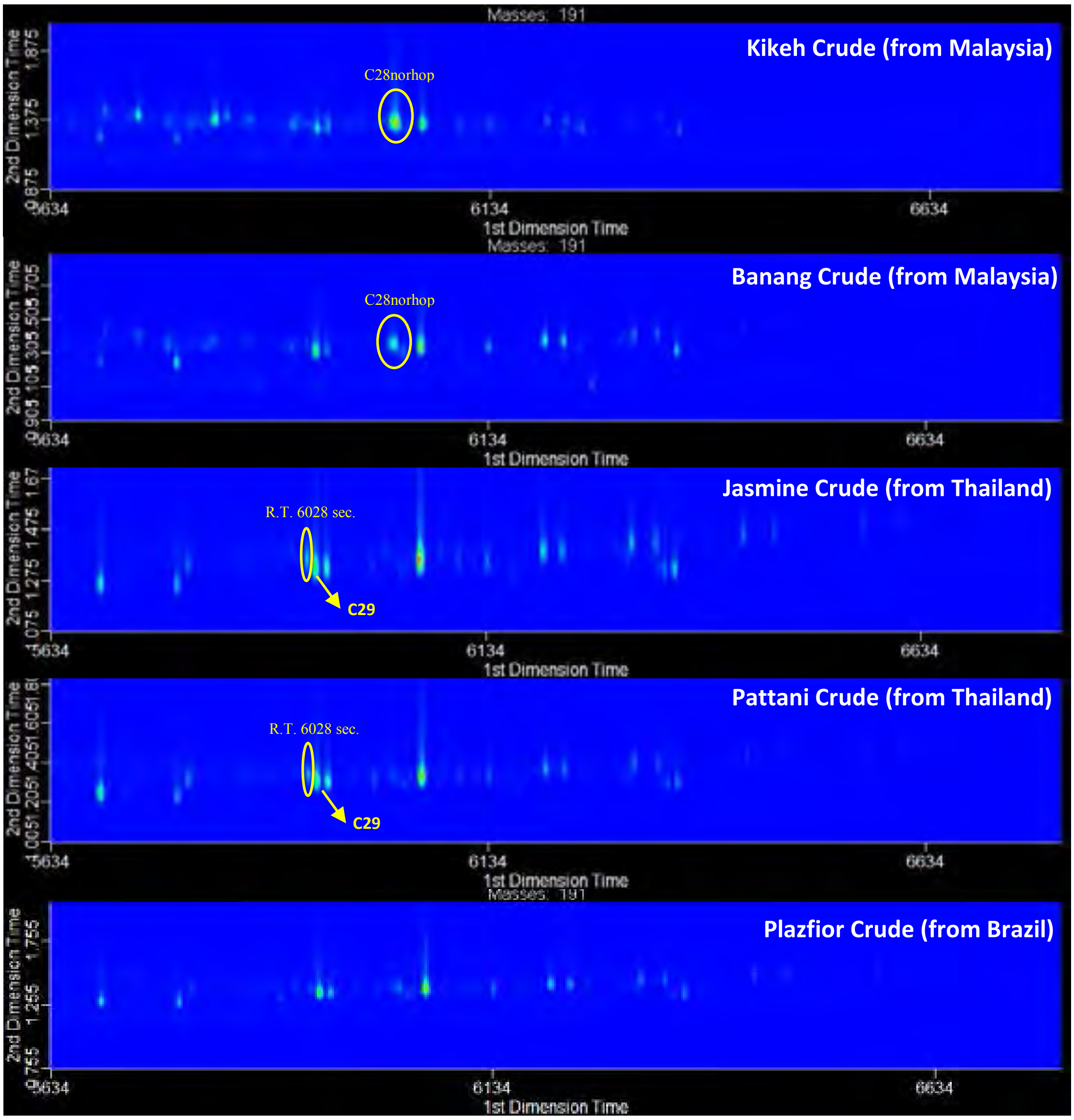


Figure 4.9 m/z 191 mass chromatograms of fresh crude oils from Far East.

Moreover, the peak of 28-nor-spagulane also indicated the feed stock of fuel oil. For example, fuel oil 2 (FO2) which has Murban, Banang, Upper zakum and Marine as a main feed stock demonstrated the peak of 28-nor-spagulane as shown in

Figure 4.10. This peak is not observed in fuel oil 3 (FO3) and fuel oil 4 (FO4) because these fuel oils are not have Banang crude as a feedstock. The chromatograms of m/z 191 of fresh and weathered fuel oil 3 are shown in Figure 4.11.

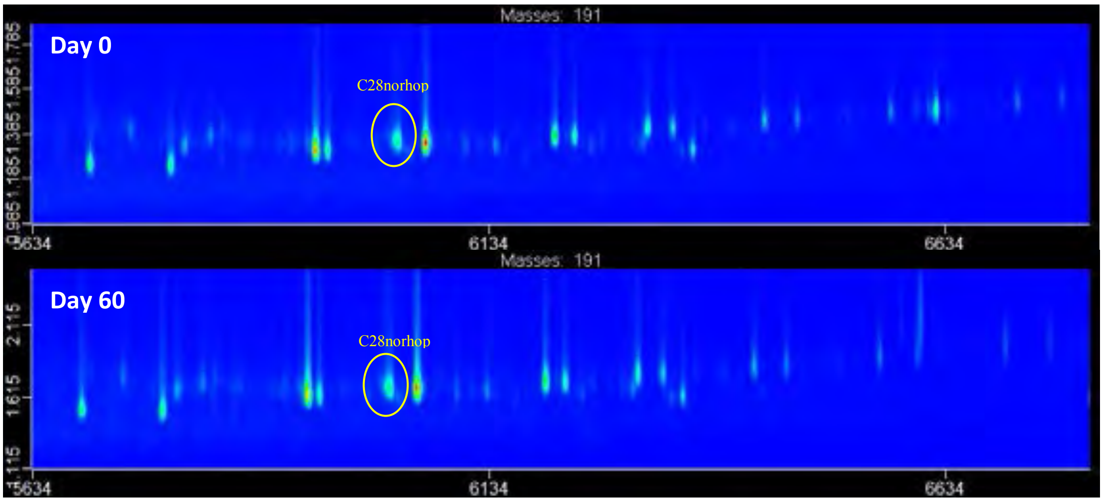


Figure 4.10 m/z 191 mass chromatograms of fresh and weathered FO2 (fuel oil 2).

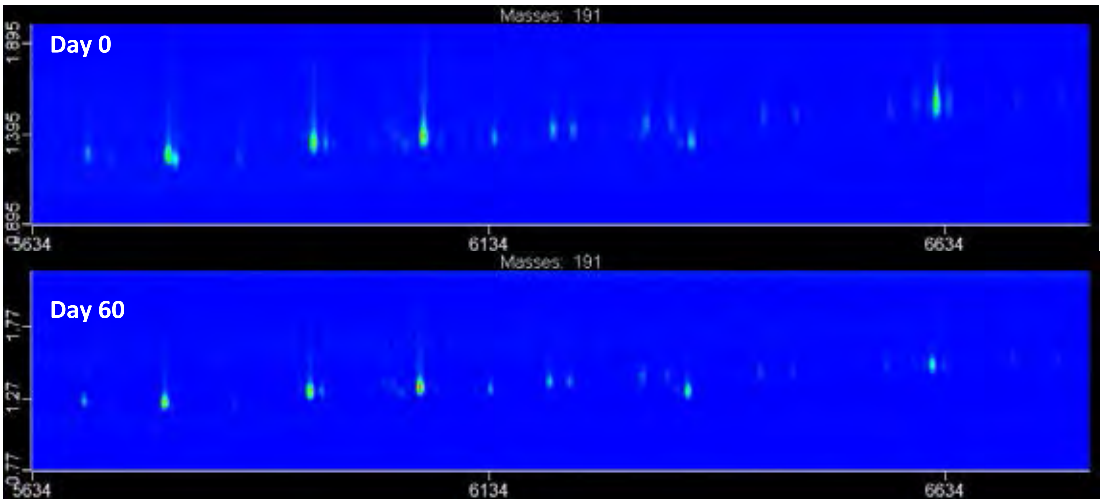


Figure 4.11 m/z 191 mass chromatograms of fresh and weathered FO3 (fuel oil 3)**.**

In addition, on day 60 all of chromatograms showed Gammacerane peak, which indicated a stratified water column due to high hyper salinity or evaporitic environment. This peak support the result of dramatic evaporation process in weathering simulation. However, comparing of two chromatograms of selected mass ion 191 between fresh (day0) and weathered (day 60) oil still showed similar pattern. This imply strong anti-weathering of the hopane group and can be useful for identification the oil samples. The chromatograms of m/z 191 of fresh and weathered Murban crude oils are shown in Figure 4.12 and the diagnostic ratios of hopane group are shown in Table 4.6-4.7.

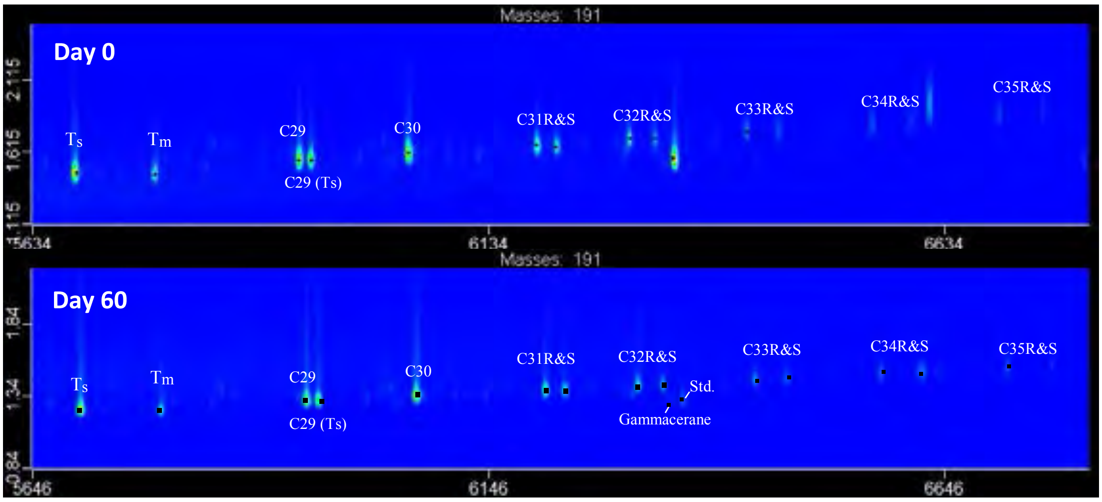


Figure 4.12 m/z 191 mass chromatograms of fresh and weathered Murban crude oil.

The results of diagnostic ratios of the biomarkers in Tables 4.6 and 4.7 demonstrate in the correlation plot. The result of fresh and weathered oil were plotted in the same graph, which the result performed as a linear in x-y plane. The conclusion of the graphs depend on the overlap between error bar and x=y line. The values of error bar were calculated as the relative variation at a 95% confidence interval in triplicate samples by using the “student’s t” statistic tool. The graphs are shown in Figures 4.13 – 4.14. Both the correlation plots of fuel oils and crude oils show positive match between fresh and weathered oils on day 60. Thus, it can be implied that the biomarkers in hopane group are suitable and reliable for using as the diagnostic ratios.

Table 4.6 Diagnostic ratio of fresh and weathered crude oil samples

Name of biomarker	**CO1**		**CO2**		**CO3**		**CO4**		**CO5**	
	D0	**D60**	**D0**	**D60**	**D0**	**D60**	**D0**	**D60**	**D0**	**D60**
Ts	51	48	13	14	29	31	26	21	31	25
Tm	29	29	25	22	29	29	34	28	31	26
C29H	45	49	43	40	52	51	49	48	47	48
C29H(Ts)	37	38	15	14	26	26	23	19	25	21
C29M	0	0	39	39	0	0	0	5	12	0
C28norhopane	0	0	11	12	0	0	4	4	6	0
C30H	50	50	50	50	50	50	50	50	50	50
C30M	0	4	15	16	4	7	7	4	7	0
C31HS	32	33	24	24	32	32	38	36	38	38
C31HR	23	25	21	20	26	24	28	25	29	26
C31M	0	0	0	0	9	7	9	6	18	0
C32HS	24	26	12	13	23	23	28	26	31	29
C32HR	17	18	10	12	17	18	23	17	23	19
Gammacerane	0	2	0	1	3	3	5	2	0	0
C33HS	14	16	0	5	16	16	20	15	21	18
C33HR	0	11	0	3	11	11	13	9	15	13
C34abs	0	13	0	2	11	12	14	10	16	15
C34abr	0	9	0	1	8	8	10	5	11	11
C35abs	0	10	0	0	10	11	15	12	14	15
C35abr	0	6	0	0	6	7	10	7	10	0

Table 4.7 Diagnostic ratio of fresh and weathered fuel oil samples

Name of biomarker	**FO1**		**FO2**		**FO3**		**FO4**	
	D0	**D60**	**D0**	**D60**	**D0**	**D60**	**D0**	**D60**
Ts	28	31	28	28	17	13	17	13
Tm	40	35	28	27	42	39	42	42
C29H	49	56	48	47	42	42	44	44
C29H(Ts)	23	25	27	24	14	9	13	9
C29M	0	11	38	35	0	0	0	0
C28norhopane	0	0	12	0	0	0	0	0
C30H	50	50	50	50	50	50	50	50
C30M	0	5	11	13	15	11	16	12
C31HS	0	16	31	30	19	17	19	15
C31HR	0	10	25	23	13	11	13	9
C31M	0	7	9	9	1	0	0	0
C32HS	0	10	21	17	13	11	14	11
C32HR	0	8	18	19	10	7	10	7
Gammacerane	0	4	0	6	5	0	4	3
C33HS	0	6	14	13	8	0	8	6
C33HR	0	4	10	9	7	0	5	4
C34abs	0	4	11	7	4	0	2	0
C34abr	0	0	7	7	2	0	2	0
C35abs	0	0	9	6	1	0	2	0
C35abr	0	0	6	2	1	0	1	0

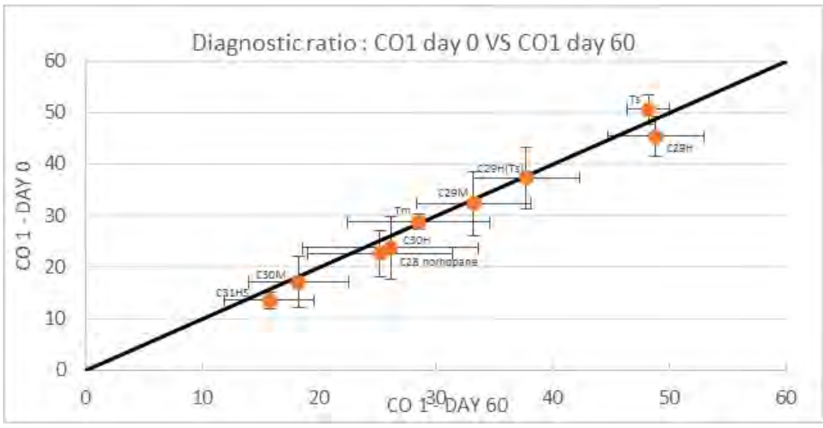


Figure 4.13 The correlation plot between CO1 on day 0 and day 60**.**

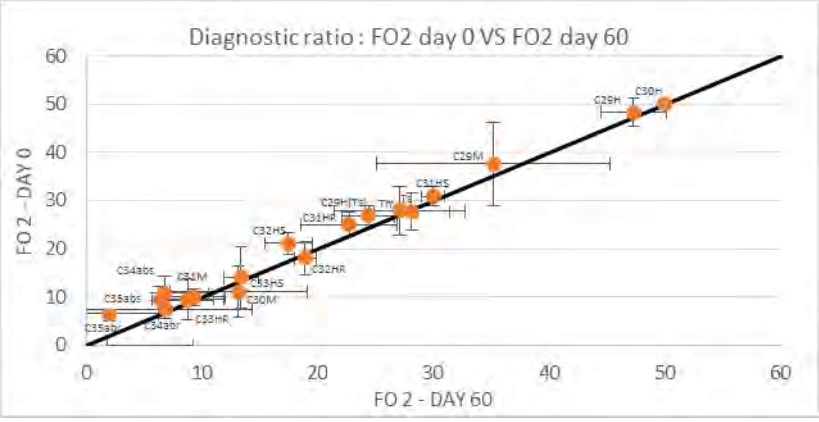


Figure 4.14 The correlation plot between FO2 on day 0 and day 60.

Since the distributions of hopane biomarkers are different between crude oils and fuel oils. The result of correlation plot of the diagnostic ratio between crude oil and fuel oil indicated to be non-match. Although, FO2 has CO1 as a main feedstock. It was observed that some of biomarkers were not overlapped with the straight line x=y as illustrated in Figure 4.15. In addition, the correlation plot also indicated non-match between different types of crude oils (CO1 and CO2) as shown in Figures 4.16-4.17. There were several hopanes not overlapping the straight line x=y, especially in Far East crudes (CO2 in Figure 4.16). Thus, it can be concluded that correlation plot is appropriate technique for oil fingerprinting.

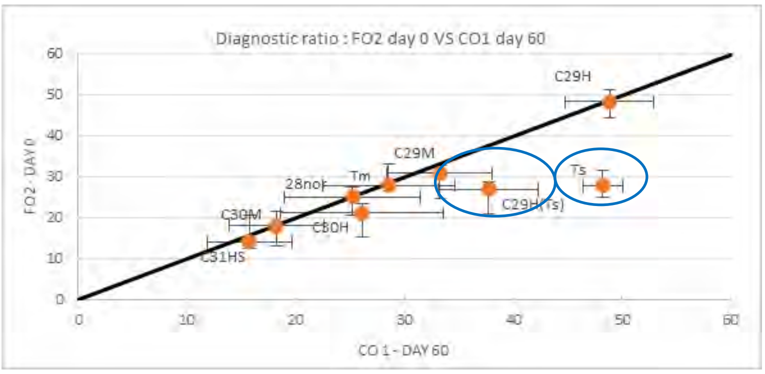


Figure 4.15 The correlation plot between FO2-day 0 and CO1-day 60.

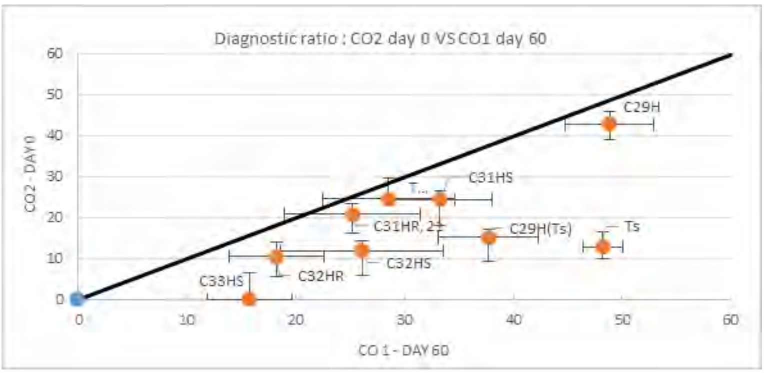


Figure 4.16 The correlation plot between CO2-day 0 and CO1-day 60.

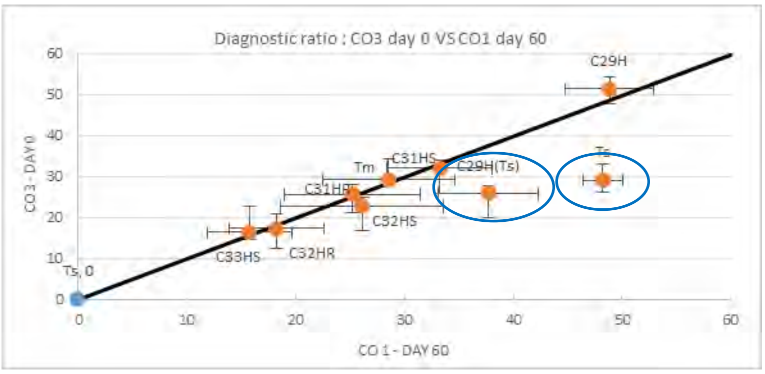


Figure 4.17 The correlation plot between CO3-day 0 and CO1-day 60.

4.4 Summarized Protocol for the Identification Types of Spilled Oil

From the results in previous section, the protocol to identification types of oil spill is summarized in Figure 4.18. Firstly, the extracted samples are analyzed by GC-FID in order to identify basic information such as the range of hydrocarbon and weathering degree. If the chromatogram of GC-FID provides a huge unresolved complex mixture (UCM) area, the sample probably identified as a lube oil. If only small UCM rise up in the chromatogram, it could not be identified since the sample is weathered oil. Then, the second step is identified type of oil by measuring asphaltenes content. If the asphaltenes contents are less than 10 %, it probably be a crude oil. On the other hand, if the asphaltenes contents are higher than 10 %, it could not identified types of oils since the sample might be both crude oil and fuel oil which highly degraded light hydrocarbon. After that, GCxGC-TOFMS is used to characterize the distribution of polycyclic aromatic hydrocarbons (PAHs) (m/z 192) and biomarkers in hopane group (m/z 191). In order to confirm the types of oils, Pyrogenic index (PI) is applied in this stage. If PI higher than 0.1, it could be fuel oil. In contrast, if PI less than 0.01, the sample could be crude oil. Moreover, this step can be applied with the distribution of selected mass ion 192. The distribution patterns of methyl-anthracenes and methyl-phenanthrenes are different in most of crude oils and fuel oils. The common 3-, 2-, 9- and 1- methyl phenanthrene (MP) appear in all of oil types while 4-MP and 2-MA appears only in the fuel oils and crude oils from Malaysia basin. However, the differentiation of 4-MP and 2-MA patterns are suitable for the samples that less degree of weathering. Thus, it can be concluded that the sample having PI less than 0.01 with the presence of 4-MP and 2-MA is crude oil from Malaysia basin. Finally, all of samples were created the correlation plot of hopanes in order to identify and confirm source of spilled oil. The sample is concluded positive match, if all of diagnostic ratios overlap the straight line x=y. On the other hand, it can be concluded non-match, if some of biomarkers not overlap the straight line x=y.

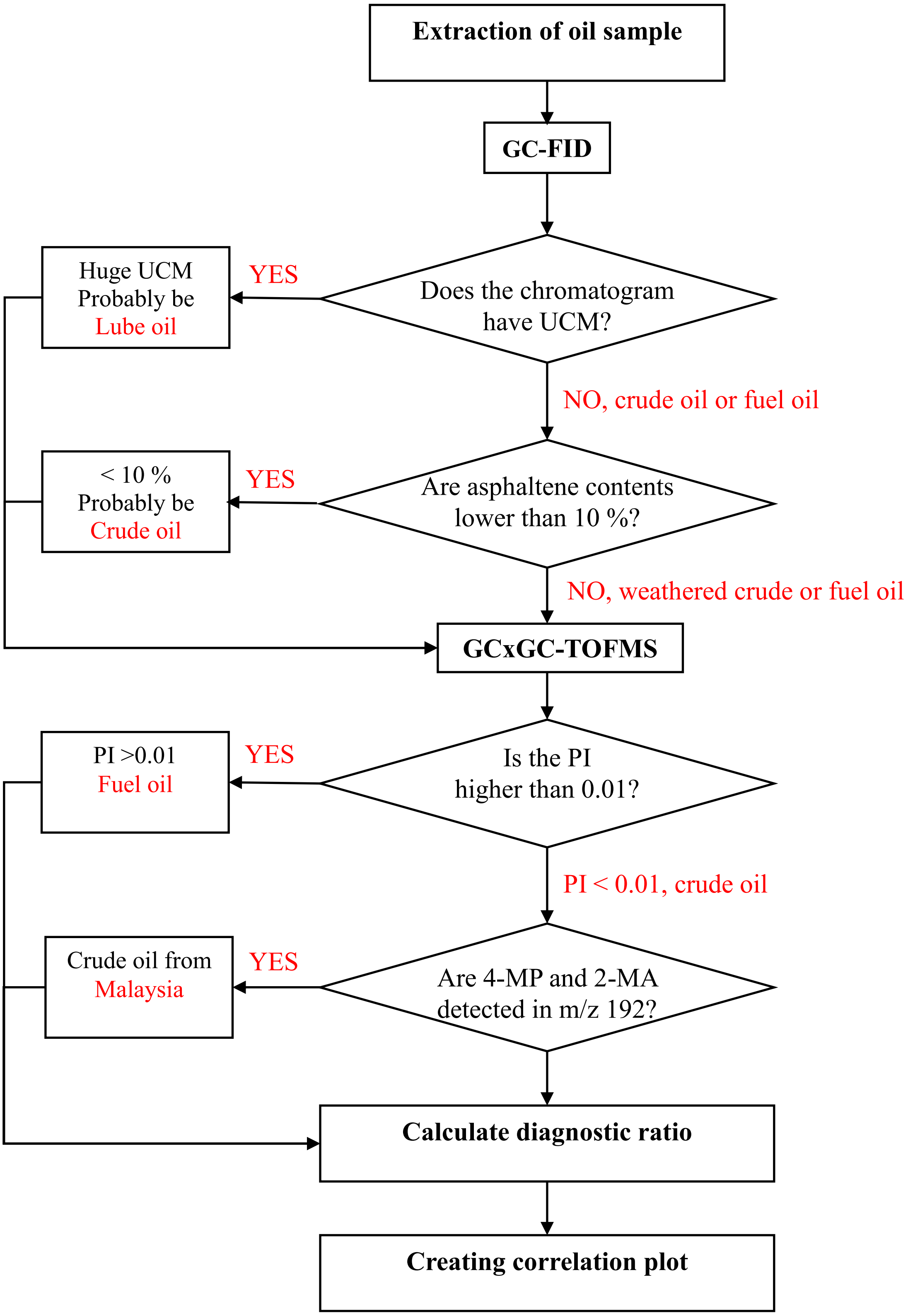


Figure 4.18 Proposed protocol chart for identification types of oil spill

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This work studied the differentiation of crude oils and processed oils by focusing on the distribution patterns and general diagnostic ratios of PAHs and their alkylated including biomarkers in hopane group. Moreover, this research also focus on measuring asphaltenes and Al/Si contents. Nine crude oils and four fuel oils were investigated in this research. GC-FID was used to analyze basic information of hydrocarbon and effect of weathering processes. GCxGC-TOFMS was used to analyze the distribution pattern of biomarkers and PAHs. ICP-OES was used to measure Al and Si contents while asphaltenes were measured following ASTM method. The conclusions of this study are summarized as follow:

1. The results from GC-FID show the similar distribution of crude oil and fuel oil. The light hydrocarbon dramatically decreased within one week and UCM rose up within 60 days which indicated biodegradation stage of weathering. Therefore, the result from GC-FID could not clearly identify the source of oil spill. It can be used as a first screen for forensic oil spill.
2. The distribution pattern of MA and MP were different between crude oils and fuel oils except Banang crude oil. This pattern can be used only to differentiate between fuel oil and crude oil from Middle East crude.
3. The results of pyrogenic index show different values between crude oils and fuel oils. All crude oil samples have value less than 0.01 while fuel oil samples have value higher than 0.01. Therefore, this index is suitable for using as indicator identifying types of oil both Far East and Middle East crude from fuel oils.
4. Al and Si contents are not suitable for oil differentiation because measuring of Al and Si content were interfered by the salt crystal.

Moreover, after weathering it is difficult to estimate degree of oil concentration which significant affect to fraction of oil.

5. Asphaltenes contents is a support information for oil identification. The results show that crude oils have asphaltene contents lower than 10 % while fuel oils have asphaltenes contents higher than 10%. However, it should be noted that the asphaltene contents in crude oils can be increased with weathering time.
6. The distribution of biomarker in hopane groups are useful for oil fingerprinting. The 28-nor-spagulane can be used to identify oil from Malaysia because this component was observed only in Banang and Kikeh crude. Moreover, this peak is also strong anti-weathering since it was observed on days 60. At retention time 6028 sec, it shows peak which observed only in crude oil from offshore of Thailand. It can be concluded that this peak is an important indicator to identify crude oil from reservoir zipping or leaking pipeline. In addition, the distribution of biomarkers are an important key to identify source since they are anti-weathering and have similar distribution pattern on day 0 and days 60.
7. The diagnostic ratio of m/z 191 is reliable and provides accuracy correlation plot between day 0 and days 60. This technique is appropriate for oil fingerprinting because the samples were analyzed three times and an error of the values were calculated with 95 % confident interval.

5.2 Recommendations

There are some limitations of my research that need to be developed. First, Collecting the samples should be used a large bottle to collect the sample and the samples should be filtrated the water and algae before extraction. Second, analysis of Al and Si contents need to be eliminated the salt before analysis in order to avoid interference of result from ICP-OES. Moreover, for weathering simulation, it should be poured the oil sample more than 30 g because the light crude oil such as Murban crude disappear and is hard to collect after weathering for 60 days

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APPENDICES

Appendix A GCxGC-TOFMS Total Ion Chromatogram Result

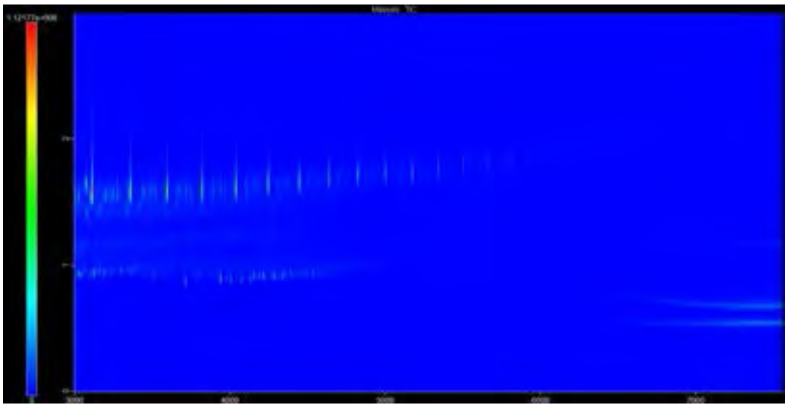

Figure A1 Total ion chromatogram of CO1-day0.

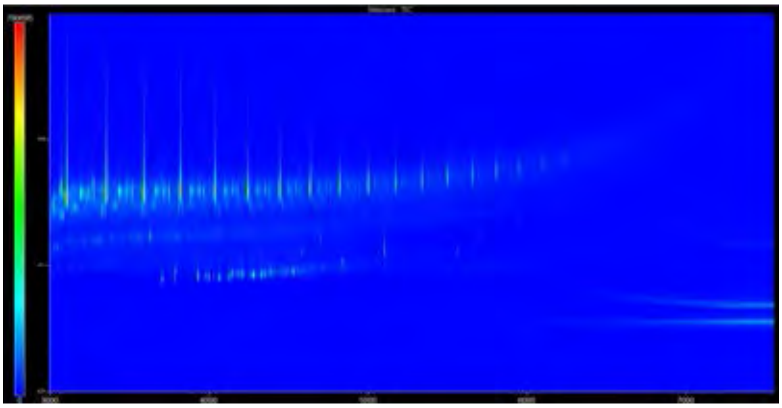

Figure A2 Total ion chromatogram of CO1-day7.

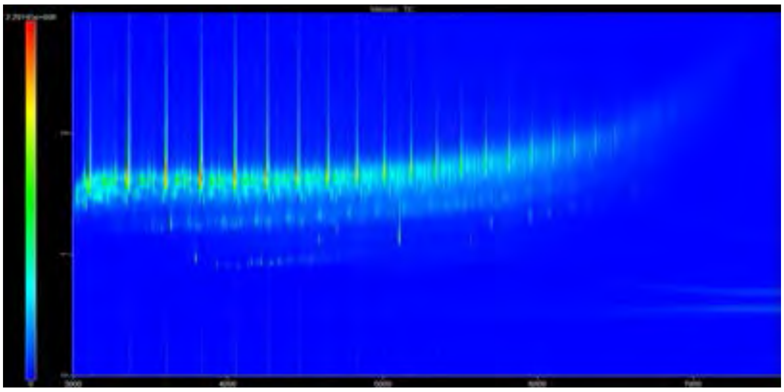

Figure A3 Total ion chromatogram of CO1-day60.

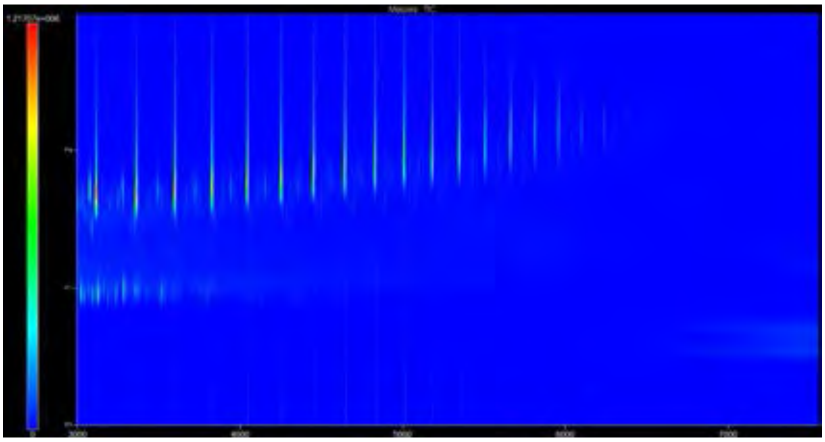

Figure A4 Total ion chromatogram of CO2-day0.

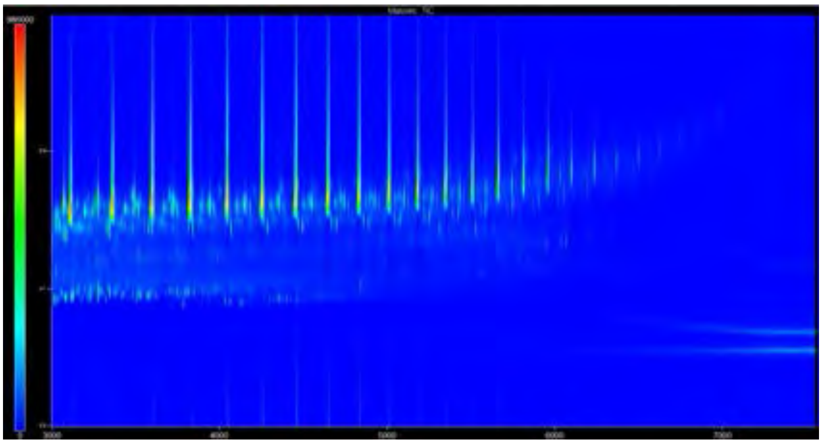

Figure A5 Total ion chromatogram of CO2-day7.

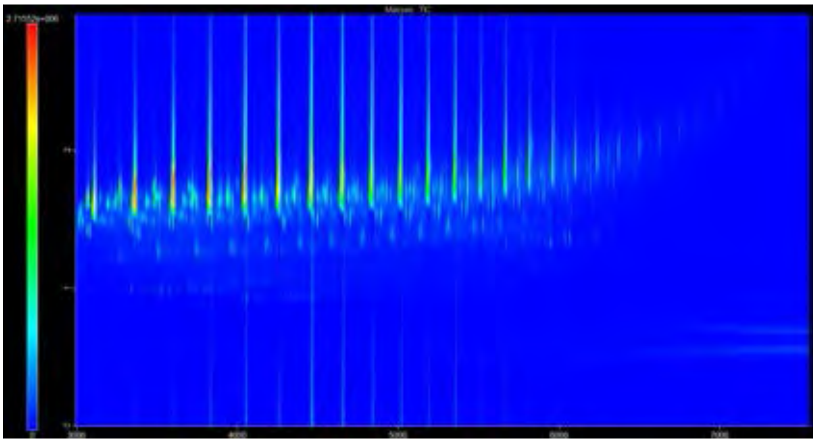

Figure A6 Total ion chromatogram of CO2-day60.

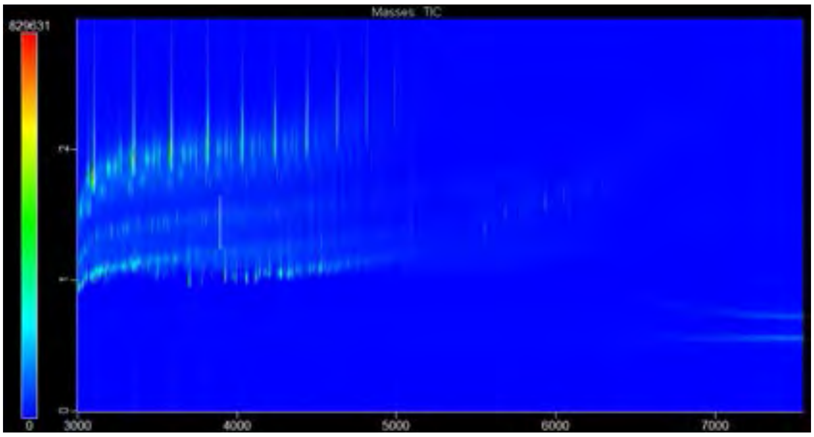

Figure A7 Total ion chromatogram of CO3-day0.

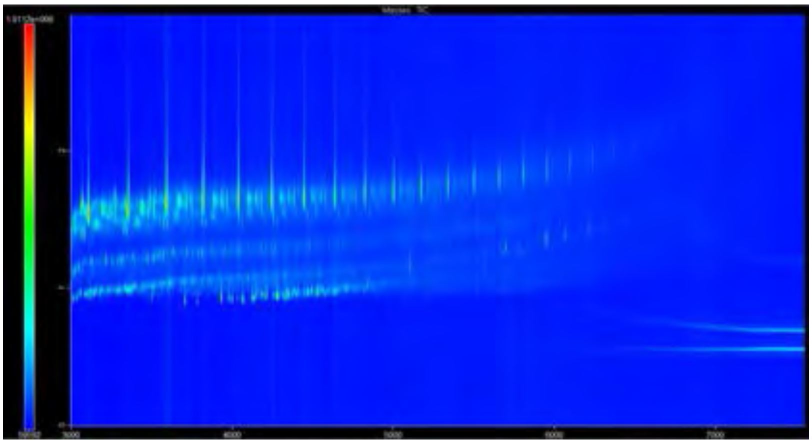

Figure A8 Total ion chromatogram of CO3-day7.

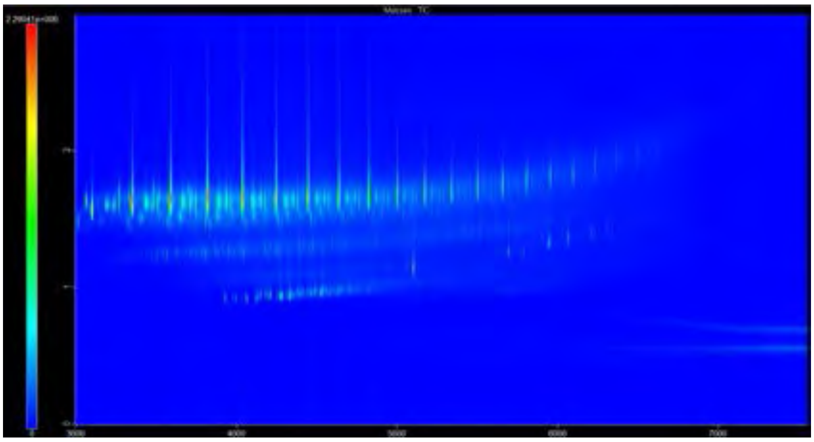

Figure A9 Total ion chromatogram of CO3-day60.

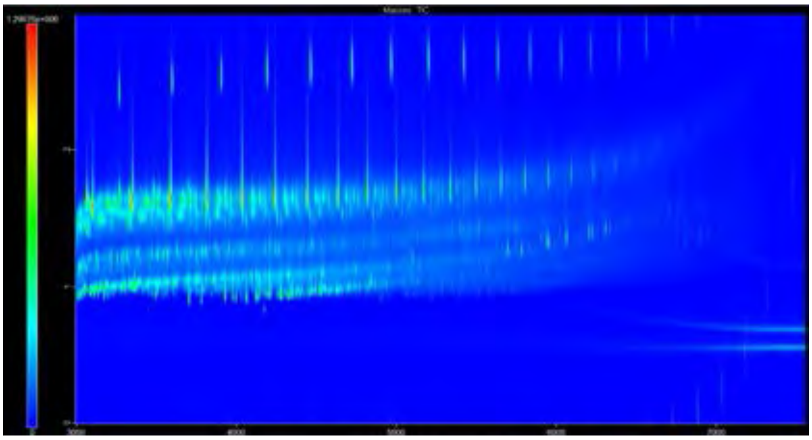

Figure A10 Total ion chromatogram of CO4-day0.

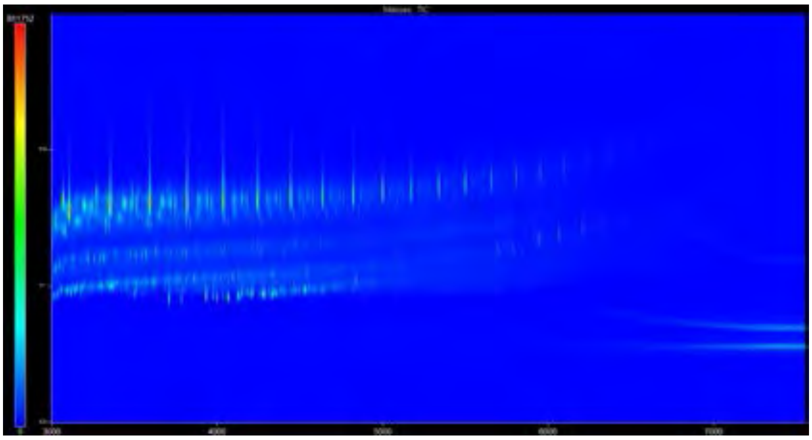

Figure A11 Total ion chromatogram of CO4-day7.

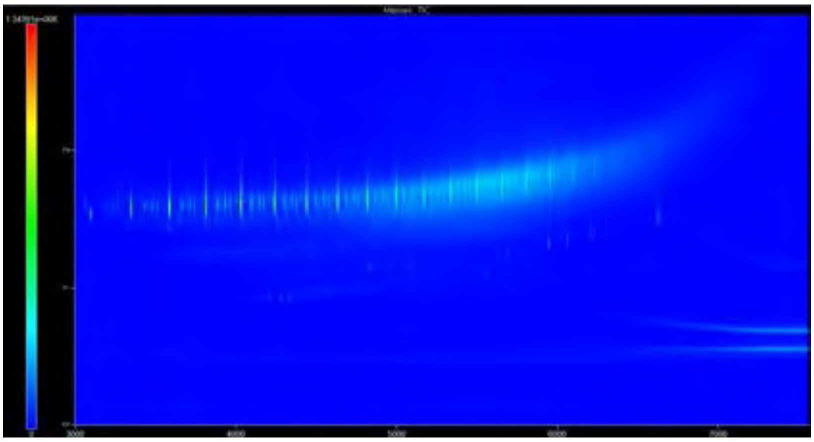

Figure A12 Total ion chromatogram of CO4-day60.

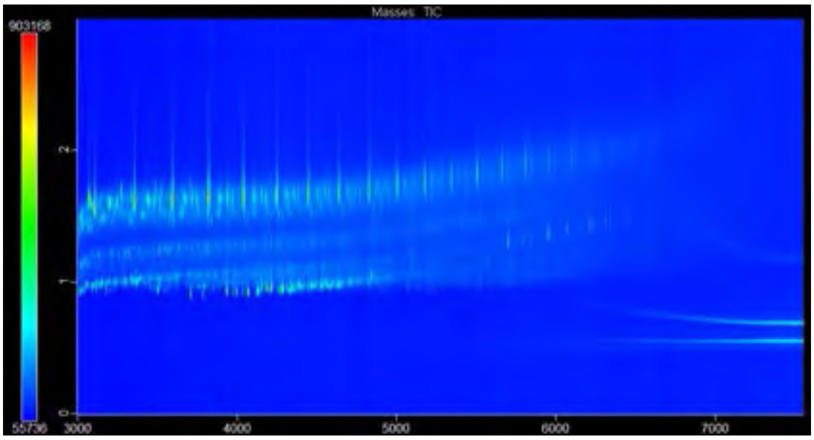

Figure A13 Total ion chromatogram of CO5-day0.

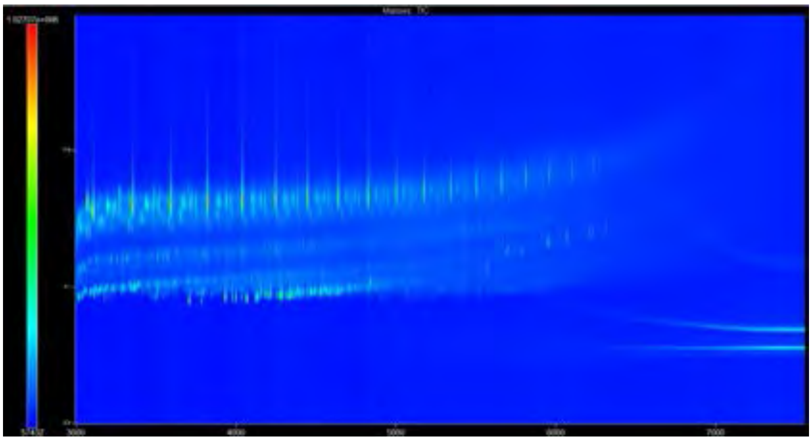

Figure A14 Total ion chromatogram of CO5-day7.

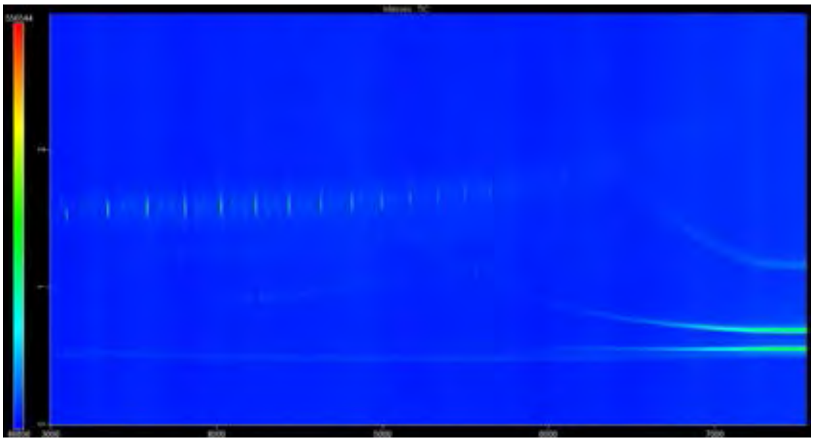

Figure A15 Total ion chromatogram of CO5-day60.

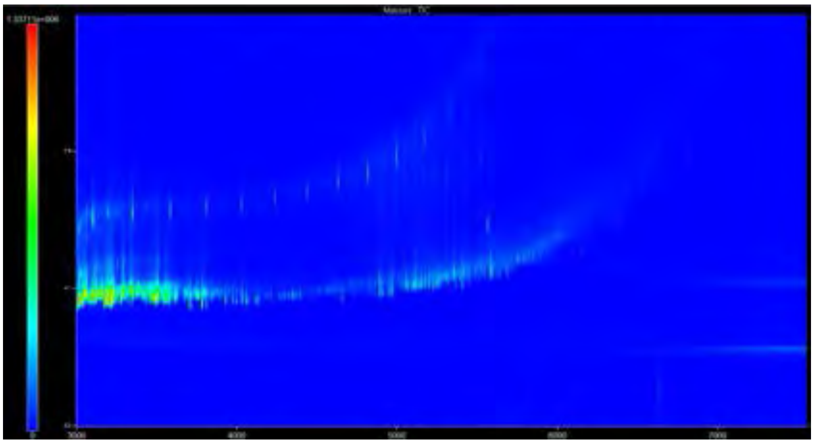

Figure A16 Total ion chromatogram of FO1-day0.

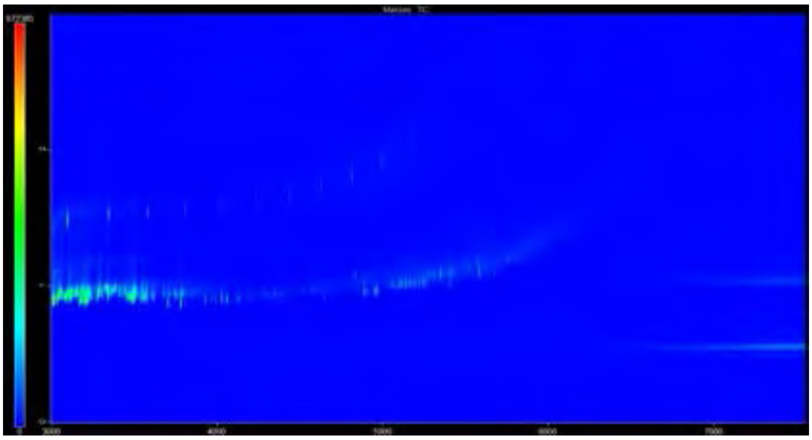

Figure A17 Total ion chromatogram of FO1-day7.

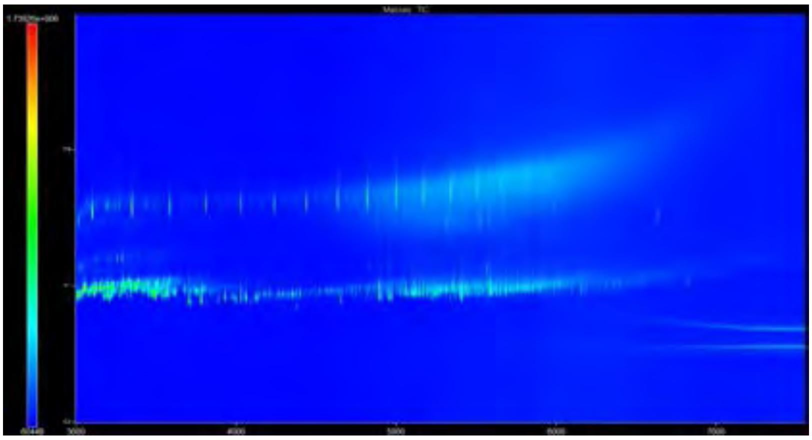

Figure A18 Total ion chromatogram of FO1-day60.

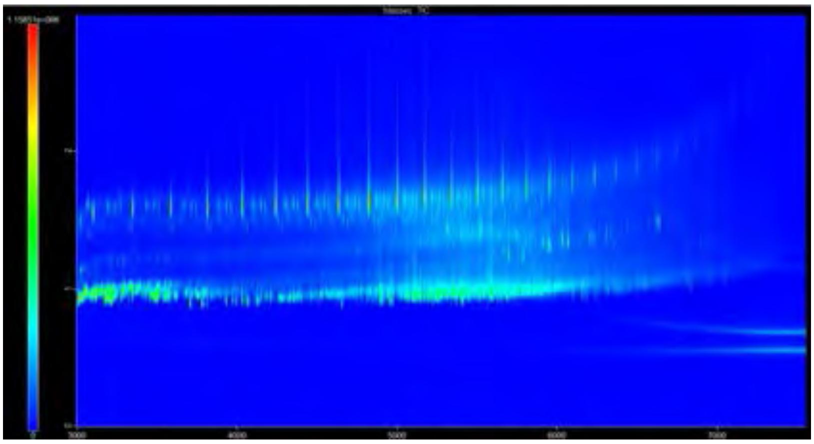

Figure A19 Total ion chromatogram of FO2-day0.

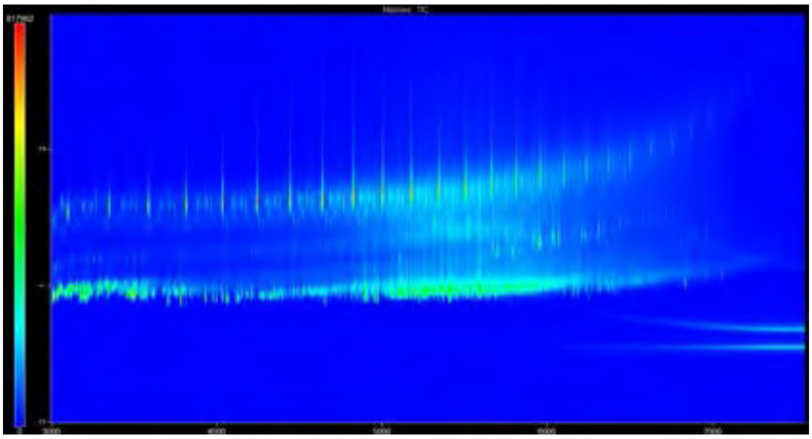

Figure A20 Total ion chromatogram of FO2-day7.

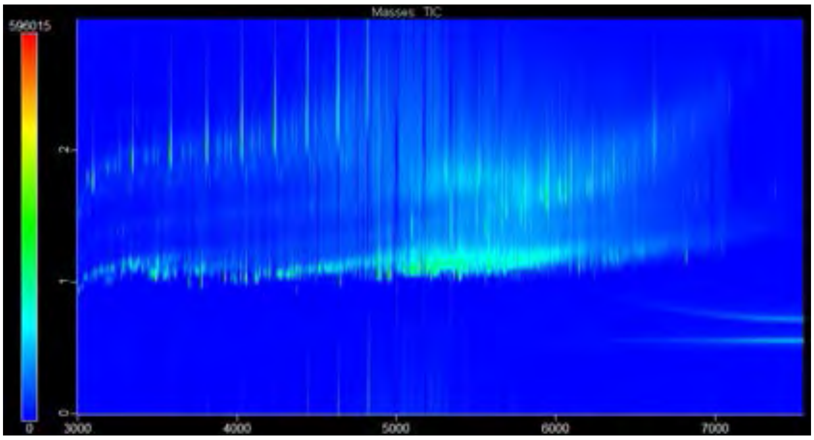

Figure A21 Total ion chromatogram of FO2-day60.

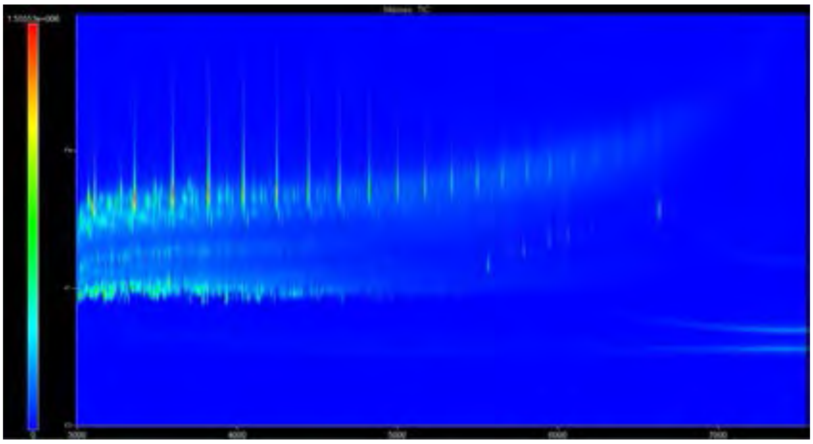

Figure A22 Total ion chromatogram of FO3-day0.

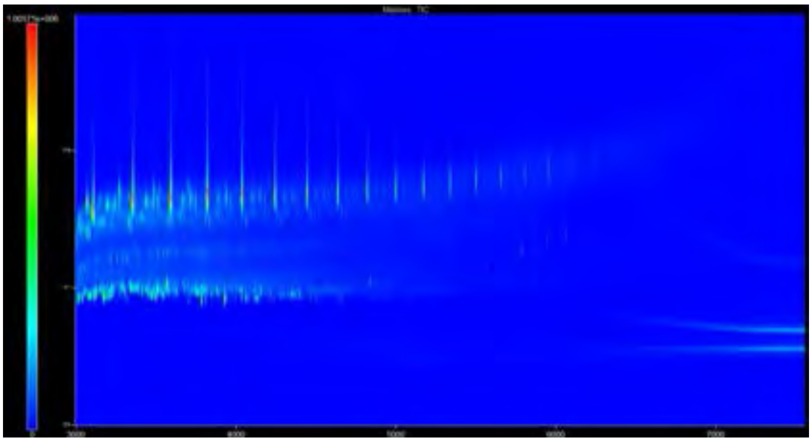

Figure A23 Total ion chromatogram of FO3-day7.

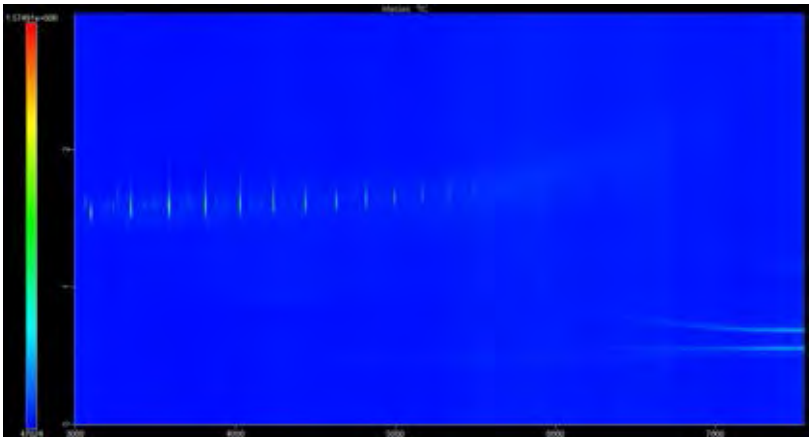

Figure A24 Total ion chromatogram of FO3-day60.

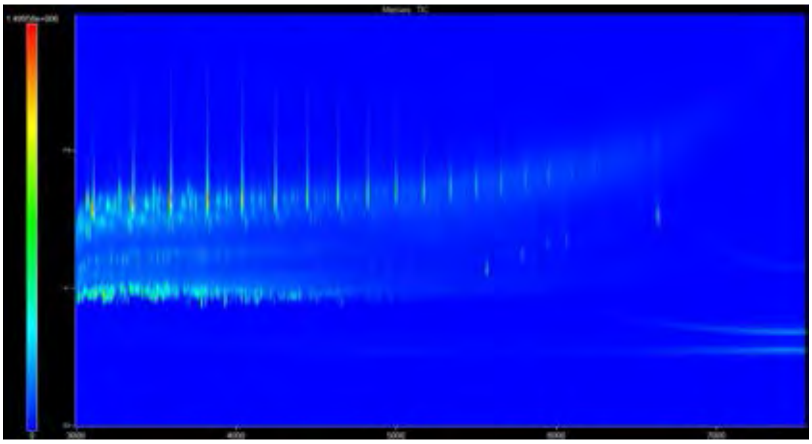

Figure A25 Total ion chromatogram of FO4-day0.

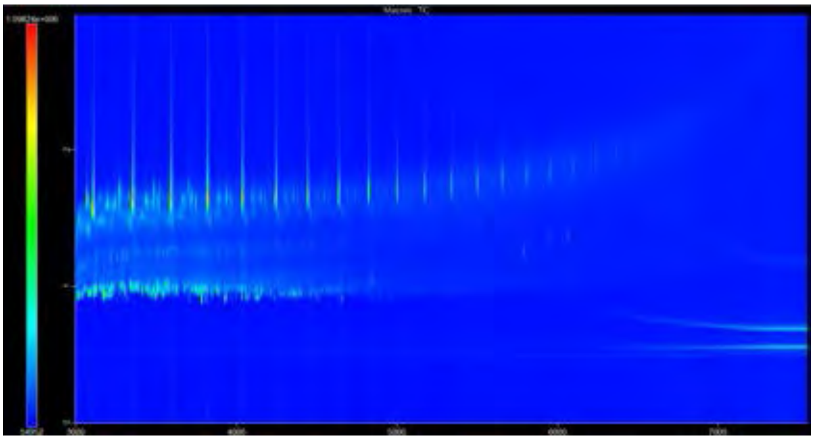

Figure A26 Total ion chromatogram of FO4-day7.

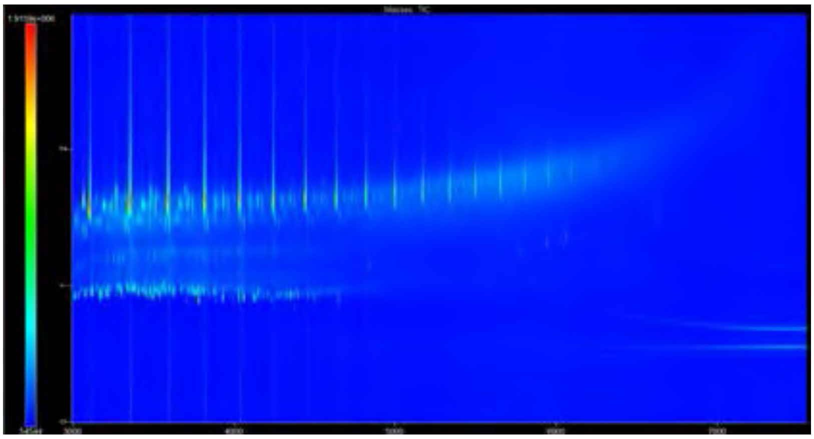

Figure A27 Total ion chromatogram of FO4-day0.

Appendix B GCxGC-TOFMS Target Ion (m/z 191) Contour Plot Result

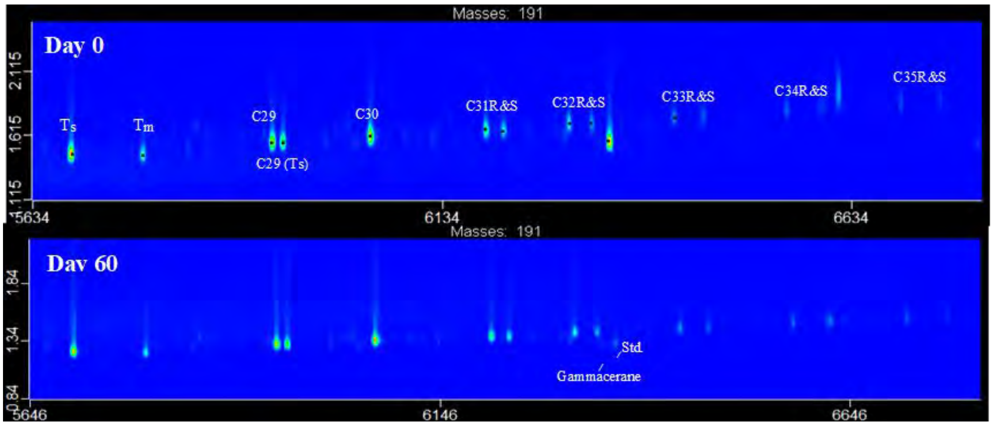

Figure B1 Target ion (m/z 191) surface plot of CO1-day 0 and day-60.

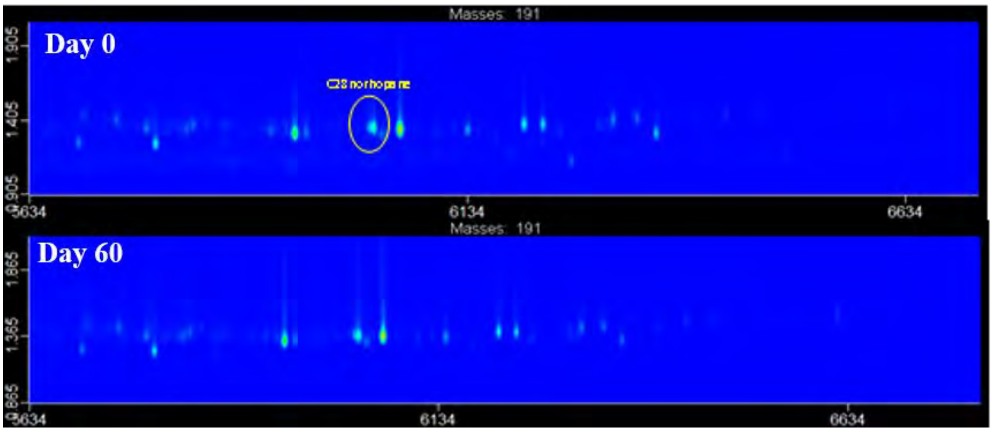

Figure B2 Target ion (m/z 191) surface plot of CO2-day 0 and day-60.

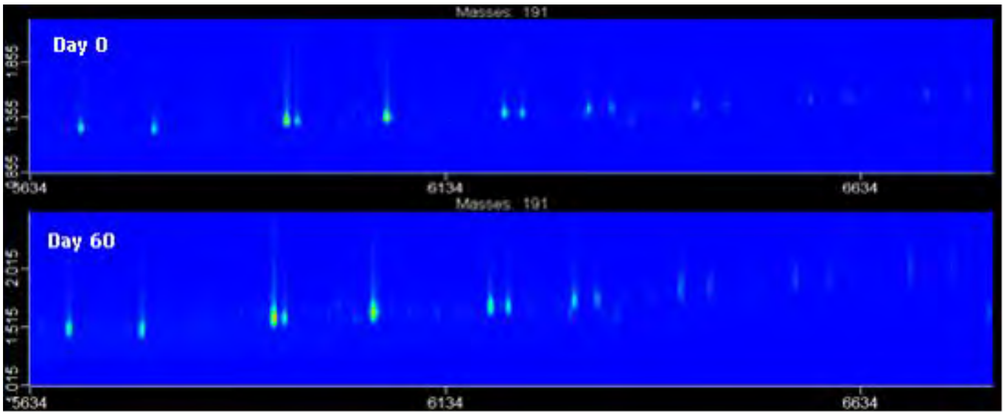

Figure B3 Target ion (m/z 191) surface plot of CO3-day 0 and day-60.

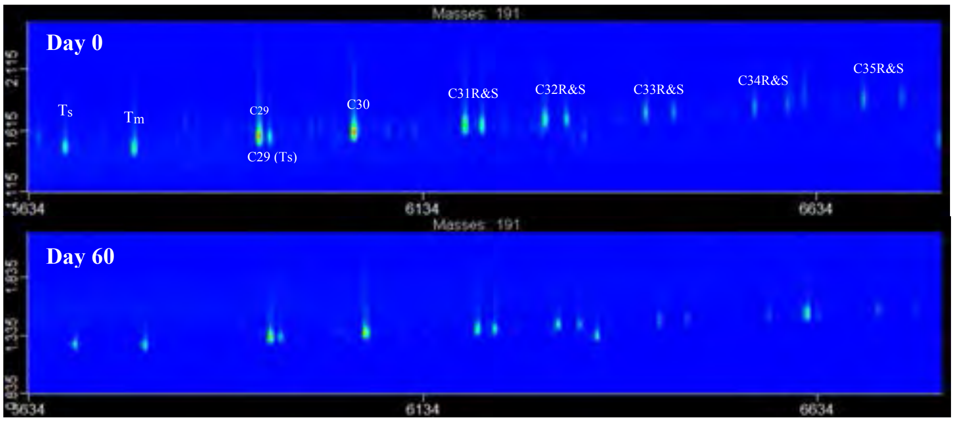

Figure B4 Target ion (m/z 191) surface plot of CO4-day 0 and day-60.

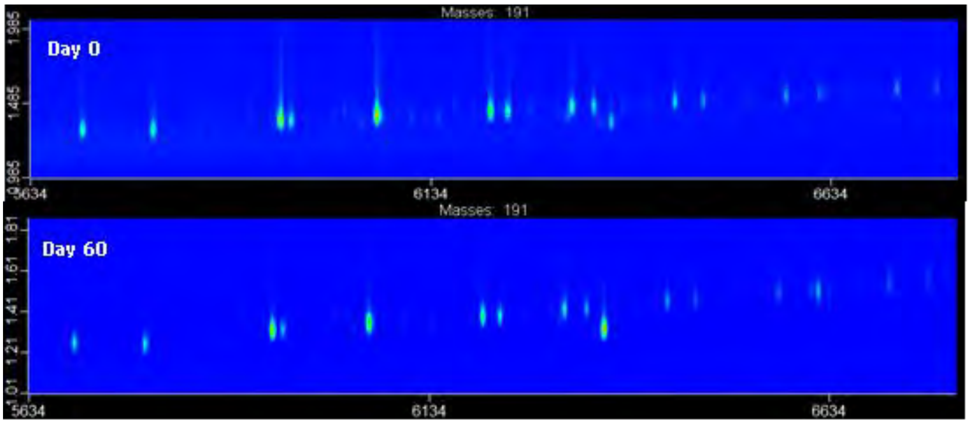

Figure B5 Target ion (m/z 191) surface plot of CO5-day 0 and day-60.

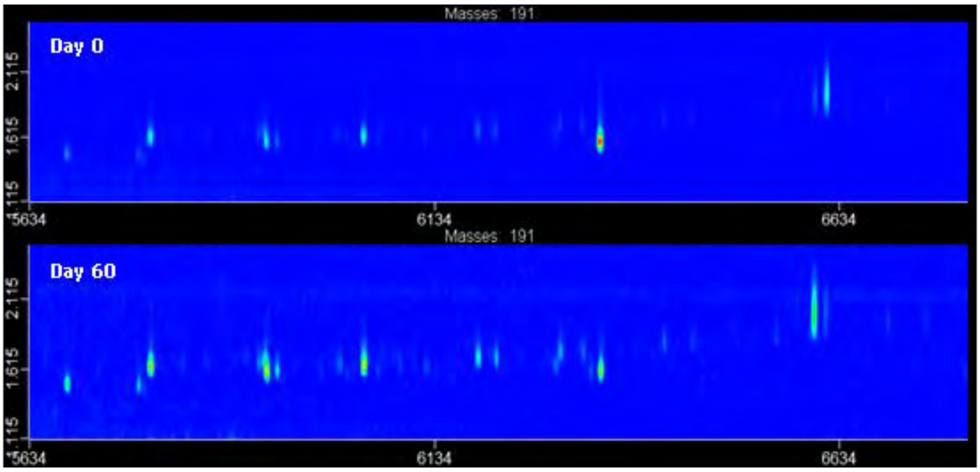

Figure B6 Target ion (m/z 191) surface plot of FO1-day 0 and day-60.

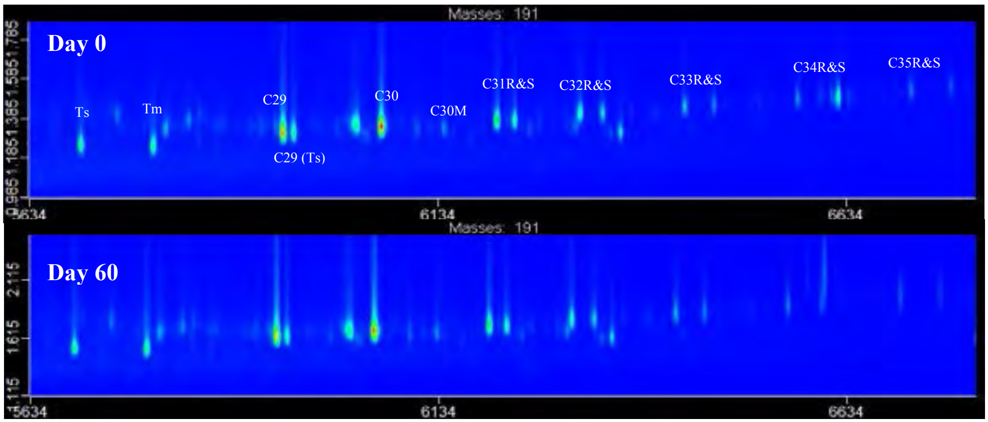

Figure B7 Target ion (m/z 191) surface plot of FO2-day 0 and day-60.

Figure B7 Target ion (m/z 191) surface plot of FO2-day 0 and day-60.

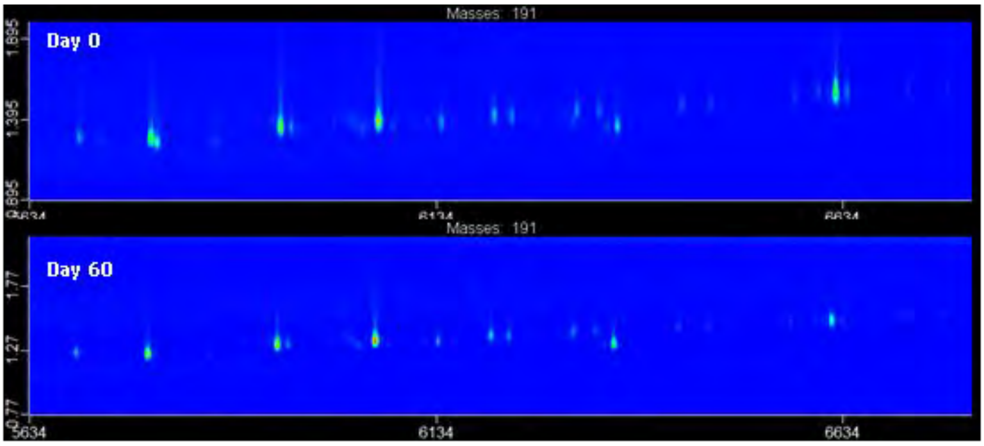

Figure B8 Target ion (m/z 191) surface plot of FO3-day 0 and day-60.

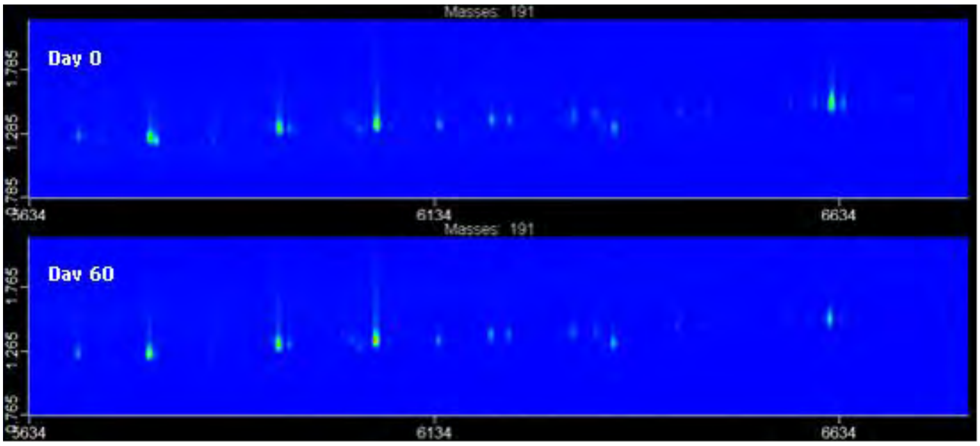

Figure B9 Target ion (m/z 191) surface plot of FO4-day 0 and day-60.

Appendix C The Correlation Plot between Fresh and Weathered Oil Samples

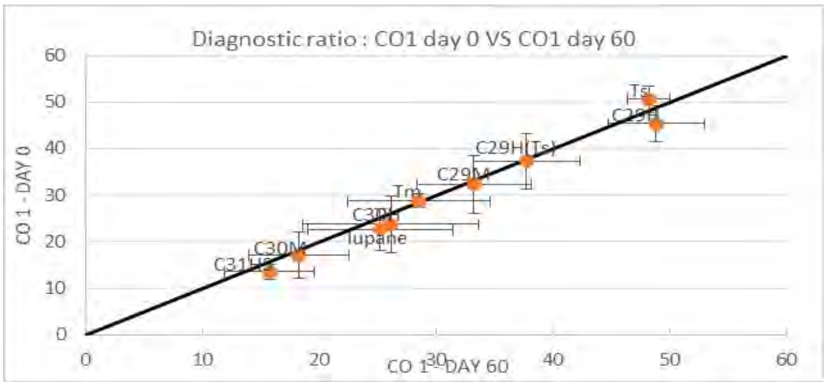

Figure C1 The correlation plot between CO1 on day 0 and day 60.

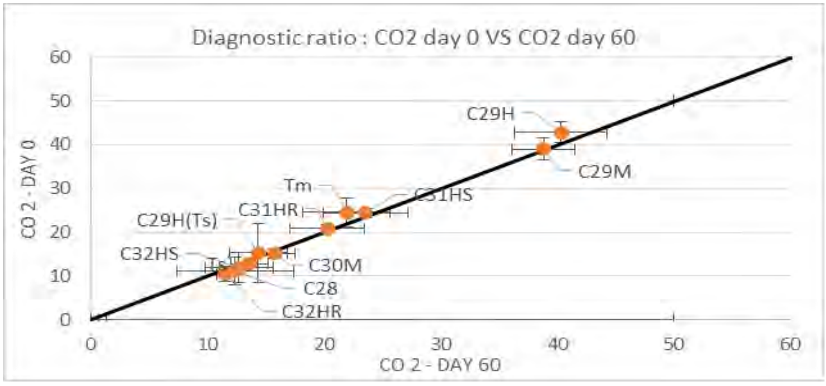

Figure C2 The correlation plot between CO2 (Banang) on day 0 and day 60.

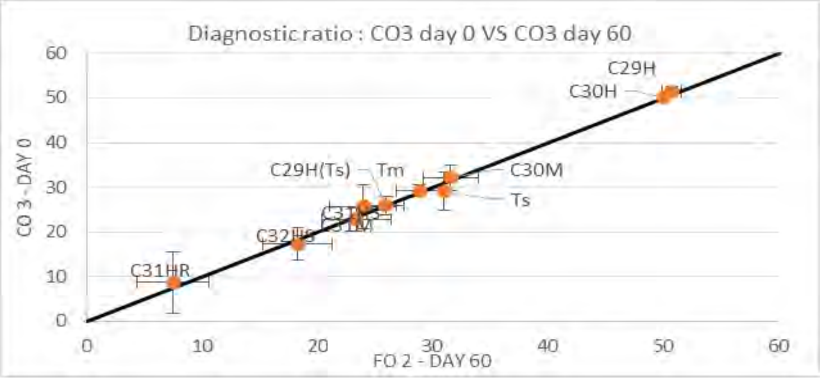

Figure C3 The correlation plot between CO3 (Upper zakum) on day 0 and day 60.

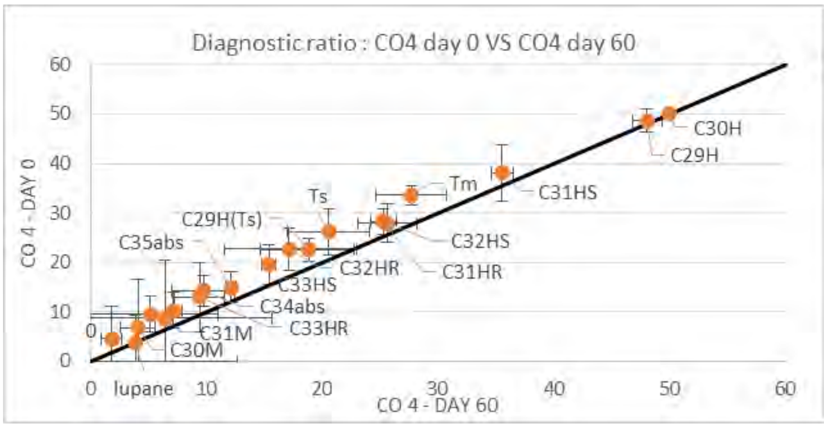

Figure C4 The correlation plot between CO4 (Qatar marine) on day 0 and day 60.

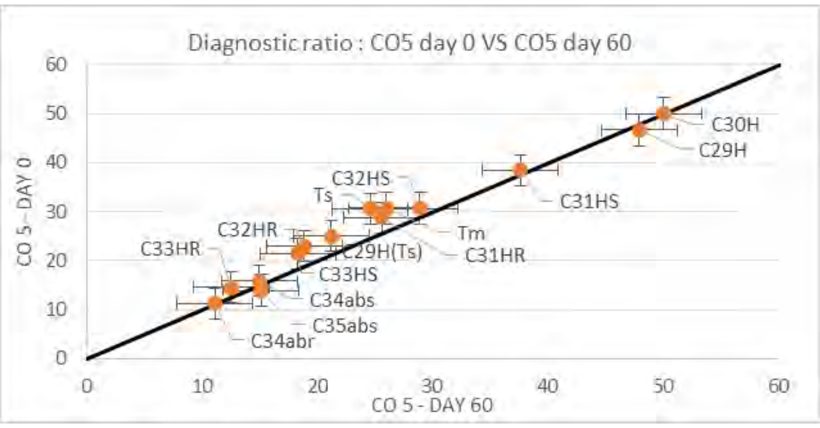

Figure C5 The correlation plot between CO5 (Alshaheen) on day 0 and day 60**.**

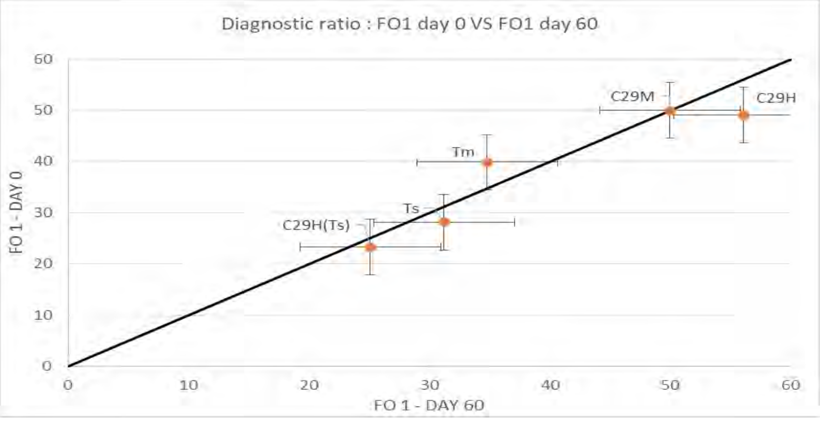

Figure C6 The correlation plot between FO1 on day 0 and day 60**.**

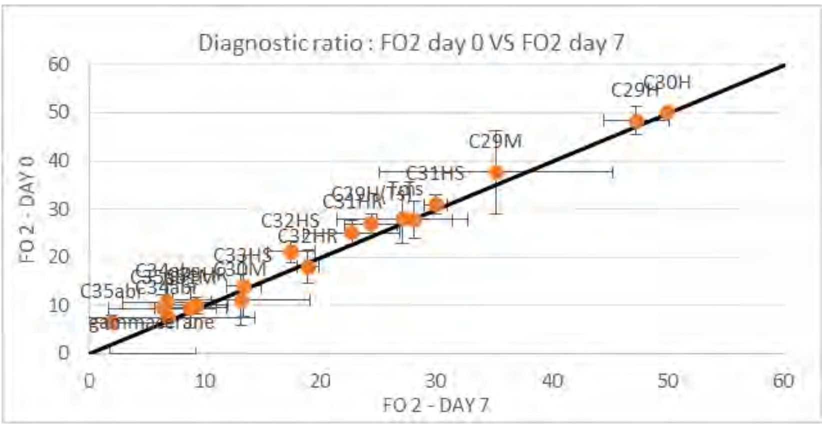

Figure C7 The correlation plot between FO2 on day 0 and day 60.

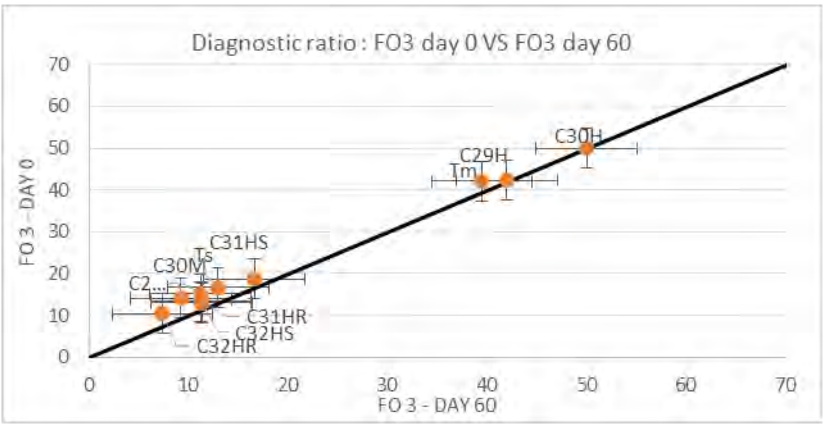

Figure C8 The correlation plot between FO3 on day 0 and day 60.

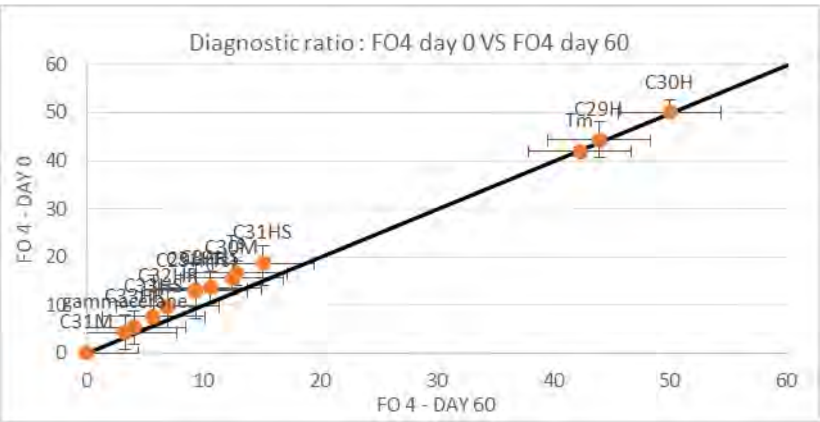

Figure C9 The correlation plot between FO4 on day 0 and day 60.

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Proceedings:

1. Thongkorn, H. and Jongpatiwut, S. (2018, June 5) Identification Types of Spilled Oil, Using Analysis of Biomarker and Asphaltenes Contents. Proceedings of the 24th PPC Symposium on Petroleum and Petrochemicals and Polymers and the 9th Research Symposium on Petrochemical and Materials Technology, Bangkok, Thailand.

Presentations:

1. Thongkorn, H., Jongpatiwut, S. (2018, June 5) Identification Types of Spilled Oil, Using Analysis of Biomarker and Asphaltenes Contents. Poster presented at 24th PPC Symposium on Petroleum and Petrochemicals and Polymers and the 9th Research Symposium on Petrochemical and Materials Technology, Bangkok, Thailand.
2. Thongkorn, H., Jongpatiwut, S. (2018, August 25-29) Identification Types of Spilled Oil, Using Fingerprinting Techniques and Aluminium Contents. Poster presented at 23rd International Congress of Chemical and Process Engineering CHISA 2018, Prague, Czech Republic.