THE STUDY OF SULFUR COMPOUNDS FOR OILS FINGERPRINTING APPLICATION

Titiparn Prasantongkolmol

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The Study of Sulfur Compounds for Oils Fingerprinting Application

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การศึกษาสารประกอบซัลเฟอร์ในน้ำมันเพื่อใช้ในการระบุหาแหล่งที่มา

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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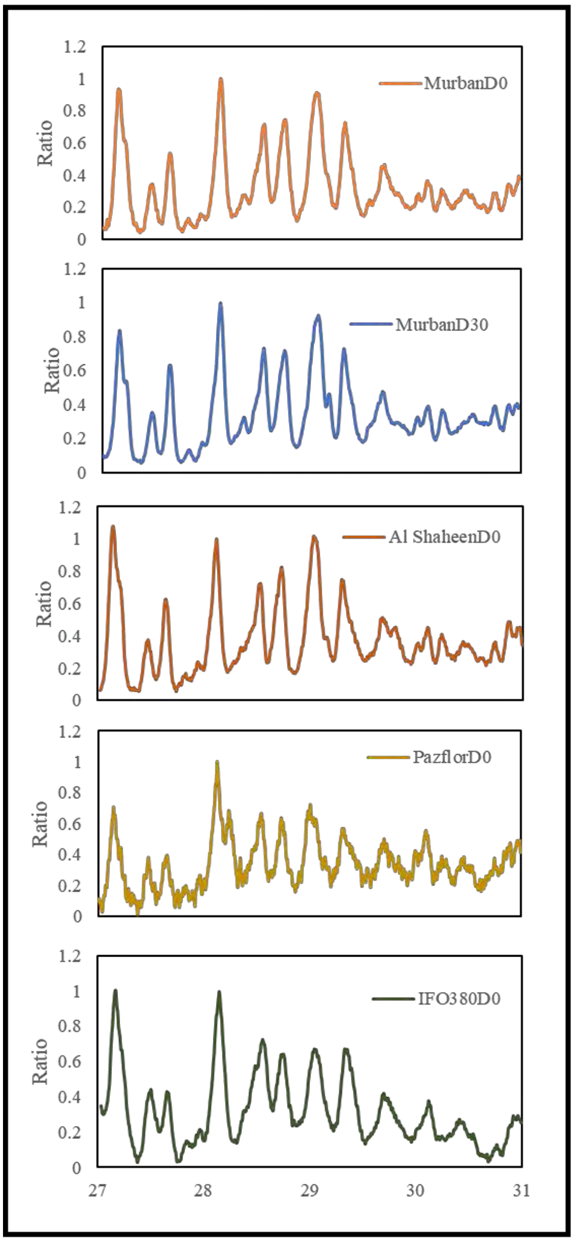
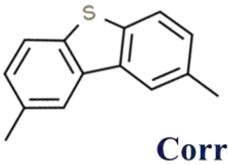
GRAPHICAL ABSTRACT

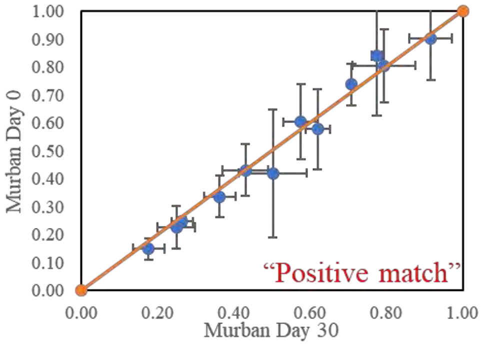
OIL FINGERPRINTING

Sulfur Compounds Distribution

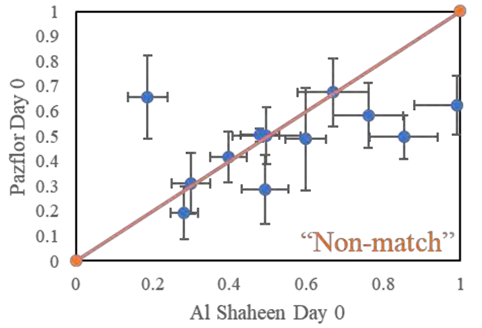




Correlation Plot



Sulfur compounds in oil can resist the weathering process and can be use to support the oil spill identification



GC-SCD

ธิติพันธ์ ประสานทองโกมล : การศึกษาสารประกอบซัลเฟอร์ในน้ำมันเพื่อใช้ในการระบุหาแหล่งที่มา. (The Study of Sulfur Compounds for Oils Fingerprinting Application) อ.ที่ปรึกษาหลัก : รศ. ดร.ศิริพร จงผาติวุฒิ

เหตุการณ์น้ำมันรั่วไหลในทะเลเป็นปัญหาที่สำคัญที่ส่งผลต่อสิ่งแวดล้อมทางทะเล และบริเวณชายฝั่งเป็นอย่างมาก นอกจากเหตุการณ์น้ำมันรั้วที่ทราบ ยังมีเหตุการณ์น้ำมันรั่วอื่น ๆ อีกมากที่ยังไม่ทราบสาเหตุ ไม่ว่าจะเป็นจากอุบัติเหตุ หรือการลักลอบปล่อยน้ำมันลงสู่ทะเล ซึ่งเหตุการณ์เหล่านี้จะส่งผลให้เกิดก้อนน้ำมันดินขึ้นตามชายหาด ซึ่งที่มาของก้อนน้ำมันยังไม่มีใครทราบแน่ชัด ดังนั้น การพัฒนาวิธีที่จะระบุหาแหล่งที่มาจึงเป็นสิ่งที่สำคัญ เพื่อที่หาแหล่งที่มาของน้ำมันที่รั่วกับก้อนน้ำมันดิน โดยทั่วไปเทคนิคที่ใช้ในการระบุหาแหล่งที่มาของน้ำมัน จะใช้ไบโอมาร์คเกอร์กลุ่มโฮปเพนโดยใช้เครื่องแก๊สโครมาโตกราฟชนิดแก๊สแบบสองมิติแบบมีแมสสเปกโทรมิเตอร์ (GCxGC-TOFMS) แต่อย่างไรก็ตามเทคนิคนี้มีข้อเสีย คือ มีราคาแพงและใช้เวลานานในการวิเคราะห์ นอกจากสารไบโอมาร์คเกอร์กลุ่มโฮปเพน สารประกอบกลุ่มซัลเฟอร์ เป็นสารอีกกลุ่มหนึ่งที่สามารถใช้เป็นไบโอมาร์คเกอร์เพื่อที่จะระบุหาแหล่งที่มาของน้ำมันได้ สารประกอบกลุ่มซัลเฟอร์จะมีอยู่หลากหลายรูปแบบในน้ำมัน และมีปริมาณที่แตกต่างกันขึ้นอยู่กับแหล่งที่มาของน้ำมัน ในงานวิจัยนี้ได้ทำการพัฒนาเทคนิคใหม่ขึ้นมา คือ การดูรูปแบบการกระจายตัวของสารกลุ่มซัลเฟอร์ในน้ำมันโดยใช้เครื่องแก๊สโครมาโตกราฟีชนิดแก๊สแบบมีซัลเฟอร์ดีเทคเตอร์ (GC-SCD) อัตราส่วนของสารประกอบซัลเฟอร์ได้ถูกคำนวณเพื่อใช้ในการสร้างกราฟแสดงความสัมพันธ์ (correlation plot) ผลการทดลองจากซัลเฟอร์โครมาโตแกรมแสดงให้เห็นว่า น้ำมันก่อนและหลังผ่านกระบวนการทางธรรมชาติ มีรูปแบบของสารประกอบกลุ่มซัลเฟอร์ที่คล้ายกัน ยิ่งไปกว่านั้น รูปแบบของสารประกอบกลุ่มซัลเฟอร์ยังสามารถแยกน้ำมันดิบและน้ำมันเตาแต่ละชนิดได้ ดังนั้น จึงสามารถสรุปได้ว่า เทคนิคการใช้รูปแบบการกระจายตัวของสารกลุ่มซัลเฟอร์ในน้ำมันสามารถใช้ในการสนับสนุนการระบุหาแหล่งที่มาของน้ำมันได้ นอกจากนี้ สารกลุ่มซัลเฟอร์ที่ใช้ในการระบุหาแหล่งที่มา ได้ถูกพบว่าคือสารกลุ่ม ไดเมทิลไดเบนโซไทโอฟีน

สาขาวิชา เทคโนโลยีปิโตรเคมี

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Titiparn Prasantongkolmol : The Study of Sulfur Compounds for Oils Fingerprinting Application. Advisor: Assoc. Prof. SIRIPORN JONGPATIWUT, Ph.D.

Oil spills are one of the serious problems to marine and coastal environment worldwide. Besides the known incidents, a number of oil spills are unknown, which may come from both accident and unauthorized drainage. Moreover, the spills cause tarball to arise on the beach and the origin of tarballs are still subtle. Thus, the development of oil fingerprinting is important in order to identify the origin of oil spills and tarballs. Generally, the current standard technique is using GCxGC-TOFMS to analyze the biomarker compounds in oil such as hopane groups. However, this technique is expensive and requires long time for analysis. Beside the hopane groups, the sulfur compounds in oil is the other groups which can be used as biomarkers for oil fingerprinting application. The sulfur compounds in oil are present in various types with a different amount depending on the source of oil. In this study, the new sulfur compounds distribution technique is developed by using GC-SCD instrument. This technique is cheaper and easier for analysis as compared to GCxGC-TOFMS. Moreover, the sulfur compound ratio is calculated and then created the correlation. The result from GC-SCD chromatogram shows a similar pattern of fresh and weathered oil samples. In addition, the GC-SCD chromatogram can differentiate each type of crude oil and fuel oil samples. Thus, the sulfur compounds distribution technique can be used to support the oil spill identification. Furthermore, the sulfur compound species which used for oil fingerprinting are identified to be C2-alkylated dibenzothiophene groups.

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CHAPTER 1
INTRODUCTION

The oil spill incident is one of the serious problems to marine and coastal environments worldwide. In the past, there were many oil spills incidents such as the Exxon Valdez in Alaska in 1989, Gulf War in Persian in 1991 and BP's Deepwater Horizon in Mexico in 2010. In Thailand, there was a large oil spill in Rayong province in 2013. This incident caused tarballs covering the beach, which lead to serious impact on environment, economy, and tourism. Later, even though, there was no large oil spill incident, from time to time, tarballs have been found on beaches. The origins of the tarballs are still subtle. Thus, the development of oil fingerprinting methodology is significant in order to identify the oil spill source. After oil spills into the seawater, oil has undergone weathering processes (e.g. evaporation, dissolution, photo-oxidation, and biodegradation) that cause the change of physical and chemical composition in oil (Tarr *et al.*, 2016). Hence, analytical development for oil fingerprinting becomes an interesting and challenging.

In general, the current standard method for oil fingerprinting is CEN method. This method involves the evaluation by a gas chromatograph equipped with flame ionization detector (GC-FID) followed by gas chromatograph equipped with mass spectrometry (GC-MS), then considering specific diagnostic ratios to confirm the analysis of oil fingerprinting. However, one-dimensional GC-MS has a limitation to identify complex mixtures in oils (Bayona *et al.*, 2015). Comprehensive two-dimensional gas chromatograph with time of flight mass spectrometry (GCxGC-TOFMS) become a new technique for oil fingerprinting application. This technique has high-resolution capacity and is suitable for the analysis of complex mixtures in oils. The GCxGC-TOFMS instrument consists of a two-dimensional column, which allows separation by both boiling point and polarity that could provide a better analysis of complex chemicals (Bayona *et al.*, 2015). Thus, analysis of oil spills by using comprehensive two-dimensional column to identify biomarkers in oils make the oil fingerprinting more effective.

In general, crude oil contains sulfur compounds content varies from 0.1 – 3.0% by weight. The sulfur compounds in crude oil are present in various structures such as hydrogen sulfides, mercaptans, thiophenes, benzothiophenes, and dibenzothiophenes. The amount and type of sulfur are different depending on the source of crude oil (Bajia *et al.*, 2017). There are various analytical techniques to detect the sulfur compound in crude oils such as X-ray fluorescence spectrometry (XRF) and inductively coupled plasma atomic emission spectrometry (ICP-AES). For gas chromatograph (GC), sulfur chemiluminescence detectors (SCD) is a popular for analyzing sulfur compounds in petroleum since it has a linear and equimolar response to all sulfur compounds and has high sensitivity and selectivity (Hua *et al.*, 2004). Furthermore, the cost of analysis by GC-SCD technique is cheaper and easier for analysis as compared to GCxGC-TOFMS technique. Among the types of sulfur compounds in oil, The sulfur compound that are larger than 4,6-Dimethyldibenzothiophene (4,6-DMDBT) seem to be the interesting compound in petroleum biomarker since these components are stable, less reactivity, and difficult to remove from oil(Hegazi *et al.*, 2016). Moreover, these components might not be affected by the weathering process and could be used as a fingerprinting of oil. Hence, the analysis of heavy sulfur compounds in oil by using GC-SCD instrument will be a complementary method that can support a biomarker method by GCxGC-TOFMS.

The aim of this research is to study and develop the sulfur compounds distribution method by GC-SCD to support the identification of crude oils and simulated tarballs by GCxGC-TOFMS.

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Crude Oils

Crude oil is an unrefined petroleum product composed of a mixture of hydrocarbons and other organic materials such as sulfur, nitrogen, and certain metals (e.g. nickel, vanadium, and so on). Crude oil is originated from remained plants and animals that live millions of years ago in the environment. The remainders of these organisms were covered by sand, slit and rock layers. After undergone by heat and pressure, the remain of plants and animals turn into crude oils (EIA, 2017). The process of crude oil forming is shown in Figure 2.1.

The composition of crude oil is different depending on its source. Normally, crude oil has been classified by using hydrocarbon type (e.g. paraffinic crudes, naphthenic crudes, and Asphaltenic crudes), American Petroleum Institute (API) gravity which shows the light and heavy of crude and sulfur content such as sweet and sour crude. Therefore, the difference of crude oil compositions that come from different source can be used to differentiate and fingerprinting of crude oil (Vermeire, 2012).

Source: Adapted from National Energy Education Development Project (public domain)

Figure 2.1 Petroleum and natural gas formation (EIA, 2017).

2.2 Processed Oil

Process oils or refined petroleum products are products of crude oil when passing the process in refinery such as distillation, treating and cracking. The chemical compositions of process oils are significantly different from crude oil. The major processes are gasoline, kerosene, diesel, lubricating and fuel oil. The chemical composition of process oils is significantly different from crude oil. The distillation process of crude oil is shown in Figure 2.2.

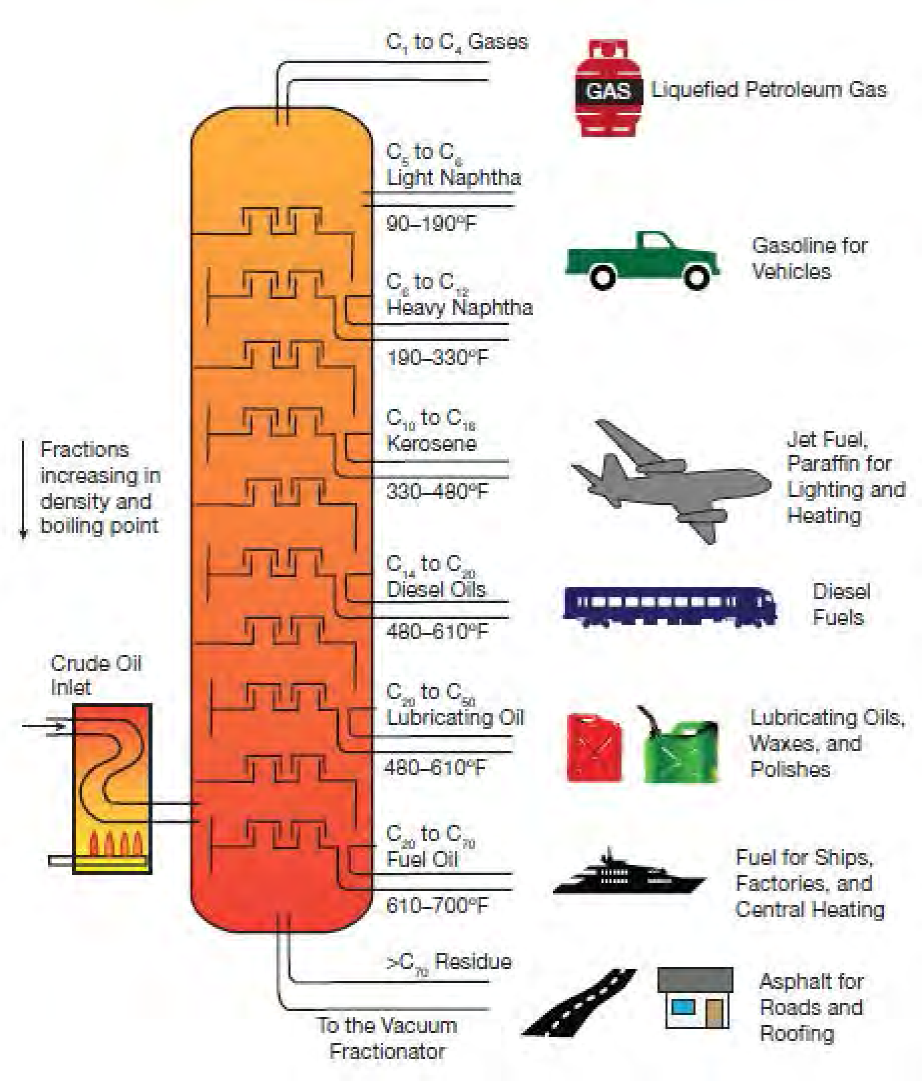


Figure 2.2 The distillation process of crude oils (Olsen, 2014).

Fuel oil which use as a fuel in the ship is called bunker fuels. The naming of bunker fuel is generally used to describe the different grade of marine fuel. Typically, the bunker fuels can be classified in to 3 types which are Bunker A, Bunker B and Bunker C. Bunker A was also call No. 2 fuel oil, Bunker B was also call No. 4 or No. 5 fuel oil and Bunker C which is a commonly used bunker fuel was also call No. 6 fuel oil. Due to the high grew demand of marine fuels. The International Organization for Standardization (ISO) was developed standardized specifications for marine fuel oils which were classified into 14 grades of marine fuels including four distillate and ten residual grades.

The ISO was using viscosity, pour point and sulfur, carbon, and metal residual content as a principle features to distinguish residual marine fuel oils into ten grades. Practically, only five of these are widely used for marine transport. These five widely used fuel occur within two groups. The first groups are intermediate fuel oil 180s (IFO180s). The second groups are intermediate fuel oil 380s (IFO380s). The name of these two groups is referred to the maximum permissible viscosities of these fuel at 50 C, 180, 380 mm^2/s (cSt), respectively. IFO180s include the ISO grades RME 180 and RMF 180 and IFO380s include the ISO grade RMG 380, RMH 380, and RMK 380. These five grades are distinguished by differences of carbon residue, ash, and vanadium contents. (Uhler *et al.*, 2016).

2.3 Petroleum Chemical Fingerprinting

2.3.1 Chemical Composition of Oil

Crude oil consists of hydrocarbons and nonhydrocarbons which range from light volatile compounds to heavy nonvolatile one. Normally, petroleum compounds can be classified by their structure into four groups call SARA which is saturated, aromatic, resin and asphaltene (Wang *et al.*, 2007)

Saturates are a group of hydrocarbons predominant class in most crude oil. Saturates are composed of only carbon and hydrogen with no carbon-carbon double bonds including straight chain and branched chain (also called paraffin) and cycloalkane (also call napthenes) and some chemical biomarker such as terpanes and steranes. Alkenes or olefins are partially unsaturated hydrocarbons that compose of one or more double carbon-carbon bonds. Olefins are not normally found in crude oil but can found in some refined products such as products of oil from cracking process.

Aromatic hydrocarbons are cyclic that contain benzene ring and have stability than isolated double bonds. Aromatic in petroleum include the mono-aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene isomer (all of this also called BTEX), other alkyl-substituted benzene compounds (C_n-benzenes), and aromatics which have two or more aromatic benzene ring are called polycyclic aromatic hydrocarbons (PAHS) e.g. naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene.

Polar compounds are a compound such as nitrogen, oxygen, or sulfur that have bonding with atoms. In petroleum, the smaller polar compounds are call resin while the large polar compounds are called asphaltene. The polar heteroatom cyclic compounds such as alkylated carbazole, quinoline, pyridine, thiophene, and dibenzothiophene are present in oil and can persist in the environment despite the weathering oils. Thus, these compounds in oil are a potential source to identify the petroleum source.

Resin compounds include heterocyclic hydrocarbons, phenols, acids, and so on. Sulfur compounds in crude oil are among the important heteroatomic constituents that vary from about 0.1-3 % to 5-6 % for some heavy oils. The sulfur compound in crude oil can present in various forms such as element sulfurs, hydrogen sulfides, mercaptans, thiophenes, benzothiophenes, dibenzothiophenes, and naphthobenzothiophenes.

Asphaltenes are a class of large compounds that are not dissolved in petroleum but disperse as colloids. Table 2.1 shows the composition of crude oils and petroleum products (%) (Wang *et al.*, 2016).

Table 2.1 The composition of crude oils and petroleum products (Wang *et al.*, 2016)

Group	**Compound Class**	**Gasoline**	**Diesel**	**Light crude**	**Heavy crude**	**IFO**	**Bunker C**
Saturated		50-60	65-95	55-90	25-80	25-45	20-40
	Alkanes	45-55	35-45				
	Cyclo-alkane	~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	25-40	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	1-5	1-5
Polar compound			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
Sulfur		<0.05	0.05-0.5	0-2	0-5	0.5-2	2-4
Metals (ppm)				30-250	100-500	100-1000	100-2000

2.3.2 Petroleum Biomarkers

Biomarkers or biological markers are complex molecules which come from formerly living organisms. Biomarkers present in crude oils, rocks, and sediments show little change from their organic molecules (also called biogenic precursors) in the living organism. Furthermore, they can show the information about the nature, source, type, geological condition of these organisms. In many years, biomarkers have been widely used in petroleum exploration and reservoir geochemistry to achieve the valuable information to geochemists such as thermal maturity of the oil, the type, and age of source material and rock and degree of biodegradation of oil. Nowadays, Biomarkers become the significant hydrocarbon groups in petroleum for chemical fingerprinting since biomarkers such as hopenoids, steroids, and aromatic steroids have more resistant to degradation in the environment. Moreover, different geological conditions and ages of forming biomarker might show different biomarker fingerprint. Thus, the analysis of biomarker in oil provides important information for determining of oil spill source (Wang *et al.*, 2016).

The basic structure of biomarker compounds in petroleum is isoprene and the compound that consists of isoprene subunits is called terpenoids or isoprenoids. Moreover, terpenoids are classified into families based on the approximate number of isoprene subunits as shown in Table 2.2.

Table 2.2 Families of terpenoids (Wang *et al.*, 2007)

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

Normally, petroleum biomarkers are classified into 2 groups which are acyclic terpenoids and cyclic terpenoids

2.3.2.1 Acyclic Terpenoids or Isoprenoids

Acyclic or aliphatic isoprenoids hydrocarbons have found in large number in oils. The number of carbon atoms in terpenoids family is depending on source material, diagenesis, thermal maturity, and in-reservoir biodegradation. For instance, phytane ($C_{20}H_{42}$) and pristane ($C_{19}H_{40}$) is the most common acyclic terpenoid in oils biomarker having different carbon atom. Phytane and pristane ($C_{19}H_{40}$) are isoprenoid compounds having a lot in oils which have widely used for studying oil biodegradation in the environment. Figure 2.3 shows an example of acyclic terpenoid compounds structure in oil including 2,6- dimethyloctane (monoterpene, C_{10}), pristane and phytane (diterpene, C_{19}, and C_{20}) and so on (Wang *et al.*, 2016).

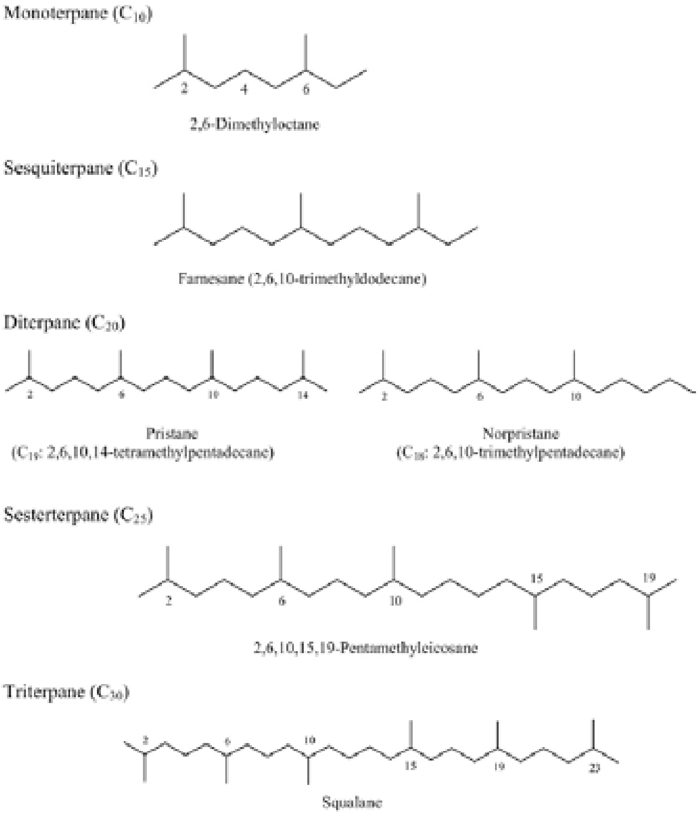


Figure 2.3 The structure of acyclic terpenoids (Wang *et al.*, 2016).

2.3.2.2 Cyclic Terpenoids

The most common cyclic terpenoids in oil are terpanes, steranes (cyclic terpenoid compounds), and aromatic steranes. In most crude oils, terpanes, including bicyclic, tricyclic, tetracyclic and pentacyclic, are found. Hopanes are one of the examples of pentacyclic triterpanes normally containing 27-35 carbon atoms. Hopanes with the 17α, 21β-configuration are characteristic of petroleum due to their great abundance and thermodynamic stability compared to other epidemics (ββ and βα) series. Steranes are a four-ring class of biomarkers that contain 21-30 carbon atoms including regular steranes, rearranged diasteranes, and mono- and tri- aromatic steranes. The carbon atom of 27 (cholestane), 28 (ergostane), 29 (stigmastane) of sterane series are very useful for chemical fingerprinting due to their source specificity. Another group of biomarker compounds in oil is aromatic steranes. These compounds also give significant information for source identification (Wang *et al.*, 2016). Figure 2.4 shows a molecular structure of cyclic terpenoids compound.

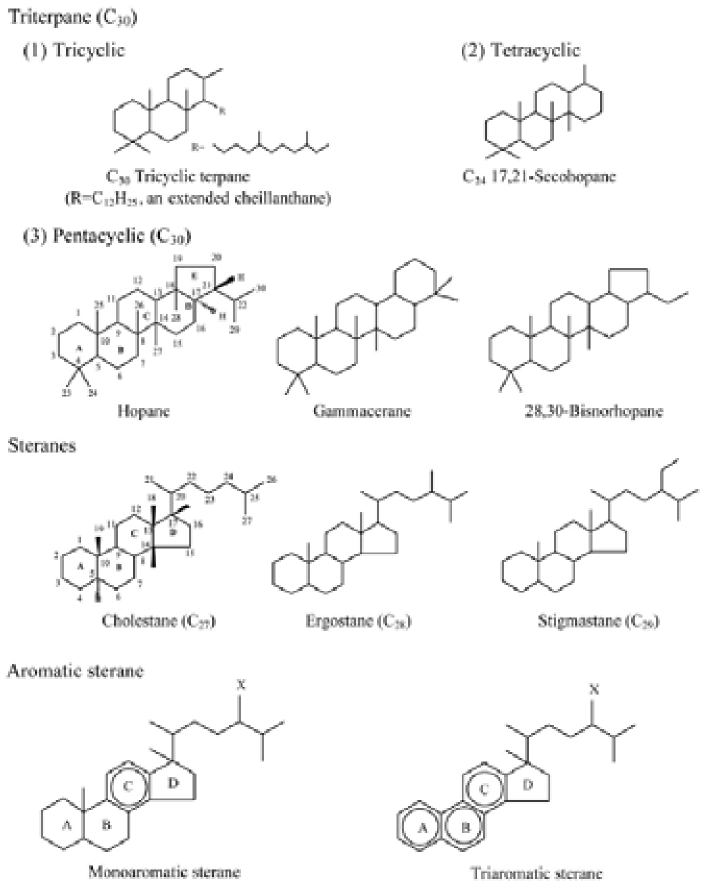


Figure 2.4 The structure of cyclic terpenoid compound (Wang *et al.*, 2016).

Table 2.3 The summary of petroleum biomarker regularly used for oil spill identification (Wang *et al.*, 2016)

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
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

Compound	Empirical formula	Target ions
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-tetrakishomohopane4	$C_{19}H_{34}$	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 Polycyclic Aromatic Hydrocarbon (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that widespread in environment found in soil, sediments, and air particle. The PAHs are composing of two or more or fused benzene rings with pair of carbon atom shared between molecule bonded in linear, cluster, or angular arrangement. The molecular arrangements of PAHs are shown in Figure 2.5. The general properties of PAHs are high boiling points, low vapor pressure, and low solubility in water. Moreover, PAHs have resistance in weathering process including oxidation and reduction (Abdel-Shafy *et al.*, 2016, Emsbo-Mattingly *et al.*, 2016).

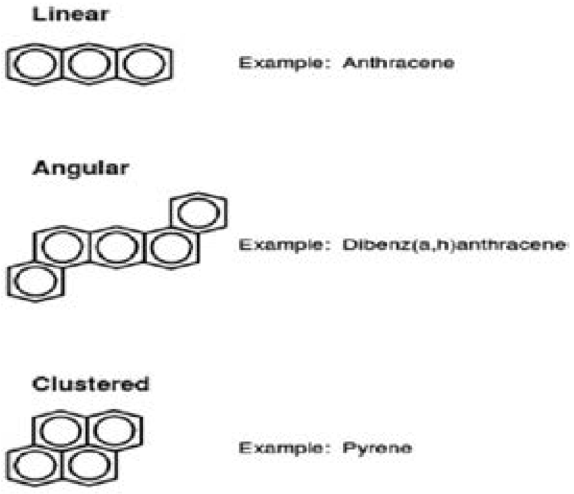


Figure 2.5 The molecular arrangement of PAHs (Abdel-Shafy *et al.*, 2016).

The sources of PAHs are classified into three main groups including pyrogenic, petrogenic, and biological. Pyrogenic PAHs are formed in high temperatures under low oxygen conditions. For example, the thermal cracking process of petroleum residual. In addition, PAHs can also be formed in low temperature condition which is called petrogenic during crude oil maturation process. This petrogenic PAHs are commonly found in petroleum products.

The temperature of formation is one of the important information to provide PAHs sources identification. For instance, high formation temperature might produce PAHs with fewer alkylate chain than low temperature and have different PAHs distribution pattern. Thus, it is beneficial in source identification of oil spill.

2.3.4 Polycyclic Aromatic Sulfur Heterocycles (PASHs)

Sulfur in petroleum is generally the most abundant hetero element. The total sulfur content in most crude oils is in a range between 0.1 – 3 % but vacuum residue of heavy crude can reach 8 %. Organic sulfur compounds in crude oils are present in various molecular structures such as aliphatic thiols, mono, disulfide, sulfoxide, and alkyl phenyl disulfide. However, a large amount occurs in an aromatic structure such as alkylated thiophene, benzothiophenes (BTs), dibenzothiophene (DBT), and alkylated dibenzothiophene (DBTs). These sulfur compound might represent over 70 % of the sulfur present in middle distillate fractions (Hegazi *et al.*, 2016). The structure of sulfur compound in petroleum are shown in Figure 2.6.

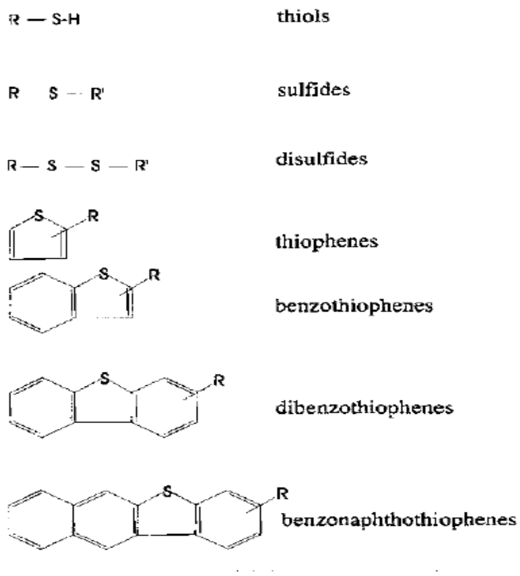


Figure 2.6 The structure of sulfur compound in petroleum (Beens *et al.*, 1997).

When the oil spill into the environment, it will be undergone weathering process. Photo-oxidation and biodegradation are an important mechanism in the chemical change in crude oils. From Dutta *et al.* (2000), they studied the combine effect of the photo-oxidation and biodegradation of crude oil. Almost complete depletion of alkanes and naphthalene derivative and less extensive removal by biodegradation in the order of n-alkane > naphthalene > branched alkanes > fluorenes > phenanthrenes > dibenzothiophene. The aromatic with larger chain were less sensible to biodegradation.

The study of biodegradation of sulfur compound in crude oils showed that the sensible of the sulfur heterocycles in homologous series in the order of C2-BTs > C3-BTs, DBT > C1-DBTs > C2-DBTs > C3-DBTs (Fedorak *et al.*, 1983, Dutta *et al.*, 2000).

Hegazi *et al.* (2012) studied the effect of weathering on the distribution pattern of the high molecular weight sulfur-containing aromatic by using FT-ICR MS technique. They showed that dibenzothiophene and naphthenodibenzothiophenes have a weathering stability. Therefore, it might be used as a marker in crude oil for spilled oil source identification (Hegazi *et al.*, 2012).

Misselwitz *et al.* (2013) studied the fingerprint of crude oils by using comprehensive two-dimensional gas chromatography. They showed that the diagnostic biomarker such as hopane and sterane can be used to identification crude oil sample. Moreover, they found that adding alkylated dibenzothiophenes and phenanthrene to the diagnostic ratio provide a better distinction between crude oils (Misselwitz *et al.*, 2013).

2.3.5 Weathering Process

When the oil spill into the sea, the oil will be undergone the physical and chemical processes that cause the change of compounds in oil. This process is called weathering process including spreading, evaporation, dispersion, dissolution, oxidation, and biodegradation as shown in Figure 2.7. From ITOPF (2014), the speed of these processes occurs depending on weathering condition (location, wind, wave, and sun) and properties of oil such as API gravity, volatility, and viscosity. Moreover, spreading, evaporation, dispersion and emulsification are rapidly in the early stage of oil spills while photo-oxidation, sedimentation, and biodegradation are long-term processes (ITOPF, 2014, Tarr *et al.*, 2016). The estimated time of each weathering process is shown in Figure 2.8.

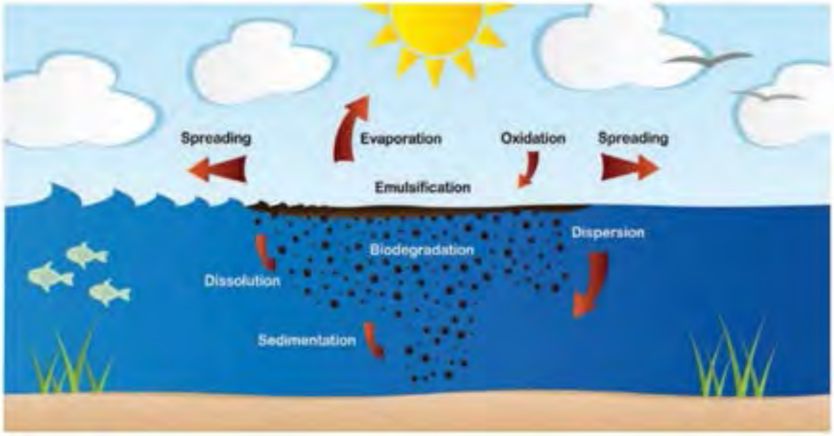


Figure 2.7 Weathering process of oil spill in the sea (ITOPF, 2014).

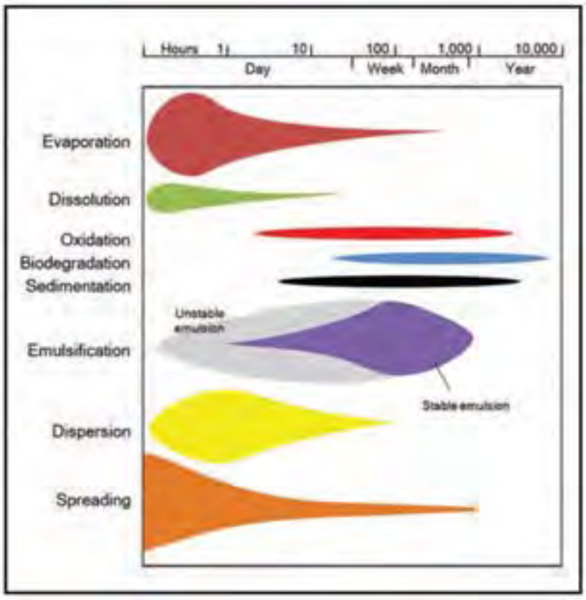


Figure 2.8 The estimated time of each weathering process (ITOPF, 2014).

2.3.5.1 Spreading

As soon as after the oil spilled, it starts to spread over the sea surface. The speed is depending on viscosity and volume spilled. Furthermore, the rate of spread is also affected by waves, turbulence, tidal streams, and currents. The oils initially spread as a coherent slick but faster begin to break up because of wind and wave and will tend to form narrow bands.

2.3.5.2 Evaporation

The light component in oil will evaporate to the atmosphere. The rate of evaporation is depending on ambient temperatures, wind speed, and volatility of oil. For instance, the oil with higher proportional of light component or low boiling point component will have higher degree of evaporation. Furthermore, oil component with a lower boiling point less than 200 °C will evaporate within a period of 24 hours in temperature conditions. The rate of evaporation also affects by initial spreading rate. For example, the large surface area has a higher evaporation rate. Moreover, rough sea, high wind speeds, and warm temperatures will also be increasing evaporation. Thus, spill of light oil products such as kerosene and gasoline might evaporate completely within a few hours.

2.3.5.3 Dispersion

The dispersion rate of oil is greatly depending on the nature of oil and the sea state. The wave and turbulence of the sea will cause a slick to break into a droplet which becomes spread into the upper layer of seawater. The increased surface area by dispersed oil might increase some weathering processes such as biodegradation, dissolution, and sedimentation.

2.3.5.4 Emulsification

Oil spill will mix with water and form water-in-oil emulsions. This process could increase the volume of pollutant. However, the formation of water-in-oil emulsion can reduce the rate of other weathering processes and can cause the persistence of light and medium crude oils on the sea surface.

2.3.5.5 Dissolution

The rate of oil dissolve into the sea is depending on composition, spreading, the water temperature, turbulence, and degree of dispersion. The heavy components in oil are almost insoluble in the sea while light components (e.g. benzene and toluene are slightly soluble. Normally, the rate of evaporation of light components is much higher than dissolving.

2.3.5.6 Photo-oxidation

Photo-oxidation is a process that promoted the oil by sunlight which might lead to formation of soluble products or persistent tars. The effect of oxidation is minor compared to other weathering processes. In general, thin oil films break down slowly usually at below 0.1 % per day, and may oxidize to persistent residues more than degrade. The example of this process is tarballs which consist of solid outer crust in order to prevent softer to oxidize.

2.3.5.7 Sedimentation and Sinking

Sedimentation is a process which oil droplets will interact sediment particles and organic matter suspended in the sea and then the droplet will slowly sink to the sea. Moreover, sedimentation is one of the long-term processes which leads to accumulating of spilled oil in the sea. However, sinking of bulk oil is observed only in shallow water close to shore.

2.3.5.8 Biodegradation

Biodegradation is a process which micro-organism in the sea including bacterial, yeast, fungi, unicellular algae, and protozoa can change the component in oil into the energy source. The factors that affect the rate and extent of biodegradation are properties of oil, the availability of oxygen and nutrients, and temperature. Although, the variety of factors affect biodegradation makes it difficult to predict. Biodegradation is a long-term mechanism for the removal of a trace of oil from shorelines.

2.3.6 Weathering Effect on Chemical Fingerprinting

From Zhang *et al.* (2015), they studied the weathering effect on alkanes, biomarkers, and polycyclic aromatic hydrocarbons of Dalian crude oil by using gas chromatography equipped with mass spectrometry (GC-MS). The result of aliphatic hydrocarbon shows that the volatile hydrocarbons of *n*-alkane and *i*-alkane (less than C-13) are absence and the Unresolved complex mixture (UCM) arises which indicates that n-alkane will seriously affect by the weathering process. However, pristane (Pr) and phytane (Ph) show strong capability of anti-weathering and become dominant peak. Moreover, the ratios of *n*-C17/Pr, *n*-C18/Ph, and Pr/Ph has been used to indicate oil biodegradation. The value of Pr/Ph decrease can indicate that Ph is a strong capability of resistance compared to Pr. For biomarkers, the hopanes (m/z 191) and sterane (m/z 217) have similar distributions of initial oil and oil after the weathering process. In addition, Wang *et al.* (2004) also studied the biomarker distribution in weathered oil. The result indicated that biomarker distribution of terpane and sterane might be unchanged by weathering process. Therefore, the biomarkers compound can be used as fingerprinting of source oil identification. For polycyclic aromatic hydrocarbon (PAHs), PAHs compounds compose of naphthalene (N), phenanthrenes (P), dibenzothiophene (D), fluorenes (F) and chrysenes (C). Naphthalene and alkylated homologous seem to be significantly composition change by weathering process (Wang *et al.*, 2004, Zhang *et al.*, 2015).

2.4 Oil Spill Identification Methodology and Oil Spill in Thailand

2.4.1 Chemical Fingerprinting Techniques

Nowadays, there have many different instruments and non-instrument technique for analysis of fingerprinting in oils such as gas chromatograph (GC), gas chromatograph equipped with mass spectrometry (GC-MS), high performance chromatograph (HPLC), thin layer chromatograph (TLC), Ultraviolet (UV) spectroscopy and so on (Ned *et al.*, 2013). In general, gas chromatography is the most widely used methodologies following the European Committee for Standardization (CEN) TR15522-2 and the ASTM5739-00. For other methodologies, it can support GC-technique to get a better result.

Chromatograph is a separation technique of a mixture of compounds into their individual component depending on their volatiles. There are many types of chromatography techniques such as liquid chromatography (LC) and gas chromatography (GC). The GC technique is widely used in many applications include fingerprinting of oil since it can analyze both qualitative and quantitative of sample (Dhanarasu, 2012).

Gas chromatograph (GC) is composed of three main parts which are injector, column, and detector. The sample is start injecting into the column by injector and will be vaporized into vapor. Then, the streams of samples are transported to a column by carrier gas including Helium or Nitrogen in order to separate several components and the amount of each component is then measured by the detector. The detector converts the amount of each component to an electrical signal and sends these signals to data processing (Dhanarasu, 2012, Shimadzu, 2019). Figure 2.9 shows diagram of gas chromatography (GC) instrument. Figure 2.10 shows diagram of gas chromatography (GC) processes.

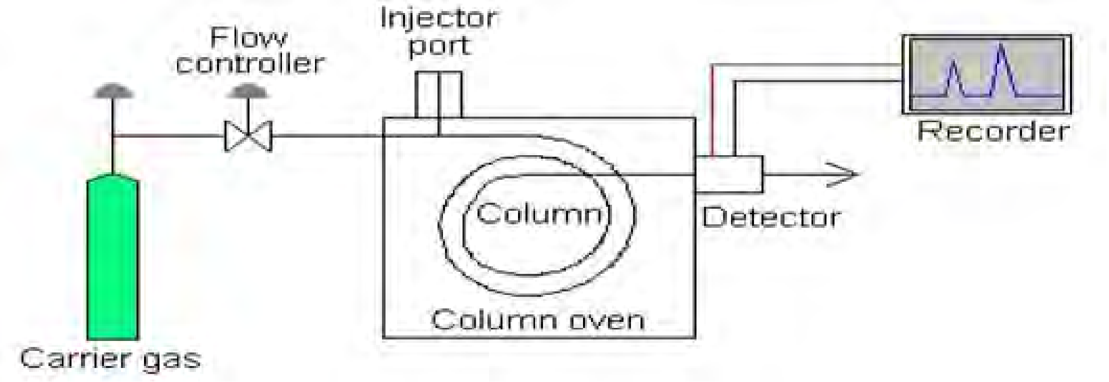


Figure 2.9 The diagram of gas chromatograph instrument (Dhanarasu, 2012).

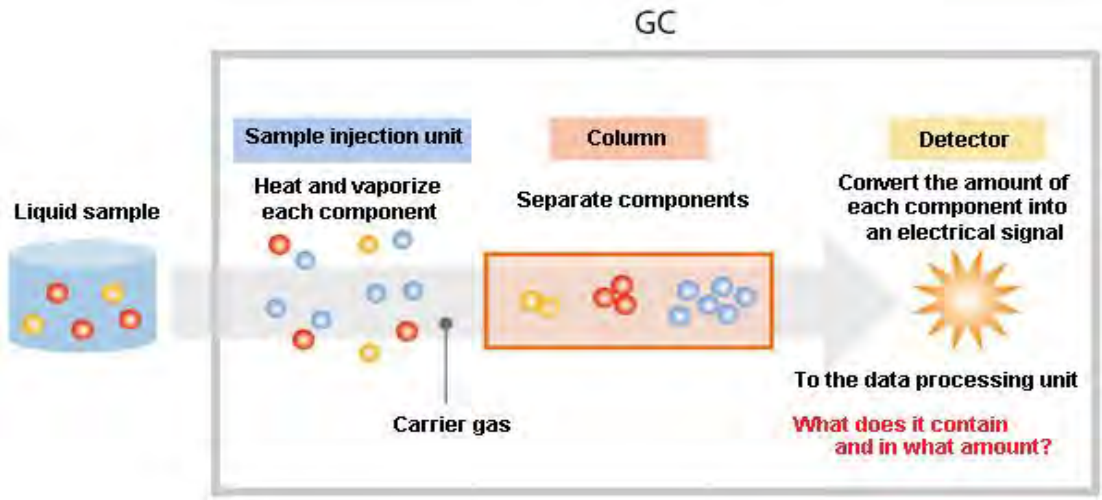


Figure 2.10 The diagram of gas chromatography process (Shimadzu, 2019).

In GC instrument, the column is a very important part of the system since the separation of various component occur in this area. In GC column, there consists of stationary phase and packed material which influence the separation of compound and affect the time of separation (retention time). Column can be classified into two types including packed column and capillary column. Normally, capillary column has a better resolution to give finely structured chromatography fingerprinting. The column is placed in an oven where the temperature will be controlled over a wide range of temperatures. The picture of packed column and capillary column of Gas chromatography (GC) are shown in Figures 2.11 and 2.12. For GC detector part, there have many detector types and the selected is depending on its application. Most of the detectors used in GC were usually invented for this technique. Mass spectrometry is one of the detectors of GC which become a popular now since it can analyze both quantitative and quantitative of unknown compounds in sample even if it has only micrograms of sample. When GC is combined with mass spectrometry, electron ionization (EI) or chemical ionization (CI) are ionized the compound the elute from GC column into charge fragment. Next, charge fragment will be forced to accelerate into a mass analyzer. The difference of mass to charge ratio will create a different signal. Therefore, the mass analyzer will be able to detect the compound that produces ions within the mass range. However, sometimes one-dimensional gas chromatography has a limitation on complex samples since coelute interference might obstruct the information in GC. Hence, comprehensive gas chromatography becomes a new technique for fingerprinting of oil since it has high resolution capacity and selectivity and can provide a resolution capability of coeluted biomarkers(Piantanida *et al.*, 2014, Bayona *et al.*, 2015).

Figure 2.11 Packed column of gas chromatography (GC) (Piantanida *et al.*, 2014).

Figure 2.12 Capillary column of gas chromatography (GC) (Piantanida *et al.*, 2014).

2.4.1.1 GC x GC-TOFMS

Nowadays, comprehensive two-dimensional gas chromatography (GC x GC) is useful in oil fingerprinting application. TOFs (time of flight) detection system have an ability of confirmation of fingerprinting and resolution of coeluted biomarkers. In addition, TOF-MS detector could complement to FID detection (Bayona *et al.*, 2015). The operating principle of GCxGC is shown in Figure 2.13. Sample are separated in two different columns with difference length and affinity such as one column is polar column and the another one is non-polar. The modulator is connected between 2 columns to collects the separated compounds from the first column and periodically sent them to the second column. This make the GCxGC have high peak capacity and great separation of coeluting compounds. For example, In Figure 2.13, peak A has one component whereas peak B has two component that can separate in the second column (Shields *et al.*, 2015).

Normally, the GC x GC column composes of two-dimensional column which the first column is non-polar and the second one is polar column. However, some research was studied the opposite sequence and can get a better result of non-polar component (Bayona *et al.*, 2015). Figure 2.14 shows the simple diagram of GCxGC-TOFMS instrument.

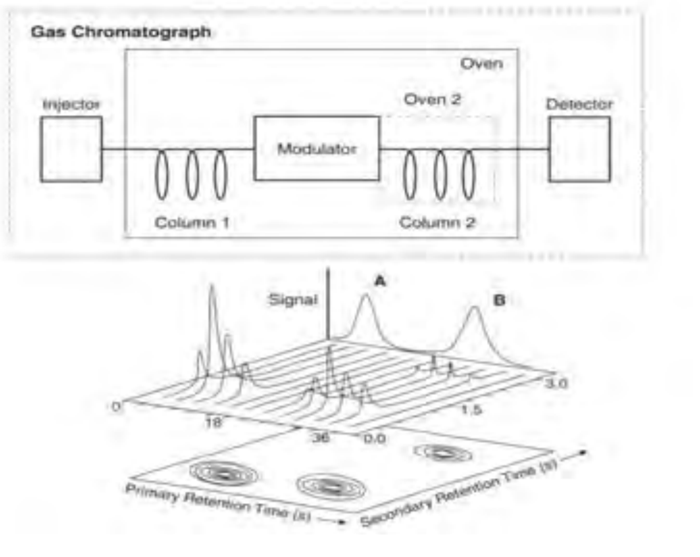


Figure 2.13 The operating principle of GCxGC (Shields *et al.*, 2015).

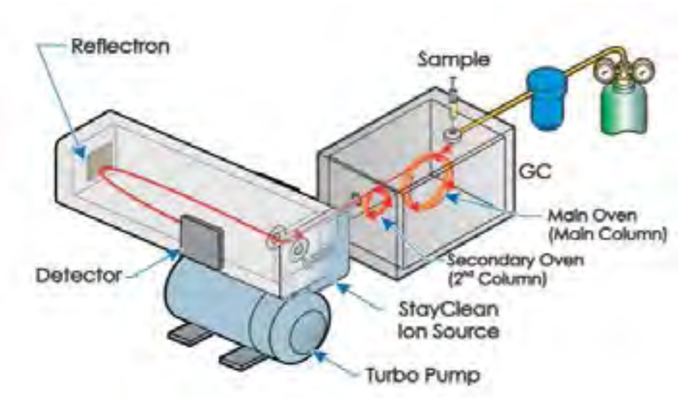


Figure 2.14 The diagram of GCxGC-TOFMS instrument (LECO, 2019).

2.4.1.2 GC-SCD

The gas chromatograph coupled with sulfur chemiluminescence detector (GC-SCD) is a popular technique to characterize sulfur compound in petroleum. The sulfur chemiluminescence detector (SCD) has equimolarity or equimolar response, great linearity, high precision, high sensitivity and selectivity and detection limit in the pg of Ss^{-1} range (Luong *et al.*, 2016).

Gas phase ozone induced chemiluminescence reactions are the basis for detection method of sulfur in analytical sample. The reaction of ozone and certain sulfur species will generate the chemiluminescence emission which might be sulfur monoxide or other gaseous molecule containing sulfur. However, this previous idea is only the principle and may not truly occur. In general, the sulfur component may not react with ozone or may not volatile enough to react with ozone at room temperature condition. Therefore, the chemiluminescence detection step should be preceded via a conversion step generally a high temperature pyrolytic reaction in order to achieve universal sulfur detection. This reaction will convert all of sulfur compounds in the sample to the common chemiluminescent species that can detect with ozone-induced chemiluminescence.

For SCD detection mechanism, the reaction in the dual plasma burner at approximately 800 ^{o}C under reduced pressure and in the presence of an appropriate catalyst such as alpha alumina in ceramic tube is shown in reaction (2.1).

$$Sulfur\ compounds\ \rightarrow SO + H_2O + other\ products \qquad (2.1)$$

And the reaction in ozone reactor with excess ozone under reduced pressure is show in reaction (2.2).

$$SO + O_3 \rightarrow SO_2^* \rightarrow SO_2 + O_2 + h\nu\ (300 - 400\ nm) \qquad (2.2)$$

The excited state of sulfur dioxide (SO_2^*) emit light and then the light produced by subsequence reaction is optically filtered and detected with a blue sensitive photomultiplier tube. The signal obtained is amplified for output of a chromatographic data system (Yan, 2006, Luong *et al.*, 2016). A simplified diagram of the GC-SCD detector is shown in Figure 2.15.

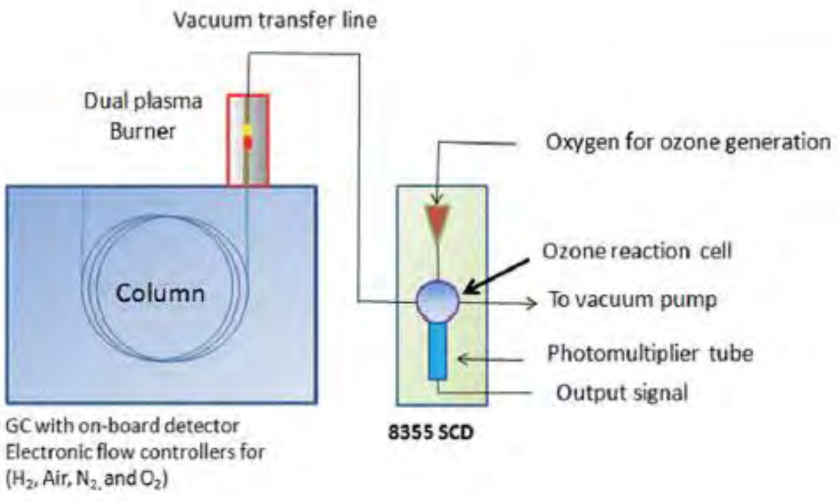


Figure 2.15 A simplified diagram GC-SCD detector (Luong *et al.*, 2016).

2.4.2 NORDTEST Methodology for Oil Spill Identification

The NORDTEST oil spill identification system has formed since 1991. This method is composed of three-step procedure. The first one is GC-FID screening of spill sample and suspect source. Next, GC-MS is used to fingerprint the spill and suspect source samples. After comparison the GC-MS result, the last step is analyzing the spill sample to the result of identify or non-identify (Hansen *et al.*, 2002).

This methodology has been continuously used for oil spill identification since 1991. Until April 2000, NORDTEST was starting the project called "Revision of the Nordtest Methodology for oil spill identification. The project collaborates many national laboratories including Finland, Denmark, Norway, Sweden, and USA. The main objectives of this NORDTEST project are improve the existing methodology into a technically more robust and legally and to adjust the NORDTEST methodology into a guideline for the European Committee for Standardization (CEN). The improvement of NORTEST methodology is on the same procedures which are GC-FID, GC-MS and analyzing the result. Figure 2.16 shows the protocol or the decision chart of NORDTEST methodology. The analysis of oil spill identification procedure is in the following step (Nordtest, 1991):

Level 1: GC-FID screening: After the sample preparation such as oil extraction, the result of this screening level can provide information including an overall boiling range of spill oiled, the total distribution of hydrocarbons (n-alkane) and weathering effect on oil spilled. At this level, the GC-FID can provide both quantitative and qualitative information. It can possible to be non-match when comparison between suspected source and spill source have a different distribution of n-alkane, isoprenoid or unresolved complex mixture (UCM). Therefore, it will consider moving to the next levels of analysis.

Level 2: GC-MS fingerprinting: This level will use gas chromatography with mass spectrometry operated in the selected ion monitoring mode (GC/MS-SIM) to analyzing spill sample and suspected source. This technique is beneficial for analyzing petroleum biomarker and polycyclic aromatic hydrocarbons (PAHs) in oil spill sample.

Level 3: Analyzing data and diagnostic ratio calculation: This level analyzes the result from Levels 1 and 2. The results are used to calculate the analytical standard deviation (RSD). Next, the result of diagnostic ratio that more robust (i.e., RSD > 95 %, precisely measured and weathering resistant) will be selected by "Student's t" stastical tool. After that, the result of spill sample and suspect source will plot in x-y plot with linear regressions. The conclusion will base on the fit between spill and source samples.

The overall conclusions will be classified into 4 results including Positive match, Probable match, Inconclusive and Non-match depending on degree of difference between spill and sample source within criteria.

Positive match: The chromatographic patterns of the spill and suspected sources are virtually identical and the only differences are caused by acceptable analytical variance or weathering.

Probable match: The chromatographic pattern of the spill and suspected sources are similar. The different may cause from weathering processes like loss of lower molecular weight peaks or wax redistribution and contamination.

Inconclusive: The chromatographic patterns of the spill and suspected source are quite similar except the difference that is impossible to ascertain. The different may cause from heterogeneities of the oil quality either within spill or suspected source.

Non-match: The chromatographic patterns of the spill and suspected source are unlike(Faksness *et al.*, 2002).

The conclusion above should go along with correlation plot analysis. For the correlation plot analysis, the result will triplicate analyzes to calculate the analytical relative standard deviation.

Observation's diagnostic could be calculated by equation (2.3)

$$Diagnostic\ ratio = \frac{100 \times A}{(A+B)} \qquad (2.3)$$

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

For biomarker with no corresponding standard, the value of A and B were (area of analyst/area of internal standard).

The accuracy of correlation analysis (equation 2.4) and calculation of diagnostic ratio depends on the measurement of triplicate analyses (preferably the spill sample). The result could be calculated as the relative variation at a 95 % confident interval or confident limit (CL) in triplicate sample using the “Student’s t” statistic tool.

Correlation analysis of diagnostic ratio (2.4)

$$\mu = x \pm \frac{t \times s}{\sqrt{N}} \qquad (2.4)$$

Where s is standard deviation between triplicate sample, N is the number of observations, x is mean value and t is the Student’s t from Table 2.3.

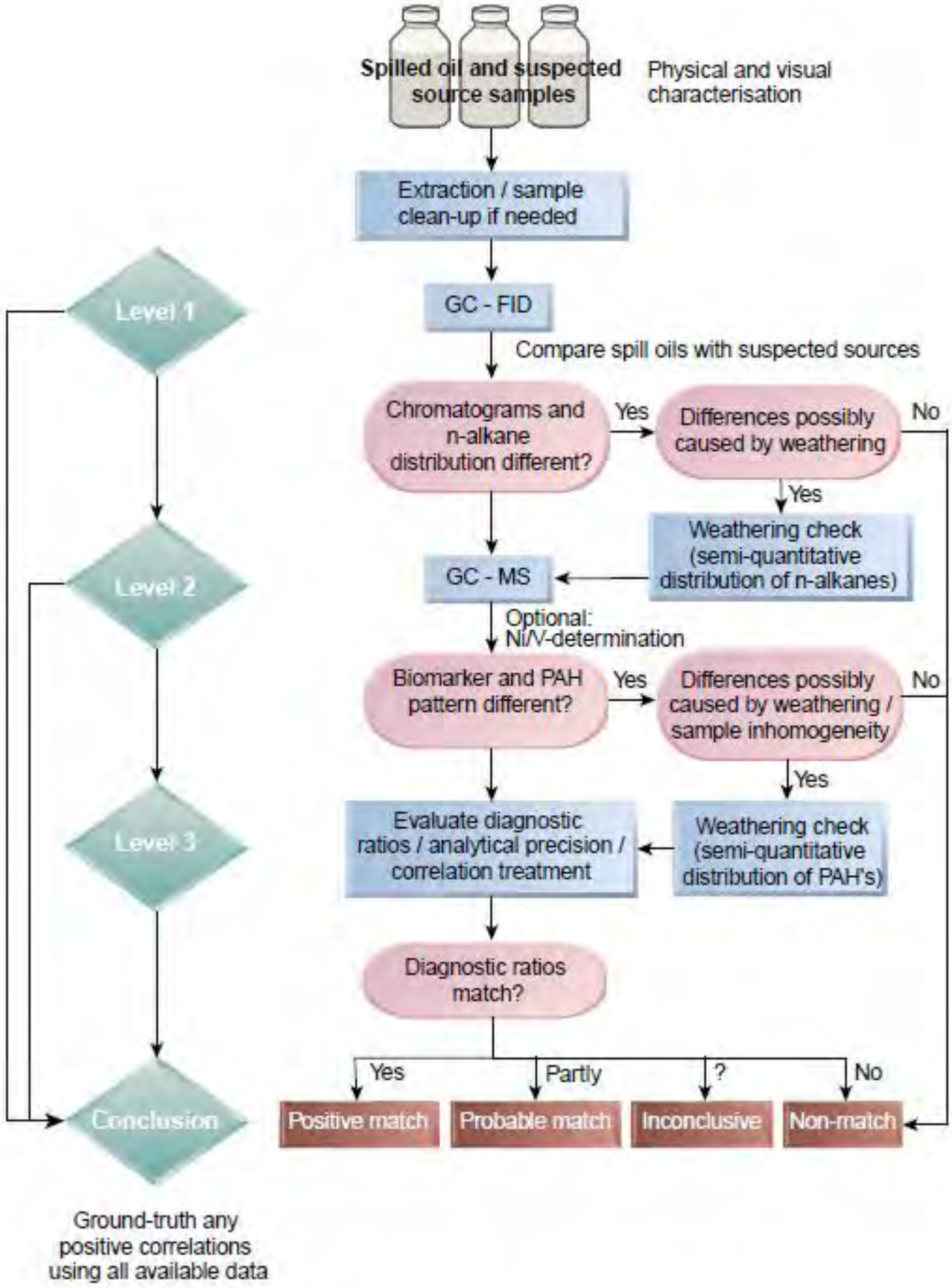


Figure 2.16 The protocol or decision chart of Nordtest methodology (Faksness *et al*., 2002).

Table 2.4 Value of student's t (Herris, 1995)

Degree of freedom	Confident level (%)		
	95	98	99
1	12.706	31.821	63.657
2	4.303	6.965	9.925
3	3.182	4.541	5.841
4	2.776	3.747	4.604
5	2.571	3.365	4.032
∞	1.960	2.236	2.576

For confident level, it recommends a definition of positive match at a 95 % confident interval. The example is from Round Robin study that is co-operation with twelve laboratories from ten countries in order to analyze oil spill and improve the methodology. These examples are shown in Figures 2.17 to 2.22. In addition, the recommended criteria for classification of spill sample based on the experiment from Round Robin test are shown in Table 2.4 (Faksness *et al.*, 2002, Faksness *et al.*, 2002).

Table 2.5 Recommended criteria for correlation studies of diagnostic ratios (Faksness et al., 2002)

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

DR = Diagnostic ratio

According to Round Robin study, the comparison result of the spill sample and suspected source are present in x-y plot with linear regressions and conclusion based on the "fit" between spill and source sample for the selected suite of the measured diagnostic ratios can be made.

The straight line (x=y) can be concluded perfect match when all DRs for the spill sample is the same as for the source oil. If the error bars of all diagnostic ratios are overlapping the linear line, the spill sample concludes positive match to the suspected source as shown in Figure 2.17 and 2.19. If some DRs is not overlapping the linear line, it can be concluded no-match as shown in Figure 2.18 and 2.20.

Figures 2.20, 2.22 and 2.22 show an example of the use of different confident level including 95%, 98%, and 99% respectively. It will able to see that some of the ratios are still outside the linear line, even if increase confident interval to 98% or 99% which have the same conclusion: no match.

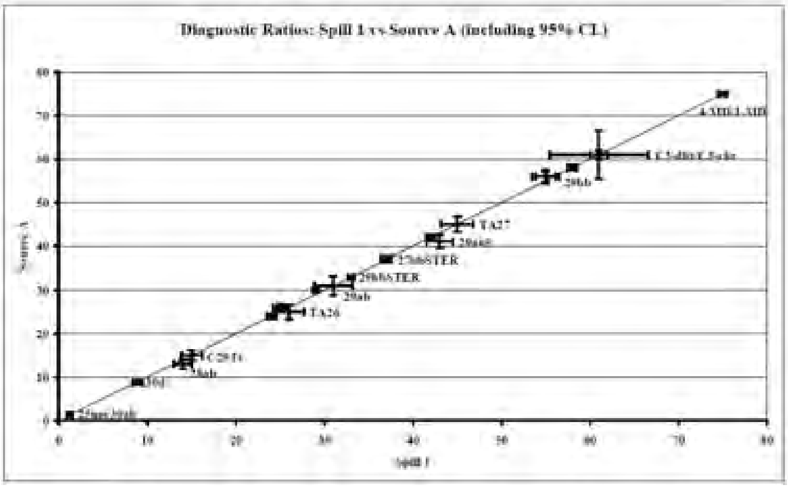


Figure 2.17 Correlation between spill 1 and source A, using a 95% confidence limit (positive match) (Faksness *et al.*, 2002).

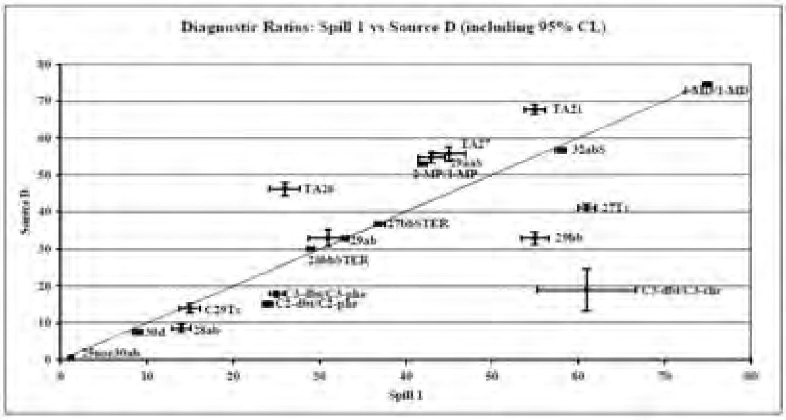


Figure 2.18 Correlation between spill 1 and Source D, using a 95% confidence limit (Non match) (Faksness *et al.*, 2002).

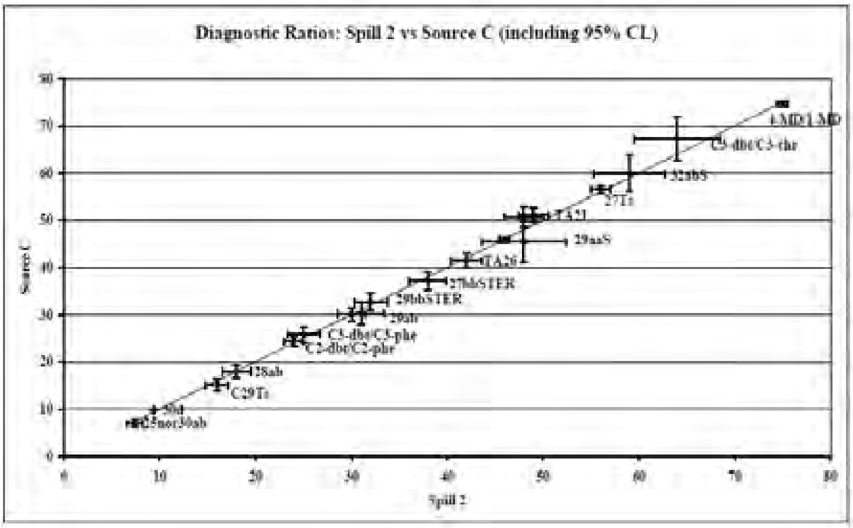


Figure 2.19 Correlation between spill 2 and source C, using a 95% confidence limit (Positive match) (Faksness *et al.*, 2002).

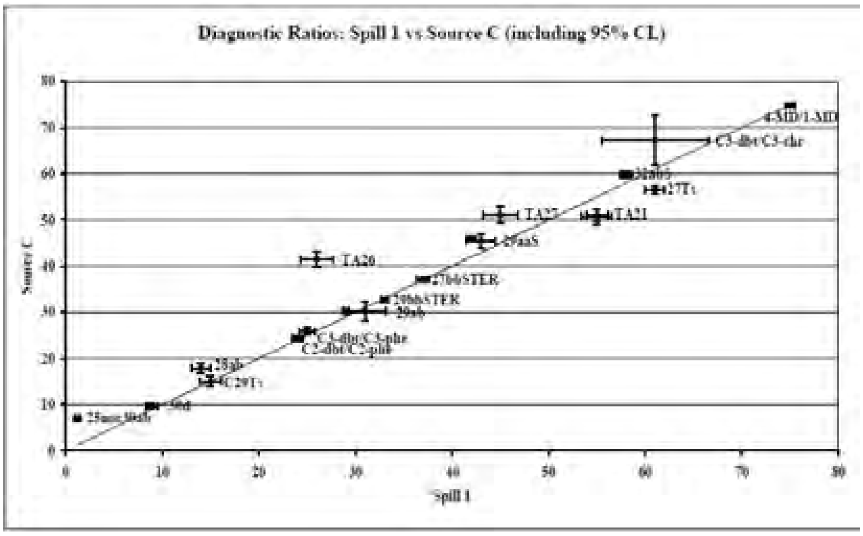


Figure 2.20 Correlation between spill 1 and source C, using a 95% confidence limit (Non match) (Faksness *et al.*, 2002).

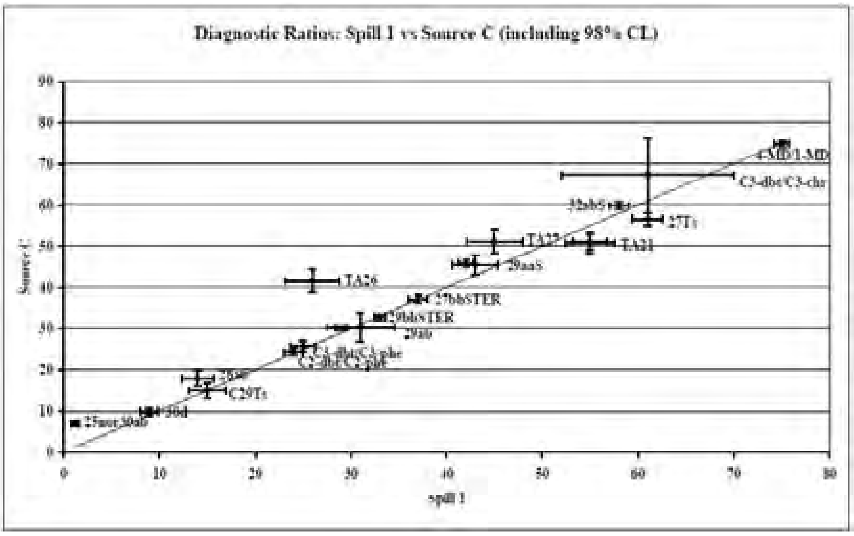


Figure 2.21 Correlation between spill 1 and source C, using a 98% confidence limit (Faksness *et al.*, 2002).

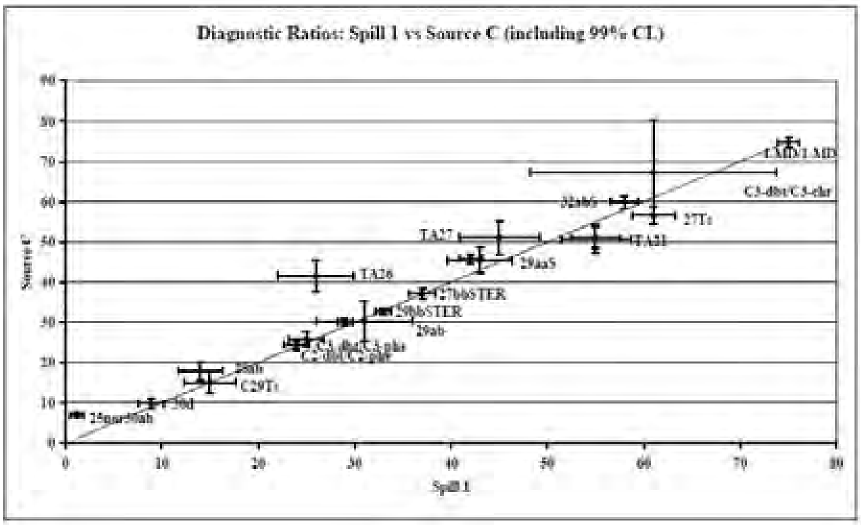


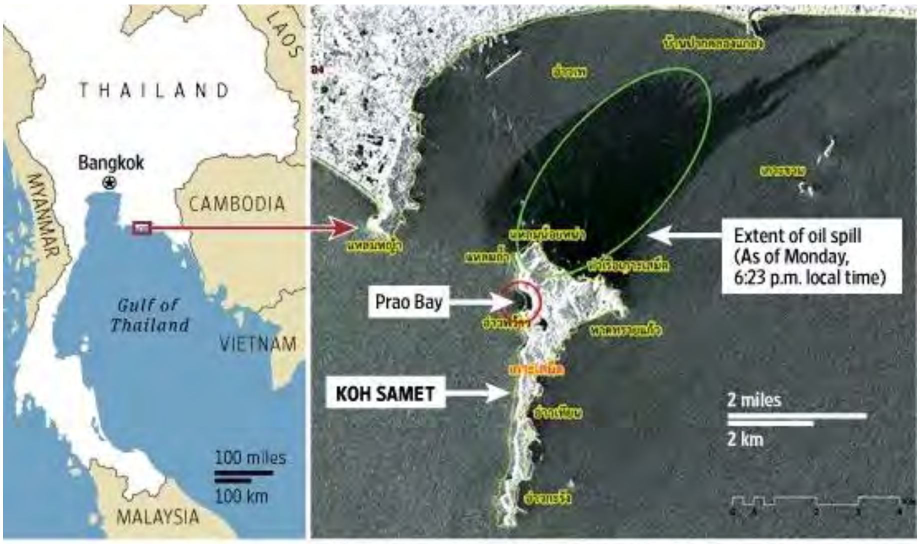
Figure 2.22 Correlation between spill 1 and source C, using 99% confidence limit (Faksness *et al.*, 2002).

2.4.3 Example of Oil Spill in Thailand

On July 27, 2013, there was an accident in the Gulf of Thailand that makes Rayong province confront with large oil spill problem. The accident caused by leakage of pipeline near Koh Samet owned by PTT Global Chemical Public Company Limited. At least 50,000 tonnes of crude oil were released into the sea and move from the north of Koh Samet island and cover the Ao Phrao and later other beaches. This oil spill incident has many serious impacts such as toxic to the coastal environment and no tourist coming to travel. Figure 2.23 shows the approximate of the oil spill incident in Rayong province (Maierbrugger, 2013).

Besides, on Oct 27, 2015, on Hua Hin beach in Prachuap Khiri Khan province fled with a large quantity of oil that coated garbage, leaves, wood and sea animal along several kilometers of sandy beach as shown in Figures 2.24 and 2.25. From the satellite map shows the oil spill will cover the 10 km stretch of coast of Hua Hin to Khao Takiab. The causes of this oil spill are still unknown, but the possible origin may from oil tanker or fishing boat (Fernquest, 2015).

In addition, there have been many oil spills in the sea and tarballs on the beach every year in Thailand, but no one can knows the origins



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

Figure 2.23 Approximate area of oil spill incident in Rayong (Maierbrugger, 2013).

Figure 2.24 Approximate area of oil spill in Hua Hin (Fernquest, 2015).

Figure 2.25 Oil coating on animal on Hua Hin beach (Fernquest, 2015).

CHAPTER 3
EXPERIMENTAL

This Chapter is divided into 2 main parts. The first one is Extraction and Analysis of Oils. The second one is Data Collection and Analysis.

PART 1 Extraction and Analysis of Oils

3.1 Material and Equipment

3.1.1 Source of Oil Samples

The oil samples that use in this research are list in Table 3.1. All crude oil samples are obtained from PTTGC. Two fuel oils (FOA, IFO380) and one diesel oil are obtained from PTT Oil and Retail Business Public Company Limited and NAVEE GROUP. All crude oil samples are generally used as a feedstock in Thailand petroleum refinery. The fuel oil and diesel oil samples are used as a marine fuel for ship in the sea.

Table 3.1 Information of seven crude oils, two fuel oils, and 1 diesel oil samples

No	Sample Name	Description
1	Murban Crude	Crude Oil, Middle East
2	Banang Crude	Crude Oil, Malaysia
3	Pattani Crude	Crude Oil, Thailand
4	Pazflor Crude	Crude Oil, Africa
5	Jasmine Crude	Crude Oil, Thailand
6	Alshaheen Crude	Crude Oil, Middle East
7	Upper Zakuum Crude	Crude Oil, Middle East
8	Fuel Oil 600	Fuel Oil type 1, Bunker Fuel A
9	Fuel oil 380 (IFO380)	Intermediate Fuel Oil
10	DieselB7	Diesel oil

3.1.2 Gas

The ultra-high purity (UHP) nitrogen for GC-TOFMS, and GC-SCD

The ultra-high purity (UHP) hydrogen for GC-SCD

The high purity (HP) helium for GC-TOFMS and GC-SCD

The zero grade air is used for FID and SCD detector

3.1.3 Chemicals

n-Hexane AR grade from RCI Labscan

Dichloromethane from Burdick Jackson

Silica gel from Merck, Germany

Sodium carbonate and sodium sulfate from Asia Pacific Specially Chemicals Limited, Australia.

17β (H), 21β (H)-hopane solution from Fluka

4,6-Dimethyldibenzothiophene from Sigma-Aldrich

3.1.4 Equipment

Agilent© 7890 comprehensive two-dimensional gas chromatography with a LECO Pegasus 4D time-of-flight mass spectrometry (GCxGC-TOFMS)

Agilent© 7890A with 355 sulfur chemiluminescence and dual plasma controller (GC-SCD)

Nylon syringe filter 0.45 μm and 0.2 μm

3.2 Methodology

3.2.1 Weathering Simulation

The weathering simulation experiment is simulated by placing 2 L of seawater from Phetchaburi province into a container with dimension of 4" width 4" long and 10" high. Next, 10 mL of oils were poured into the seawater. The containers were placed outdoor to get exposed to the sunlight for 60 days in order to simulate all weathering processes. In addition, all oil samples were collected at Day 0, Day 7, Day 30, Day 45, and Day 60 for analysis.

3.2.2 Extraction of Oil Samples

The extraction of oil samples method was performed following the method by Zhang *et al.* (2015) and Ho *et al.* (2015). In the first step, 0.20 – 0.25 g of oil sample was introduced into a 20 mL vial. Next, high purity *n*-hexane/dichloromethane (1:1, v/v) 10 mL was added to extract the oil. Then 0.5 g of anhydrous sodium carbonate was added to remove water. Next, the mixture in the vial was vortexed for 5 min and then the solutions were left to settle at room temperature for 4 h. The supernatant in vial was filtered through 0.45 µm nylon syringe to another vial and then 0.25 g of silica gel and 0.25 g of anhydrous sodium sulfate were added to remove water. After that, vial containing oil and silica gel was vortexed for 2 min and settled for 2 min. Finally, the samples were filtered through a 0.2 µm nylon syringe filter and transfered to a vial (Ho *et al.*, 2015, Zhang *et al.*, 2015).

3.2.3 Analysis of Oil Sample Using GC x GC -TOFMS

The extracted oil samples were analyzed by a LECO Pegasus 4D GC x GC- TOFMS using the following GC conditions:

Inlet:	Spitless
Detector	Time of flight mass spectrometry
Column:	First dimension (1D): 60 m long x 0.25 mm internal diameter, and 0.25 µm film thickness, capillary RTX-PAH column.
	Second dimension (2D): 1 m long x 0.25 mm internal diameter, and
0.25	µm film thickness, capillary RTX-1HT column.
Gas:	Helium 1 mL/min
Temperature:	Injection port 300 ^{o}C
	Transfer line 300 ^{o}C
	MS source 250 ^{o}C
Injection ratio:	10:1 split

The 1D oven conditions were isothermally at 40 ^{o}C for 1 min and increase the temperature to 340 ^{o}C with ramping rate at 2.5 ^{o}C/min, hold time 5 min.

The 2D oven conditions were the same with 1D except the temperature offset higher 5 °C from 1D.

Quantitative analysis: Selection ion monitoring mode (SIM)

3.2.4 Analysis of Oil Sample Using GC-SCD

The sulfurs in extracted oil sample were analyzed by an Agilent 7890A gas chromatograph coupled with sulfur chemiluminescence detector (GC-SCD) and dual plasma controller using the following conditions:

Inlet:	Spit	
Detector:	355 sulfur chemiluminescence detector and dual plasma controller	
Column:	30 m long x 0.320 mm internal diameter, and 0.25 μm film thickness, high resolution capillary HP-5 column	
Gas:	Helium	
	Hydrogen	50 mL/min
	Air zero	400 mL/min
	Nitrogen	5 mL/min
Temperature:	Injection port: 300 °C	

Injection ratio: 10:1 split

The oven conditions were initial temperature at 80 °C and then the ramped at 5 °C/min to 300 °C, hold time 5 min.

The straight run gas oil standard mixture was used as daily calibration.

3.2.5 Analysis of Sulfur Content in Pattani Crude Oil

According to the unavailable data of sulfur content in Pattani crude oil, the sulfur content of Pattani crude oil was determined by ASTM D2622 using an XOS Sindie model sulfur analyzer. Firstly, the sample was poured into a cup. Then, the sample was covered with Mylar film before analyzing. The test conditions were carried on at very low pressure and “Low (PPM) Range” mode. The sulfur content was calculated by the calibration curve.

Part 2 Data Collection and Analysis

3.3 Software

3.3.1 ChromaTOF Software

Data is acquired and processed using Leco ChromaTOF software. Both PAH 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 are calculated using equation (2.3),

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 is used to perform the calculation of diagnostic ratios using the statistical theory that concerns about the confidence interval relatives to the student’s constant value which depends on number of observations.

Microsoft Excel is also used to calculate the normalization of signal by SCD and perform the calculation of sulfur compound ratios.

CHAPTER 4

RESULT AND DISCUSSION

This Chapter shows experimental result of five crude oils including Murban, Al Shaheen, Upper Zakum, Pattani, Pazflor, two fuel oils (Fuel oil 600, IFO380), and one diesel oil from both fresh and after weathering process. The physical appearance of the oil samples before and after weathering was observed. The result shows physical appearance, distribution of hopanes group, and sulfur compounds by using GCxGC-TOFMS and GC-SCD. Furthermore, the sulfur compounds species identification is also discussed in this Chapter.

4.1 Weathering of Oils

The weathering of crude oils, fuel oils, and diesel oil in seawater was performed. The appearances of the oil samples were observed daily.

4.1.1 The Appearance of Oil in Seawater

4.1.1.1 Crude Oil

Figures 4.1 (a)-(e) show the physical appearance of crude oil during the weathering simulation. On Day 0, all crude oils spread over seawater instantly. The appearance of crude oil seems to be the same in all crude. After 7 days of oil spill, all crude oils spread over seawater and the amount of oil loss by the weathering process like evaporation which can be observed from fading of oil over the seawater especially in Murban crude. Moreover, due to the evaporation of seawater, the salt crystal on the oil and container wall was observed. In the middle phase and last phase of weathering (Days 30, 45, 60), The amount of all crude oils was significantly lost especially Murban crude and some part of oil stuck on container wall. In addition, all oils appeared to be more viscous since the light component in oil disappeared by the weathering processes. In the last day of weathering (Day 60), the appearance of Murban and Pattani crude are looked similar to tarball which is very viscous. In these periods, moss and algae were observed appear in all containers so the oil might have the effect of biodegradation process.

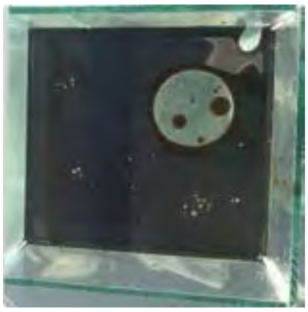
4.1.1.2 Fuel Oil

Figures 4.2 (a), (b) show the physical appearance of fuel oils during the weathering simulation. On Day 0, both fuel oils (Fuel oil 600, IFO380) have the same physical appearance which were not spread over the seawater instantly after oil spill unlike with crude oil. After 7 days of oil spill, all fuel oils (Fuel oil 600, IFO380) spread over and formed a brunch sheet on the seawater surface. In the middle phase and last phase of weathering (Days 30, 45, 60), both fuel oils have same physical appearance which look more viscous than weathered crude oil similar to tarball and can see some part of oil stuck on container. Due to the fuel oil comprised of high heavy components, the weathering processes might not significantly affect the fuel oil in last phase of weathering. Furthermore, as same with crude oil, in these phases, I can observe the moss and algae grew up so it will have the biodegradation effect.

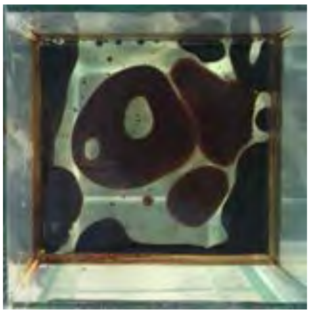
4.1.1.3 Diesel Oil

Figure 4.3 shows the physical appearance of diesel oil during the weathering simulation. On day 0, The physical appearance of DieselB7 (DB7) showed a clear color. However, the color of diesel oil changed to yellow after weathering. This happened since the diesel oil have the effect of weathering process such as photo-oxidation when exposed to the sunlight. The physical appearance was still the same until the last day of weathering (Day 60) which is spread over seawater, low viscous, and no tarball formed. Moreover, the amount of diesel oil was dramatically lost since the diesel oil does not contain heavy component so there was no sample for further analysis.

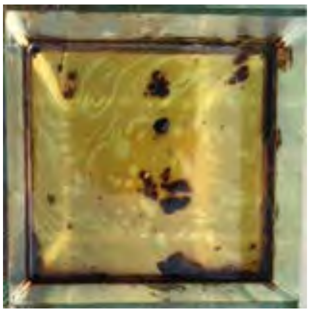
(a) Murban
Crude



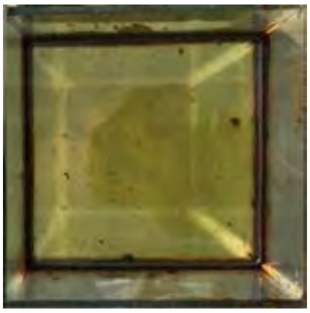
Day 0



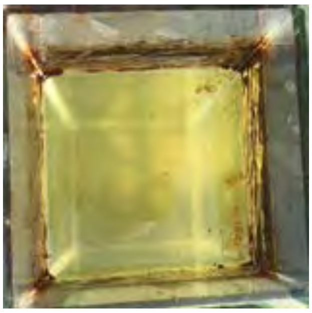
Day 7



Day 30



Day 45

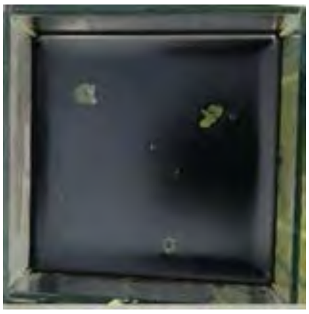


Day 60

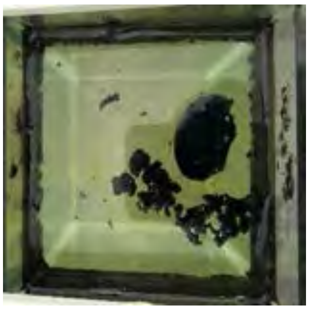
(b) Pattani
Crude

Day 0

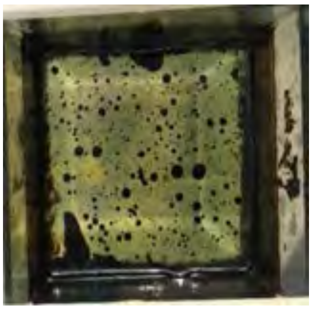
Day 7



Day 30



Day 45



Day 60

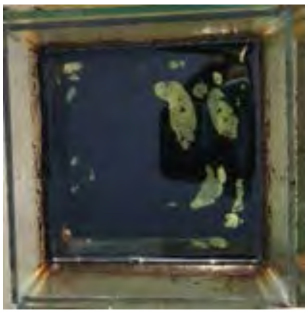
(c) Pazflor Crude

Day 0

Day 7

Day 30

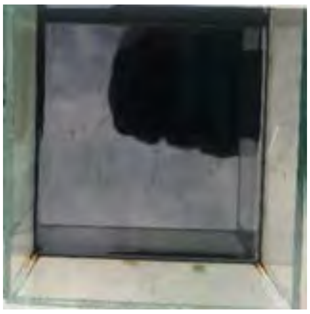
Day 45



Day 60

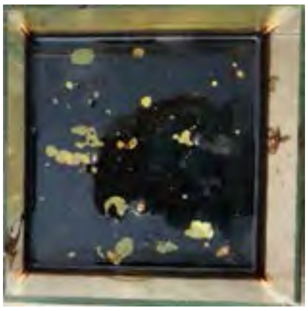
(d) Al Shaheen Crude

Day 0

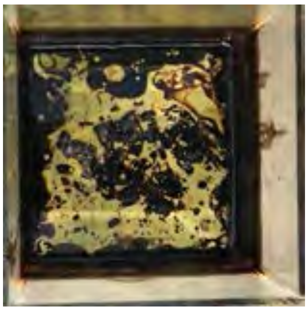


Day 7

Day 30

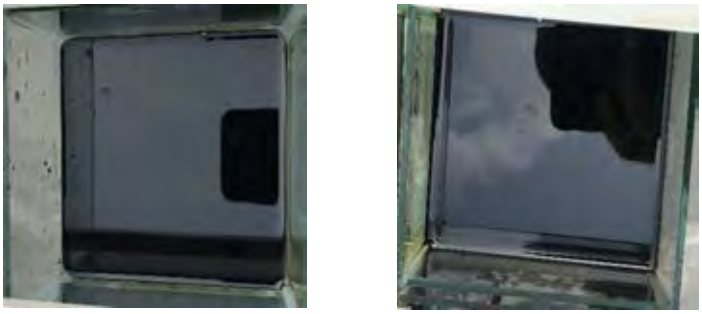


Day 45

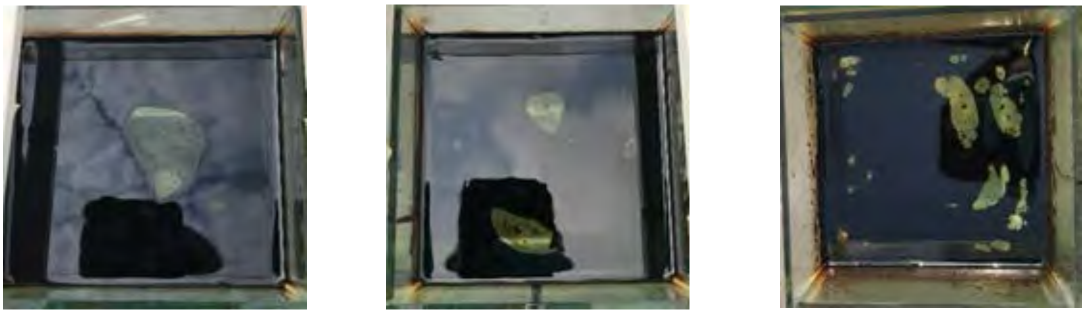


Day 60

(e) Upper Zakum Crude



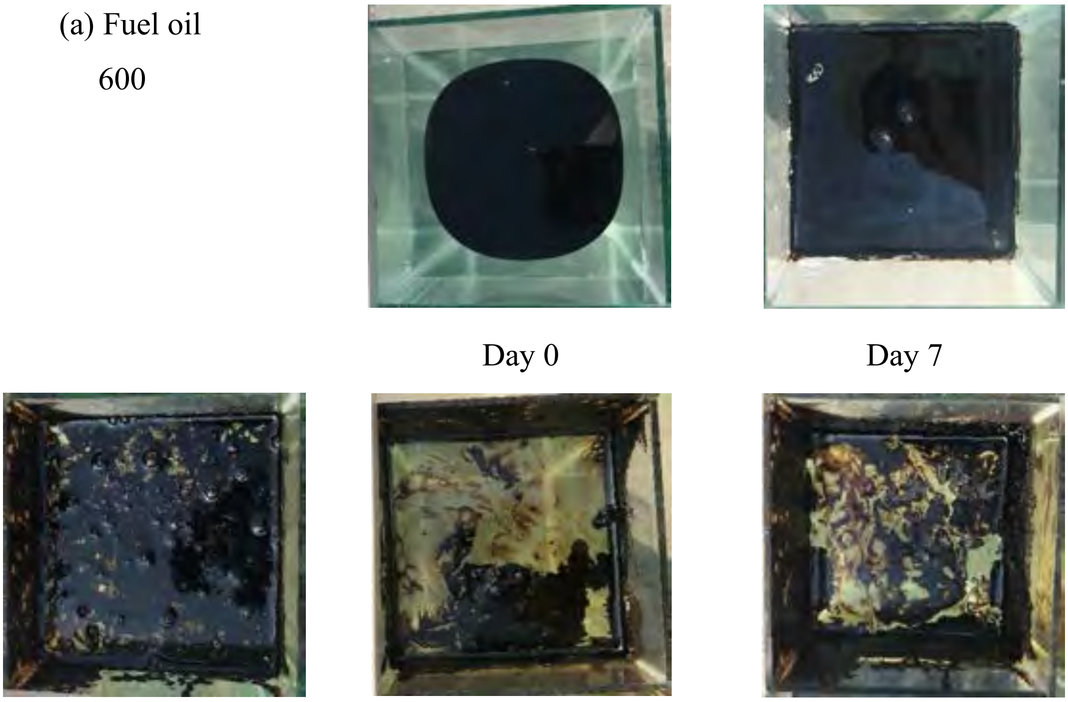
Day 0 Day 7



Day 30 Day 45 Day 60

Figure 4.1 Physical appearance of crude oil sample in seawater on Day 0, 7, 30, 45 and 60.

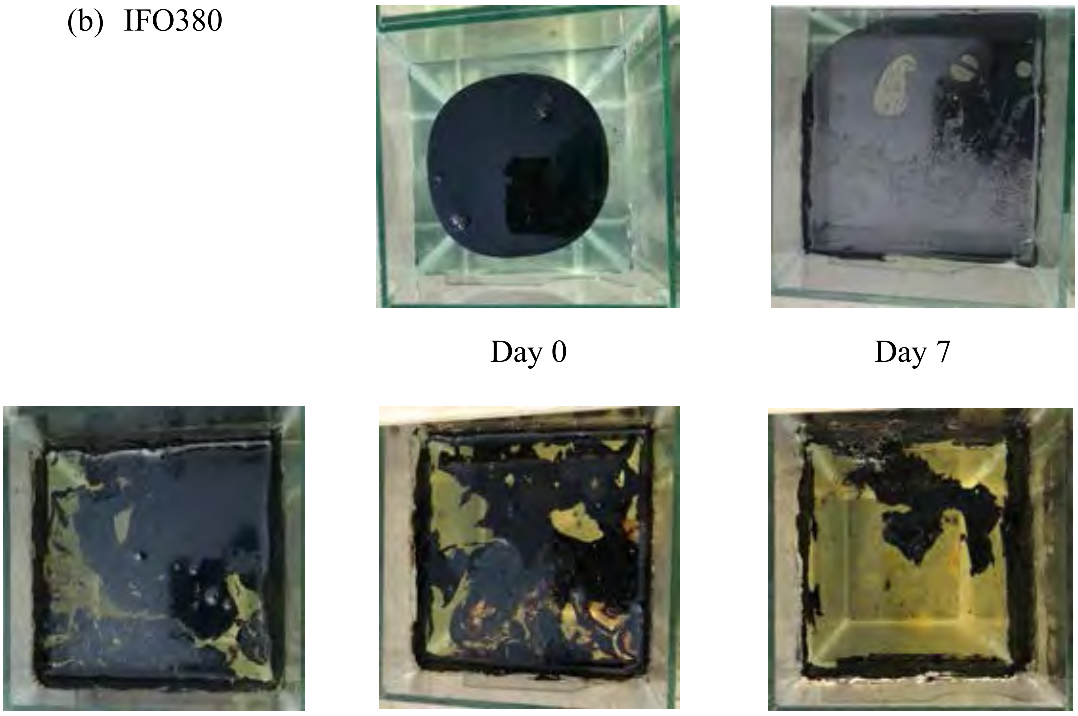
(a) Fuel oil
600



Day 0 Day 7

Day 30 Day 45 Day 60

(b) IFO380



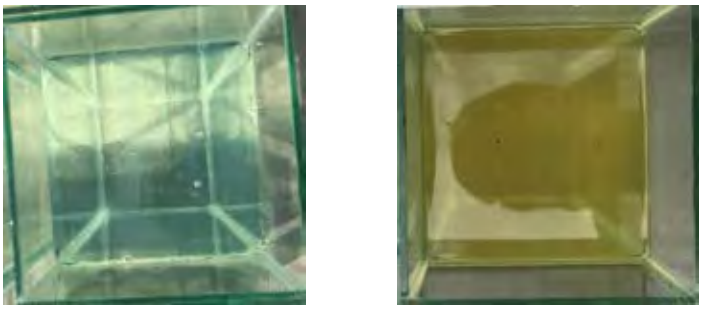
Day 0 Day 7

Day 30 Day 45 Day 60

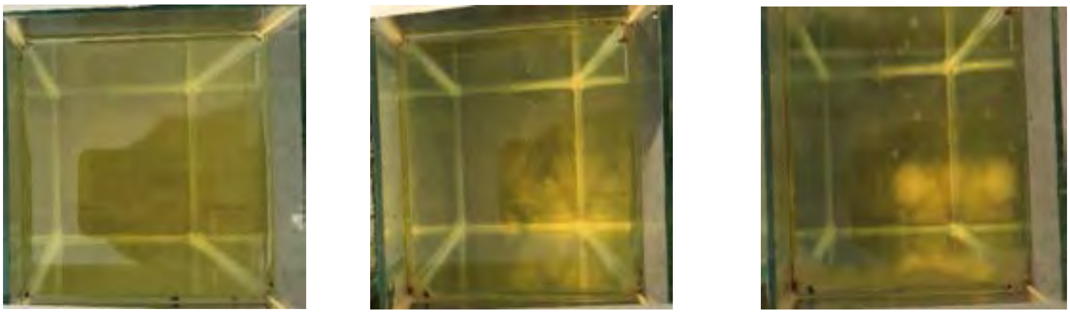
Figure 4.2 Physical appearance of fuel oil sample in seawater on Day 0, 7, 30, 45 and 60.

DieselB7

(DB7)



Day 0 Day 7



Day 30 Day 45 Day 60

Figure 4.3 Physical appearance of diesel oil sample in seawater on Day 0, 7, 30, 45 and 60.

4.2 Analysis of Biomarker

The analysis of hopanes group (m/z 191) in crude oils and fuel oils was investigated by GCxGC-TOFMS.

4.2.1 Standard Analysis

The 1 μL of internal standard (IS) was added to all oil samples before analyzing with GCxGC-TOFMS in order to confirm the retention time. Figure 4.4 shows the chromatogram of IS 17β(H), 21β(H) – hopane solution with selected ion mass 191 (m/z 191) which has the retention time appear at 6330 s.

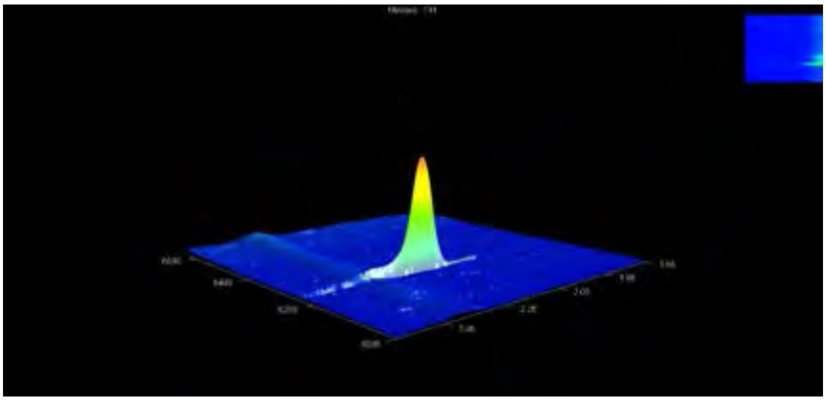


Figure 4.4 The surface chromatogram of IS 17β(H), 21β(H) – hopane solution.

4.2.2 General Total Ion Chromatograms of Oil Samples

Figure 4.5 shows the total ion chromatograms (TIC) of Murban crude oil sample. All oil samples were analyzed by GCxGC-TOFMS with reverse phase column and acquisition time delay 3000 sec to cut the peak of solvent. The chromatogram in Figure 4.5 shows the dividing of hydrocarbon in crude oil sample into n-alkane, cycloalkane, polycyclic aromatic hydrocarbon (PAHs), hopane groups, and other series. According to two-dimensional gas chromatograph (GCxGC) reverse phase column principle, the first dimension (column) is polar column which provides a high resolution for polar compound as shown in Figure 4.5. The second dimension (column) is short non-polar column which provides better resolution of co-eluting compounds of first dimensional column. Figure 4.6 shows the chromatogram of selected mass ion (m/z 191) of hopanes group in a) 1D chromatogram b) 2D chromatogram.

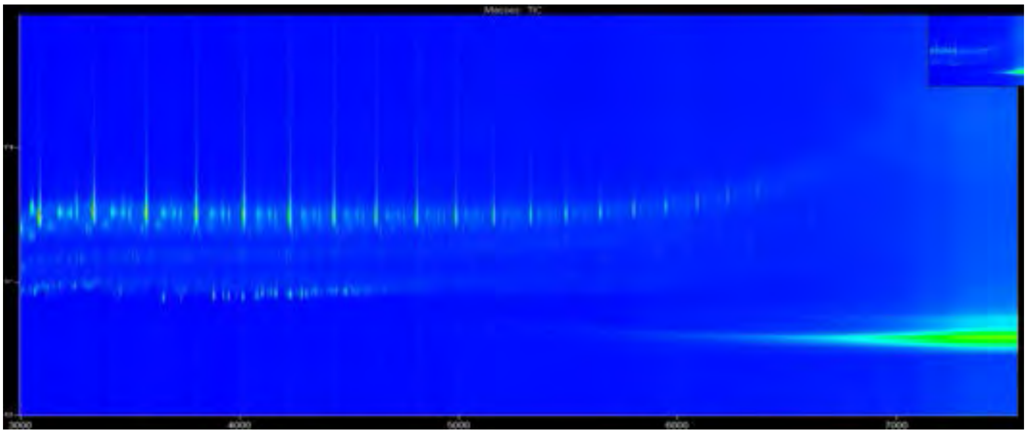


Figure 4.5 Total ion chromatogram (TIC) of Murban crude oil sample by GCxGC-TOFMS.

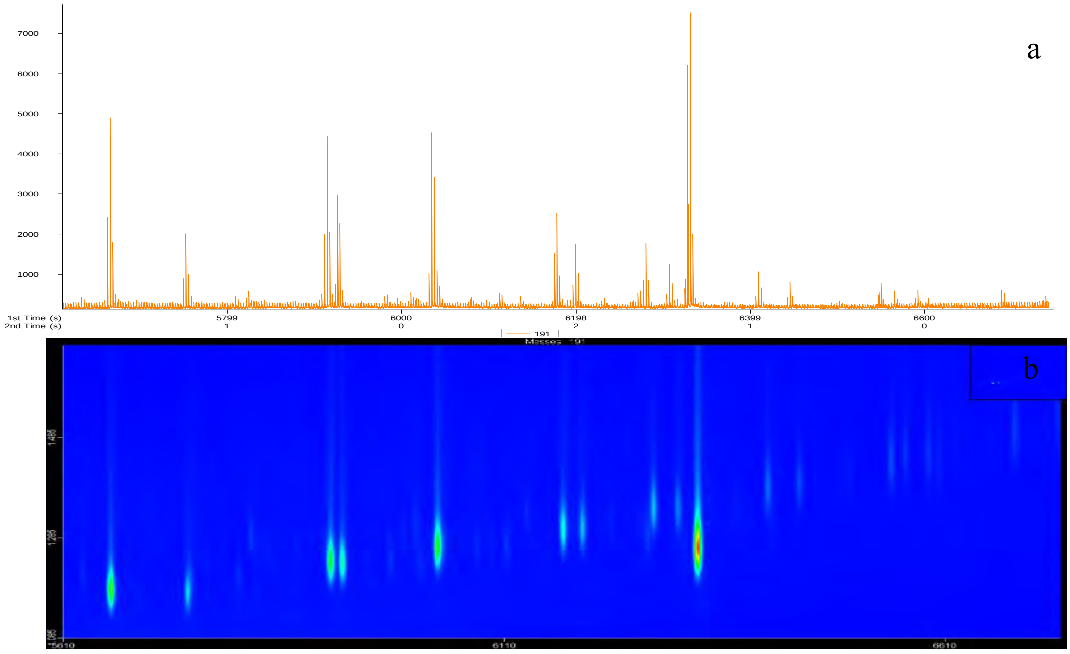


Figure 4.6 Selected ion chromatogram (m/z 191) of Murban crude oil a) 1D chromatogram b) 2D chromatogram.

4.2.3 The Hopanes Group Distribution by GCxGC-TOFMS

Figures 4.7, 4.8, and 4.9 show the hopanes group distribution of Murban crude, Pazflor crude, and IFO380 fuel oil before and after weathering for 30 days. The result from the selected mass ion 191 shows that the hopanes distributions had a similar pattern between fresh and weathered crude oil and fuel oil. This can conclude that the hopanes group can resist the weathering process. Thus, the hopanes group can be used to support the identification of oil samples.

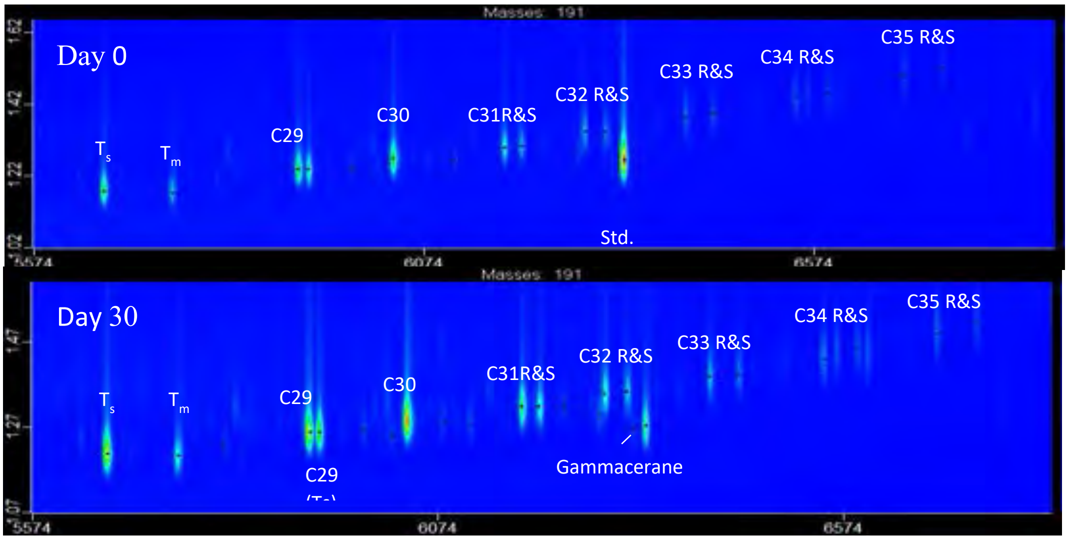


Figure 4.7 Selected ion chromatogram (m/z 191) of fresh and weathered Murban crude oils.

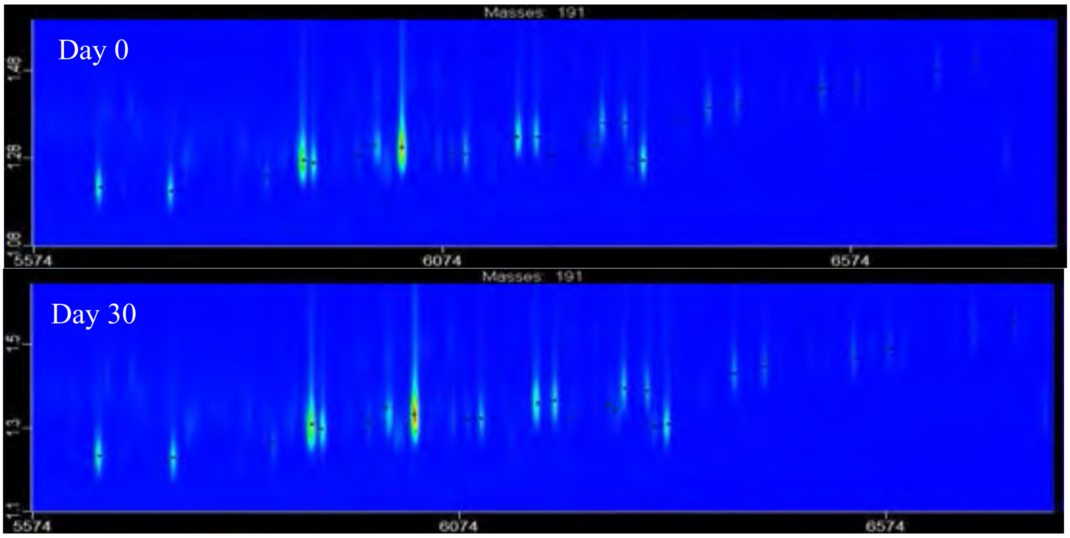


Figure 4.8 Selected ion chromatogram (m/z 191) of fresh and weathered Pazflor crude oils.

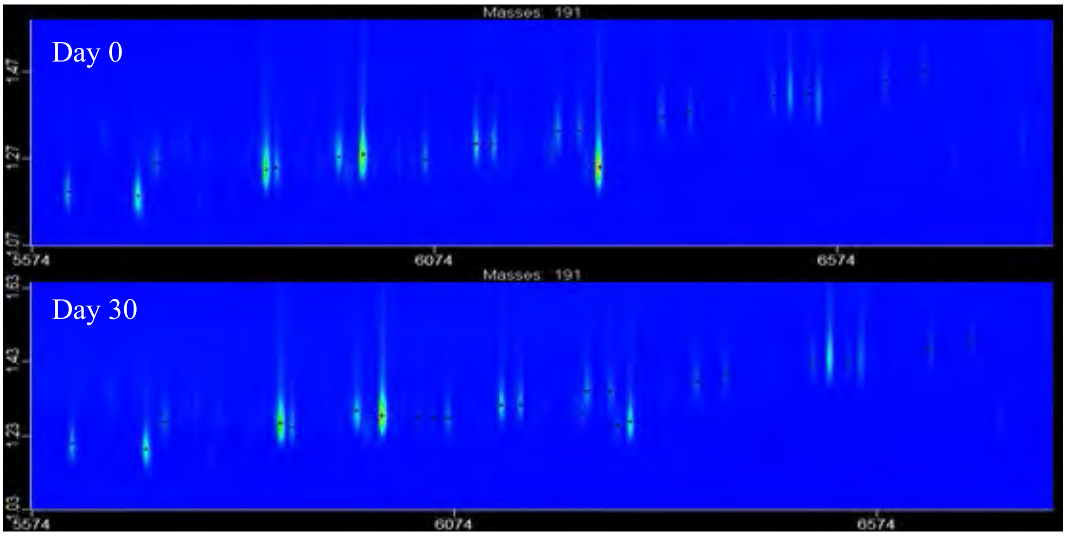


Figure 4.9 Selected ion chromatogram (m/z 191) of fresh and weathered IFO380 fuel oil.

Considering different crude oils, the crude oils that come from the same region seem to have a similar hopane distribution as compared to those from different regions. For example, the hopane distributions of Murban and Al Shaheen crude which both come from Middle East had similar hopane groups distribution as compared to those of Murban and Pazflor crude which come from different regions as shown in Figures 4.10 and 4.11 respectively.

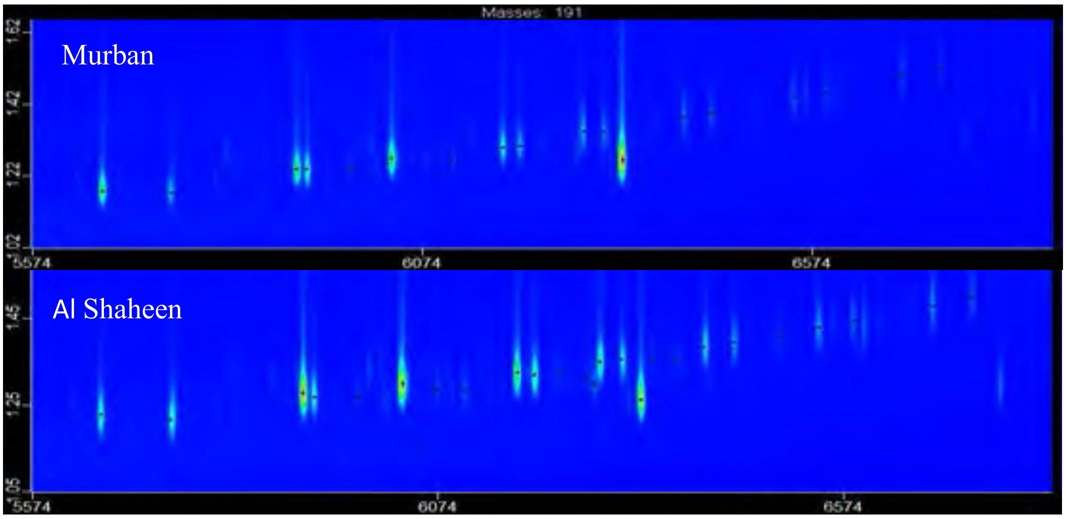


Figure 4.10 Selected ion chromatogram (m/z 191) of Murban and Al Shaheen crude oil.

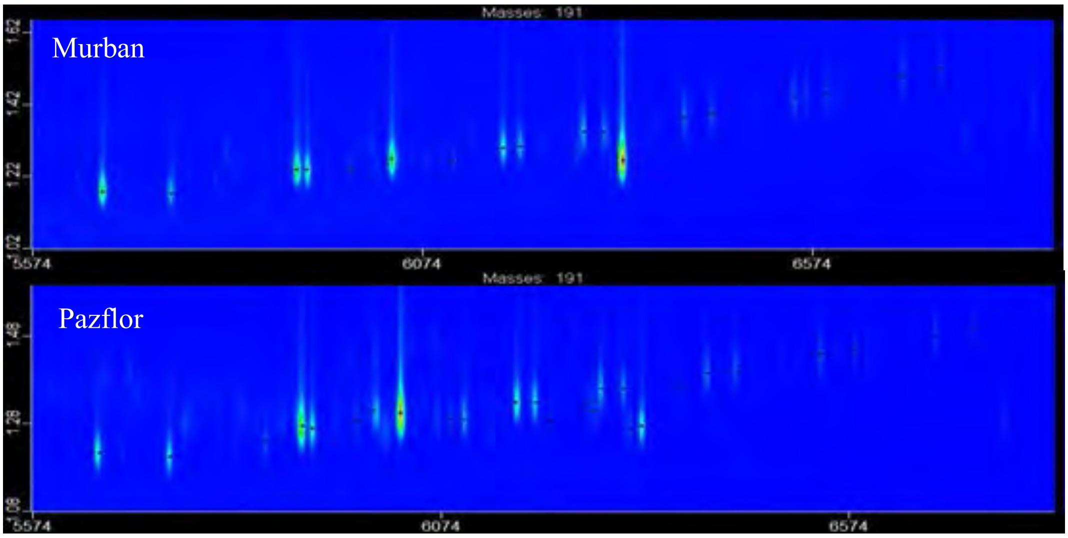


Figure 4.11 Selected ion chromatogram (m/z 191) of Murban and Al Shaheen crude oil.

Figure 4.12 shows the hopanes distribution of Murban crude oil and IFO380 fuel oil. The result shows different patterns between crude oil and fuel oil. However, when compared between Fuel oil 600 and IFO380, the hopanes distribution showed a similar pattern. Thus, in order to confirm the potential match of the two different oil samples, the diagnostic biomarker ratios are calculated to create the correlation plot that will be discussed in the next topic.

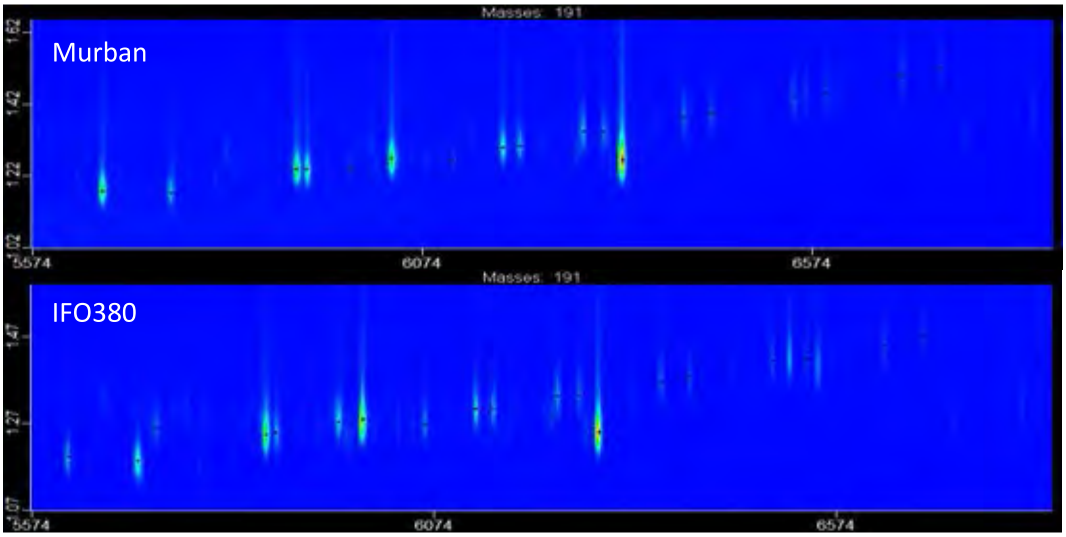


Figure 4.12 Selected ion chromatogram (m/z 191) of Murban crude and IFO380 fuel oil.

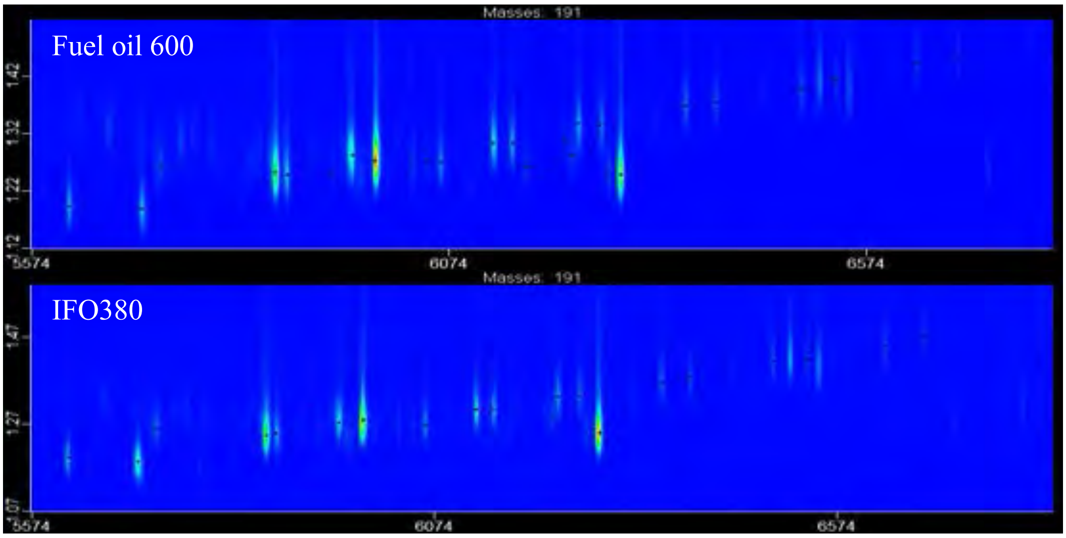


Figure 4.13 Selected ion chromatogram (m/z 191) of Fuel oil 600 and IFO380 fuel oil.

4.2.4 Identification of Oil Sample by Using Diagnostic Ratios

The plot of diagnostic ratios of biomarkers is a technique widely used for oil correlation, oil spill studies, and environmental forensics. The benefit of this technique is minimization of the concentration effect when comparing diagnostic ratios of spilled oil and suspected source. Moreover, the use of diagnostic ratio tends to introduce a self-normalizing effect. Diagnostic ratio can calculate both quantitative (i.e., compound concentration) and semiquantitative data (i.e., peak areas or heights) (Wang *et al.*, 2016). The selection of biomarkers and accuracy of instrument will indicate the reliability of diagnostic ratios. In this research study, the diagnostic ratios were calculated from (area of biomarker1)/ (area of biomarker1+ area of biomarker2).

After the selected mass ion 191 chromatogram (hopanes group) was obtained from GCxGC-TOFMS, the diagnostic ratios of hopanes group are calculated from the area of hopanes group. The diagnostic ratios result of biomarkers in crude oils and fuel oils are summarized in Tables 4.1 and 4.2 respectively.

Table 4.1 Diagnostic ratio of fresh and weathered crude oil samples

Name of Biomarker	Murban		Al Shaheen		Upper Zakum		Pattani		Pazflor	
	D0	**D30**	**D0**	**D30**	**D0**	**D30**	**D0**	**D30**	**D0**	**D30**
Ts	46.9	45.8	28.9	28.9	30.0	29.3	33.0	34.2	22.4	22.4
Tm	30.0	27.6	29.9	30.7	28.3	28.8	15.4	17.1	17.1	19.0
C29H	47.6	47.7	48.6	47.7	50.1	49.3	46.1	47.5	41.2	41.3
C29H(TS)	38.8	37.7	24.9	26.5	25.5	25.4	29.3	30.7	22.9	22.9
C29M	5.0	7.4	6.0	5.9	4.7	5.8	12.9	10.6	5.5	3.7
C28norhopane	0.0	2.9	5.4	11.2	0.0	3.9	6.3	19.7	13.0	18.8
C30H	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
C31HS	8.2	9.7	7.7	7.5	2.9	8.9	3.5	14.0	15.5	15.4
C31HR	35.8	34.6	37.2	37.9	34.4	33.8	18.7	20.8	25.1	25.2
C31M	26.0	27.4	32.7	30.8	26.3	27.1	14.6	16.3	19.6	18.9
C32HS	11.9	10.0	9.5	15.9	12.4	11.4	6.0	7.2	6.4	7.4
C32HR	27.6	28.3	30.8	30.7	25.4	25.0	13.5	14.8	15.2	16.2
Gammacerane	25.3	23.7	25.1	25.4	20.7	23.6	12.2	14.5	14.8	15.2
C33HS	0.0	5.4	0.0	3.3	1.7	0.0	7.8	9.3	5.3	5.2
C33HR	20.8	20.4	22.1	23.5	18.0	18.6	7.8	7.6	11.6	12.0
C34abs	13.9	13.6	18.0	16.0	13.3	13.4	5.9	6.5	8.7	8.2
C34abr	17.1	15.0	18.4	17.6	14.5	14.7	4.5	5.7	6.7	7.0
C35abs	10.3	10.4	13.0	12.0	10.1	9.6	2.8	3.8	4.2	4.4
C35abr	12.4	12.3	17.4	15.5	13.4	13.3	1.8	2.0	4.4	4.3

Table 4.2 Diagnostic ratio of fresh and weathered fuel oil samples

Name of Biomarker	**Fuel oil 600**		**IFO380**	
	D0	**D30**	**D0**	**D30**
Ts	15.1	-	18.5	18.3
Tm	19.0	-	33.9	31.5
C29H	39.9	-	44.0	45.9
C29H(TS)	21.3	-	21.2	18.0
C29M	5.6	-	0.0	1.4
C28norhopane	37.7	-	30.6	28.9
C30H	50.0	-	50.0	50.0
C31HS	17.4	-	16.6	13.8
C31HR	22.2	-	23.7	23.9
C31M	17.0	-	18.5	18.4
C32HS	7.8	-	6.6	7.5
C32HR	15.8	-	18.0	20.1
Gammacerane	15.7	-	17.8	17.5
C33HS	6.4	-	0.0	4.4
C33HR	10.6	-	13.4	13.0
C34abs	8.5	-	9.2	10.7
C34abr	8.3	-	10.8	11.4
C35abs	5.6	-	4.1	7.8
C35abr	5.2	-	8.7	8.8

The diagnostic ratios from Tables 4.1 and 4.2 were selected and then used to create the correlation plot.

Figures 4.14 and 4.15 show the correlation plot of crude oil before and after weathering process for 30 days. The results show that all crude oil has a positive match result which can indicate the strong anti-weathering of hopanes group in oil. The results are in line with what reported earlier by Misselwitz *et al.* (2013), Wang *et al.* (2016) and Thongkorn (2018).

When compared the fuel oil samples before and after weathering process for 30 days, the correlation plot result exhibited that some of diagnostic biomarker ratios were not overlapped with the linear line x = y at the 95% confidence interval as shown in Figure 4.16. However, when the confidence interval was changed to 98%. All biomarkers are overlapped with the linear. Hence, the result can be concluded to be a “possible match” as shown in Figure 4.17.

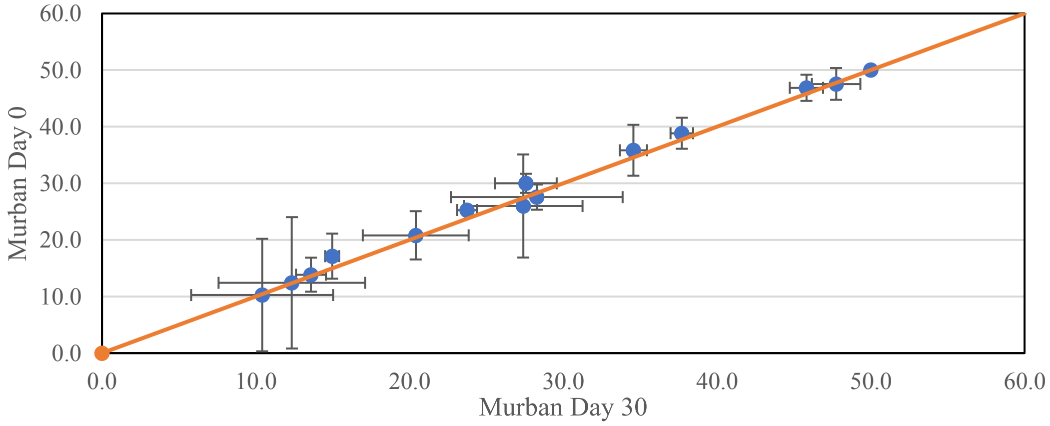


Figure 4.14 The correlation plot at 95% confidence interval of Murban crude Day 0 and Day 30.

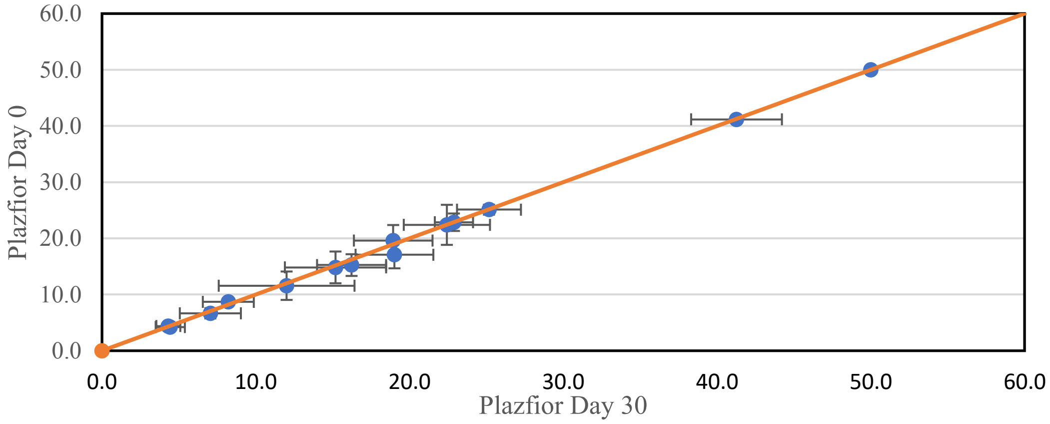


Figure 4.15 The correlation plot at 95% confidence interval of Pazflor crude Day 0 and Day 30.

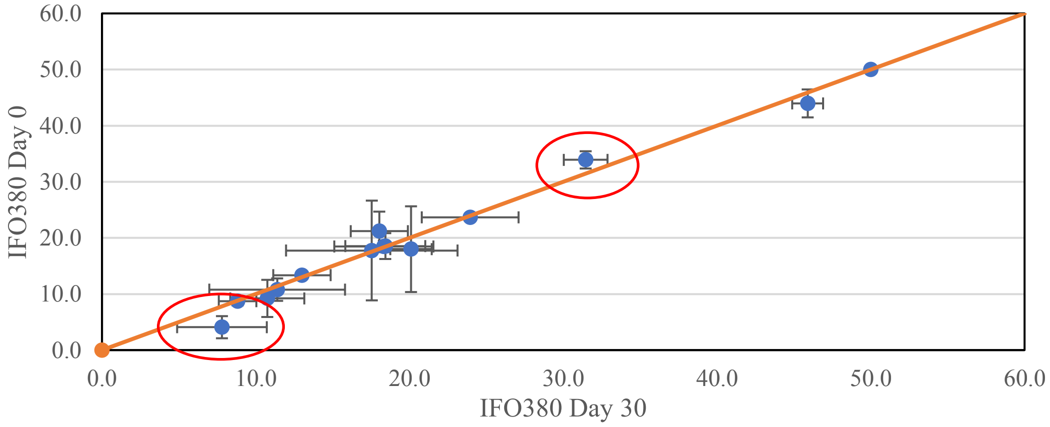


Figure 4.16 The correlation plot at 95% confidence interval of IFO380 fuel oil Day 0 and Day 30.

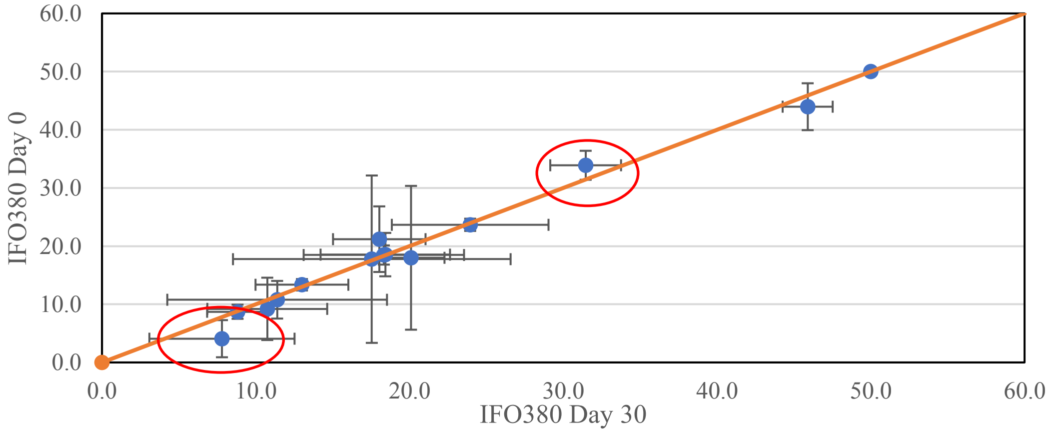


Figure 4.17 The correlation plot at 98% confidence interval of IFO380 fuel oil Day 0 and Day 30.

Figure 4.18 shows the correlation plot of Murban crude Day 0 and Al Shaheen crude Day 30 which both come from the Middle East. The correlation plot can observe some diagnostic biomarker ratios were not overlapped the linear line x=y. Thus, the result was “non match”. When comparing Murban crude Day 0 and Pazflor crude Day 30 which come from the different regions, the correlation plot can exhibited that almost all diagnostic biomarker ratios were not overlapped the linear line. The result was “non match”. In conclusion, the hopanes group can be used to differentiate different crude oils. Furthermore, crude oils which come from the same region seem to have a similar hopanes group as compared to those from different regions.

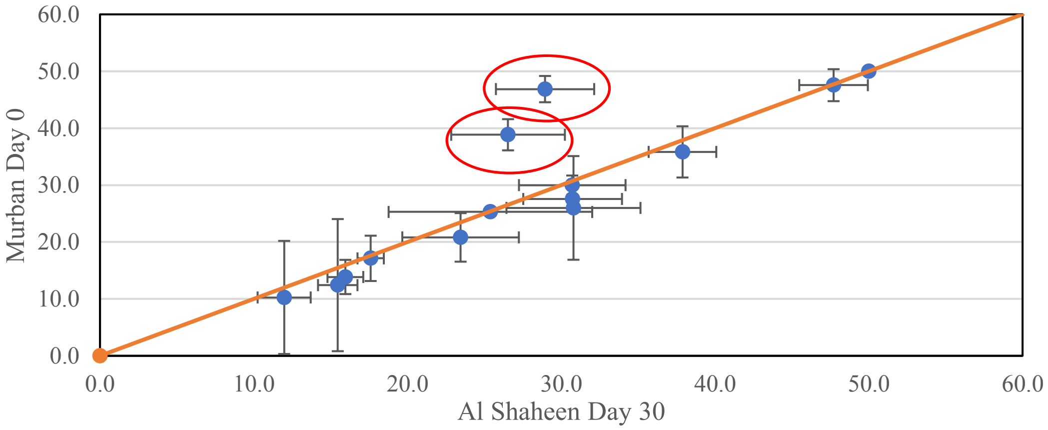


Figure 4.18 The correlation plot at 95% confidence interval of Murban crude Day 0 and Al Shaheen crude Day 30.

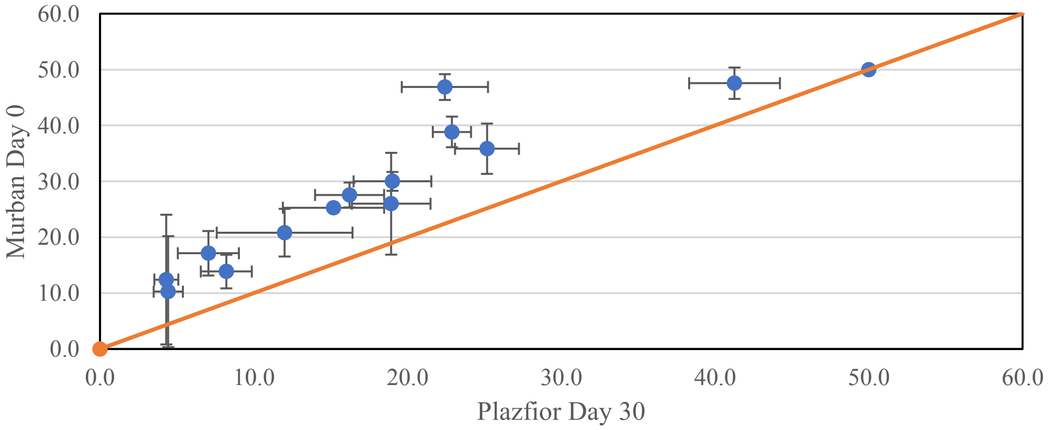


Figure 4.19 The correlation plot at 95% confidence interval of Murban crude Day 0 and Al Shaheen crude Day 30.

Figures 4.20 and 4.21 show the correlation plot of Murban crude and IFO380 fuel oil and Pazflor crude and IFO380 fuel oil respectively. The correlation plot showed “non match” result. When comparing the Fuel oil 600 and IFO380 fuel oil, the correlation plot exhibited that some diagnostic biomarker ratios were not overlapped the linear line x=y as shown in Figure 4.22. Thus, the result showed the “non match”. However, the Fuel oil 600 and IFO380 had a similar hopanes distribution and diagnostic biomarker ratios. It is possible that the two fuel oils might come from the process that utilize crude oils from the same regions. In conclusion, the hopanes group can be used to differentiate the crude oil and fuel oil samples. Furthermore, the hopanes group can also distinguish the different fuel oil samples.

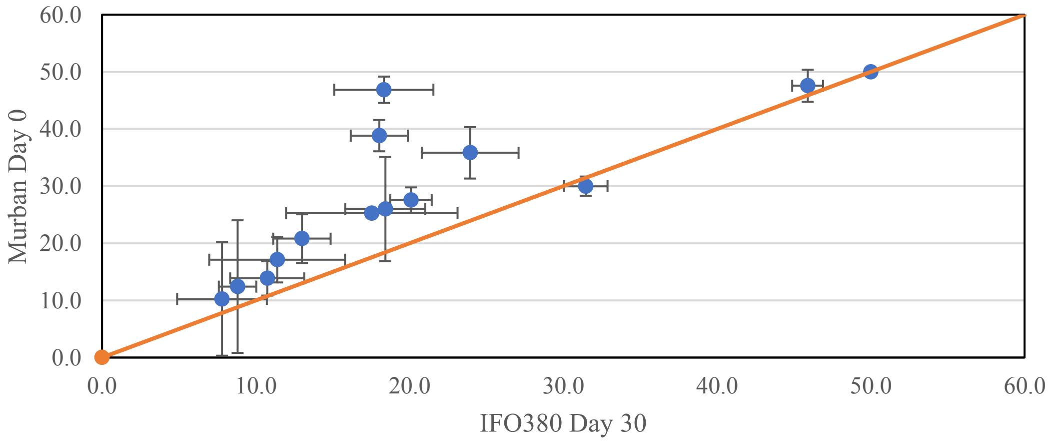


Figure 4.20 The correlation plot at 95% confidence interval of Murban crude Day 0 and IFO380 fuel oil Day 30.

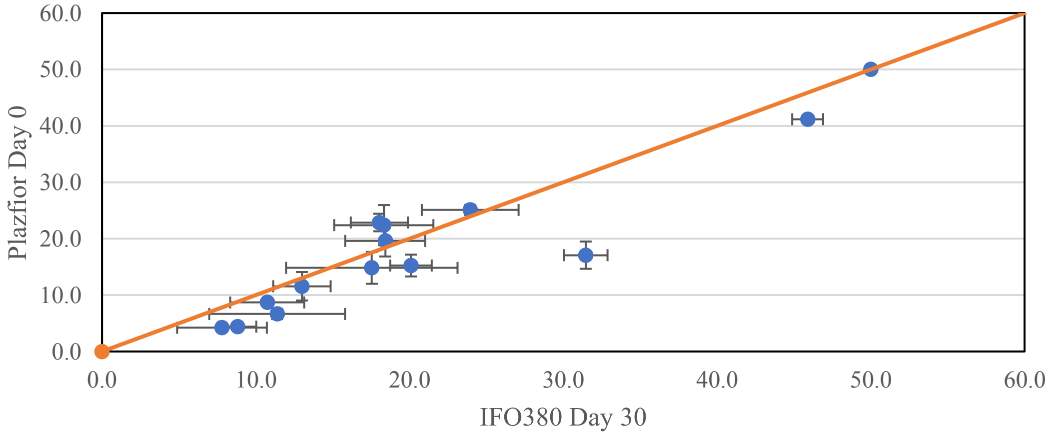


Figure 4.21 The correlation plot at 95% confidence interval of Pazflor crude Day 0 and IFO380 fuel oil Day 30.

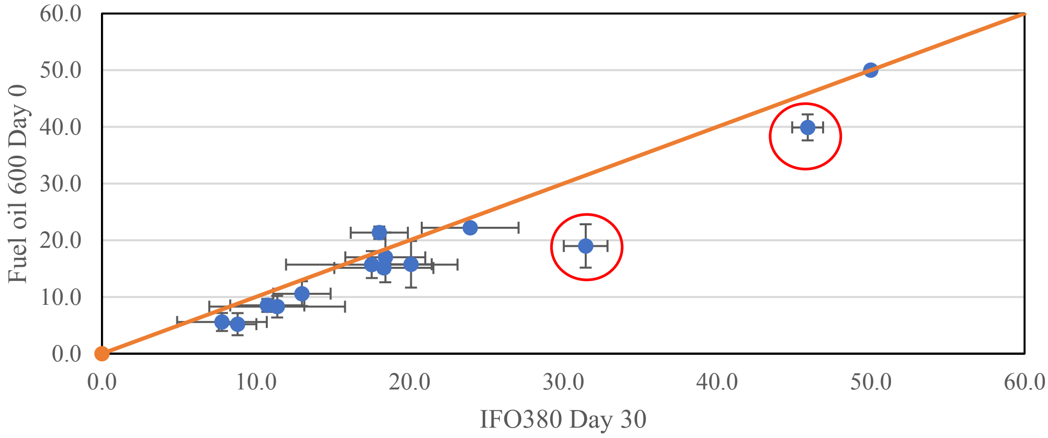


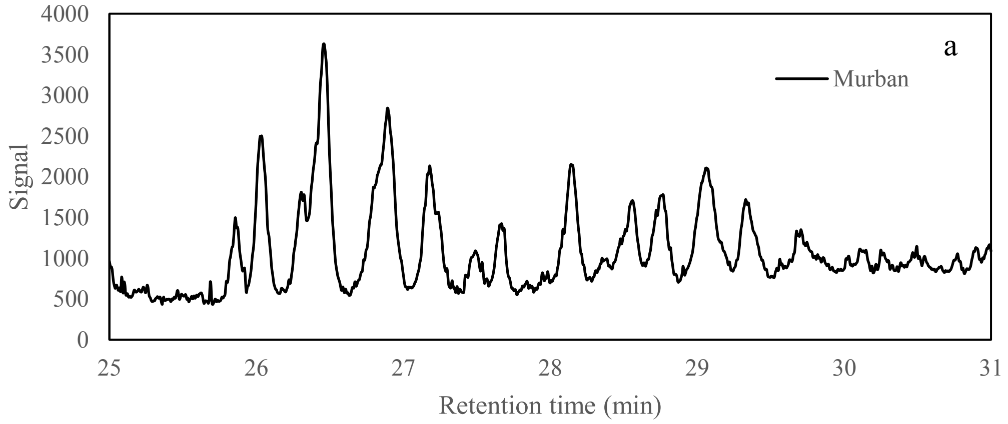
Figure 4.22 The correlation plot at 95% confidence interval of Fuel oil 600 Day 0 and IFO380 fuel oil Day 30.

4.3 Analysis of Sulfur Compounds

The analysis of sulfur compounds in crude oils, fuel oils and diesel oil were investigated by using GC-SCD instrument.

4.3.1 The Sulfur Compounds Distribution from GC-SCD

The chromatograms of crude oil and fuel oil samples on Day 0 and Day 30 are shown in Figures 4.23 (a)-(g) and Figures 4.24 (a)-(g) respectively. The result of crude oil on Day 30 showed the dramatic loss of light sulfur compounds (e.g. thiophene, dibenzothiophene) due to the weathering process such as evaporation while the heavy sulfur compounds (e.g. 4,6 dibenzothiophene or larger compounds, retention time after 26 min) noticeable decreased. For fuel oil, the chromatogram of both fuel oil showed slightly difference of heavy sulfur compounds between Day 0 and Day 30. This result indicated that the heavy sulfur compounds can be used as chemical fingerprinting since they can resist the weathering processes. However, this method cannot be applied for all types of crude oil. Some crude oils contains low amount of sulfur content such as Pattani crude which has sulfur content of 0.057 %wt calculated by ASTM D2622. Therefore, the GC-SCD chromatogram cannot detect the peak in chromatogram as seen in Figures 4.23 (d) and 4.24 (d).



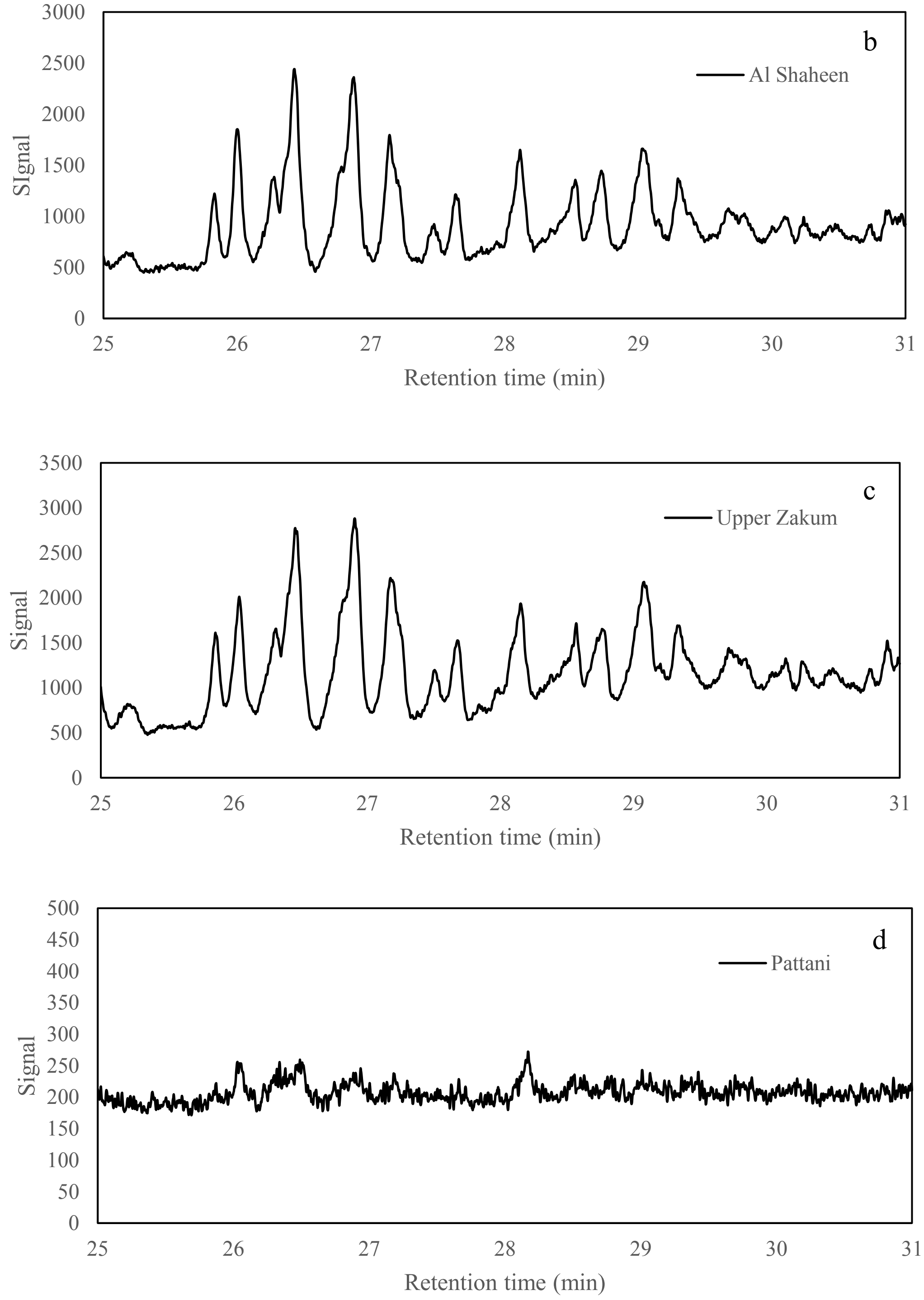


Figure 4.23 GC-SCD chromatograms of crude oils and fuel oils sample.

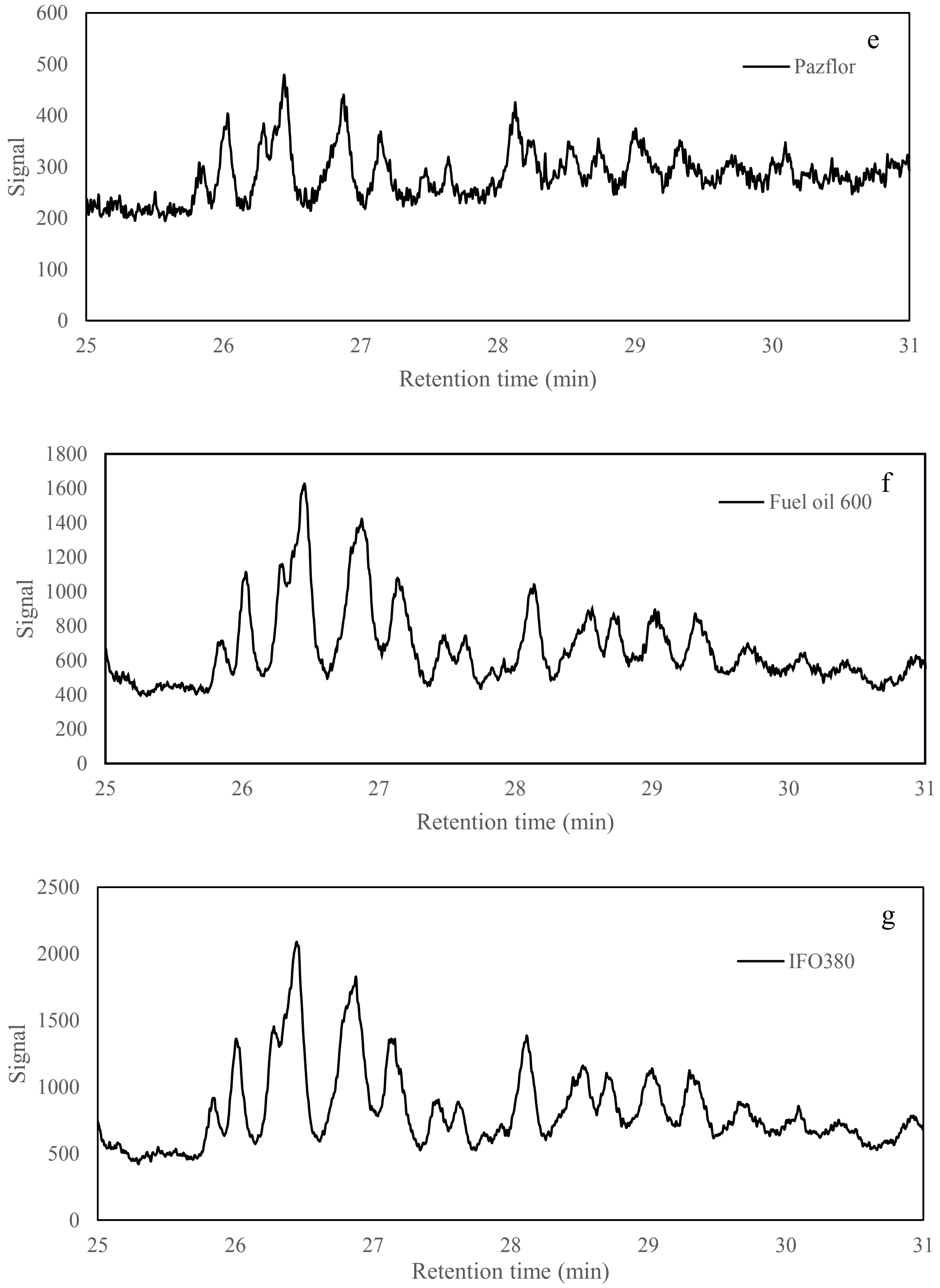


Figure 4.23 (Cont.) GC-SCD chromatograms of crude oils and fuel oils sample.

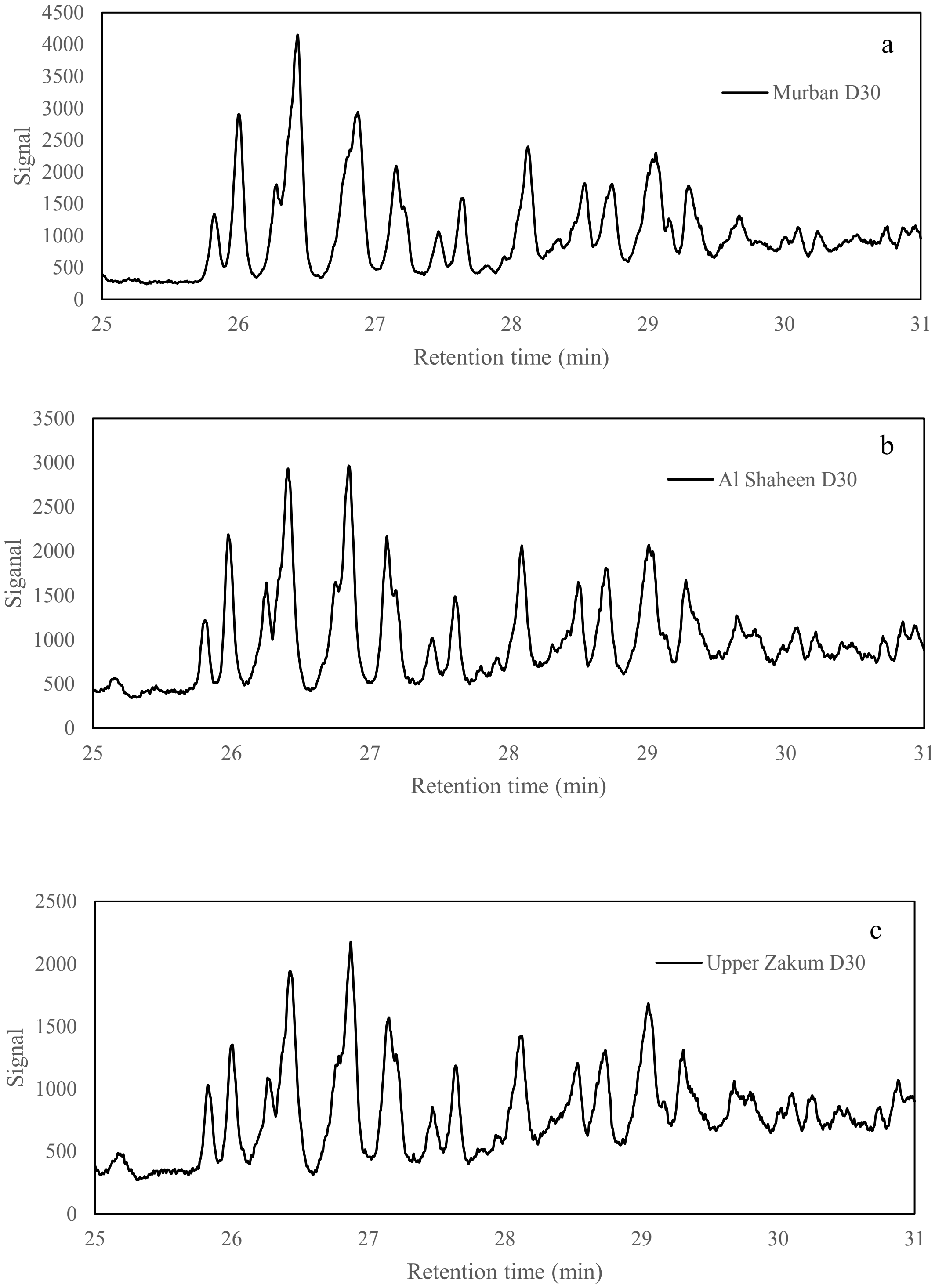


Figure 4.24 GC-SCD chromatograms of crude oils and fuel oils sample after weathering for 30 day.

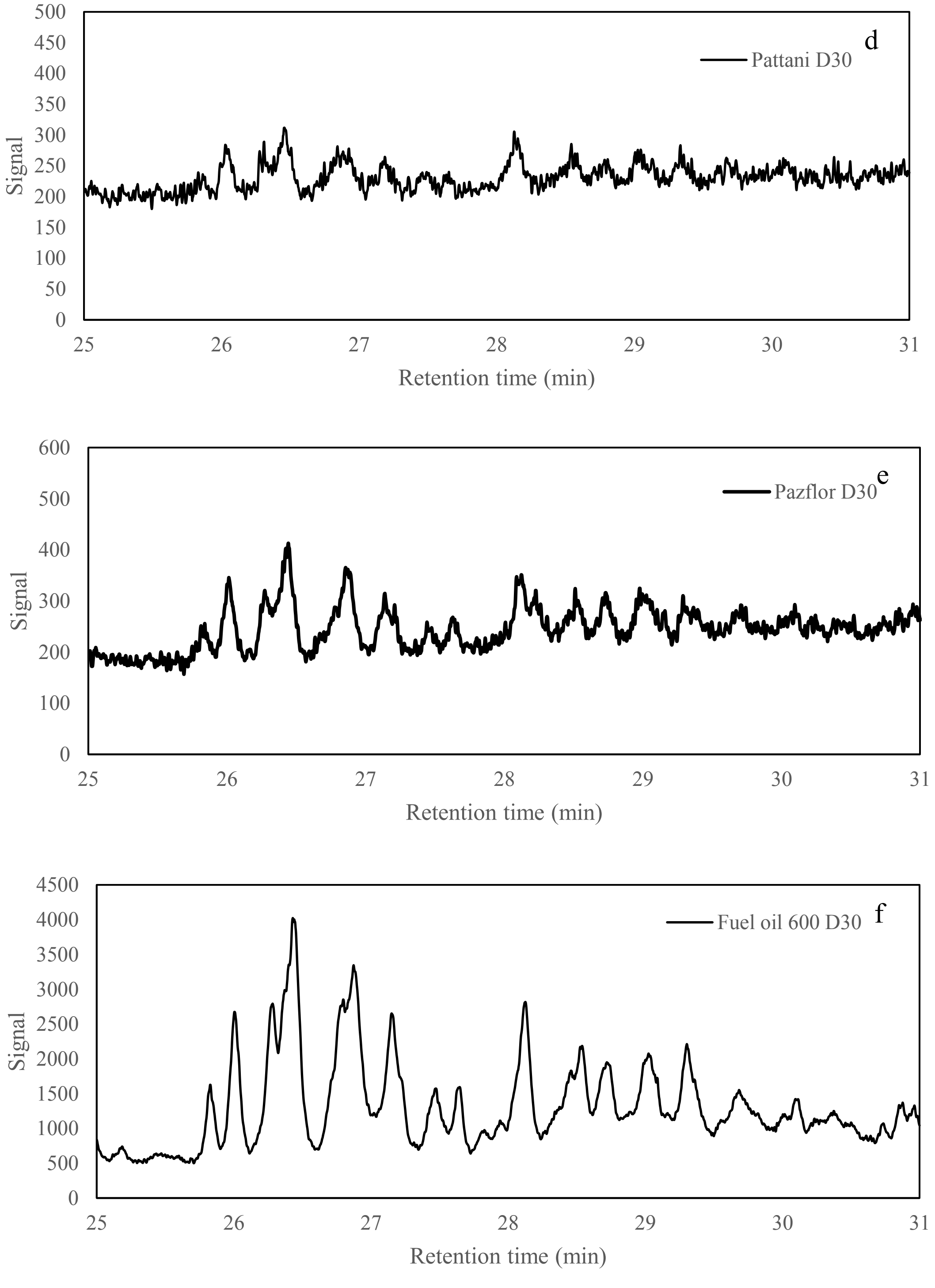


Figure 4.24 (Cont.) GC-SCD chromatograms of crude oils and fuel oils sample after weathering for 30 day.

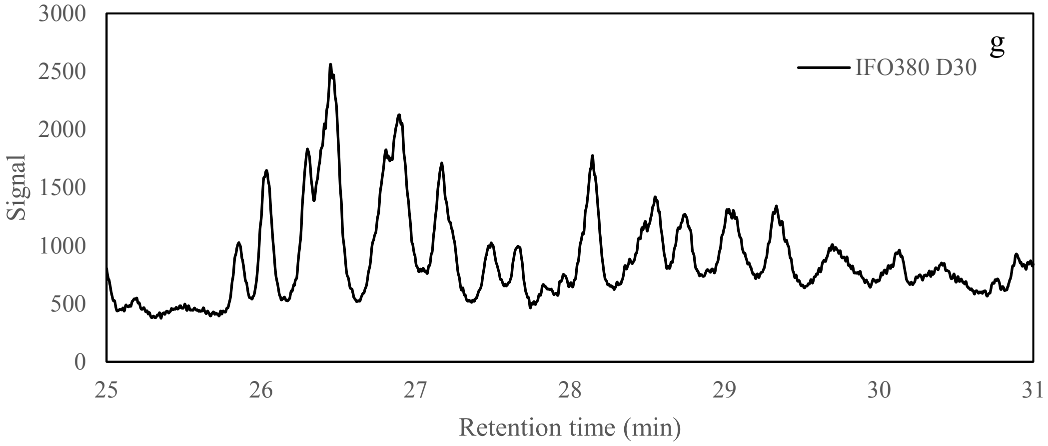


Figure 4.24 (Cont.) GC-SCD chromatograms of crude oils and fuel oils sample after weathering for 30 day.

4.3.2 Identification of Oil Samples

The analysis of sulfur compounds by GC-SCD was performed with these following steps. Firstly, each oil sample was analyzed three times. Next, the normalization of chromatogram was done by normalizing all signals at retention time between 27 to 31 min with retention time about 28 min. Finally, the 3 times analysis were averaged before comparing with other oil samples. Figures 4.25 and 4.26 show the chromatogram of Murban crude Day 0 and Day 30 after normalization with three times analysis. The result shows similar pattern indicating that GC-SCD instrument has good repeatability.

Figures 4.27 – 4.30 and 4.35, 4.36 show the chromatogram of fresh oil (Day 0) and weathered oil (Day 30) of crude oils and fuel oil after normalization. The chromatogram of both crude oil and fuel oil show a similar pattern between fresh and weathered oil sample. Among all signals at retention time between 27 to 31 min, the signal which is a peak from both chromatograms was selected. The selected sulfur compounds ratio of crude oil and fuel oil before and after weathering are shown in Tables 4.3 and 4.4 respectively. Moreover, the correlation plot of the data from Tables 4.3 and 4.4 was created in order to evaluate the potential match of 2 different oil samples.

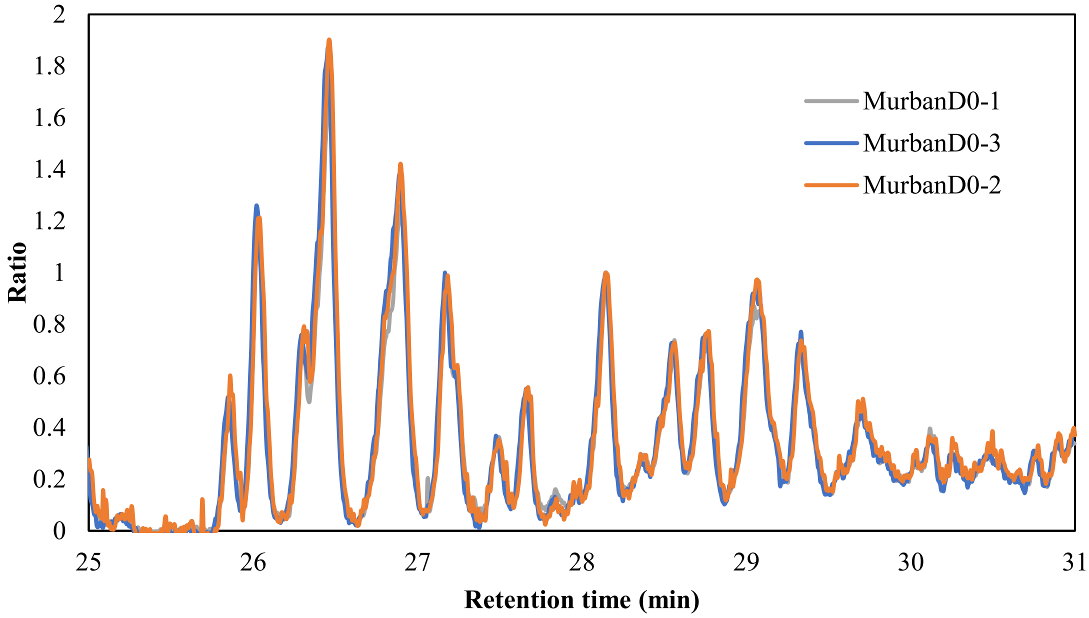


Figure 4.25 GC-SCD chromatogram of Murban crude Day 0 after normalization.

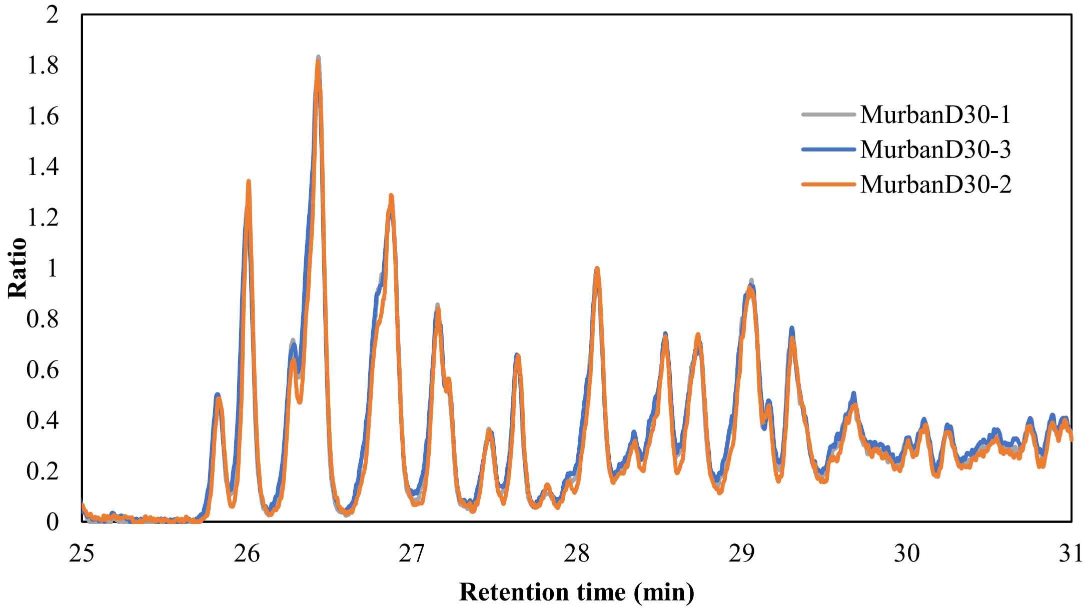


Figure 4.26 GC-SCD chromatogram of Murban crude Day 30 after normalization.

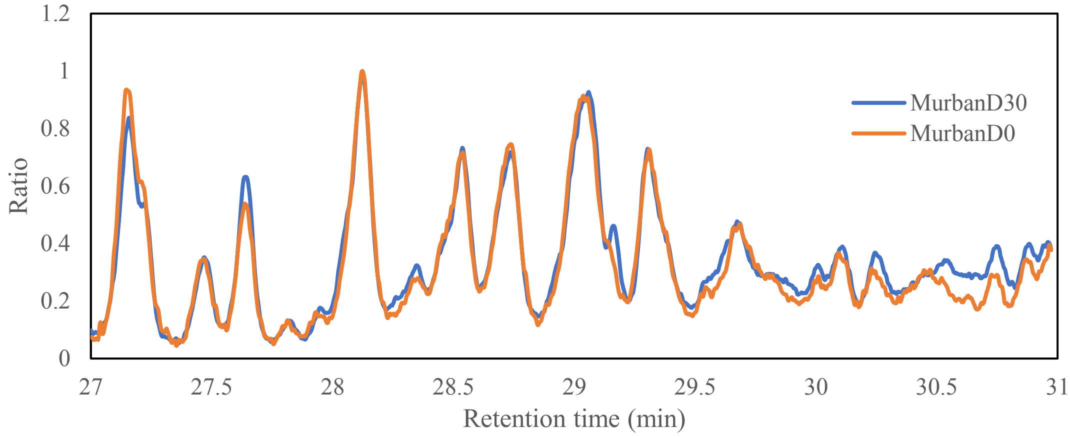


Figure 4.27 GC-SCD chromatogram compared with Murban crude on Day 0 and Day 30.

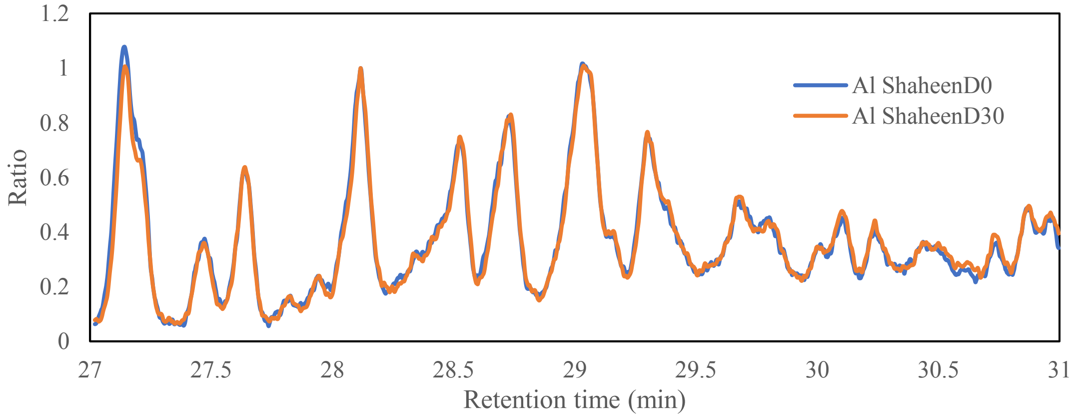


Figure 4.28 GC-SCD chromatogram compared with Al Shaheen crude on Day 0 and Day 30.

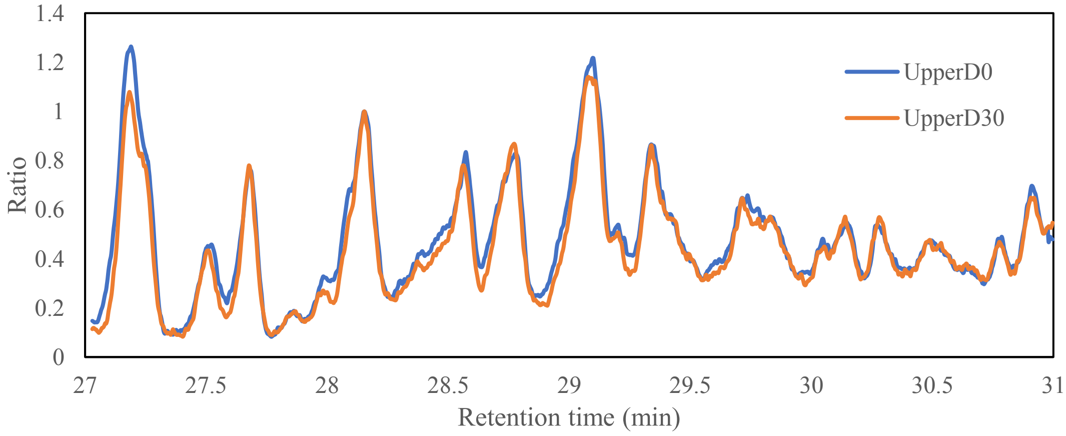


Figure 4.29 GC-SCD chromatogram compared with Upper Zakuum crude on Day 0 and Day 30.

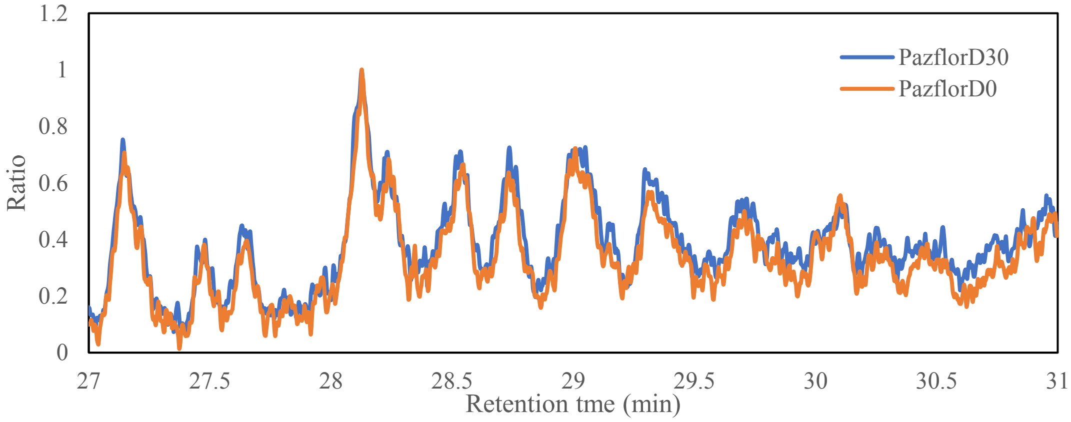


Figure 4.30 GC-SCD chromatogram compared with Plazfior crude on Day 0 and Day 30.

Table 4.3 Sulfur compound ratio of fresh and weathered crude oil samples at different retention time

Murban		**Alshaheen**		**UpperZakuum**		**Pazflor**	
D0	D30	D0	D30	D0	D30	D0	D30
0.84	0.77	0.76	0.67	1.22	0.99	0.54	0.60
0.23	0.25	0.18	0.15	0.44	0.35	0.22	0.28
0.42	0.50	0.27	0.25	0.69	0.67	0.35	0.43
0.80	0.79	0.43	0.45	0.86	0.80	0.81	0.82
0.15	0.18	0.21	0.18	0.25	0.24	0.64	0.71
0.58	0.62	0.30	0.32	0.74	0.64	0.62	0.60
0.74	0.71	0.52	0.54	0.82	0.87	0.57	0.65
0.90	0.92	0.91	0.92	1.18	1.13	0.60	0.70
0.60	0.58	0.52	0.53	0.76	0.69	0.50	0.60
0.43	0.43	0.46	0.44	0.63	0.60	0.45	0.54
0.34	0.36	0.31	0.34	0.54	0.51	0.50	0.52
0.25	0.26	0.34	0.34	0.36	0.36	0.31	0.35

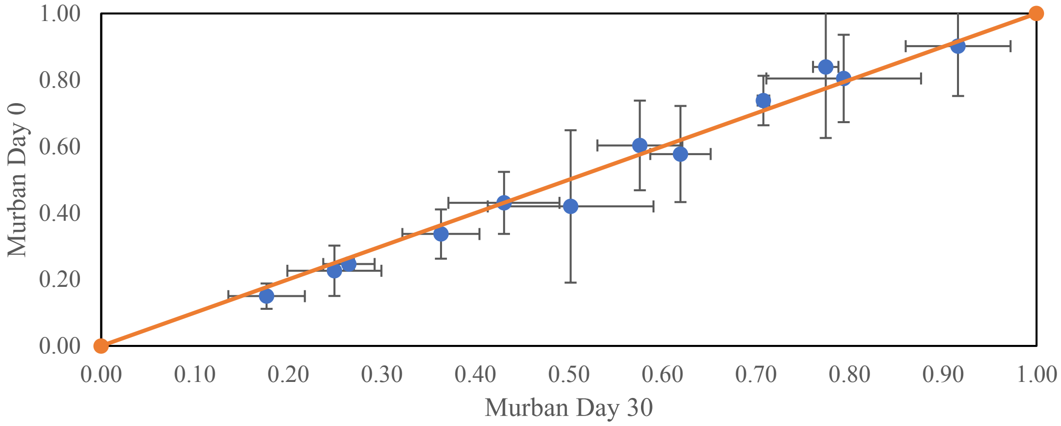


Figure 4.31 The correlation plot at 95% confidence interval between Murban Day 0 and Day 30.

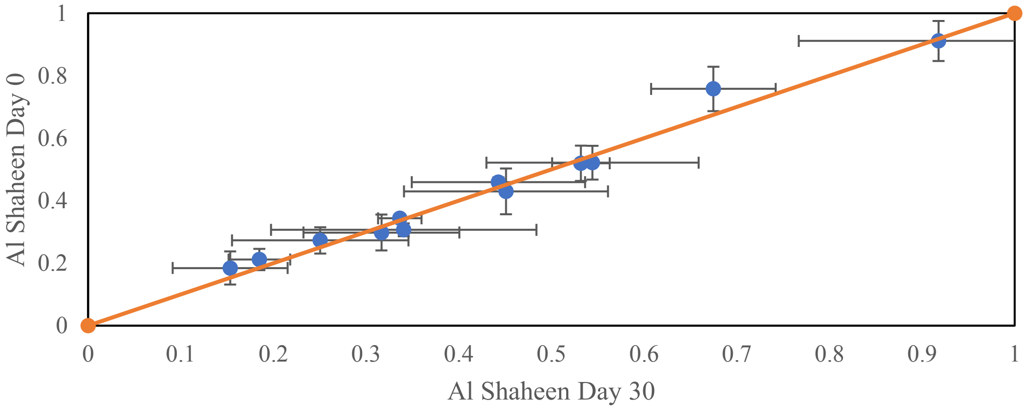


Figure 4.32 The correlation plot at 95% confidence interval between Al Shaheen Day 0 and Day 30.

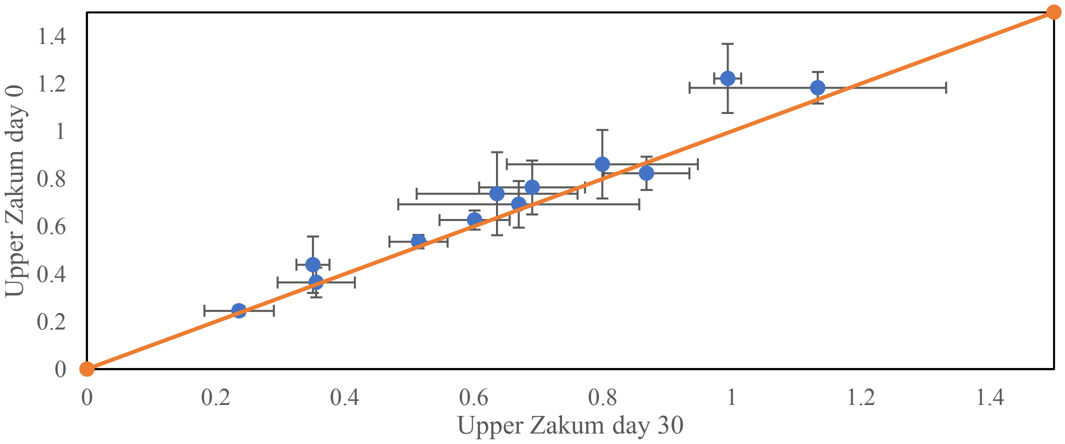


Figure 4.33 The correlation plot at 95% confidence interval between Upper Zakum Day 0 and Day 30.

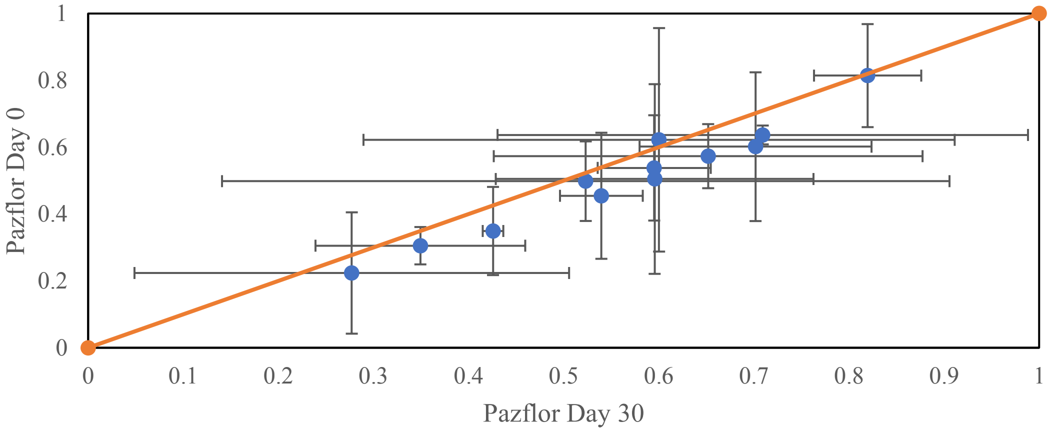


Figure 4.34 The correlation plot at 95% confidence interval between Pazflor Day 0 and Day 30.

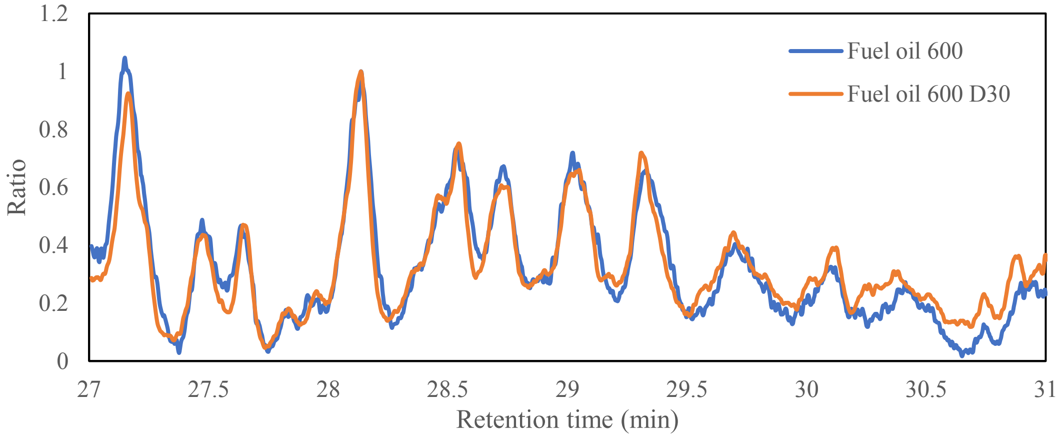


Figure 4.35 GC-SCD chromatogram compared with Fuel oil 600 on Day 0 and Day 30.

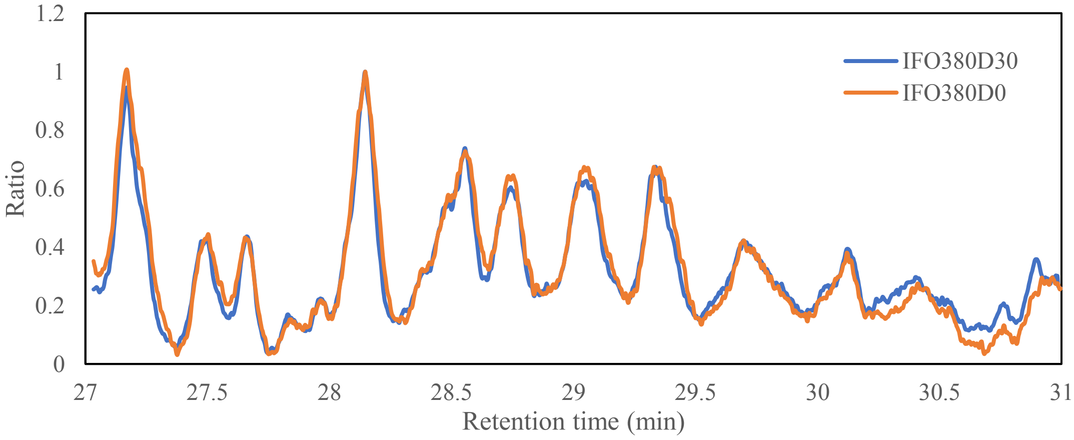


Figure 4.36 GC-SCD chromatogram compared with IFO380 on Day 0 and Day 30.

Table 4.4 Sulfur compound ratio of fresh and weathered fuel oil samples at different retention time

Fuel oil 600		**IFO380**	
D0	D30	D0	D30
0.91	0.84	1.01	1.01
0.39	0.34	0.44	0.44
0.33	0.35	0.42	0.42
0.85	0.81	1.00	1.00
0.18	0.14	0.27	0.27
0.66	0.64	0.73	0.73
0.62	0.60	0.63	0.63
0.60	0.61	0.66	0.66
0.62	0.56	0.66	0.66
0.40	0.42	0.42	0.42
0.28	0.36	0.38	0.38
0.27	0.27	0.25	0.25

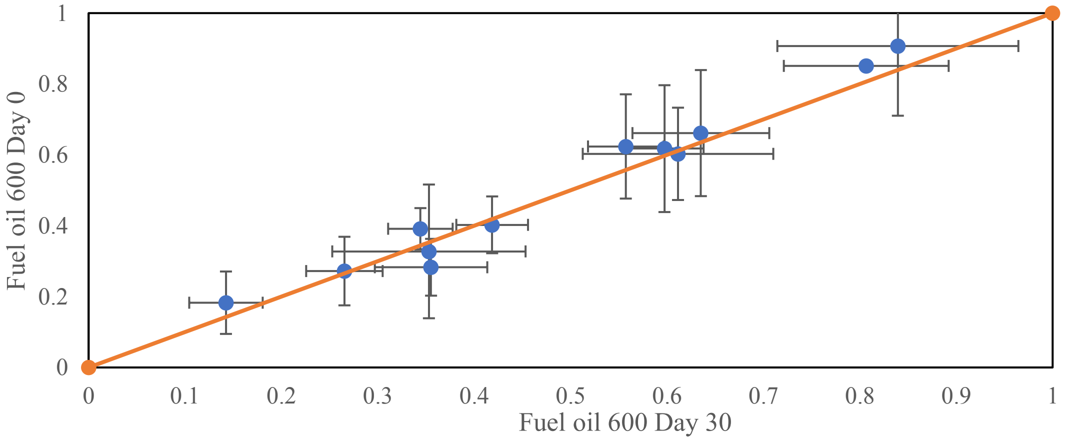


Figure 4.37 The correlation plot at 95% confidence interval between Fuel oil 600 Day 0 and Day 30.

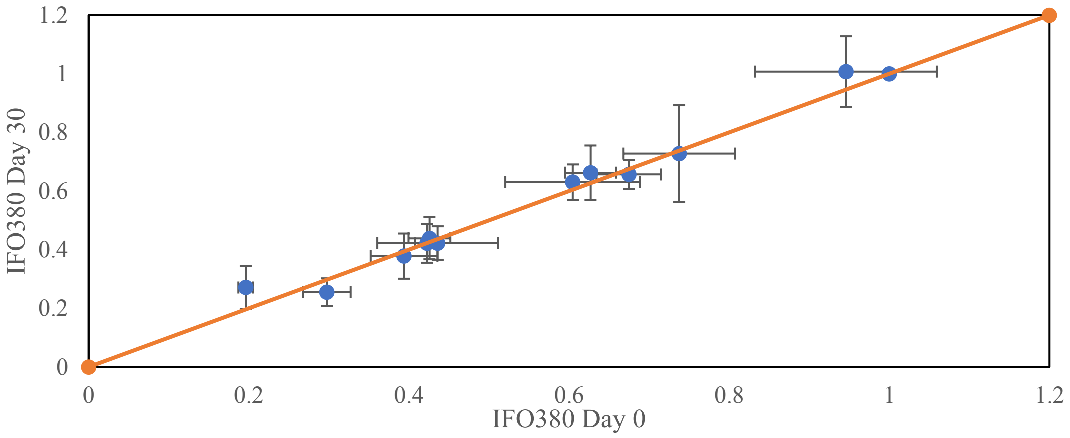


Figure 4.38 The correlation plot at 95% confidence interval between IFO380 Day 0 and Day 30.

The GC-SCD chromatogram result of both crude oil and fuel oil before (Day 0) and after (Day 30) weathering show a similar pattern. In addition, the correlation plot between fresh and weathered oil shows a positive match result as shown in Figures 4.31 – 4.34 and 4.37, 4.38 respectively. Thus, the result indicated that the sulfur compounds in oil at the retention time of 27 to 31 min can be used as chemical biomarkers for oil fingerprinting application. This result agreed well with the fact that several polycyclic aromatic sulfur heterocycles (PASHs) markers are stable and not affect by weathering processes (Hegazi *et al.*, 2016).

Hence, it can be concluded that the GC-SCD chromatogram can be used to identify the origin of crude oil and fuel oil. However, as mentioned previously, this method cannot be applied for all types of crude oil since some crude oil contains small sulfur amount so the heavy sulfur components are too low to detect in the SCD detectors.

4.3.2.1 Differentiation of Crude Oils and Fuel Oils

Figures 4.39 shows the GC-SCD chromatogram compared with Murban crude and Al Shaheen crude on Day 0. The chromatograms were slightly different. Moreover, the correlation plot showed the “non-match” result as shown in Figure 4.40. This is because both Murban crude and Al Shaheen crude come from Middle East so the sulfur compound distribution showed slightly different pattern. In addition, when comparing Murban crude with Upper Zakum crude, the chromatogram is shown in Figure 4.41, and the correlation plot as shown in Figure 4.42 shows “non match” result.

Furthermore, when comparing the GC-SCD chromatogram of Al Shaheen crude and Pazflor crude that comes from different regions, the chromatogram shows significantly different and the correlation plot showed non-match result. The result indicated that the GC-SCD chromatogram of different crude oil had a different pattern. The chromatogram and correlation plot between Al Shaheen crude and Pazflor crude are shown in Figures 4.43 and 4.44 respectively.

Hence, GC-SCD chromatogram can differentiate the different crude oil samples. In addition, the crude oils that comes from the same region seems to have a similar GC-SCD chromatogram as compared to those from different regions.

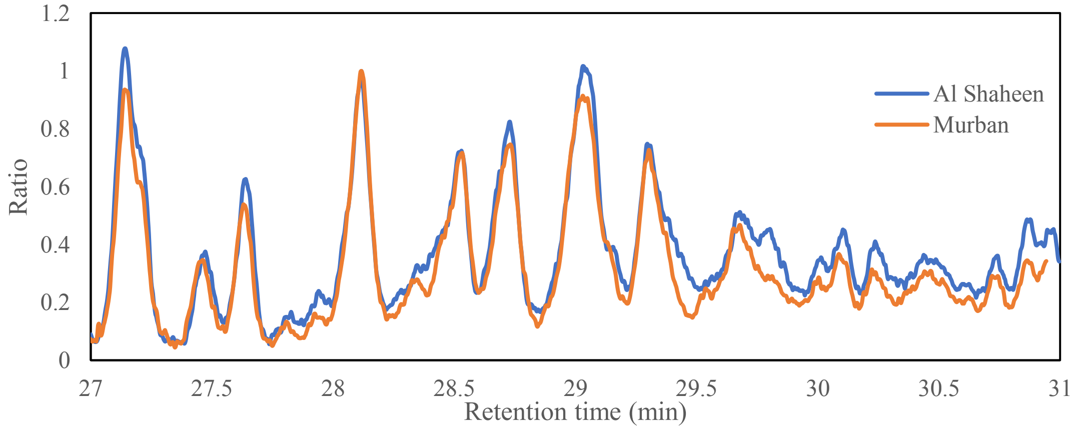


Figure 4.39 GC-SCD chromatogram compared with Murban crude and Al Shaheen crude on Day 0.

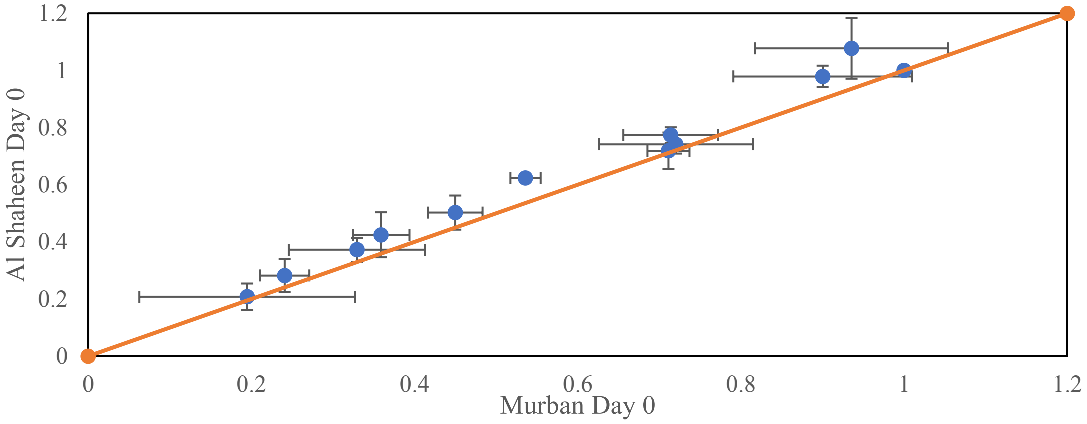


Figure 4.40 The correlation plot at 95% confidence interval between Murban crude and Al Shaheen crude Day 0.

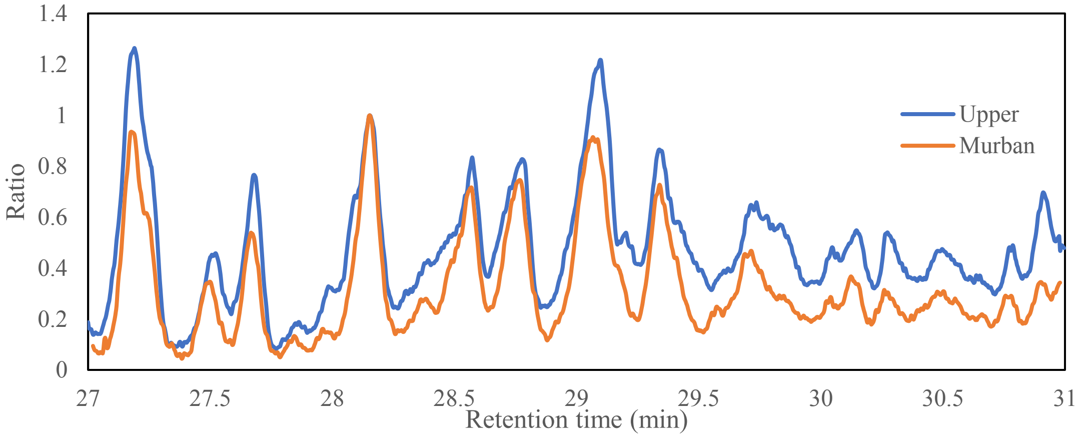


Figure 4.41 GC-SCD chromatogram compared with Murban crude and Upper Zakum crude on Day 0.

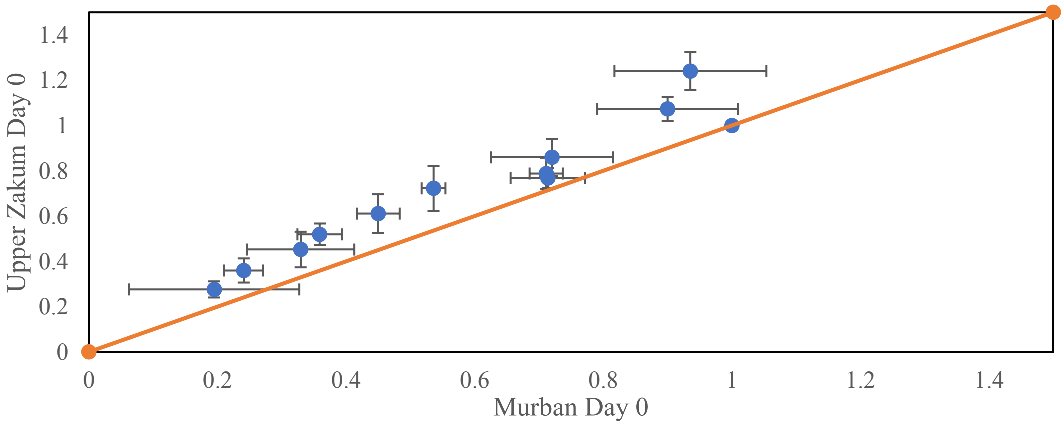


Figure 4.42 The correlation plot at 95% confidence interval between Murban crude and Upper Zakuum crude Day 0.

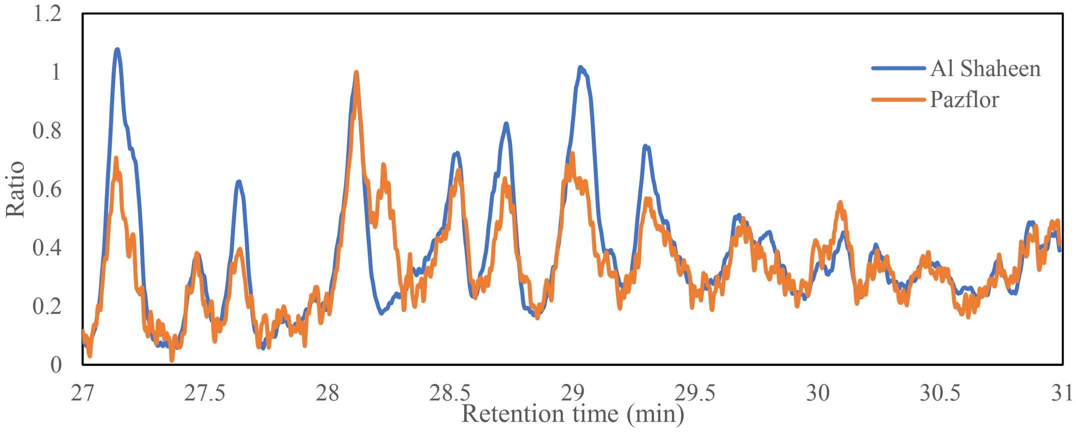


Figure 4.43 GC-SCD chromatogram compared with Al Shaheen crude and Pazflor crude on Day 0.

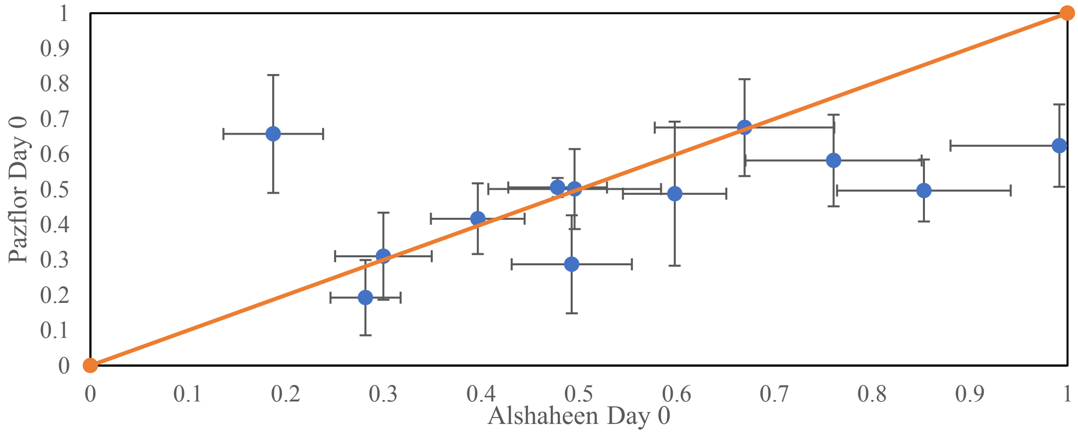


Figure 4.44 The correlation plot at 95% confidence interval between Al Shaheen crude and Pazflor crude Day 0.

Figure 4.45 shows the GC-SCD chromatogram compared with Al Shaheen crude and Fuel oil 600 on Day 0. The GC-SCD chromatograms were significantly different. Moreover, the correlation plot showed “non match” result as shown in Figure 4.46. Thus, the GC-SCD chromatogram can be used to differentiate crude oil and fuel oil samples.

However, when compared Fuel oil 600 with IFO380, the GC-SCD chromatogram shows slightly different as shown in Figure 4.47. Moreover, the correlation plot shows positive match as shown in Figure 4.48. The reason is the fuel oil is a process oil that passes through many processes to improve the quality such as blending and hydrodesulfurization. Therefore, the Sulfur compound distribution method might not appropriate to distinguish between fuel oil 600 and IFO380. However, this can’t conclude that the sulfur compound distribution is not suitable for differentiate fuel oil.

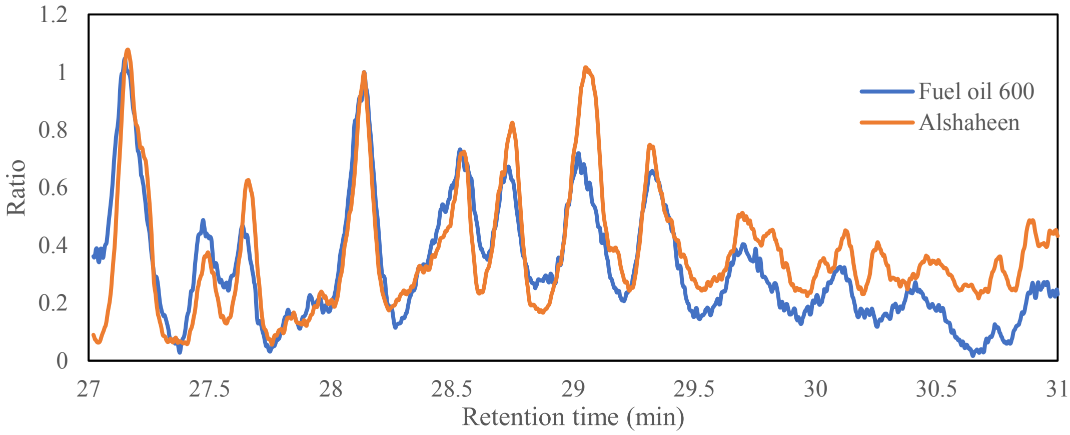


Figure 4.45 GC-SCD chromatogram compared with Al Shaheen crude and Fuel oil 600 on Day 0.

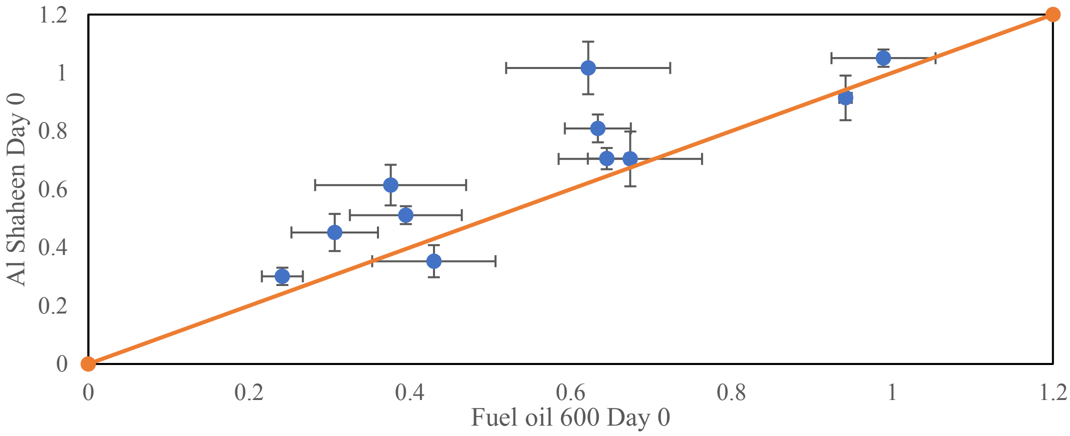


Figure 4.46 The correlation plot at 95% confidence interval between Al Shaheen crude and Fuel oil 600 Day 0.

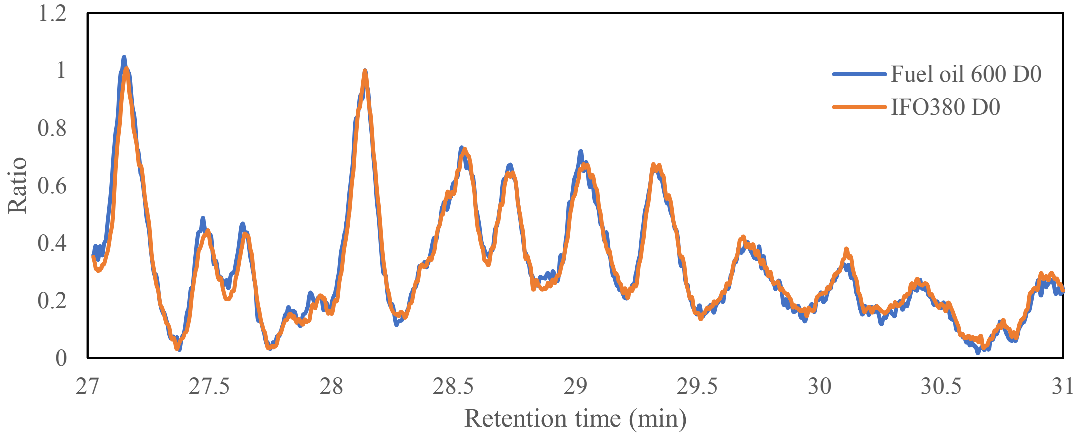


Figure 4.47 GC-SCD chromatogram compared with Fuel oil 600 and IFO380 Day 0.

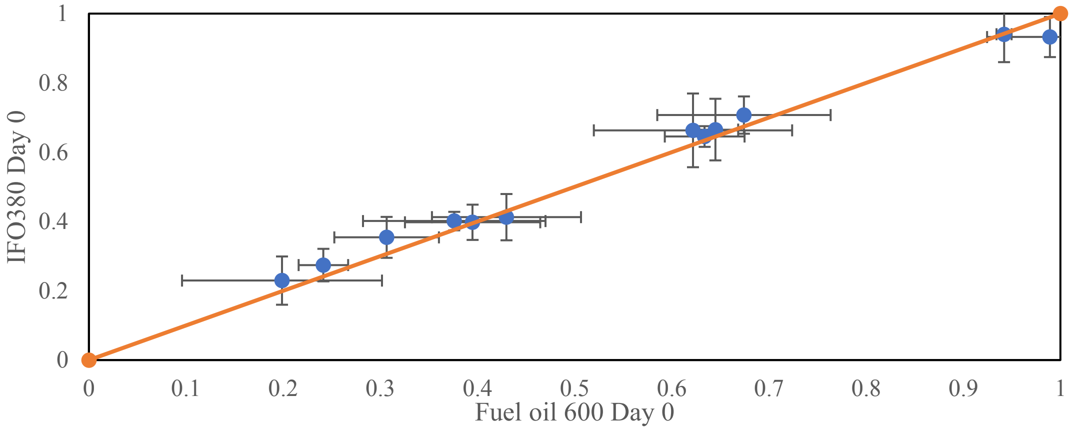


Figure 4.48 The correlation plot at 95% confidence interval between Fuel oil 600 and IFO380 Day 0.

4.3.3 Sulfur Compounds Species Identification by GCxGC-TOFMS

The oil samples were analyzed by comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) to identify the previous unknown sulfur compound biomarkers in GC-SCD chromatogram.

4.3.3.1 Sulfur Standard Analysis

According to the GC-SCD chromatogram, the sulfur compounds distribution at the retention time of 27 to 31 min can be used to support the oil spill identification. Unfortunately, the sulfur standard with the retention time over 27 min is unavailable. However, with those available standards, 4,6-Dimethydibenzothiophene (4,6-DMDBT) appears at the retention time of 26.8 min as shown in GC-SCD chromatogram in Figure 4.49. Thus, the 4,6-DMDBT in hexadecane solution was prepared and analyzed by GCxGC-TOFMS in order to confirm the retention time of sulfur compounds in chromatogram in which appeared at the actual retention time of 4089 seconds as shown in Figure 4.50.

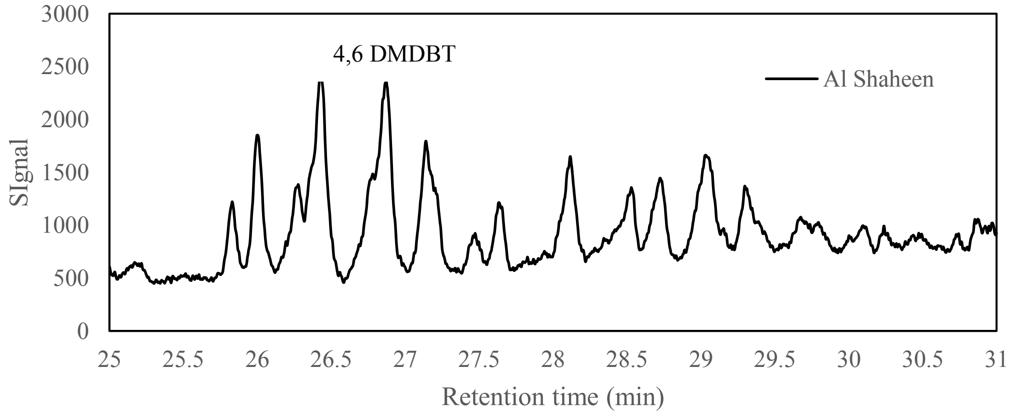


Figure 4.49 4,6-Dimethyldibenzothiophene appear at retention time about 26.8 minutes in GC-SCD chromatogram.

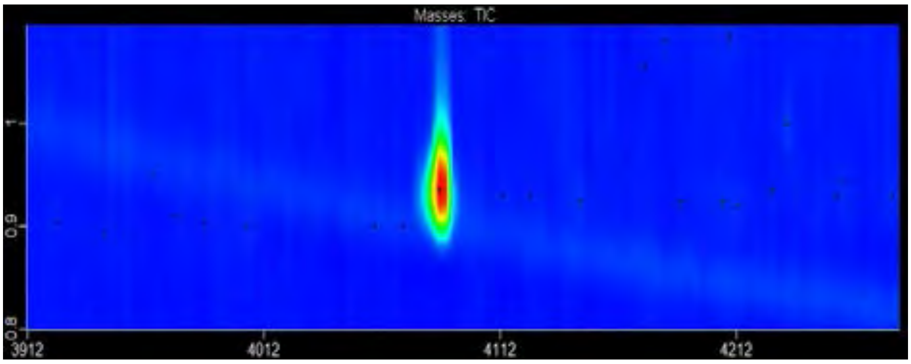


Figure 4.50 4,6-Dimethyldibenzothiophene appeared at retention time 4089 sec in total ion chromatogram (TIC).

Once the actual retention time of 4,6-DMDBT was obtained in TIC, the peaks after the 4,6 DMDBT have been used as biomarker of sulfur compounds. Figure 4.51 shows the GC-SCD chromatogram and total ion chromatogram of Murban crude oil on day 0.

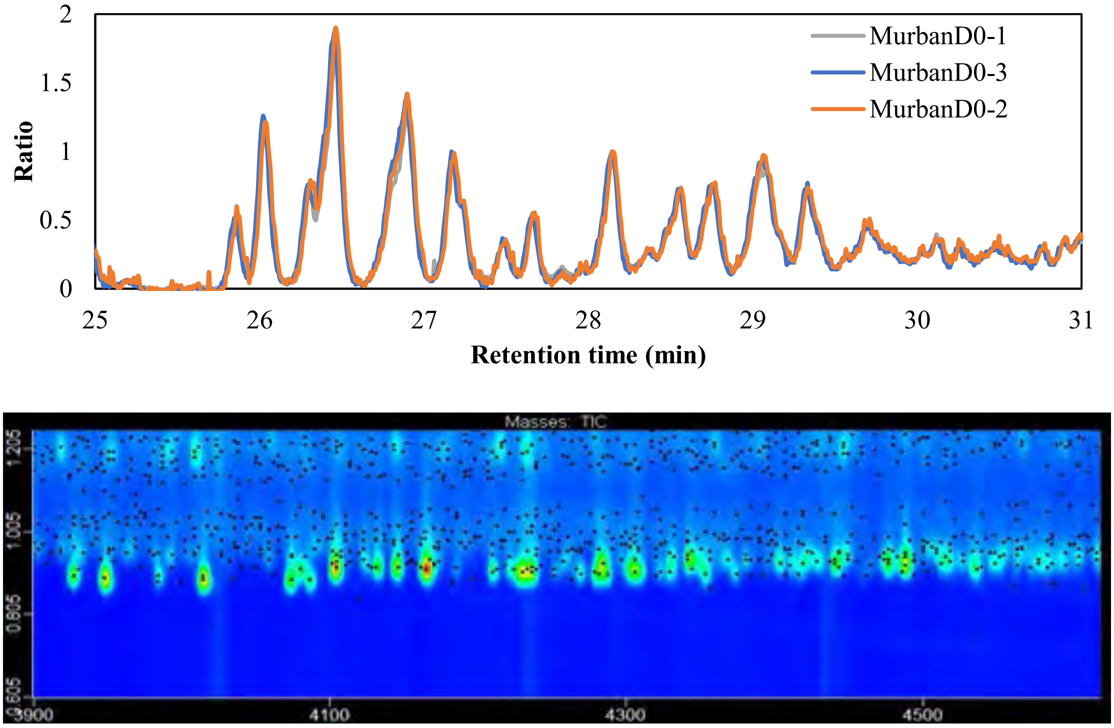


Figure 4.51 The chromatogram of Murban crude oil on day 0 a) GC-SCD chromatogram at retention time of 25 to 31 min b) Total ion chromatogram at retention time of 3900 to 4600 sec.

The peaks after the 4,6 DMDBT peak show the selected ion chromatogram (m/z 212) which is the C2 alkylated dibenzothiophene group. Hence, the result from mass spectrometry shows that the sulfur compounds species used in oil fingerprinting are C2 alkylated dibenzothiophene group. Figure 4.52 shows the sulfur distribution in GC-SCD chromatogram and selected mass ion (m/z 212) in the period that used to support the oil fingerprinting.

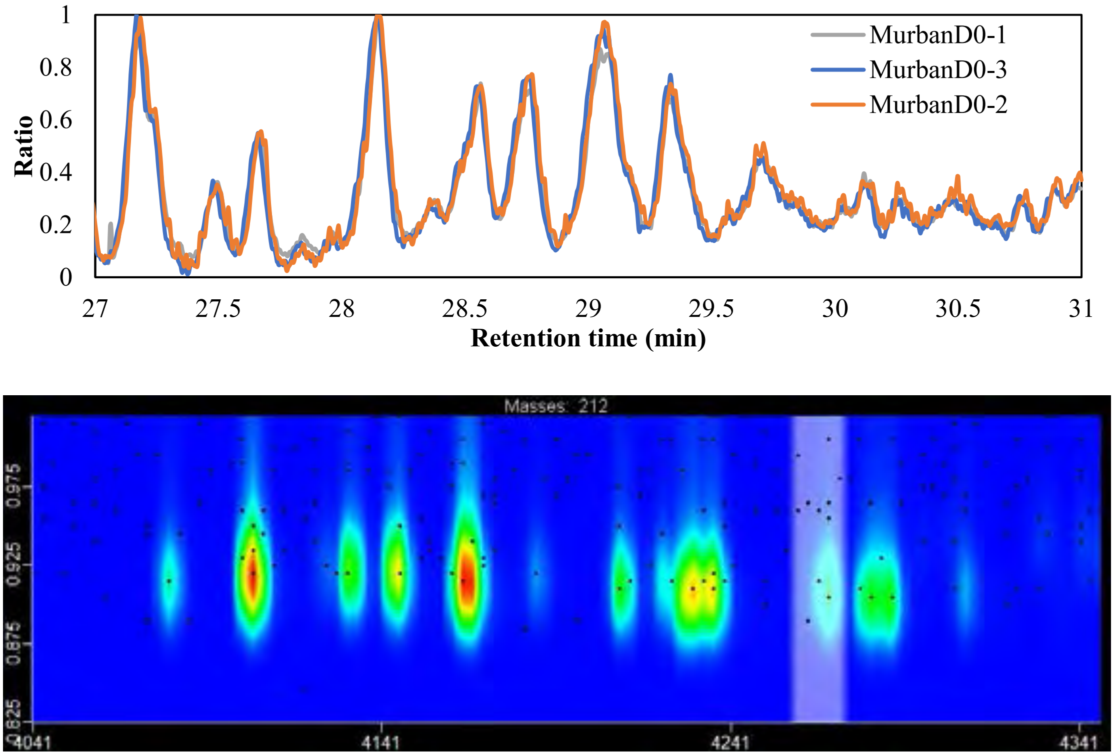


Figure 4.52 The chromatogram of Murban crude on day 0 a) GC-SCD chromatogram at retention time of 27 to 31 b) Selected mass ion chromatogram (m/z 212).

The result of sulfur compounds identification can be supported by Misselwitz *et al.* (2013) that study the fingerprinting of crude oils and tarballs. There found that the C2 alkylate dibenzothiophene group can be used as a chemical biomarker for oil fingerprinting.

4.4 Summarized Protocol for the Identification of Spilled oil

According to the result in the previous section, the protocol for identification of oil spills is concluded in Figure 4.53. Firstly, the extracted oil samples are analyzed by GC-FID in order to provide the basic information such as the distribution of hydrocarbon and degree of weathering. If the GC-FID chromatogram provides the huge unresolved complex mixture (UCM) area, the sample probably identified as lube oil. If the chromatogram has only small UCM, it can't be concluded since the oil sample might pass the weathering process (Thongkorn, 2018). Next, the oil samples are analyzed by GC-SCD. Fortunately, the GC-SCD instruments have equipped with both flame ionization detector (FID) and sulfur chemiluminescence detectors (SCD). This means that the analysis of oil sample by GC-SCD can obtain the data from FID at the same time. The GC-SCD is used to characterize the sulfur compound distribution. If the GC-SCD of different oil samples shows a different pattern, the oil sample will come from the different source. But, if the GC-SCD shows a similar pattern, the oil sample probably identified as the same oil source. In order to confirm the potential match of oil samples, the sulfur compound ratios are calculated, and the correlation plot is created. If all sulfur compound ratios overlap the linear line x = y, it can conclude to be positive match. But, if some ratio not overlaps the line, it can conclude to be non-match. Moreover, to support the identification of oil sample, the GCxGC-TOFMS is used to characterize the distribution of biomarkers (hopane groups, m/z 191). Then, the diagnostic ratios are calculated to create the correlation plot to confirm the oil spill source. However, if the GC-SCD chromatogram of oil samples does not detect or detect small peak of sulfur compounds. This means that oil samples have low sulfur content. Thus, the oil samples are required to increase concentration. Otherwise, this technique is not appropriate for this sample. The other techniques are required to support for analysis of the oil sample such as the biomarker technique by GCxGC-TOFMS.

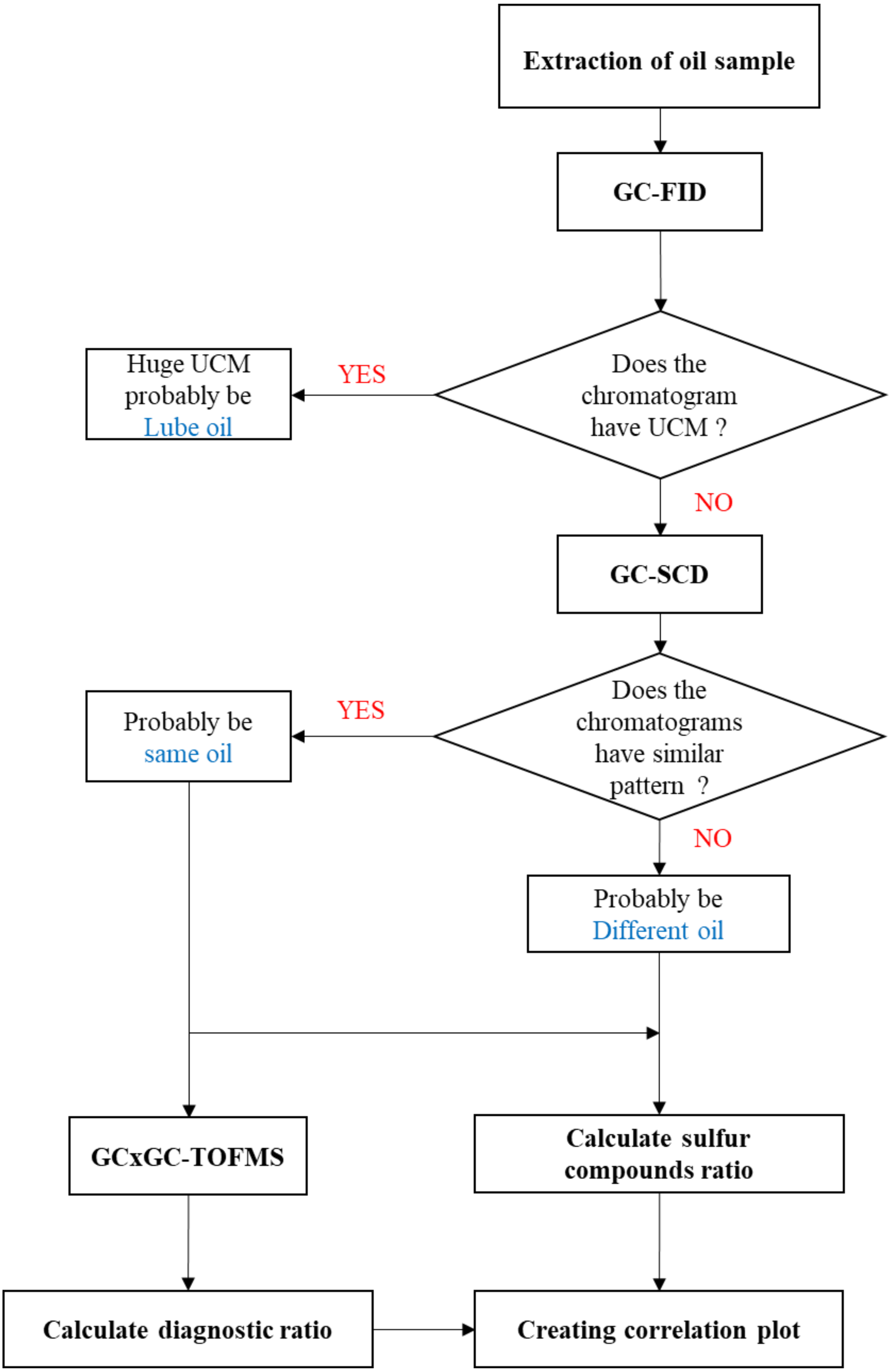


Figure 4.53 Propose summary protocol chart of oil sample identification.

CHAPTER 5
CONCLUSIONS AND RECOMENDATIONS

5.1 Conclusions

This work study and develop the sulfur compounds distribution method by GC-SCD to support the identification of crude oil and tarballs by GCxGC-TOFMS. Furthermore, this research also identifies the sulfur compound species in GC-SCD by using GCxGC-TOFMS. The sulfur compounds distribution technique by GC-SCD is a new technique for oil fingerprinting application. This technique has many advantages such as the ease of analysis and reasonable cost as compared to the common technique by GCxGC-TOFMS. The conclusions of this study are summarized as follows. Firstly, the physical appearance of crude oils after weathering processes has a different appearance depending on the type of crude oil. Some crude oils become more viscous and tarball in the last period of weathering processes. For fuel oils, both fuel oil become tarball. For diesel oil, the amount of diesel dramatically decreased and the appearance did not significantly change from fresh diesel but the color changed from a clear color to yellow. In addition, the diesel samples did not form tarball.

For analysis of biomarker, the hopanes group distribution are useful for oil fingerprinting since the distribution of hopanes group showed similar pattern on Day 0 and Day 30. Thus, the hopanes group can resist the weathering process. Moreover, the crude oils that come from near region exhibited similar hopane distribution while the crude oils that come from different regions exhibited different distribution. The diagnostic ratio of hopane groups is used to create the correlation plot for oil spill identification. This technique is reliable and provides accuracy result since the samples were analyzed three times and an error of the values were calculated with 95% confident interval.

For analysis of sulfur compounds, the sulfur compounds distribution of crude oil and fuel oil samples showed the similar characteristic on Day 0 and Day 30. The result can indicate a strong anti-weathering of sulfur compounds in oil. The sulfur compound ratios are calculated and then used to create the correlation as the same with the biomarker method. Thus, the sulfur compounds distribution by GC-SCD is useful for oil fingerprinting. Moreover, the different crude oil samples had a different sulfur compound patterns. The crude oils which comes from near region exhibited similar sulfur compounds pattern while the crude oils which come from different regions exhibited different pattern. In addition, the crude oil and fuel oil samples had a different sulfur compound characteristic. Thus, the sulfur compounds distribution can be used to differentiate the different oil samples and can differentiate the crude oil and fuel oil samples. Finally, the sulfur compound species which are used in oil fingerprinting were C2-alkylated dibenzothiophene groups.

In conclusion, the sulfur compounds distribution by GC-SCD is a new technique in oil fingerprinting that can be used to support the oil spill identification. However, this technique is not appropriate for the oil samples that contain low sulfur content. From this study, the lower limit of sulfur contents is 0.4 %wt.

The fingerprinting of oil spills and tarballs samples might not be successful by using unique technique. Several techniques are required to support the identification of oil in order to make oil fingerprinting more robust and reliable.

5.2 Recommendations

The sulfur compounds distribution is a new technique for oil spill identification. However, the drawback of this technique is not suitable for sample which has low sulfur content. Therefore, this technique should have more study about more sample of crude oil and fuel oil to determine the lower limit of sulfur contents in oil which can be used in this technique in order to make this sulfur compound distribution technique more effective. Otherwise, there need to be improved this problem such as increasing the oil concentration for analyzing by GC-SCD. For oil spills and tarball problems, the oil fingerprinting is a solution for identifying the type and source of oil spill. The data of oil fingerprinting from various techniques should be collected properly in the database in order to manage the oil spill and tarball problems in the future.

APPENDICES

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

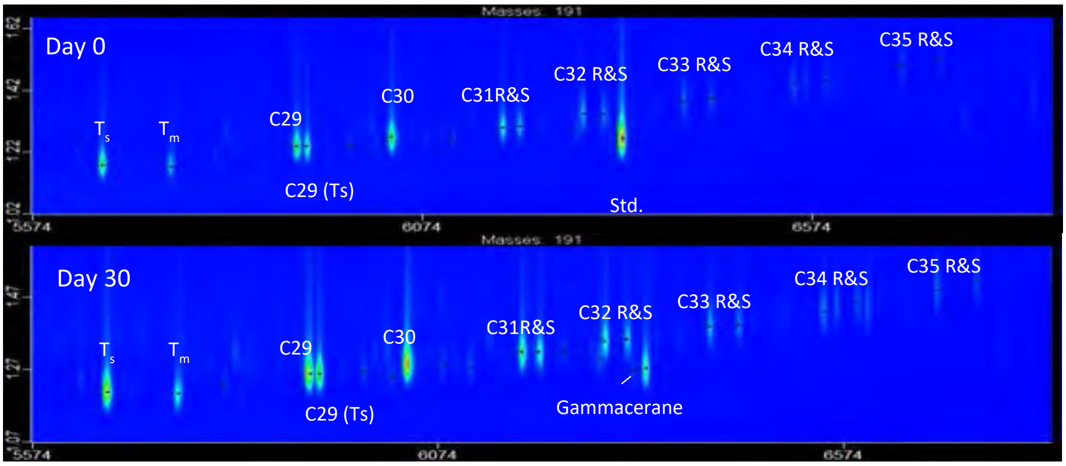


Figure A1 Target ion (m/z 191) contour plot of Murban crude Day 0 and Day 30.

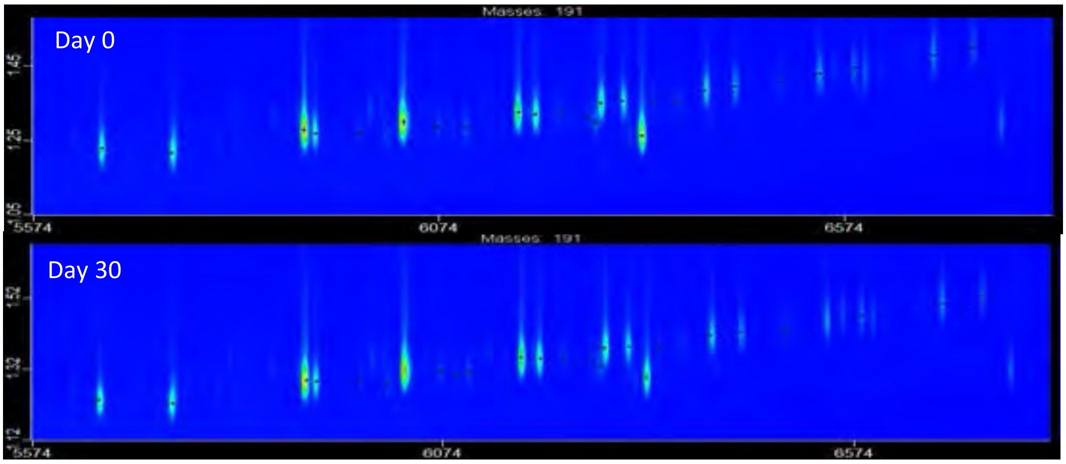


Figure A2 Target ion (m/z 191) contour plot of Al Shaheen crude Day 0 and Day 30.

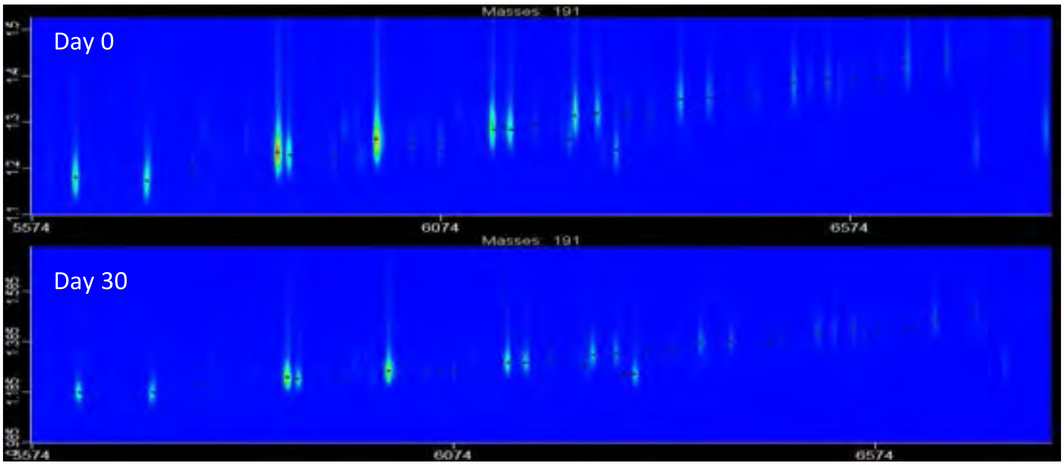


Figure A3 Target ion (m/z 191) contour plot of Upper Zakum crude Day 0 and Day 30.

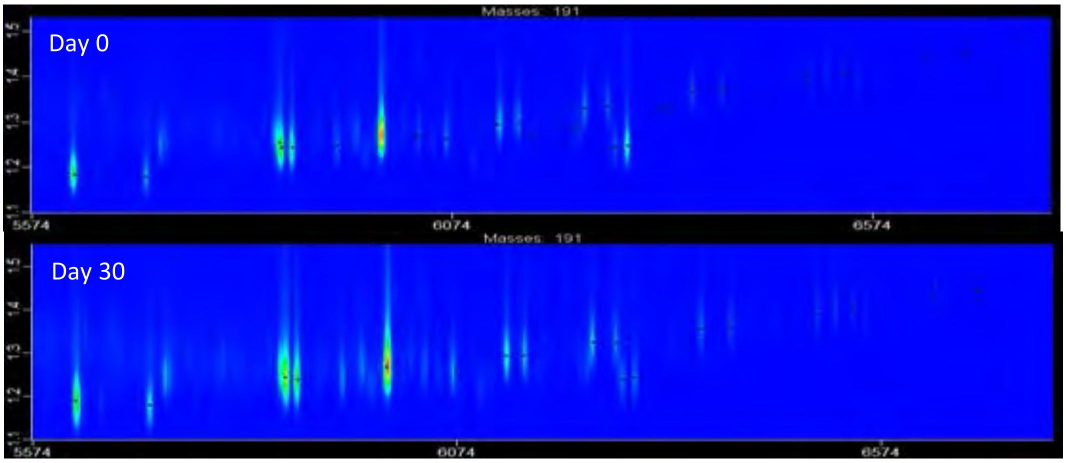


Figure A4 Target ion (m/z 191) contour plot of Pattani crude Day 0 and Day 30.

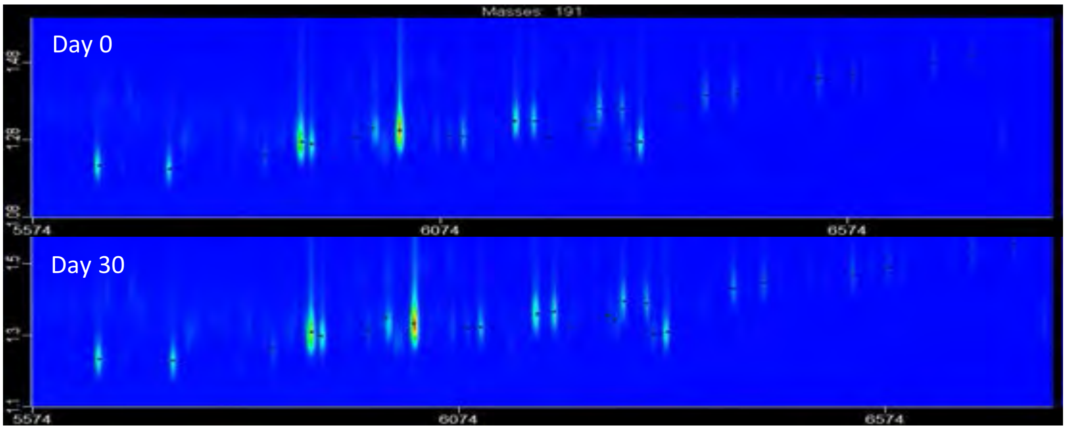


Figure A5 Target ion (m/z 191) contour plot of Pazflor crude Day 0 and Day 30.

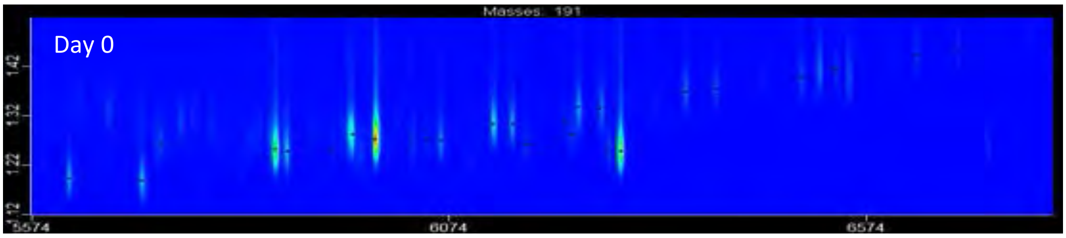


Figure A6 Target ion (m/z 191) contour plot of Fuel oil 600 Day 0.

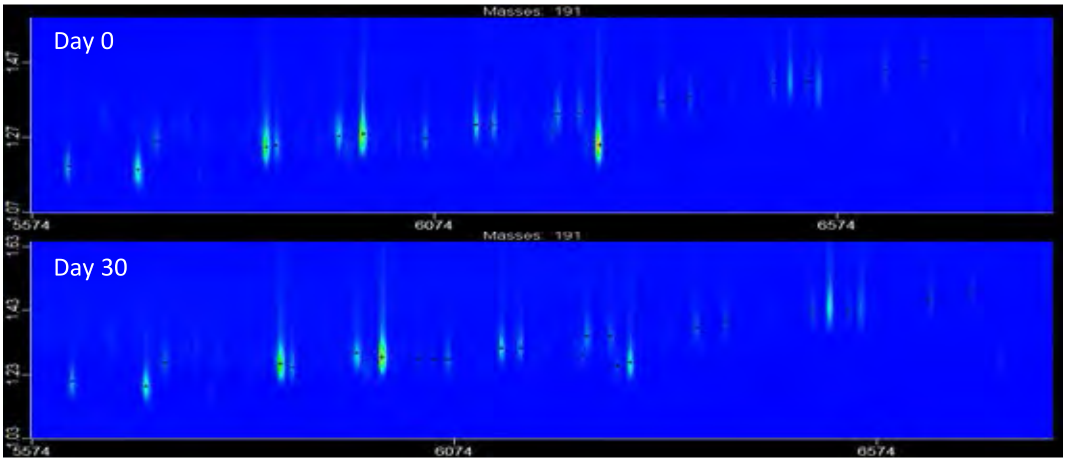


Figure A7 Target ion (m/z 191) contour plot of IFO380 fuel oil Day 0 and Day 30.

Appendix B The Correlation Plot between Fresh and Weathered Oil Samples of Hopanes Groups

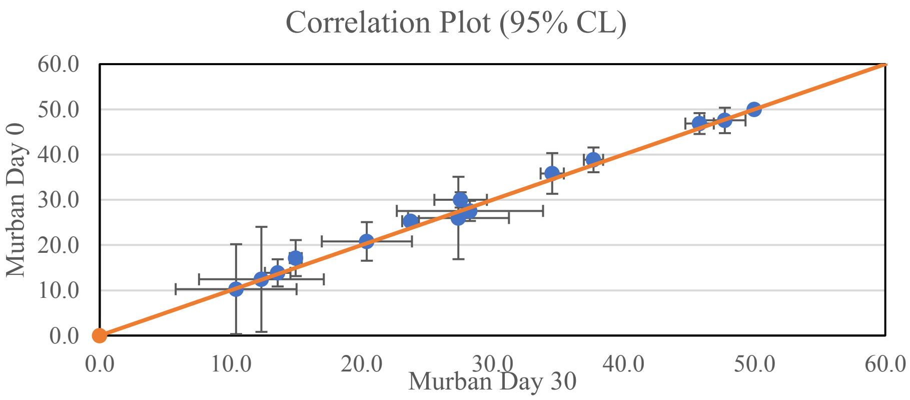


Figure B1 The correlation plot between Murban crude Day 0 and Day 30.

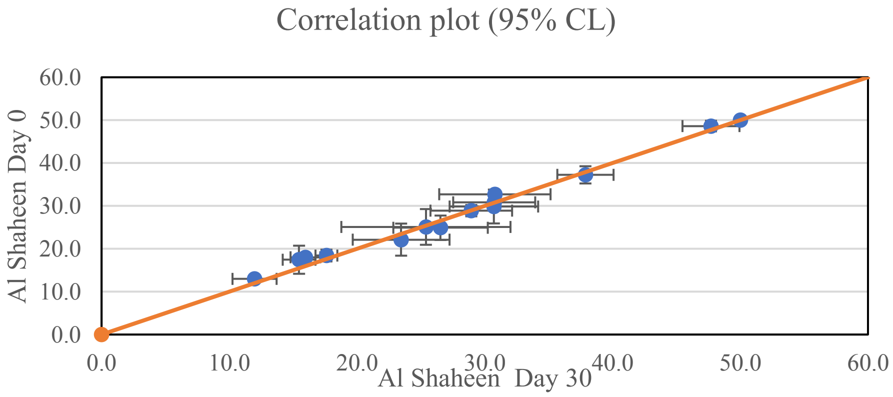


Figure B2 The correlation plot between Al Shaheen crude Day 0 and Day 30.

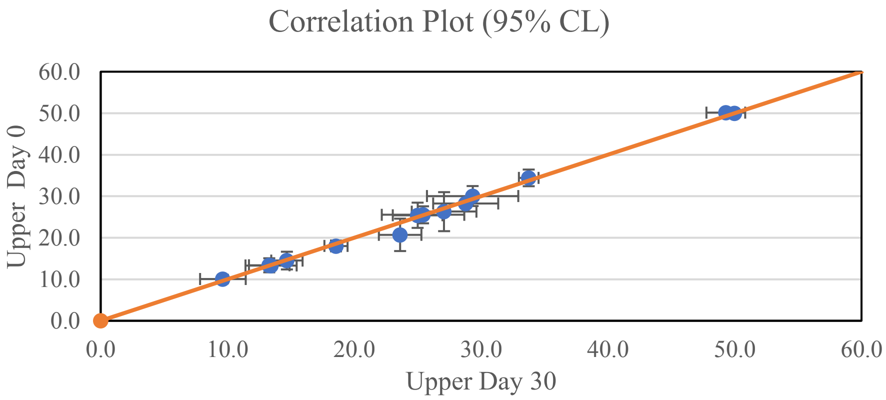


Figure B3 The correlation plot between Upper Zakum crude Day 0 and Day 30.

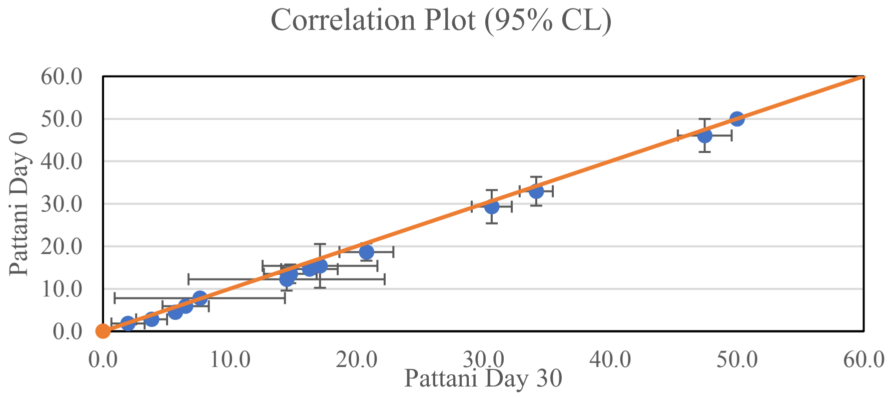


Figure B4 The correlation plot between Pattani crude Day 0 and Day 30.

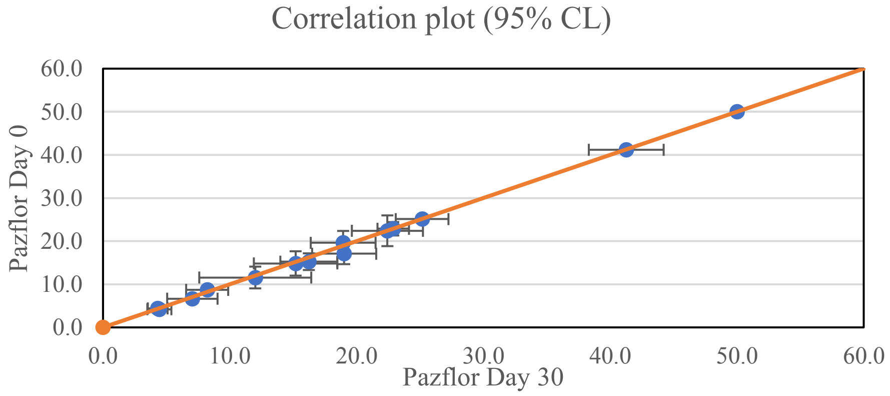


Figure B5 The correlation plot between Pazflor crude Day 0 and Day 30.

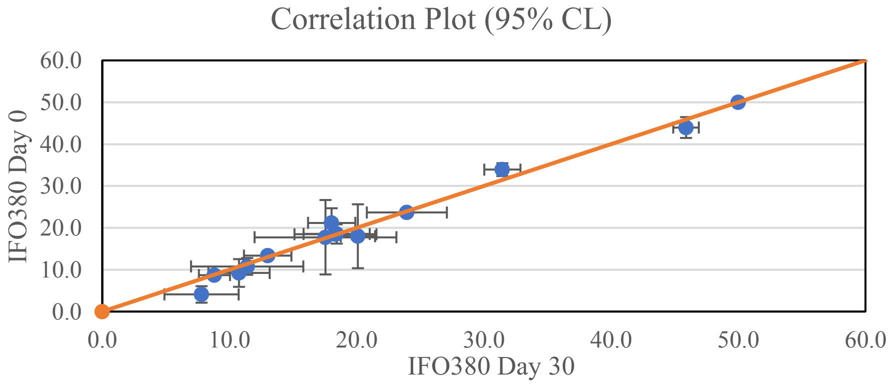


Figure B6 The correlation plot between IFO380 fuel oil Day 0 and Day 30.

Appendix C The GC-SCD Chromatogram after Normalization

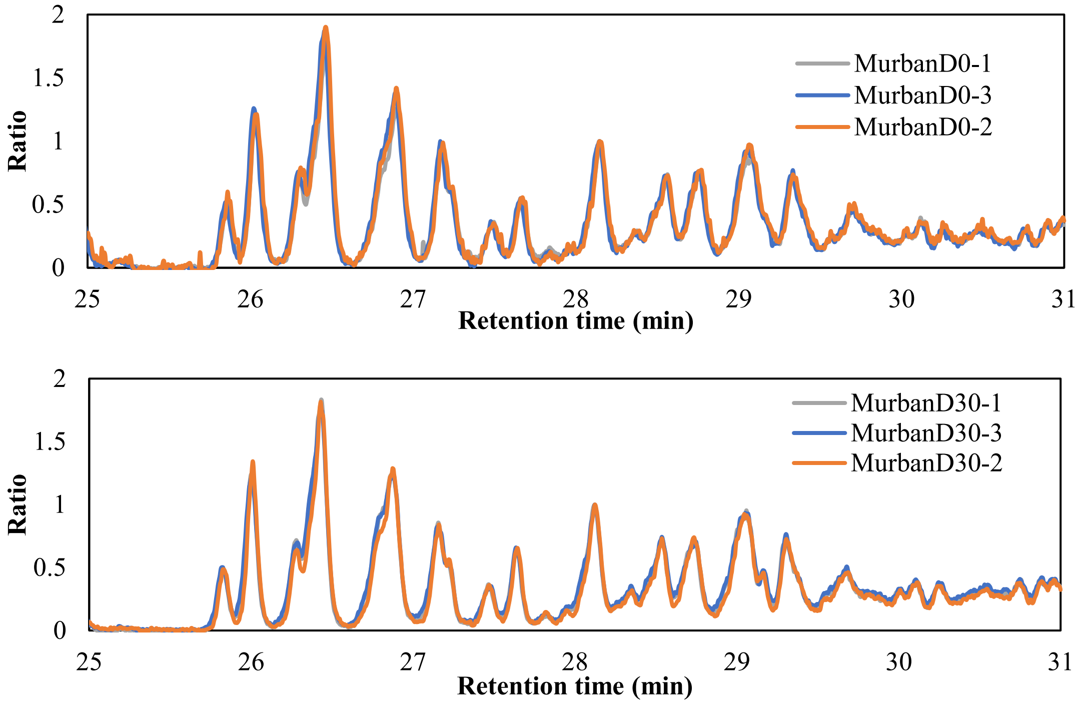


Figure C1 The GC-SCD chromatogram of Murban crude Day 0 and Day 30.

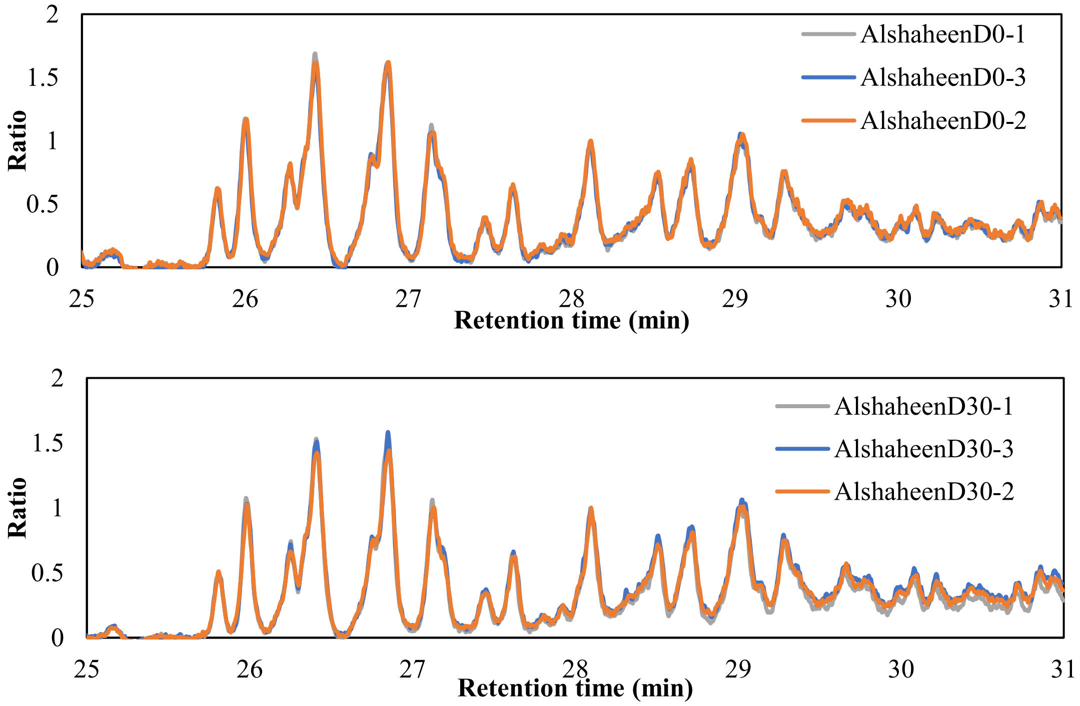


Figure C2 The GC-SCD chromatogram of Al Shaheen crude Day 0 and Day 30.

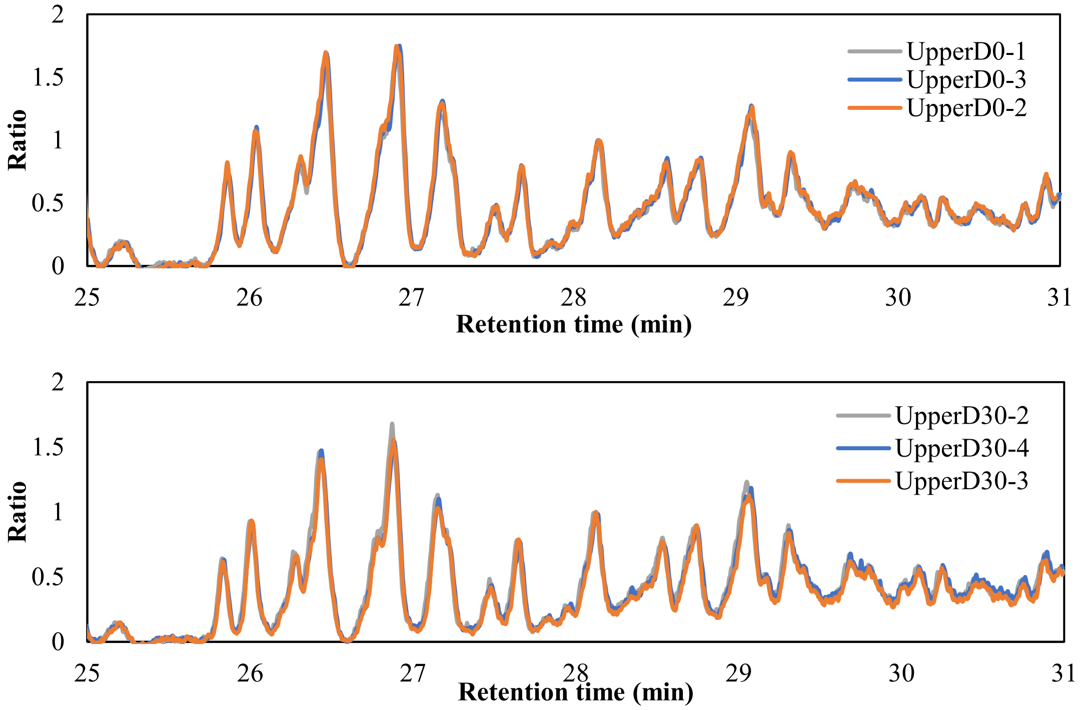


Figure C3 The GC-SCD chromatogram of Upper Zakum crude Day 0 and Day 30.

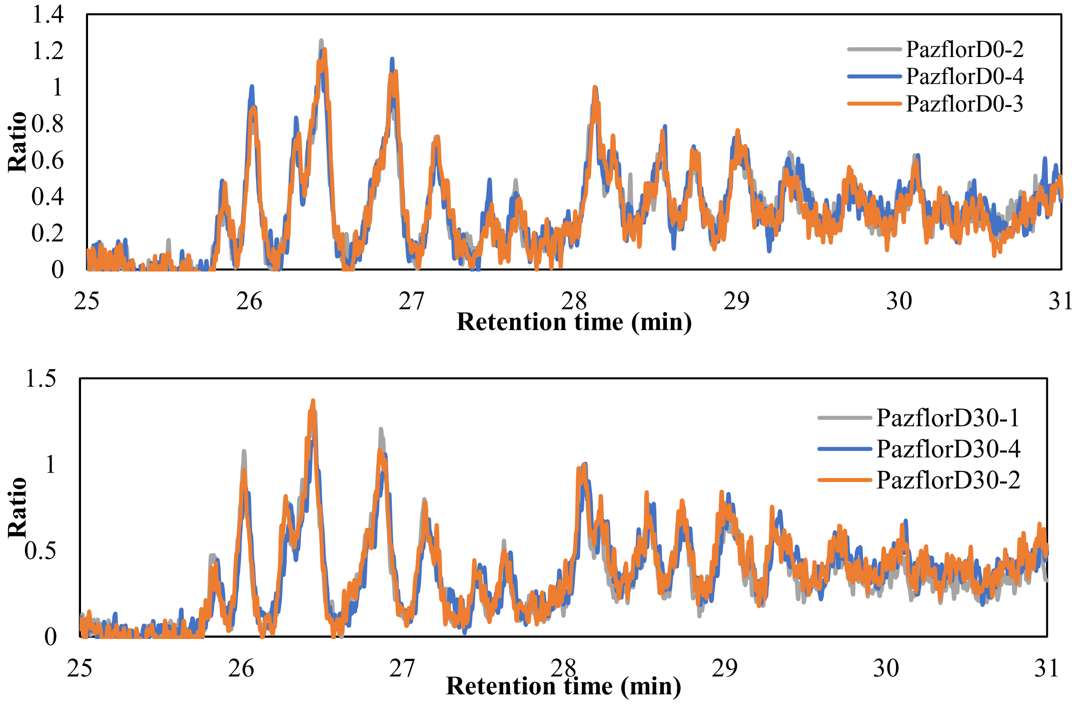


Figure C4 The GC-SCD chromatogram of Pazfior crude Day 0 and Day 30.

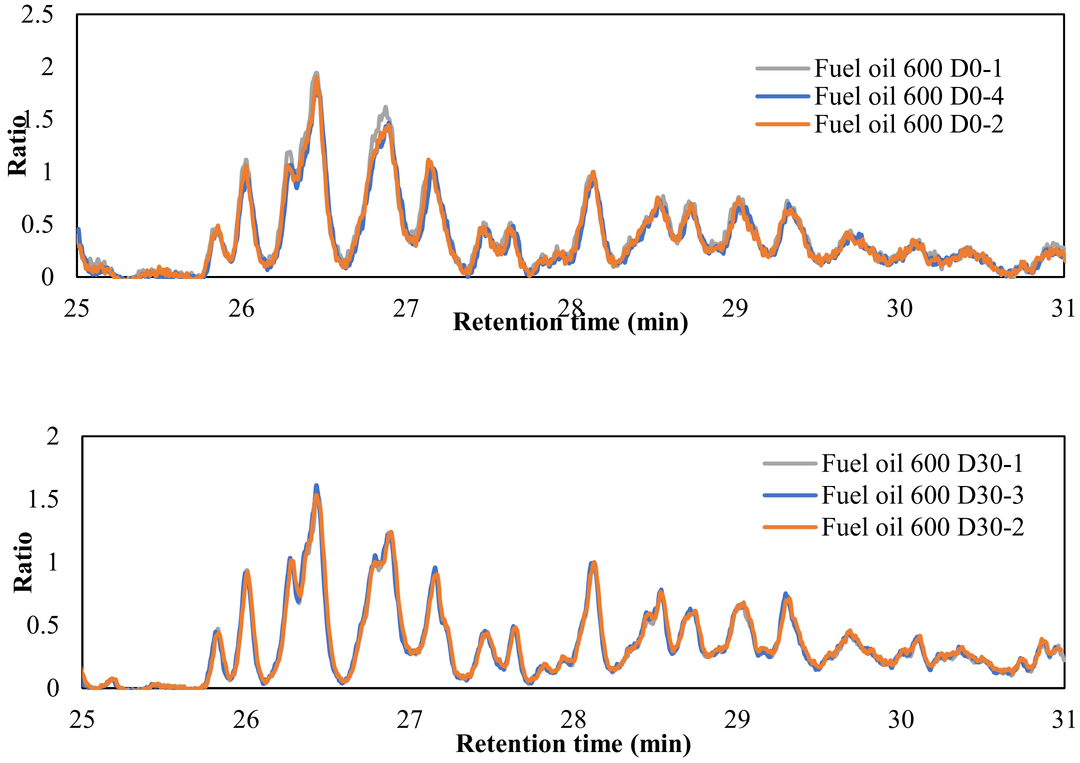


Figure C5 The GC-SCD chromatogram of Fuel oil 600 Day 0 and Day 30.

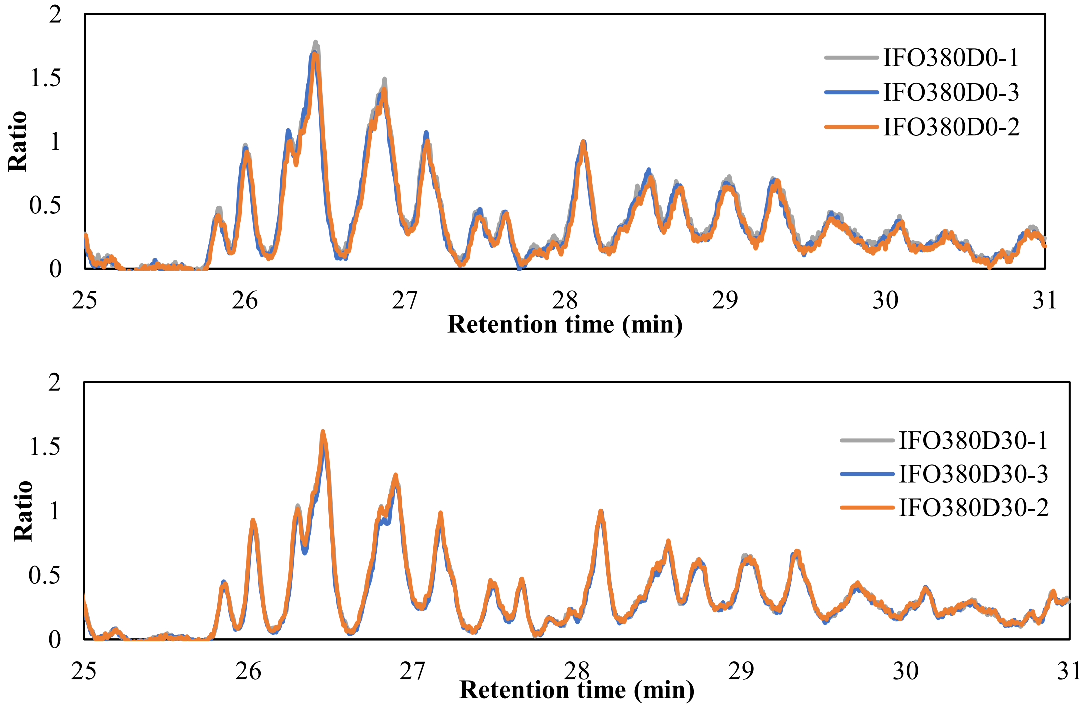


Figure C6 The GC-SCD chromatogram of IFO380 fuel oil Day 0 and Day 30.

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