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# Application Of Stir Bar Sorptive Extraction Thermal Desorption Gas Chromatography Mass Spectrometry For The Study Of Water Accommodated Fractions Of Fossil Fuels And Biodiesel

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APPLICATION OF STIR BAR SORPTIVE EXTRACTION THERMAL  
DESORPTION GAS CHROMATOGRAPHY MASS SPECTROMETRY FOR  
THE STUDY OF WATER ACCOMMODATED FRACTIONS OF FOSSIL  
FUELS AND BIODIESEL

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Dean of the Graduate School

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## **Dedication**

Investors, Friends, and Family

APPLICATION OF STIR BAR SORPTIVE EXTRACTION THERMAL  
DESORPTION GAS CHROMATOGRAPHY MASS SPECTROMETRY FOR  
THE STUDY OF WATER ACCOMMODATED FRACTIONS OF FOSSIL  
FUELS AND BIODIESELS

by

RICARDO MCCREARY JR., B.S.

THESIS

Presented to the Faculty of the Graduate School of  
The University of Texas at El Paso  
in Partial Fulfillment  
of the Requirements  
for the Degree of

MASTER OF SCIENCE

Department of Chemistry  
THE UNIVERSITY OF TEXAS AT EL PASO  
December 2014

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## **Abstract**

Even though measures are taken to decrease accidental release of crude oil and refined fuels into the aquatic environment, continued demand of such fuels—particularly in the transportation sector—pose a continued threat to the aquatic environment throughout their handling, processing, and consumption. Even though measures can be taken to remove the visible layers of fuel in water, it has been shown that constituents of these fuels—that partition into water—can have adverse health effects on the aquatic organisms at low concentrations that are not necessarily predictable through the study of the actual fuel’s original composition. Consequently, this renders the need for an extraction method that can quickly and efficiently extract these constituents from various types of water matrices so that the impact of fuels on aquatic life and the integrity of the environment can be studied and monitored in an accurate and timely manner.

The overarching goal of this project was to develop a less time consuming, effective and, environmentally friendly method to assess the composition of water accommodated fractions of refined fuel products. Diesel, having a wide variety of hydrocarbons, and its more environmentally friendly alternative biodiesel (B100) were selected for this study. More specifically, the study was aimed to: (1) optimize the stir bar sorptive extraction (SBSE) method before subsequent thermal desorption-gas chromatography mass spectrometry (TD-GCMS) to extract and analyze biodiesel fatty acid methyl esters (FAMES) and dominant diesel hydrocarbons, by varying organic solvent addition in SBSE extraction, the stir time, and pH adjustment; (2) compare the composition between the fuel and its water accommodated fraction (WAF); and (3) implement the optimized parameters on actual water samples. Water samples were collected from Long Beach, California and the Gulf of Mexico.

Methanol was chosen as the organic solvent for the SBSE optimization. Our study found that methanol percentages of 50 percent--for n-alkanes—and 30 percent for aromatic hydrocarbons—in diesel rendered the better extraction efficiency from water matrices. For



biodiesel, by 40 percent methanol content, FAMES were sufficiently extracted. For all compounds of all fuels 4 hours rendered the best extraction efficiency for all fuels as a whole.. Our result showed that no pH adjustment was deemed necessary for improving the extraction recovery of water accommodated fraction of fuels. The water accommodated fraction of diesel showed an increased presence of aromatic hydrocarbons when compared to their presence in the diesel pure source in comparison to aliphatic hydrocarbons. Using biofuel (B100) the water accommodated fraction stayed relatively the same between saturated and unsaturated FAMES. The detection limit of the optimized method was estimated to as low as 5ng/L for selected diesel alkanes, 5ug/L for selected diesel aromatic hydrocarbons, 5ppt for saturated hydrocarbons, and 0.1ug/L for unsaturated FAMES. Using the optimized methanol and stir time parameters, water samples from the Gulf coast and the shores of Long Beach, CA were found to contain non-detectable or non-quantifiable levels of diesel constituents.

Results from this study will allow us to potentially analyze the toxicity and degradation of WAFs of diesel and similar fuels in fresh and sea water samples in an efficient and more environmentally conscious manner. Future directions in this research should be aimed towards further implementing this technique and its optimized parameters on actual water samples containing oil and to validate the method before fully applying this technique over other commonly used extraction techniques for the analysis of fuels.

## Table of Contents

Acknowledgements .....	v
Abstract .....	vii
Table of Contents .....	ix
List of Tables .....	xi
List of Figures .....	xiii
Chapter 1: Introduction .....	1
1.1 Crude Oil and Refined Products in our Society .....	1
1.2 Crude Oil and Refined Products in our Environment .....	3
1.3 Extraction Methods for Study .....	4
1.3.1 Liquid-Liquid Extraction (LLE) .....	5
1.3.2 Solid Phase Extraction (SPE) .....	6
1.3.3 Solid Phase Micro Extraction (SPME) .....	7
1.3.4 Stir Bar Sorptive Extraction (SBSE) .....	9
1.4 Research Objectives/ Significance .....	10
Chapter 2: Experimental .....	12
2.1 Materials .....	12
2.2 Field Samples .....	14
2.3 Stir Bar Sorptive Extraction (SBSE) .....	14
2.4. Instrumental Analysis .....	14
2.5 Data Analysis and Quality Control .....	16
2.6 Optimization .....	17
2.6.1 Methanol Optimization .....	18
2.6.2 Stir Time Optimization .....	18
2.6.3 pH Optimization .....	19
2.7 SBSE Water Accommodated Fractions .....	20
2.8 Calibration Curve and Method Detection Limit .....	21
2.9 Field sample analysis .....	21
3.1 Optimization .....	23
3.1.1 Methanol Optimization .....	24

3.1.2 Stir Time .....	31
3.1.4 Optimizations Summary .....	45
3.2 Water Accommodated Fractions (WAFs) .....	45
3.3 Calibration Curve.....	54
3.4 Actual Water Samples.....	58
Chapter 4.....	61
Conclusion .....	61
Appendix.....	63
References.....	112
Vita.....	118

## **List of Tables**

Table 1. ....	13
Table 2. ....	18
Table 3. ....	19
Table 4. ....	19
Table 5. ....	21
Table 6. ....	22
Table 7. ....	45
Table 8. ....	57
Table 9. ....	64
Table 10. ....	66
Table 11. ....	68
Table 12. ....	69
Table 13. ....	70
Table 14. ....	71
Table 15. ....	72
Table 16. ....	73
Table 17. ....	74
Table 18. ....	75
Table 19. ....	76
Table 20. ....	77
Table 21. ....	78
Table 22. ....	79
Table 23. ....	80
Table 24. ....	81
Table 25. ....	82
Table 26. ....	83
Table 27. ....	84
Table 28. ....	84
Table 29. ....	85

Table 30. ....	108
Table 31. ....	109
Table 32.....	112

## List of Figures

Figure 1:.....	1
Figure 2: .....	2
Figure 3:.....	2
Figure 4:.....	6
Figure 5:.....	7
Figure 6:.....	8
Figure 7:.....	10
Figure 8: .....	15
Figure 9:.....	16
Figure 10:.....	17
Figure 11:.....	20
Figure 12:.....	23
Figure 13:.....	24
Figure 14 :.....	25
Figure 15:.....	26
Figure 16:.....	27
Figure 17:.....	28
Figure 18:.....	29
Figure 19:.....	30
Figure 20:.....	32
Figure 21:.....	33
Figure 22:.....	35
Figure 23:.....	36
Figure 24:.....	37
Figure 25:.....	38
Figure 26:.....	39
Figure 27:.....	40
Figure 28:.....	41
Figure 29:.....	42

Figure 30:.....	43
Figure 31:.....	44
Figure 32:.....	47
Figure 33:.....	48
Figure 34:.....	49
Figure 35:.....	50
Figure 36:.....	51
Figure 37:.....	52
Figure 38:.....	53
Figure 39:.....	54
Figure 40:.....	56
Figure 41:.....	57
Figure 42:.....	58
Figure 43:.....	59
Figure 44:.....	60
Figure 45:.....	63
Figure 46:.....	65
Figure 47:.....	67
Figure 48:.....	86
Figure 49:.....	87
Figure 50:.....	88
Figure 51:.....	89
Figure 52:.....	90
Figure 53:.....	91
Figure 54:.....	92
Figure 55:.....	93
Figure 56:.....	94
Figure 57:.....	95
Figure 58:.....	96
Figure 59:.....	97
Figure 60:.....	98

Figure 61:.....	99
Figure 62:.....	100
Figure 63:.....	101
Figure 64:.....	102
Figure 65:.....	103
Figure 66:.....	104
Figure 67:.....	105
Figure 68:.....	106
Figure 69:.....	107
Figure 70:.....	110
Figure 71:.....	111



# Chapter 1: Introduction

## 1.1 CRUDE OIL AND REFINED PRODUCTS IN OUR SOCIETY

Crude oil has been an important resource when it comes to fueling our need for energy. Still, even though there has been increased attention into various alternative resources for energy (Figure 1) the demand for liquid fuel has continued to increase this past decade and is projected to increase well into the year 2035 (1). According to the Energy Information Administration (1), electrical power, buildings, and transportation are the four major sectors that contribute to the increase in crude oil (in Figure 2). Amongst those, the transportation sector is the largest sector having a continued projected increase well into the year 2035. As illustrated in Figure 3, transportation fuels—jet fuel, diesel, and gasoline, in increasing order—are the major refined products from crude oil. With the continued demand of crude oil and its refined products, these fuels will continue being of concern to the environment during their extraction, processing and consumption.

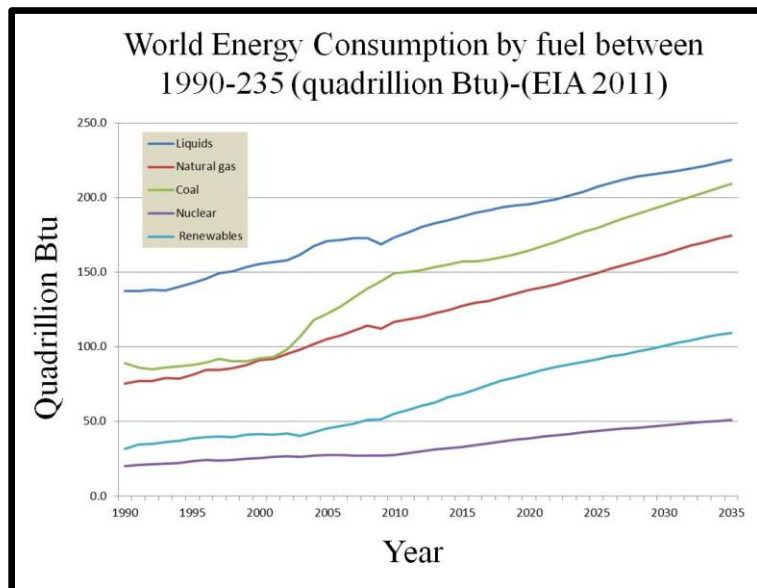


Figure 1: The consumption of various forms of sources for energy and incorporates expectations in to 2035. (1)

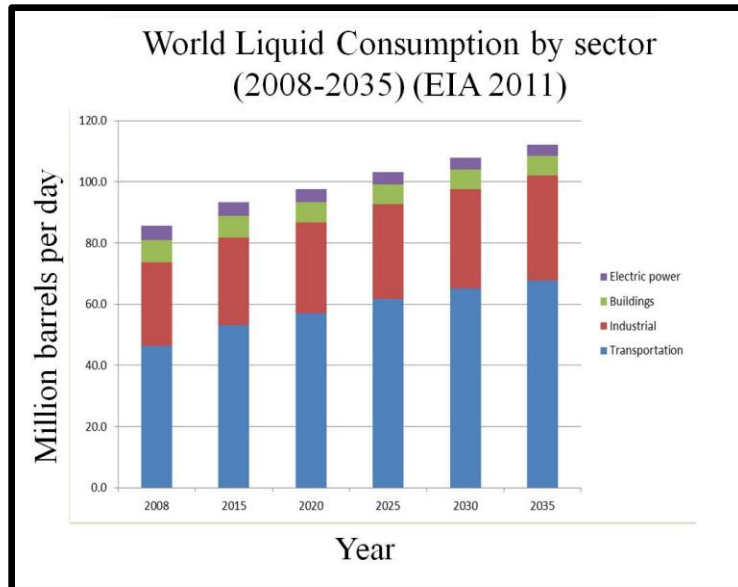


Figure 2: The consumption of fuel by sector. As illustrated, the transportation sector constitutes the largest sector and is expected to increase in EIA's forecasting into 2035. (1)

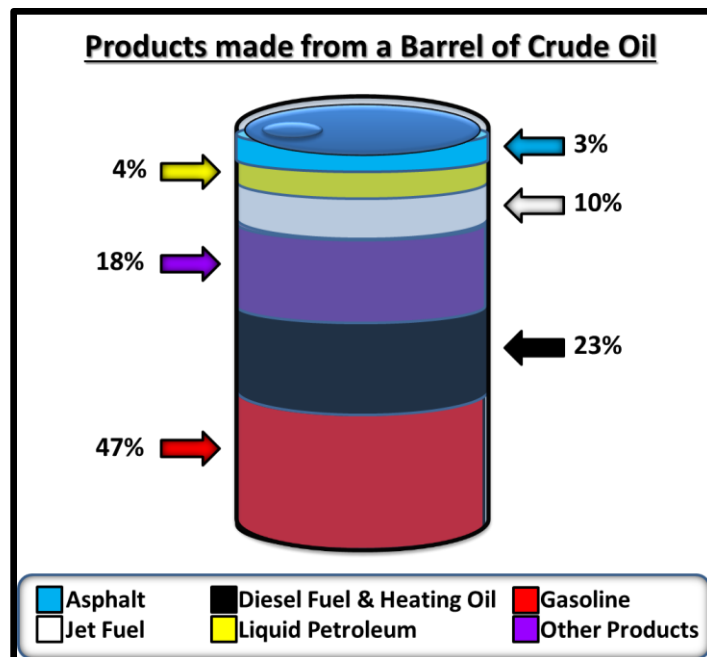


Figure 3 Products made from a Barrel of Crude Oil in the United States. (2)

## **1.2 CRUDE OIL AND REFINED PRODUCTS IN OUR ENVIRONMENT**

Crude oil is a complex mixture of hydrocarbons—alkanes, cycloalkanes, aromatic hydrocarbons, and nitrogen, oxygen, and sulfur containing hydrocarbons—found in certain rock formations in the earth (2). Visually it is a dark liquid that varies in viscosity and is highly flammable (2). Crude oil can be processed into various products other than transportation fuels—such as asphalt, and in synthetic materials (3). During various processes crude oil has a well-documented history of finding its way into the environment one way or another.

It is important to note that oil finds its way naturally into the aquatic environment through natural seepages. In areas such as the northern gulf of Mexico, there has been at least 63 individual seeps identified that release an estimated 40,000 to 100,000 tons of oil per year (4). In places where naturally occurring seepages of oil take place, there are organisms that feed-off from many of the hydrocarbons released and, thus, naturally biodegrade them to more benign molecules. Even though there the release of oil into the aquatic environment can be a naturally occurring event, concern for such a release occurs when large amounts of oil are released (due to a man-made spill) at a specific point in time, and when the spill is done in a location that is not very tolerant of the presence of such compounds where death to various species can occur.

Over our lifetime, the public has been made aware of the impact that crude oil has had in our aquatic environment after a spill (4). Aquatic organisms, such as dolphins and birds, have died due to the direct ingestion of oil, eating aquatic organisms contaminated with oil, and due to starvation (5). Furthermore, studies showed that organisms can experience reproductive problems after the exposure to high level of crude oil. In addition, feathered and furred animals can drown once they are in contact and become coated with oil, making it harder for them to float or swim. The effects of high levels of fuels in the environment are probably one of the major reasons why, once there is an oil spill in the aquatic environment, quick action is needed to “decontaminate” these areas. Many times through the use of booms—to quarantine the fuels while in water—and skimmers—to remove the oil from the water—most of the oil can be

removed. Even though with time, most of the visually noticeable oil is removed, contamination can still be present at low concentrations in the water.

Even if aquatic organisms evade the visual areas of oil, components from these fuels can accommodate themselves in water at low concentrations and still cause negative effects on their health in both short term and long term (6-12). In rainbow trout studies—carried out by Hook et al.—have shown that exposure to crude oil cause negative alterations to expressions in the liver such as processes involving protein synthesis, xenobiotic metabolism, and oxidoreductase activity (10). This also holds true for crude oil refined products. Water accommodated fractions of diesel and gasoline, have shown to pose a similar threat to that of crude oil water accommodated fractions (13-19). To further complicate matters, degradation of fuel constituents in water can lead to further variability in toxicity.

Another factor that should also be taken when studying the toxicity of crude oil derived fuels is their toxicity in more environmentally friendly blends, known as biofuels. Biofuels have gained popularity due to their ability to contribute less greenhouse emissions, their biodegradability, higher combustion efficiency, their renewability, and their potential in decreasing air pollution (20, 21). As Figure 1 illustrates, the use of renewable fuels has been increasing significantly this past decade and is projected to continue increasing in the future. Similar to what studies have shown for crude oil, gasoline, and diesel; biofuels—such as biodiesel—have their own degree of toxicity that has been studied on various organisms (22) (23). Even though there is a lower level of toxicity in biodiesel blends in comparison to diesel, the formation of methanol, for example, can still be lethal to species such as microalgae (23).

### **1.3 EXTRACTION METHODS FOR STUDY**

With the continued probability of previously mentioned scenarios demanding extraction of organic pollutants in water in effective and accurate manner, there has been significant increasing attention given towards developing and implementing environmentally friendly, simple, and efficient analytical methods for the presence of such organic pollutants in the aquatic

environment. This trend is evident through the various extraction techniques that have been developed to extract persistent organic pollutants from water prior to subsequent analysis. Extraction techniques, such as solid phase extraction (SPE), solid phase microextraction (SPME), and stir bar sorptive extraction (SBSE) have become tangible alternatives to the commonly used liquid-liquid extraction (LLE) (24). These techniques have gradually been implemented by researchers and have appeared in published studies for various compounds. A brief description and discussion of the pros and cons of each technique will be discussed.

### **1.3.1 Liquid-Liquid Extraction (LLE)**

Liquid-Liquid Extraction (LLE) is probably one of the oldest extraction techniques in use today. It involves extracting a compound, the analyte, from one solvent to another—a solvent that the analyte is more soluble in (25). For this to work, the solvent that the compound of interest is initially in must be immiscible with the extracting solvent. Once these immiscible solvents are allowed to separate and equilibrate the extracting solvent containing the analyte of interest will be removed. LLE can be repeated using new portions of extracting solvent until the desired recovery of analytes is achieved. For extracting organic pollutants from water, commonly used solvents are hexane, chloroform, acetone, dichloromethane, tert-butanol or a combination of multiple solvents.

After multiple extractions, the researcher is left with a large volume of a highly diluted solution. Not only does the organic solvent pose a potential hazard as described by the solvent's Safety Data Sheet, but further steps—such as concentration and sometimes solvent exchange—are required to obtain a more manageable sample volume and concentration for chemical analysis. It is during these extra steps that there may be significant analyte loss and/or contamination introduced to one's sample. Placing disadvantages aside, advantages of this technique include the ability or flexibility to switch the extracting solvent without major cost and the ability to reuse LLE glassware after cleaning.

### 1.3.2 Solid Phase Extraction (SPE)

Solid Phase Extraction (SPE) involves extracting compounds from an aqueous matrix, by running the liquid—the mobile phase—through a packed column—the stationary phase of a particular polarity (26, 27) There are three common types of SPE packed columns: reverse phase, normal phase, and ion exchange. The procedure to carry-out SPE can be summarized in the following steps: (1) conditioning of concentrating column; (2) passing of the sample through SPE concentrating column; (3) washing rinsing of interferences; (4) elution of compound adsorbed in SPE packing (26)—as illustrated in Figure 4.

The stationary phase, also referred to as a concentrating column, is found inside a cartridge which can be mounted on a manifold (Figure 5). The manifold is connected to a pump to draw the liquid sample through the cartridge at an adjustable flow. Numerous cartridges can run simultaneously depending on the capacity of the manifold. More advanced equipment is commercially available to automate most of the SPE process. Furthermore, different packing or sorbent material is available varying in polarity and space within the packing material to accommodate particular needs.

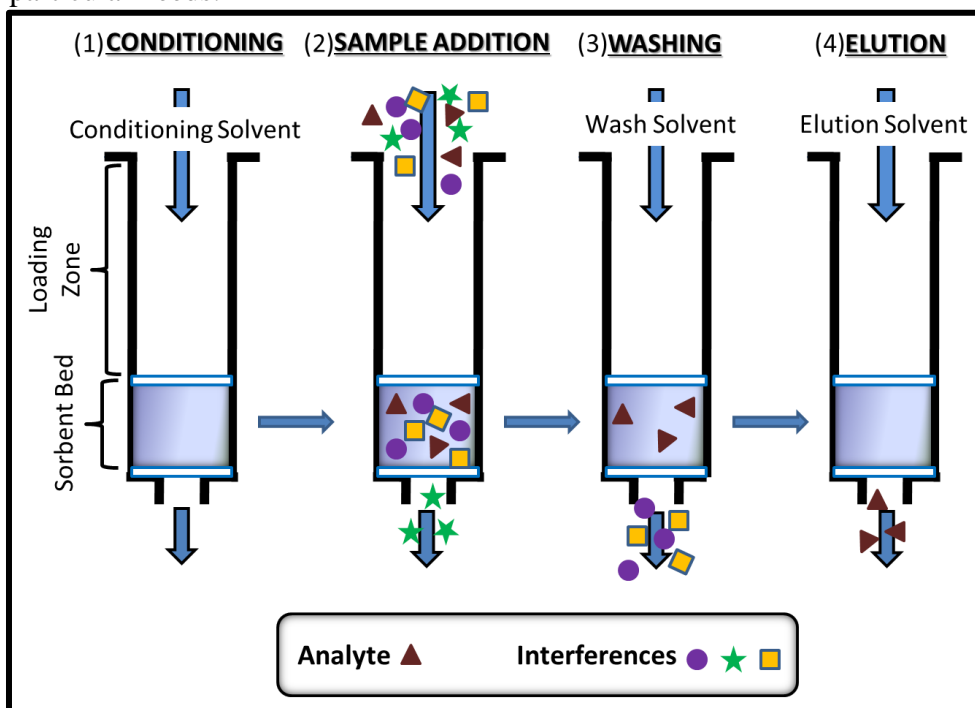


Figure 4: Basic procedures involved in Solid Phase Extraction SPE.

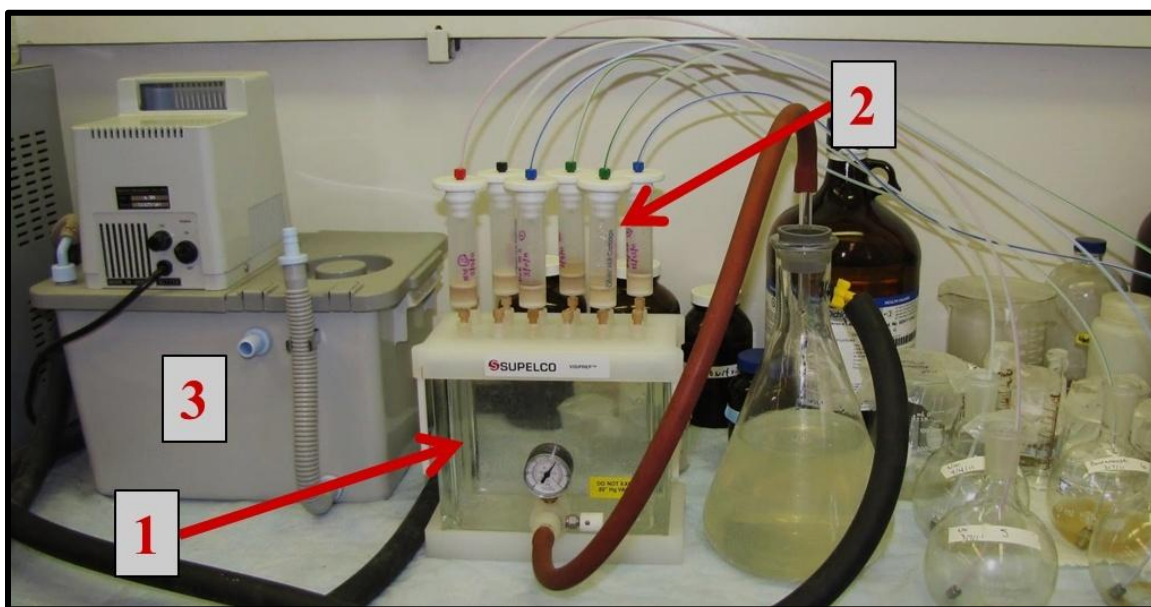


Figure 5: Illustration of the set up for SPE involving SPE cartridges “2” connected to a manifold “1” that is connected to a water vacuum pump “3”.

Some advantages that SPE are that one does not have to deal with incomplete phase separation as may be the case in LLE. SPE also requires less organic solvent. Some drawbacks though are that even though it has been reported that the cartridges can be rinsed clean and reused, SPE cartridges are commonly disposed of after use which, apart from the accruing cost, adds to the waste that must be properly disposed. This extraction technique can be more easily automated but at a considerable cost.

### 1.3.3 Solid Phase Micro Extraction (SPME)

Somewhat similar to SPE, solid phase micro extraction (SPME) also utilizes a solid stationary phase, in a shape of a fiber, to extract chemicals from liquid or gas samples. This SPME fiber is quite thin and has been commonly referred to as an inverted GC capillary column. As is illustrated in Figure 6, a syringe-like device has an extractable fiber-type segment is coated with various polymers depending on the type of compounds to be extracted. This fiber can be either submerged directly into the aqueous matrix or be used above the solution for headspace

extraction. Parameters—such as exposure time, agitation of the solution, temperature, polarity of the fiber and the surface area/thickness of the fiber—play an important role in the efficient recovery of the analyte from the liquid sample. As shown in Figure 6, this method can be carried out in a few steps that can be interpreted as being less laborious than both SPE and LLE. The steps include: (1) Exposing clean SPME fiber to aqueous matrix for a pre-determined amount of time, (2) retracting SPME fiber, and (3) directly injecting the syringe in a GC. This extraction technique has found popularity partly due to its easy set-up, automation capability, and its reusability (28-31).

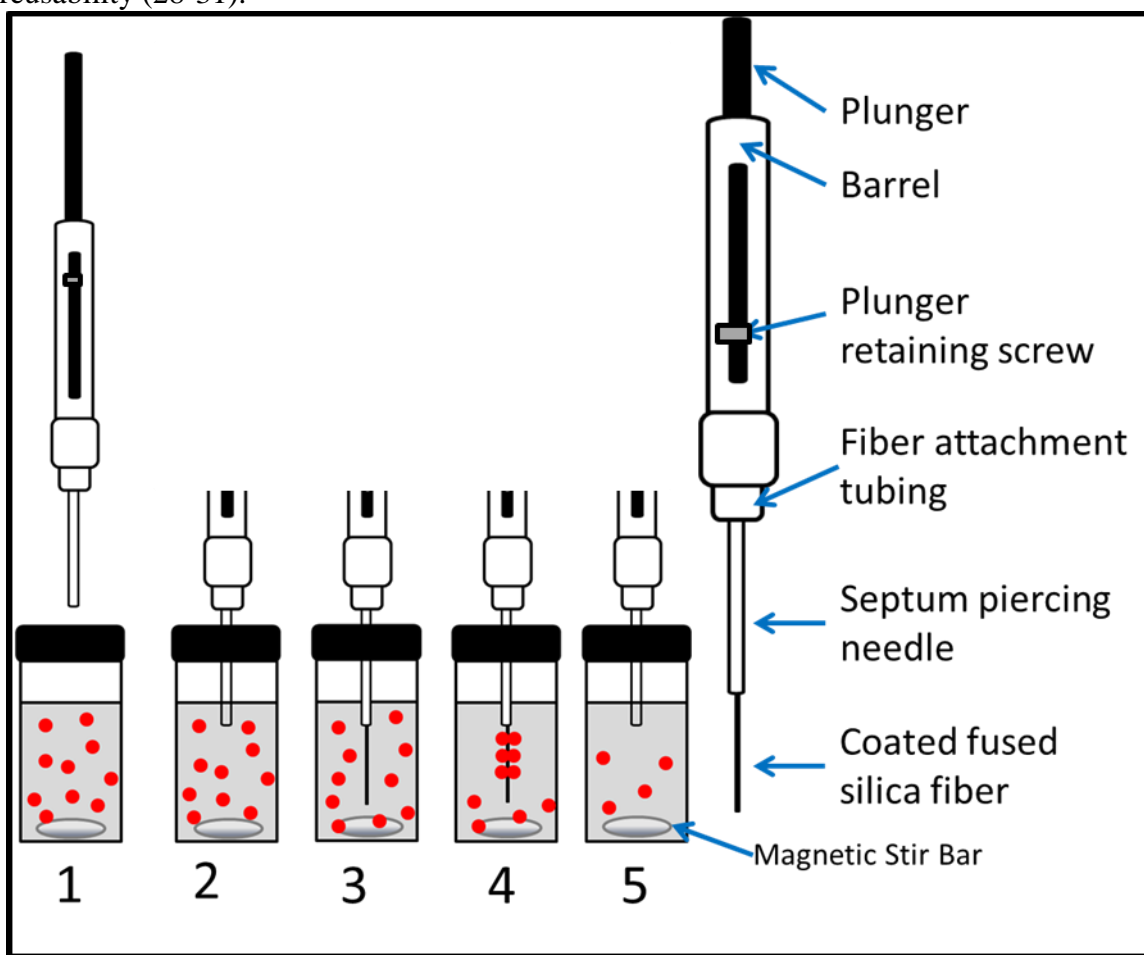


Figure 6: Illustration of a SPME syringe and the basic components and steps involved in SPME. Steps 1 and 2: Syringe-like device is inserted through the septum of a cap until submerged in the aqueous matrix. Steps 3 and 4: fiber is extracted and stir bar is used to agitate the solution to



enhance extraction efficiency. Step 5: Fiber is withdrawn and needle is removed to complete SPME process. (28-31)

After the completion of extraction the syringe is withdrawn, the syringe can be directly introduced into Gas Chromatography instrument where compounds can be thermally desorbed. Compounds can also be desorbed in various specific and effective solvents and then be analyzed by either GC or High Performance Liquid Chromatography (HPLC). Afterwards, syringe and fiber may be reused. The small amount of sample and solvent necessary in this extraction technique and the ability to reuse the fiber and syringe allows this extraction technique to be more environmentally benign than LLE and even SPE. Furthermore, the ability to reuse the SPME fibers cuts down on cost in the long run when compared to SPE. Disadvantages of this method will be that the amount and the extracting area of the sorbent on the fiber is sometimes not large enough to effectively extract analyte to where they can be detected if present at very low concentrations. Furthermore, equipment to automate this technique is not cheap.

#### **1.3.4 Stir Bar Sorptive Extraction (SBSE)**

Stir bar sorptive extraction (SBSE) involves a magnetic stir bar with various coatings—one of the first ones being a polydimethylsiloxane coating (PDMS) as shown in Figure 7 (32) (33). The stir bar or Twister®—as it is commercially known—has similar polymers and capabilities as those found in SPME. A main advantage of SBSE in comparison to SPME is the larger volume of extracting polymer that the stir bar is capable of having. Like SPME, these Twisters® can be reconditioned and reused. Upon the completion of the stirring, the organic compounds are adsorbed onto the stir bar and can then be desorbed in a thermal desorption unit or go through liquid desorption before being analyzed by gas or liquid chromatography. As shown in Figure 7, the SBSE process rivals SPME in efficiency and will be initially expensive when obtaining equipment to automate the process.

As with SPME, even though this extraction technique is relatively new, SBSE has been able to find use in various areas of chemistry as has been numerous mentioned by various

review papers (32-36). Its larger extracting polymer volume, capability of automation, the long term cost of the technique, and the techniques optimizability makes this a viable option when replacing LLE and other techniques as a way to extract organic pollutants from aqueous matrices efficiently and effectively.

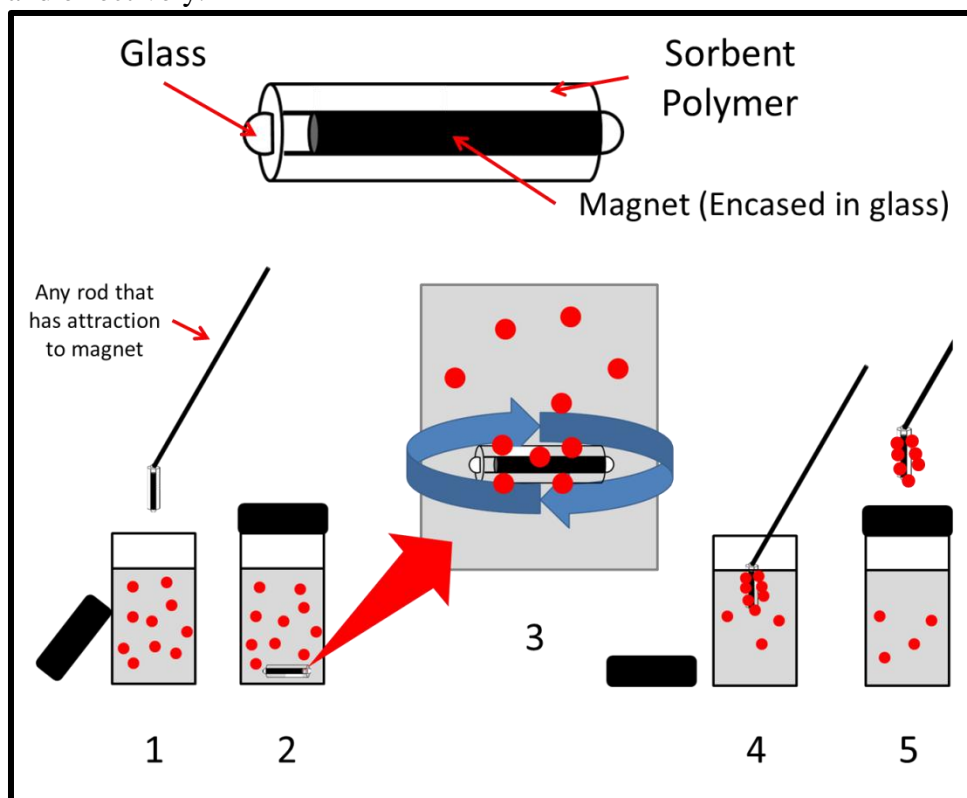


Figure 7: The basic structure of a stir bar and the procedures for SBSE. 1: Stir bar is inserted into aqueous matrix. 2: vial is closed as stir bar drops towards the bottom of the vial. 3: stir bar is placed on stir plate and is stirred at a predetermined time and rate. 4-5: stir bar is then removed and extraction is complete.

#### 1.4 RESEARCH OBJECTIVES/ SIGNIFICANCE

With the accidental release of crude oil and its refined liquid products continuing to pose a threat to the aquatic environment, there is a need to develop analytical capability for investigating their respective hydrocarbons in aqueous matrices by using more environmentally conscious, simple, and sensitive methods. The main objective of this study was to optimize and

implement stir bar sorptive extraction for the analysis of hydrocarbons in the water accommodated fractions (WAFs) of fuels in both sea and fresh water. The fraction of crude oil of focus in this study is diesel due to the wide range of hydrocarbons—various alkanes and aromatic structure—from which results should have implications to the behavior of similar compounds in other fuels such as gasoline or jet fuel. Constituents in biodiesel (B100) were also studied due to their increased use leading to inevitable environmental concern in the near future.

Specific aims in this study include: (1) optimize the SBSE process by investigating certain parameters—solvent content, stir time, and pH. Diesel and biodiesel were used as model fuel types to study their water accommodated fraction (WAF) in model fresh water (MFW, i.e. deionized water) and model sea water (MSW). (2) Compare the composition certain types of WAFs to that of actual fuel—in both MFW and MSW. (3) Use the optimized method to analyze fuel WAF constituents in actual samples from Long Beach and the Gulf Spill for diesel.

## Chapter 2: Experimental

### 2.1 MATERIALS

Aromatic Fractionation Check Standard Mix (Table 1.A), individual FAMES (Table 1.B), and Multi-State Hydrocarbon Window Defined Standard Mix (1.C), were purchased from AccuStandard (New Haven, CT, USA). HPLC grade methanol, sodium chloride, magnesium sulfate, and sodium bicarbonate were purchased from VWR (Radnor, PA, USA). Twisters® (10mm x1mm) were purchased from Gerstel Inc. (MD, USA). Gasoline and diesel were obtained from Western Refinery (El Paso, TX, USA). Vegetable oil derived biodiesel was obtained from Global Alternative Fuels (El Paso, TX, USA); while animal fat derived biodiesel was obtained from Texas Green Manufacturing LLC (Littlefield, TX, USA). Stock solutions of diesel standards were prepared in n-butanol and biodiesel (B100) were dissolved in methanol. Stock solutions of the internal standard, Mirex, were prepared in methanol. Diluted stock solutions of diesel fuel were used for optimizing parameters of SBSE process and were stored in a refrigerator at 4°C. All stock solutions and samples were stored in amber glass containers to avoid photodegradation. Distilled water (MilliQ) was used as the model fresh water (MFW), while the model sea water (MSW) synthetic sea water, was prepared according to the specifications reported by Roy et al. (34).

Table 1: List of different compounds that were included in various standard mixes.

[A] Aromatic Fractionation Check Standard	[B] Methyl Esters in Beef Tallow	[D] Multi-State Hydrocarbon Window Definition Standard
Benzene	Methyl myristate	n-Octane
Toluene	Methyl palmitate	n-Nonane
Ethylbenzene	Methyl palmitoleate	n-Decane
m-Xylene	Methyl stearate	n-Undecane
p-Xylene	Methyl oleate	n-Dodecane
o-Xylene	Methyl linoleate	n-Tridecane
1,2,3-Trimethylbenzene	Methyl linolenate	n-Tetradecane
Naphthalene	<b>[C] Fatty Acid Methyl Esters</b>	n-Pentadecane
Acenaphthylene		n-Hexadecane
Acenaphthene	Methyl caproate	n-Heptadecane
Fluorene	Methyl heptanoate	n-Heptadecane
Anthracene	Methyl octanoate	n-Pristane
Phenanthrene	Methyl nonoate	n-Octadecane
Pyrene	Methyl decanoate	n-Phytane
Fluoranthene	Methyl undecanoate	n-Nonadecane
Benz(a)anthracene	Methyl Dodecanoate	n-Eisocane
Chrysene	Methyl tridecanoate	n-Heneicosane
Benzo(b)fluoranthene	Methyl tetracosanoate	n-Docosane
Benzo(k)fluoranthene	Methyl pentadecanoate	n-Tricosane
Benzo(e)pyrene	Methyl hexadecanoate	n-Tetracosane
Benzo(a)pyrene	Methyl heptadecanoate	n-Pentacosane
Dibenz(a,h)anthracene	Methyl octadecanoate	n-Hexacosane
Benzo(g,h,i)perylene	Methyl 12-Hydroxystearate	n-Heptacosane
Indeno(1,2,3-cd)pyrene	Methyl nonadecanoate	n-Octacosane
	Methyl eicosanoate	n-Nonacosane
	Methyl heneicosanoate	n-Triacontane
	Methyl docosanoate	n-Hentriacontane
	Methyl tricosanoate	n-Dotriacontane
	Methyl tetradecanoate	n-Tritriacontane
		n-Tetratriacontane
		n-Pentatriacontane
		n-Hexatriacontane
		n-Heptatriacontane
		n-Octatriacontane
		n-Tetracontane

## **2.2 FIELD SAMPLES**

Sea water samples from Long Beach, California were collected on November 21, 2012. Louisiana Coast sea water samples were kindly provided by Dr. Ralph J. Portier at Louisiana State University. The samples were kept in a -20°C freezer until analysis.

## **2.3 STIR BAR SORPTIVE EXTRACTION (SBSE)**

All SBSE extractions were carried out in amber 20mL vials with screw caps with Teflon inserts. The following narrative describes the general SBSE procedure. Specificity of the procedures for the experiment is included in section 2.6. After all necessary substances—i.e. water, methanol, fuel, internal standard—are inserted in vial housing the SBSE process, preconditioned stir bars were inserted—one per vial—using tweezers—as shown in Figure 8. Vials were then tightly screwed and stir bars were stirred on magnetic stir plates at 1000 rpm for a predetermined period. Stir bars were then rinsed with distilled water and dried with lint free paper. Each stir bar was inserted into a thermal desorption tube to allow the extracted compounds to be thermally desorbed in a gas chromatograph by way of a thermal desorption unit.

## **2.4. INSTRUMENTAL ANALYSIS**

After the SBSE is carried out, the stir bars were thermally desorbed in a Twister® Desorption Unit (TDU) (Gerstel, US) under splitless mode. The thermal desorption process was programmed as follows: an initial temperature of 50°C, with a ramp of 60°C/min to 270°C, and holding for 10min. Transfer line temperature was set to 275°C. Cryo-fusing occurred in a cryo-injection system (CIS4) using a baffled glass liner with initial temperature of -40 ° C. CIS ramp was set at 12°C/s until reaching 275°C and held for 10 minutes. For GC, HP-5MS column (0.25 mmx30 m x 0.25  $\mu$ m, Agilent, CA, USA) was used. The oven was programmed with an initial temperature of 50°C holding for 5 minutes, ramp of 8°C/min to a final temperature of 300°C and holding for 10 minutes. The carrier gas (ultra-high purity Helium) was set to have a constant flow of 1.2 mL/min. The mass selective detector was operated in a scan mode of 40 to

500 m/z with an electron impact ionization of 70 eV. Target compounds were identified by their fragmentation pattern compared to the database by the National Institute of Standards and Technology's (NIST). An illustration of the instrument and set-up used can be found in Figure 9.

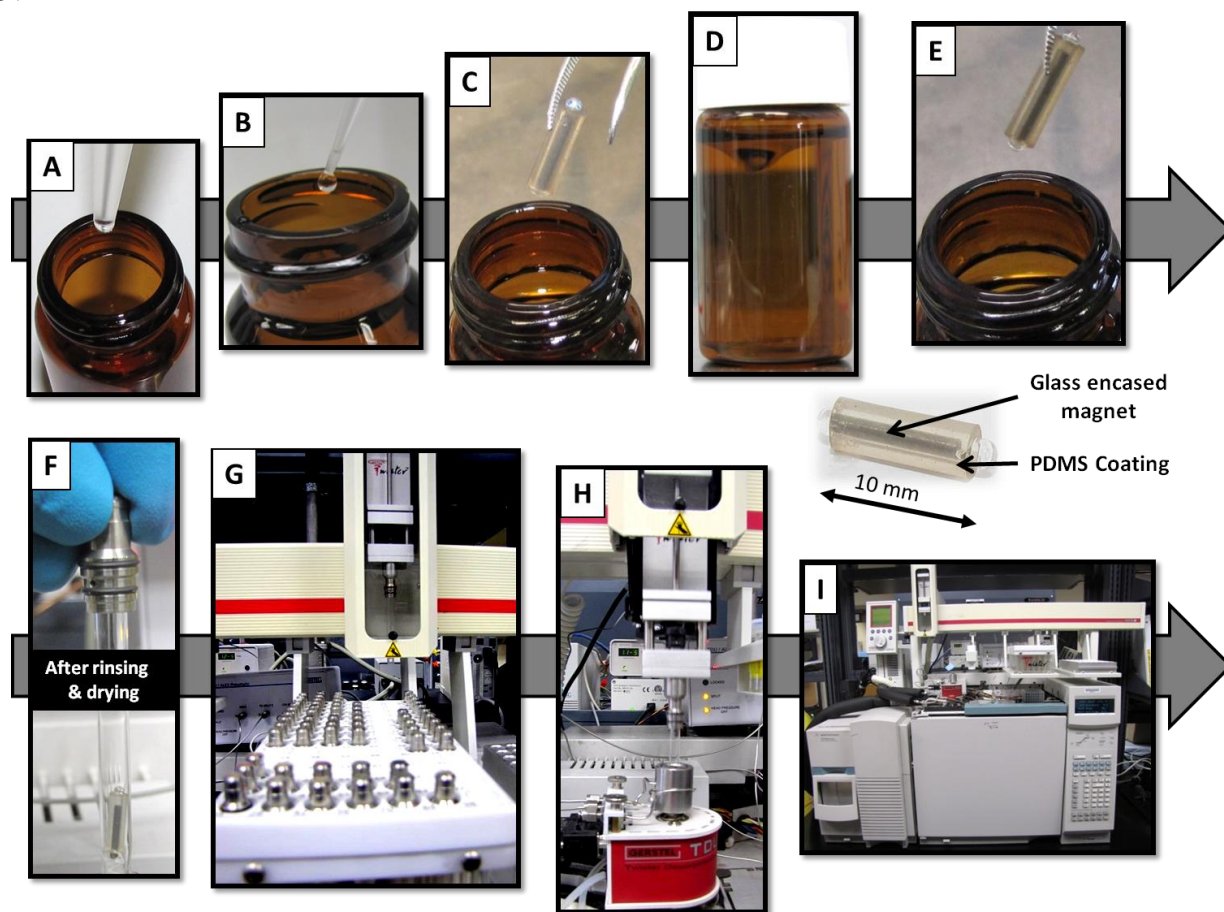


Figure 8: Illustration of basic analytical procedures: (A) Aqueous matrix was added to 20mL vial; (B) internal standard and fuel (only for the optimization and calibration curve) were spiked; (C) Twister® was added; (D) Twister® is stirred using a magnetic plate (SBSE occurs); (E) Twister® is removed and inserted (F) into a Twister Desorption Tube after being briefly rinsed with water and patted dry with a kimwipe; The Twister® is placed in a Tray (G) where it is picked up by the autosampler (H) and inserted into the Twister Desorption Unit (I) before being run on the GC/MS.

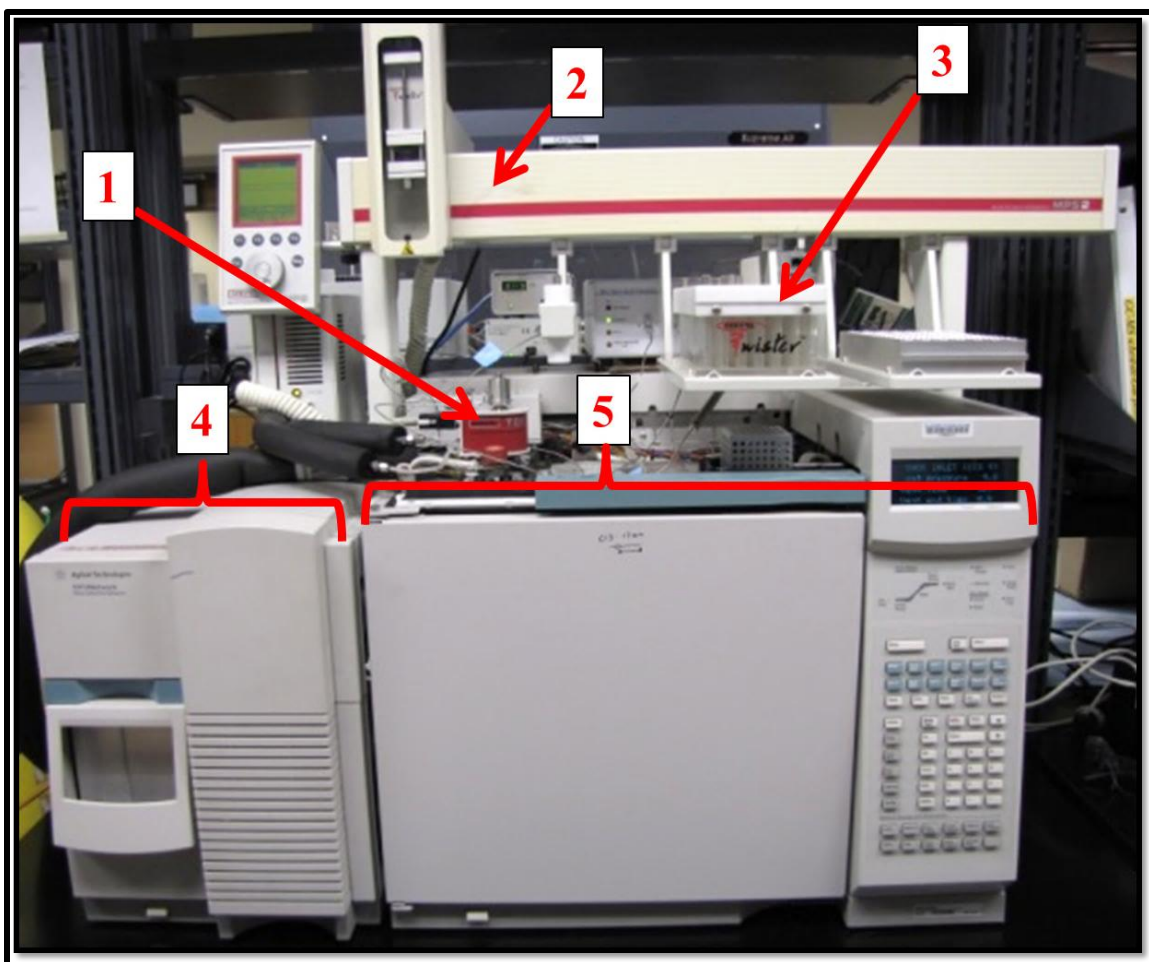


Figure 9: Illustrates the set-up used for this experiment with some major labeled components. (1) Thermal/Twister Desorption Unit (TDU); (2) Autosampler (3) Twister Tray; (4) Mass Selective Detector (MSD); (5) Gas Chromatograph (GC)

## 2.5 DATA ANALYSIS AND QUALITY CONTROL

Data analysis was performed by using MSD ChemStation: Data Analysis Application software, 2003, from Agilent Technologies to integrate various signals from chromatogram. IBM® SPSS® Statistical Software Version 22 was used to calculate significant differences between sets of data. Sets of triplicates done during optimization were taken through the Tukey Test, at 95% confidence interval, after one way ANOVA, to analyze significant difference between means of different treatments.



## 2.6 OPTIMIZATION

Diesel and biodiesel were used for method optimization. Method optimization parameters for the SBSE procedures include methanol content, stir times, and pH. Figure 10 shows the overall scheme of the experimental design for the SBSE optimization process. The best methanol content was used for stir time optimization, while the best stir time and 0 percent methanol content was used for pH optimization. These optimizations were performed for both model fresh water (MFW) and model sea water (MSW).

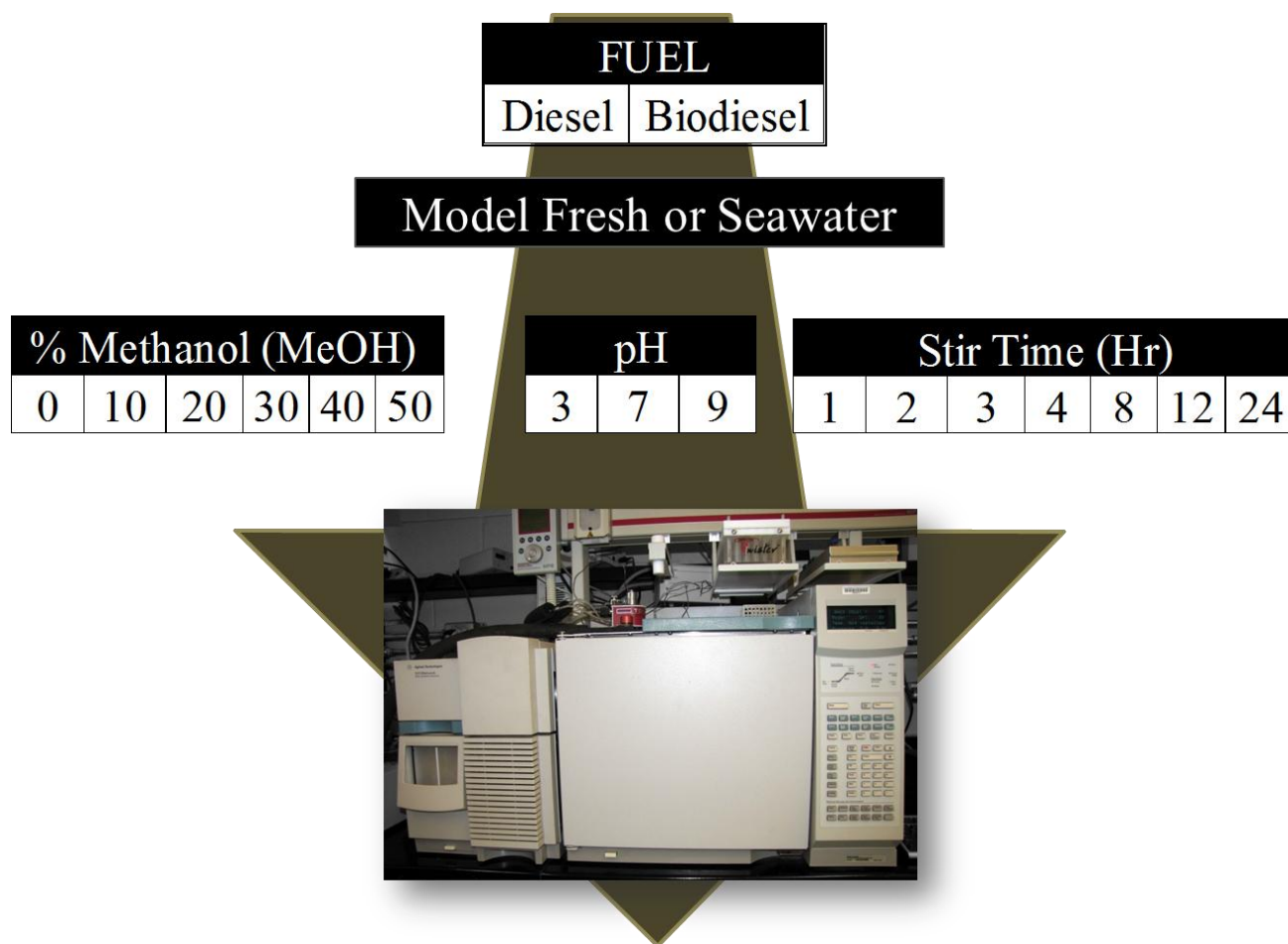


Figure 10: Illustration of the overall design of the SBSE optimization experiment. Methanol content, pH, and stir times varied in values as shown in the diagram. Subsequently, all extracts were taken through thermal desorption prior to chemical analysis by GC/MS.

### 2.6.1 Methanol Optimization

Specific amounts of each fuel (Table 2) were spiked in either the MFW or MSW containing various percentage of HPLC Grade methanol—0, 10, 20, 30, 40 and 50 percent—in replicates. All solutions were prepared to have a final volume of 20mL and the stir bar were added to the each of the solution and stirred for 4 hours. Afterwards, the Twister was removed and analyzed using thermal desorption-gas chromatography/mass spectrometry. Table 2 illustrates the amounts used in further detail.

Table 2: Experimental set-up for methanol content optimization by SBSE. [C]: Concentration of fuel in 20mL of solution; IS: Internal Standard, Mirex; N: without pH adjustment

	Methanol Optimization			
	Diesel		Biodiesel (VB100)	
	MFW	MSW	MFW	MSW
<b>Fuel [C] (ppb)</b>	250	250	2.5	50
<b>IS [C] (ppb)</b>	1	1	1	1
<b>Stir Time (Hr)</b>	4	4	4	4
<b>pH</b>	N	N	N	N
<b>Stir Rate (rpm)</b>	1000	1000	1000	1000
<b>Final Volume (mL)</b>	20mL	20mL	20mL	20mL

### 2.6.2 Stir Time Optimization

Using the methanol content that rendered the best overall recovery of fuel constituents, SBSE was carried out at various stir times—1hr, 2hrs, 3hrs, 4hrs, 8hrs, 12hrs, and 24hrs—to obtain information of the effect of stir time on the recovery of the fuel constituents. Replicates were performed for each fuel and in both MFW and MSW. A detailed illustration of the experimental set-up for each run is shown in Table 3.

Table 3: Experimental set-up for stir time optimization by SBSE. [C]: Concentration in SBSE solution; IS: Internal Standard; N: without pH adjustment

	<b>Stir Time Optimization</b>			
	<b>Diesel</b>		<b>Biodiesel (VB100)</b>	
	MFW	MSW	MFW	MSW
<b>Fuel [C] (ppb)</b>	250	250	2.5	2.5
<b>IS [C] (ppb)</b>	1	1	1	1
<b>Methanol (%)</b>	50	50	50	50
<b>pH</b>	N	N	N	N
<b>Stir Rate (rpm)</b>	1000	1000	1000	1000
<b>Final Volume (mL)</b>	20mL	20mL	20mL	20mL

### 2.6.3 pH Optimization

Due to the inability to pH adjust with 50 percent methanol content, 0 percent methanol content was used during pH optimization as well as the optimum stir time of 4 hours. Experiments were performed under the following pH levels: pH of 3, no adjustment (N), and pH of 9. Afterwards, Twisters ® were analyzed via TD-GC-MS. When no pH adjustment was performed (Labeled as “N”) the MFW had a pH of 6.5, while for the MSW the value was 7.2. Detailed conditions used for pH optimization can be summarized by Table 4.

Table 4: Experimental set-up for pH using SBSE. [C]= Concentration; IS= Internal Standard;

	<b>pH Optimization</b>			
	<b>Diesel</b>		<b>Biodiesel (VB100)</b>	
	MFW	MSW	MFW	MSW
<b>Fuel [C] (ppb)</b>	250	250	100	100
<b>IS [C] (ppb)</b>	1	1	1	1
<b>Methanol (%)</b>	0	0	0	0
<b>Stir Time (Hr)</b>	4	4	4	4
<b>Stir Rate (rpm)</b>	1000	1000	1000	1000
<b>Final Volume (mL)</b>	20mL	20mL	20mL	20mL

## 2.7 SBSE WATER ACCOMMODATED FRACTIONS

Water Accommodated Fractions (WAFs) were prepared by mixing the respective fuel of interest with water at a volumetric ratio of 1 to 9 (fuel to water) in a 500mL amber jars. The mixture was stirred for 18 hours and left to stand for 1 hour in accordance with Ramachandran et al. (35). After allowing the layers to sit out for at least 1 hour, the organic layer was removed by using a pipette. To obtain the water accommodated fraction a pipet was used using the Pasteur pipet as the intermediate or bridge between the WAF and the pipette tip—Figure 11. Only water accommodated fractions of Diesel and Animal Fat derived biodiesel (AB100) were used for the study. Table 4 shows the detailed quantities of WAFs used for SBSE process after WAFs were prepared.

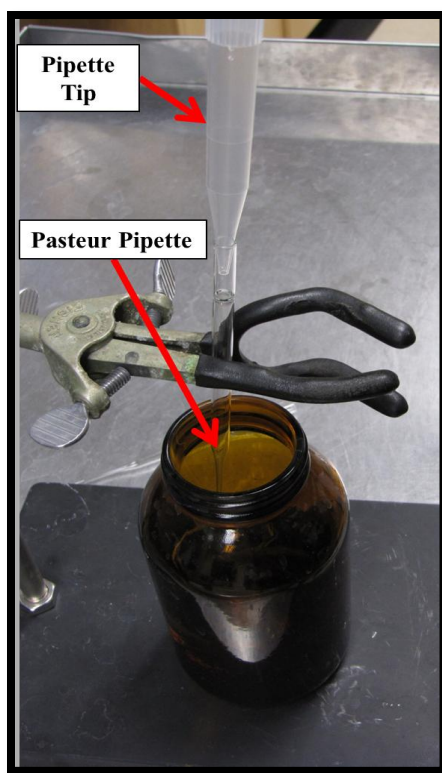


Figure 11: Setup for retrieving the water accommodated fraction (WAF) of fuel prior to SBSE. Pasteur pipette was inserted into the fuel/water mixtures. Pasteur pipette remained in the water layer as another pipette tip withdrew WAF solution.

Table 5: Experimental set-up for the SBSE of WAFs. [C]: Concentration in SBSE solution; IS: Internal Standard; N= without pH adjustment

	WAF Analysis			
	Diesel		Biodiesel (AB100)	
	MFW	MSW	MFW	MSW
<b>WAF Amount (uL)</b>	100	100	100	100
<b>IS [C] (ppb)</b>	1	1	1	1
<b>Methanol (%)</b>	50	50	50	50
<b>Stir Time (Hr)</b>	4	4	4	4
<b>Stir Rate (rpm)</b>	1000	1000	1000	1000
<b>pH</b>	N	N	N	N
<b>Final Volume (mL)</b>	20mL	20mL	20mL	20mL

## 2.8 CALIBRATION CURVE AND METHOD DETECTION LIMIT

Standard solutions of diesel in n-butanol and biodiesel in methanol as mentioned in section 2.1 were prepared. The concentration for diesel standard solution were 0.005 ppb (ug/L), 0.05 ppb, 0.01 ppb, 0.05 ppb, 1 ppb, 5 ppb, 10 ppb, 50 ppb, and 100 ppb and the levels of biodiesel standards were 0.005ppb, 0.05ppb, 0.01ppb, 0.05ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb. The standard solutions were subjected to SBSE—using 50 percent methanol content and a stirring time of four hours. For all points of data, Mirex was spiked before SBSE to obtain a final concentration of 1ppb. Method detection limit was estimated using the lowest level of the target compounds in the standard solutions after subjected to SBSE that could be distinguished by the detector.

## 2.9 FIELD SAMPLE ANALYSIS

To assess the applicability of the optimized SBSE process, two field samples were obtained to search for diesel constituents. One sea water sample was collected from the Long Beach, CA coast, while the other was from the Gulf of Mexico Coast after the Gulf Oil Spill provided by Dr. Portier from Louisiana State University (LSU). Into a 20mL amber vial 10mL of these samples and 10mL of methanol (to achieve a 50 percent methanol solution), and Mirex

(with a final concentration of 1ppb) was added as an internal standard. The solution was stirred at 1000rpm for 4 hours. The stir bar was retrieved as described in the previous sections, and the analytes were analyzed in TDU/GC/MS.

Table 6: Overall scheme of experiments carried out (experimental design) starting with the optimization phase of the SBSE process followed ending with the analysis of actual water samples.

Optimization (for each Model Fresh and Sea water)															
Methanol Content (%)						Stir Time (hours)						pH			
0	10	20	30	40	50	1	2	3	4	8	12	24	1	2	3
Water Accommodated Fractions															
Model Fresh Water Accommodated Fraction								Model Sea Water Accommodated Fraction							
Aromatic vs n-Alkanes				Saturated vs Unsaturated FAMES				Aromatic vs n-Alkanes				Saturated vs Unsaturated FAMES			
Actual Water Samples															
Long Beach, CA								Gulf Coast Water Samples							

## Chapter 3: Results & Discussion

### 3.1 OPTIMIZATION

Similar to other extraction techniques, SBSE has the flexibility of controlling various parameters—such as organic solvent content, stir time and pH—which allows this technique the possibility of being applicable for a wide range of analytes for a wide range of research areas (36) (37) (38). For the optimization component of this study, diesel and vegetable oil derived biodiesel (VB100) were chosen due to the wide variety of compounds present in the matrices. Diesel consists of a variety of both aromatic and aliphatic hydrocarbons (Figure 12) some of which will allow us to develop the optimized method and give us insight on what parameters should be used for other fuels—such as gasoline or jetfuel. For biodiesel, vegetable oil derived biodiesel (VB100) was chosen since both saturated and unsaturated fatty acid methyl esters (FAMES) were detected—Figure 13.

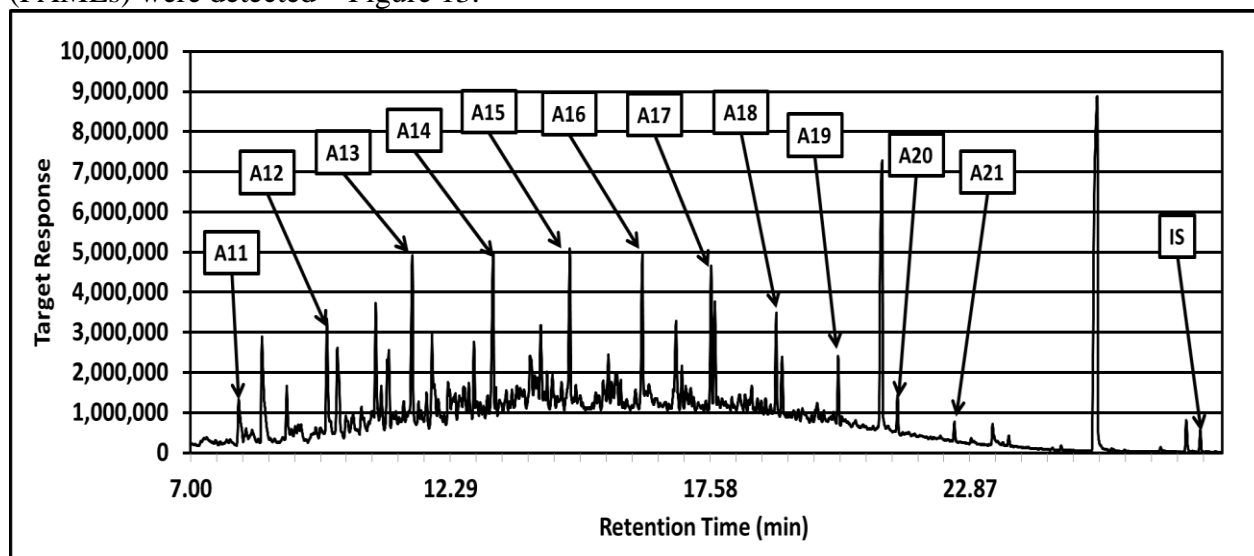


Figure 12: Chromatogram of a diesel sample showing the major n-alkanes studied: undecane (A11), dodecane (A12), tridecane (A13), tetradecane (A14), pentadecane (A15), hexadecane (A16), heptadecane (A17), octadecane (A18), nonadecane (A19), eicosane (A20), heneicosane (A21), and the Internal Standard (IS), Mirex.

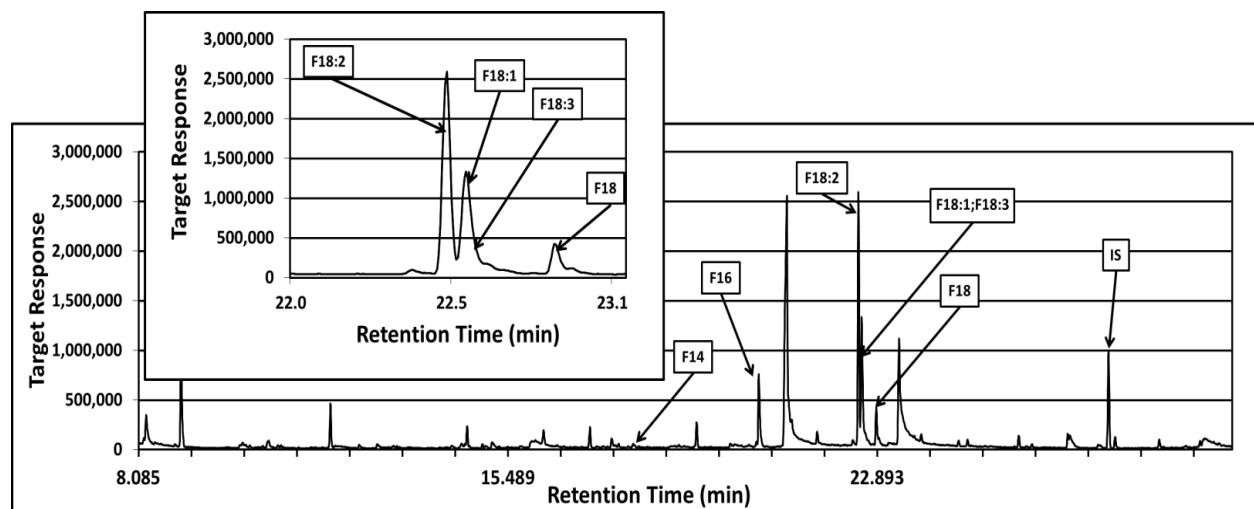


Figure 13: Chromatogram of biodiesel (VB100) showing the following compounds tetradecanoic acid, methyl ester (F14); hexadecanoic acid, methyl ester (F16); octadecanoic acid, methyl ester (F18); 9-octadecanoic acid, methyl ester (F18:1); 9, 12-octadecadienoic acid, methyl ester (F18:2); 9, 12,15-octadecanoic acid, methyl ester (F18:3); and the Internal Standard (IS), mirex.

### 3.1.1 Methanol Optimization

As with several other extraction techniques, the SBSE process is regarded as an equilibrium process of the analyte between the aqueous matrix that the stir bar is in and the polymer-coated on the stir bar. In addition, there are other equilibrium processes that can negatively affect the extraction efficiency of this technique such as the adsorption of the analyte onto the inner walls of the vial housing the SBSE process. For example, less polar compounds are more likely to be adsorbed by the glass walls and thus, may not be as accessible for the extracting polymer. To address this issue, previous studies have added organic solvents that are miscible in the aqueous matrix, such as methanol, to lower the polarity of the matrix; thus, increasing the extraction efficiency of the SBSE process by minimizing the adsorption of analyte on to the inner walls of the vials (33) (32) (39). For this study, methanol compositions of 0, 10, 20, 30, 40, and 50 percent were prepared in model fresh and model sea water to explore the effect of methanol on the extraction of target analyte in for both diesel and biodiesel.



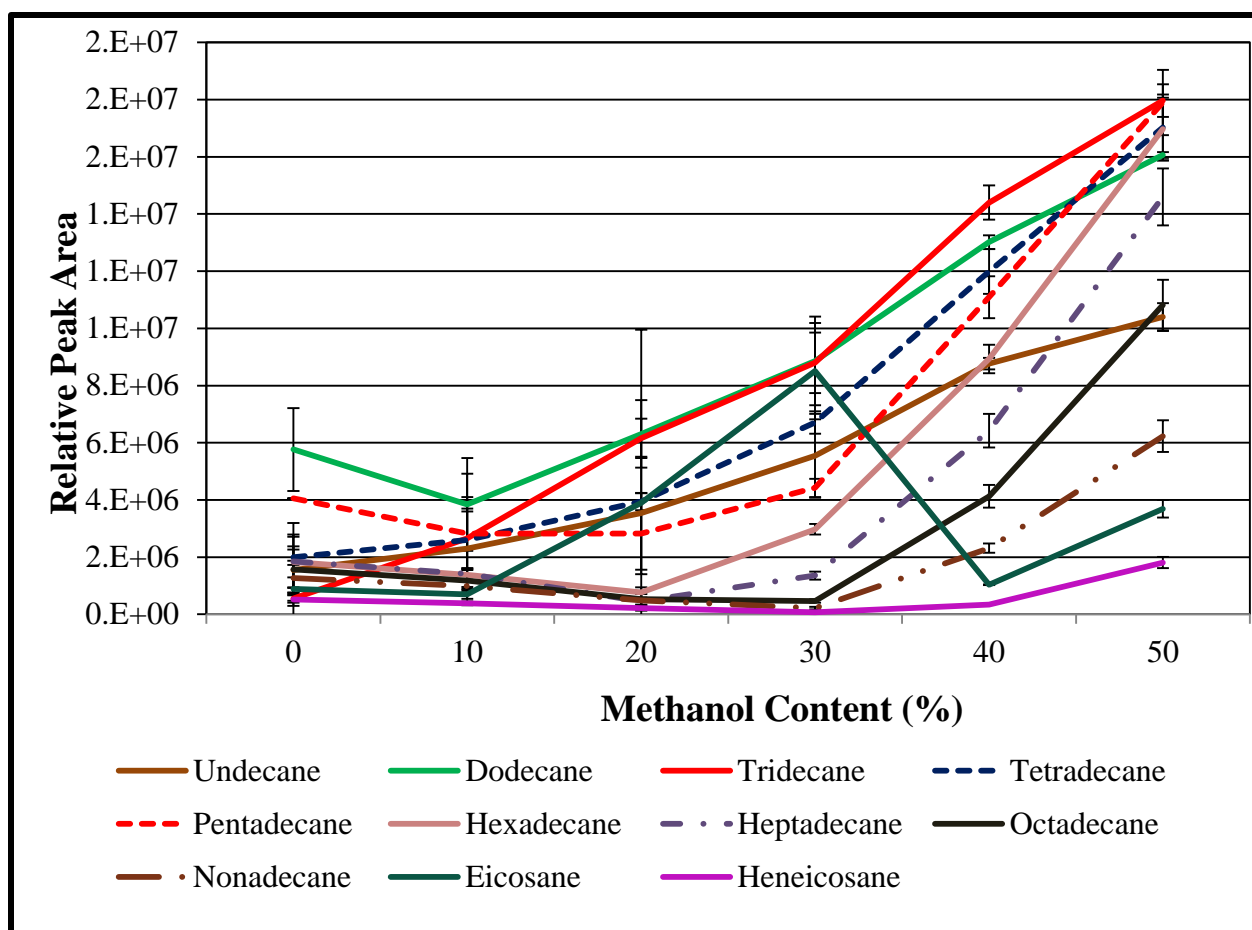


Figure 14 :Relative peak area, i.e. response, of selected aliphatic hydrocarbons found in diesel in MFW obtained from the GCMS under various methanol percentages during the SBSE process. Samples were run in triplicates (n=3) for each treatment.

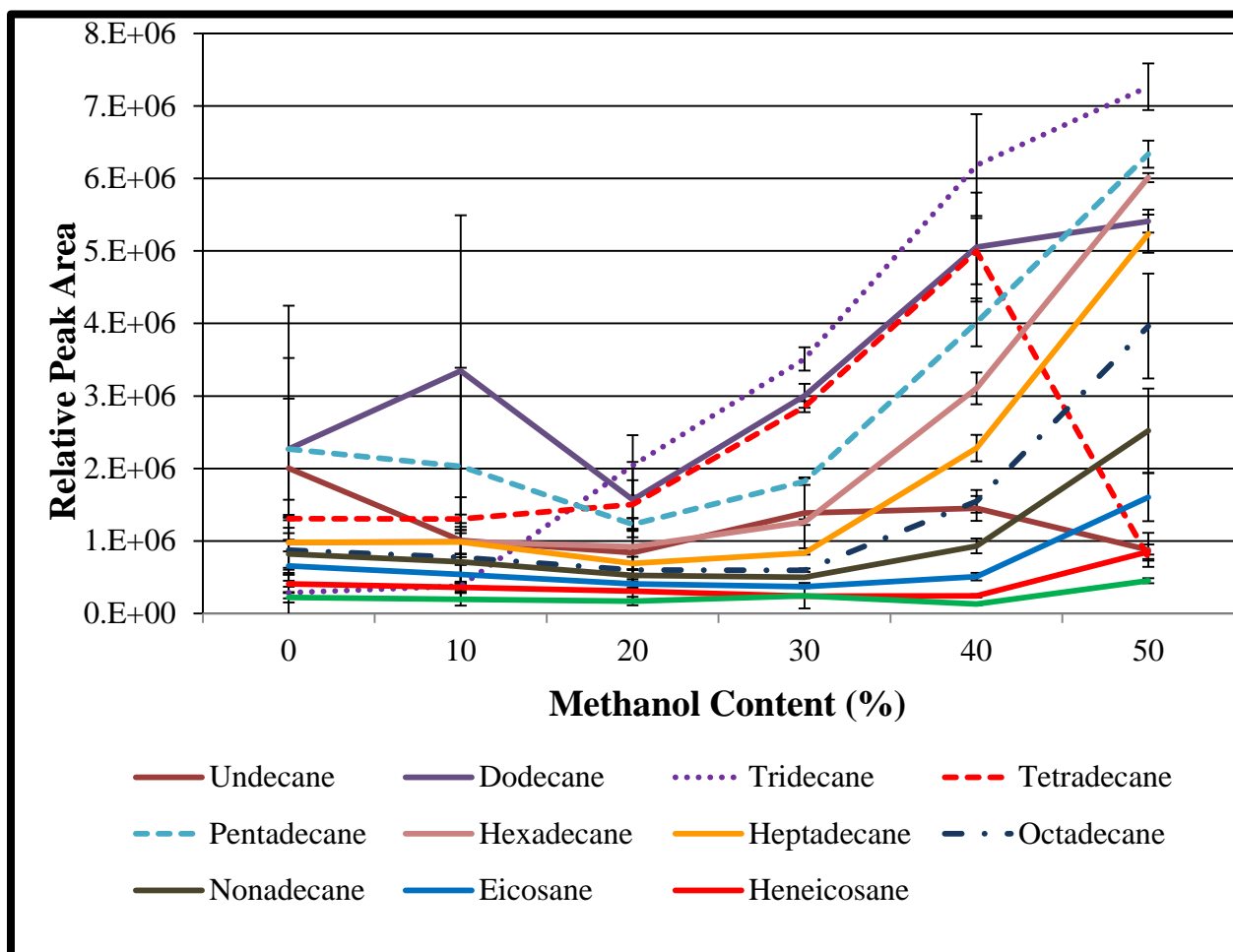


Figure 15: The relative target area of selected aliphatic hydrocarbons found in diesel in MSW obtained from the GCMS under various methanol percentages during the SBSE process. Samples were run in triplicates (n=3) for each treatment.

As shown in Figure 14 and 15, the relative peak areas for selected n-alkanes are plotted against methanol percentages used during the SBSE process in MFW and MSW, respectively. In MFW, Figure 14, for the most part, a positive trend of compounds being extracted with increasing methanol concentration was observed. There are some compounds, eicosane, that follows a rather unique trend as methanol content increases. As of now, a logical explanation for this observed behavior in this compound and others throughout the methanol optimization are

not yet well understood. In MSW, as shown in Figure 15, most n-alkanes are also showing an increase extraction with increasing methanol percentage. As explained previously, this is likely due to compounds adsorbing less on the inner glass walls of the vial with increasing methanol percentage due to the decrease in polarity of the matrix. As shown in Table 11 and Table 12 (Appendix), there is a significant difference at a 95 percent confidence interval in extraction recovery of most compounds in 0 percent and 40 and 50 percent methanol.

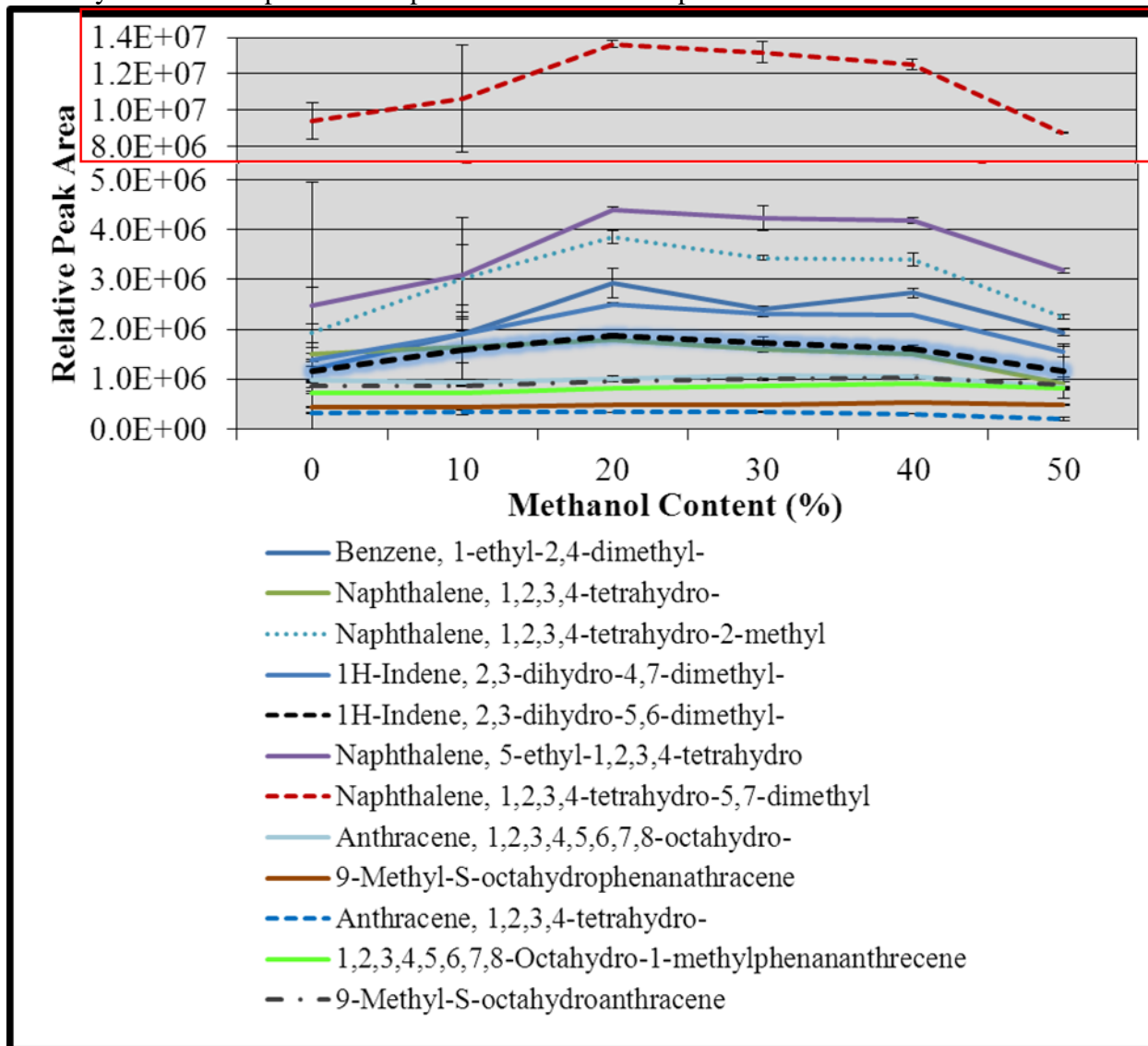


Figure 16: The relative target area of selected aromatic hydrocarbons found in diesel in MFW obtained from the GCMS under various methanol percentages during the SBSE process. Samples were run in triplicates (n=3) for each treatment.

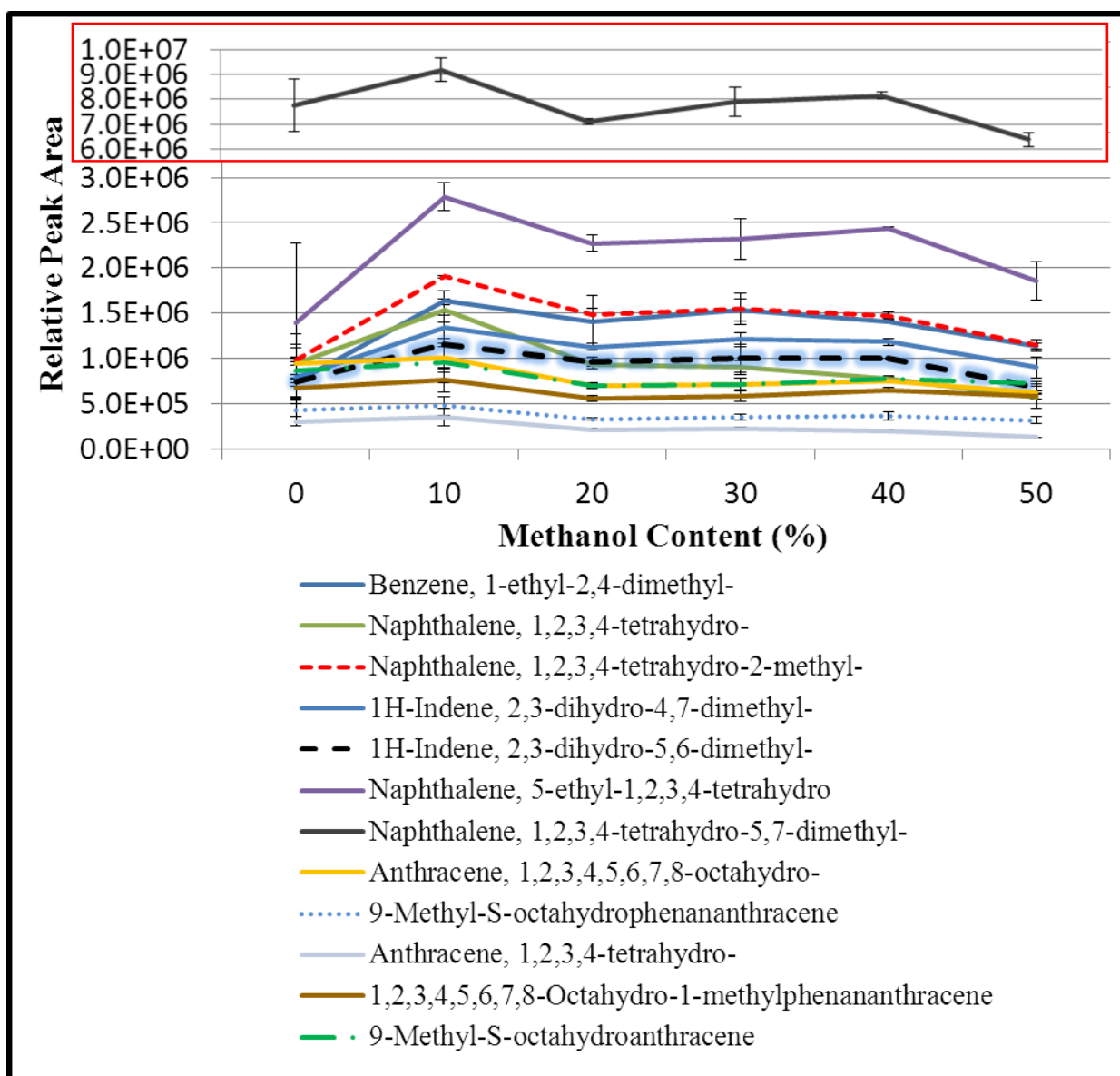


Figure 17: The relative target area of selected aromatic hydrocarbons found in diesel in MSW obtained from the GCMS under various methanol percentages during the SBSE process. Samples were run in triplicates (n=3) for each treatment.

Figure 16 and Figure 17 shows a variety of trends for selected aromatic hydrocarbons from diesel in MFW and MSW. As shown in Table 13 and Table 14 (Appendix), significant differences in extracting aromatic hydrocarbons were not observed between methanol treatments. Given the aromatic compounds have delocalized electrons density due to the presence of double bonds, it is not surprising that these compounds are less likely to be adsorbed by the glass walls

of the vial when compared to alkanes. Some functional groups in these aromatic compounds, being hydrophilic, also aid in its solubility in a polar matrix. This similar behavior can be noticed in the research conducted in our lab, where the addition of too much methanol can render slightly negative extraction efficiency starting at 50 percent methanol content (39).

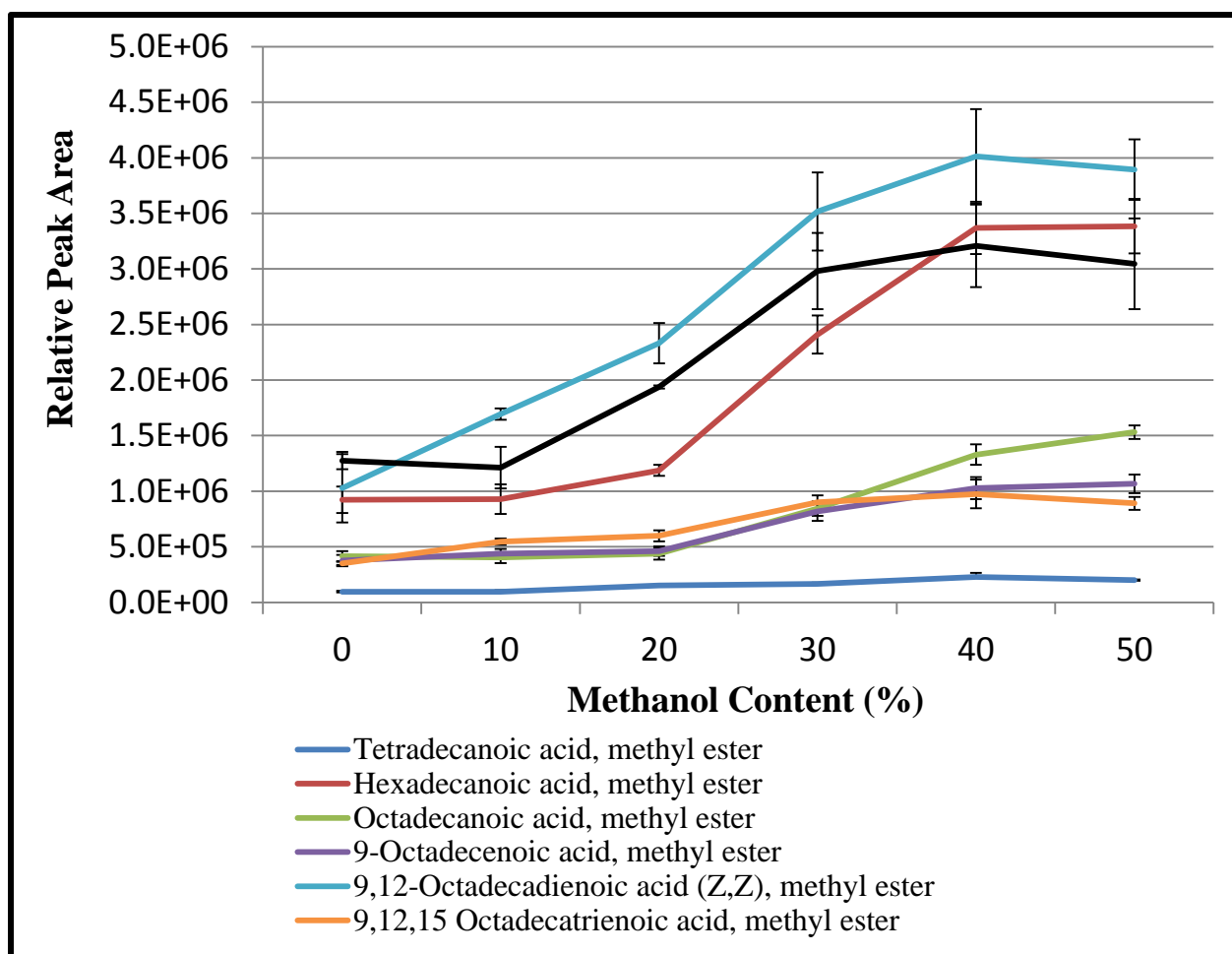


Figure 18: The relative target area of selected FAMEs found in vegetable oil derived biodiesel (VB100) in MFW obtained from the GCMS under various methanol percentages during the SBSE process. Samples were run in triplicates (n=3) for each treatment.

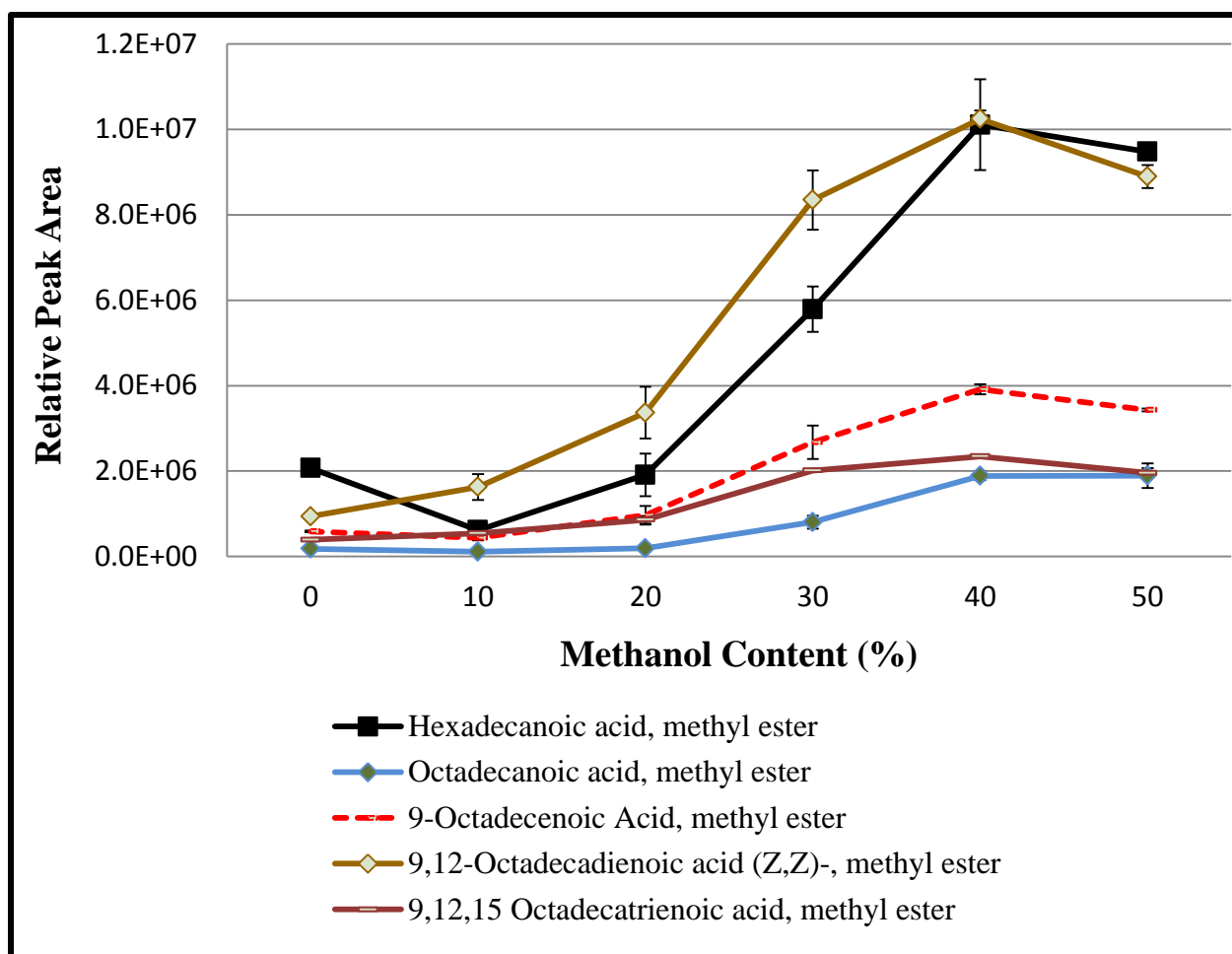


Figure 19: The relative target area of selected FAMES found in vegetable oil derived biodiesel (B100) in MSW at obtained from the GCMS after various stir times during the SBSE process. Samples were run in triplicates (n=3) for each treatment.

Figure 18 and Figure 19 show the relative response peak area from GC/MS of selected fatty acid methyl esters (FAMES) in vegetable derived biodiesel at different methanol concentration in MFW and MSW, respectively. In MFW, the amount extracted of FAMES reached the highest value for most compounds at 40 percent methanol content. For MSW, 40 percent methanol also shows the best extraction efficiency for the FAMES in biodiesel. 50 percent is also giving us about the same value for both MFW and MSW; nevertheless, 40 percent would allow higher amount of actual water samples to be used, therefore, may offer better method detection limits when comparing it to a sample containing 50 percent methanol content. As shown in Tables 15 and 16 (in Appendix), significantly higher recovery of FAMES in MFW and MSW were observed with the addition of methanol.

### **3.1.2 Stir Time**

Another parameter for method optimization was the length of stirring time at which the SBSE process was implemented (24) (32) (33). There are certain factors that can influence the time at which equilibrium is reached during SBSE such as stir rate and temperature. For this experiment stir times of 1, 2, 3, 4, 8, 12, and 24hrs were tested at a stir rate of 1000 rpm for MFW and MSW for each diesel and vegetable oil based biodiesel.

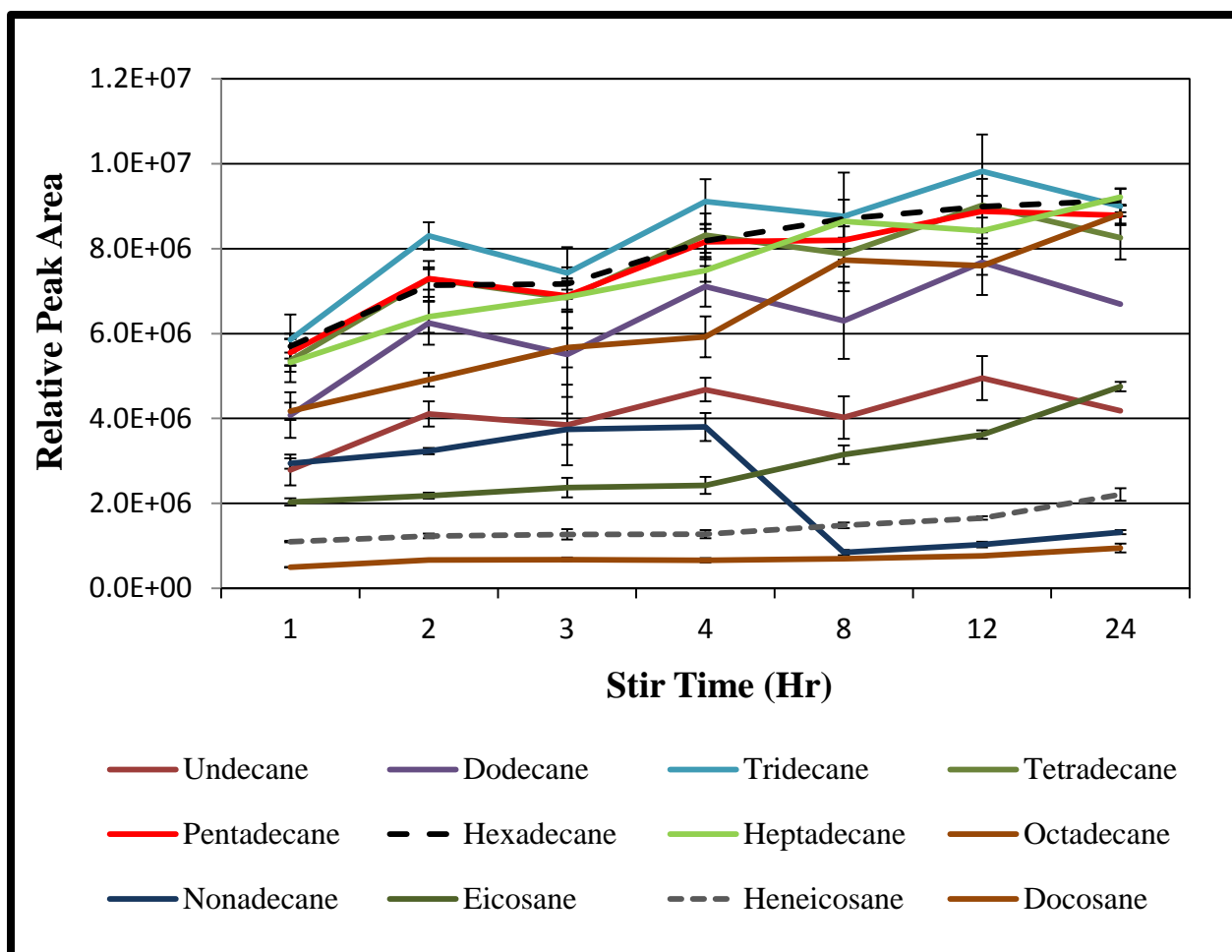


Figure 20: The relative target area of selected aliphatic hydrocarbons from Diesel in MFW obtained from the GCMS after carrying out SBSE at different stir times. Samples were run in triplicates (n=3) for each treatment.



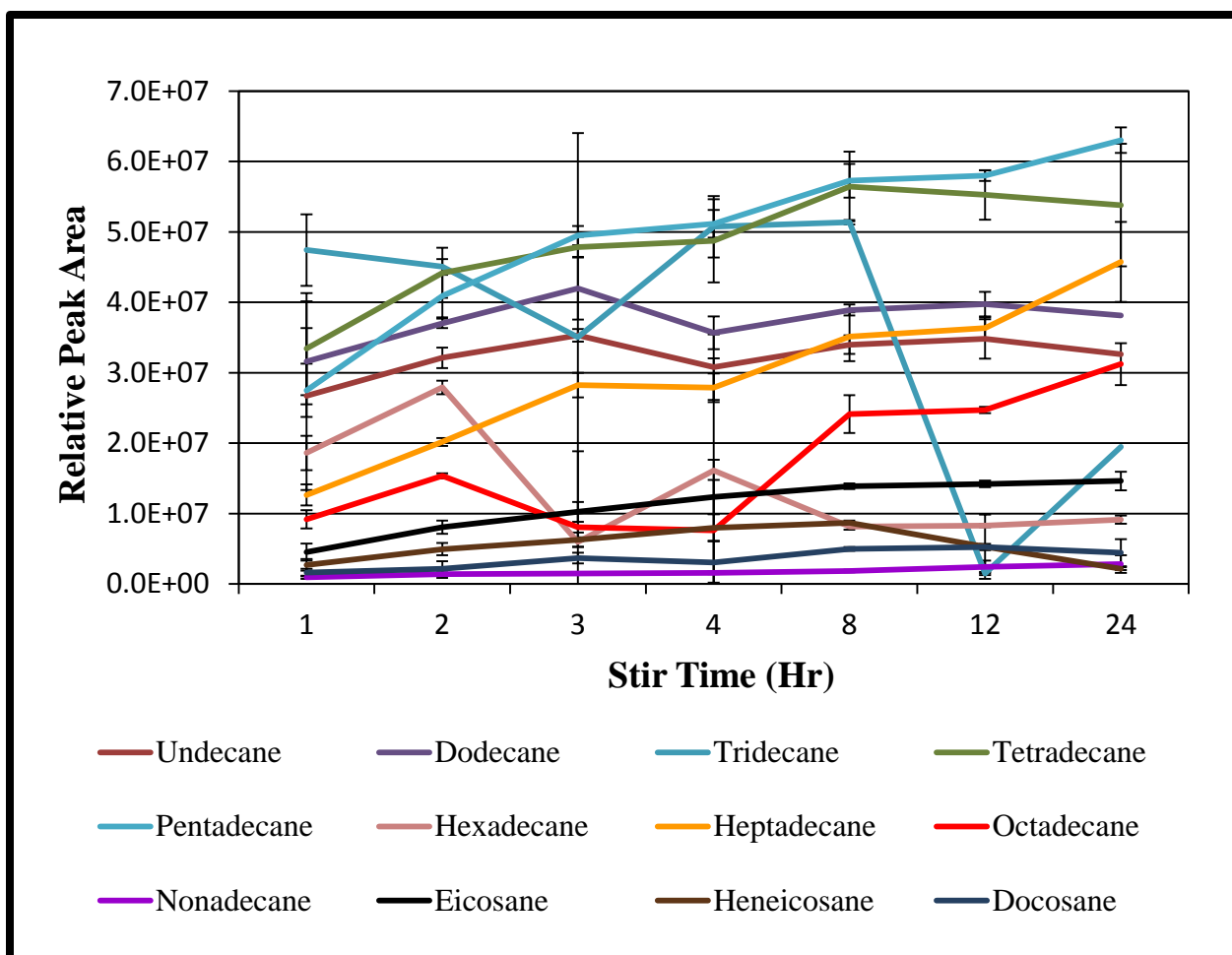


Figure 21: The relative target area of selected aliphatic hydrocarbons from Diesel in MSW obtained from the GCMS after carrying out SBSE at different stir times. Samples were run in triplicates (n=3) for each treatment.

Figure 20 and 21 show the relative peak area of aliphatic hydrocarbons from diesel at different stir times—1, 2, 3, 4, 8, 12, and 24 hours—in MFW and MSW, respectively. In MFW, the results seem to suggest an increasing trend for selected n-alkanes as the stir time reaches 24 hours; the significant improvement in extraction efficiency among the analytes generally occurred after 4 hours of stirring (Table 17 in Appendix). For MSW there were no trends observed for the extractions of hydrocarbons in diesel. The 2 hours or 4 hours of stirring time could potentially be considered a better choice as good stir times for most compounds. According to the statistical analysis shown in Tables 17 and 18 (in Appendix), it can be noticed

that differences between various compounds are not all significant in MSW until arguably 4 hours. As was the case during the methanol optimization, there are numbers compounds that do not follow expected trends. This can be seen in throughout various compounds in MSW and nonadecane in MFW. Throughout the SBSE process, it is understood that there is an equilibrium process between the PDMS coating and the aqueous environment that is continuous and cause small fluctuations in amount extracted over time, but more work needs to done to understand compounds that do not follow a consistent trend.

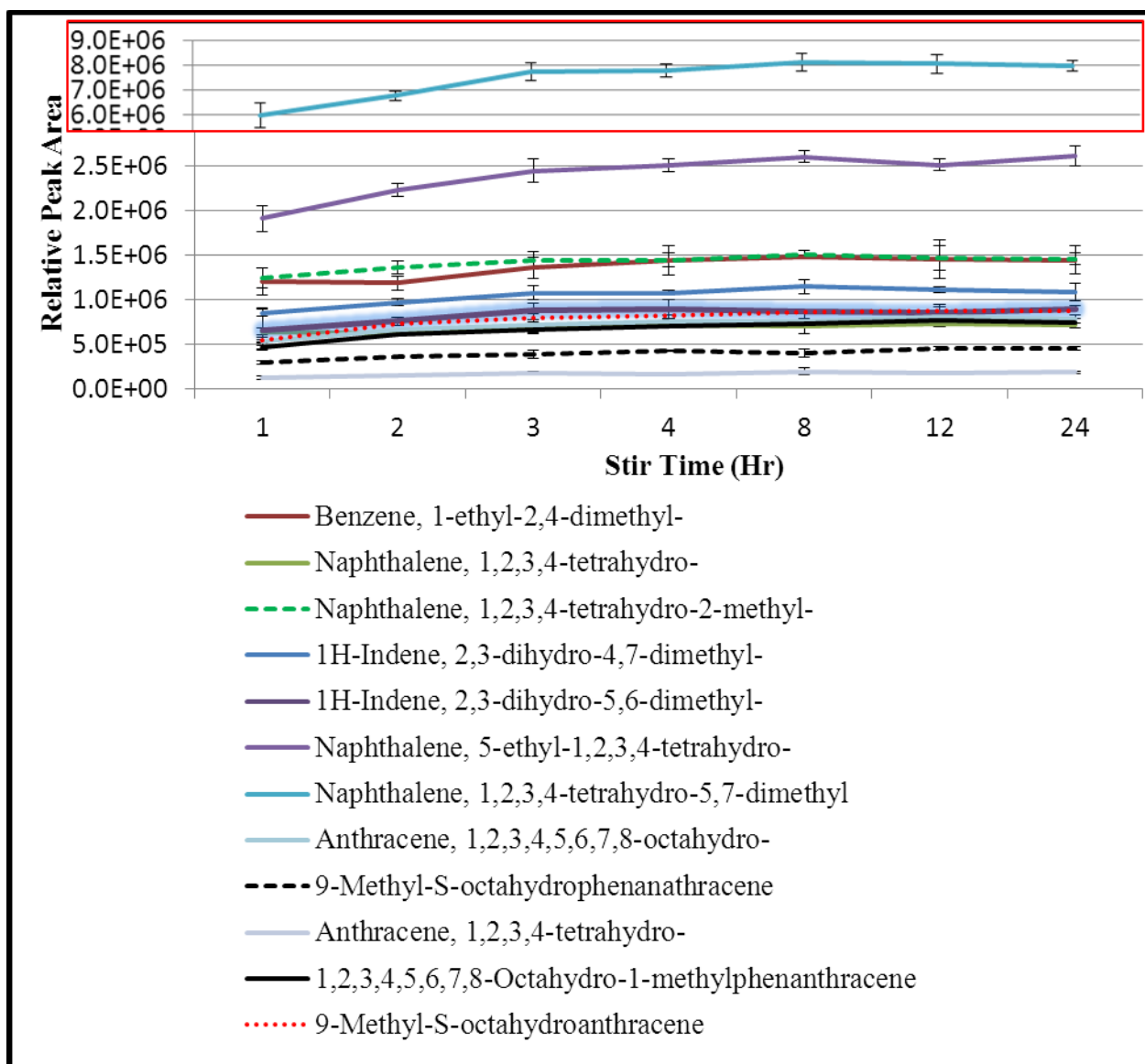


Figure 22: Relative target area of selected aromatic hydrocarbons from Diesel in MFW obtained from the GCMS after carrying out SBSE at different stir times. Samples were run in triplicates (n=3) for each treatment.

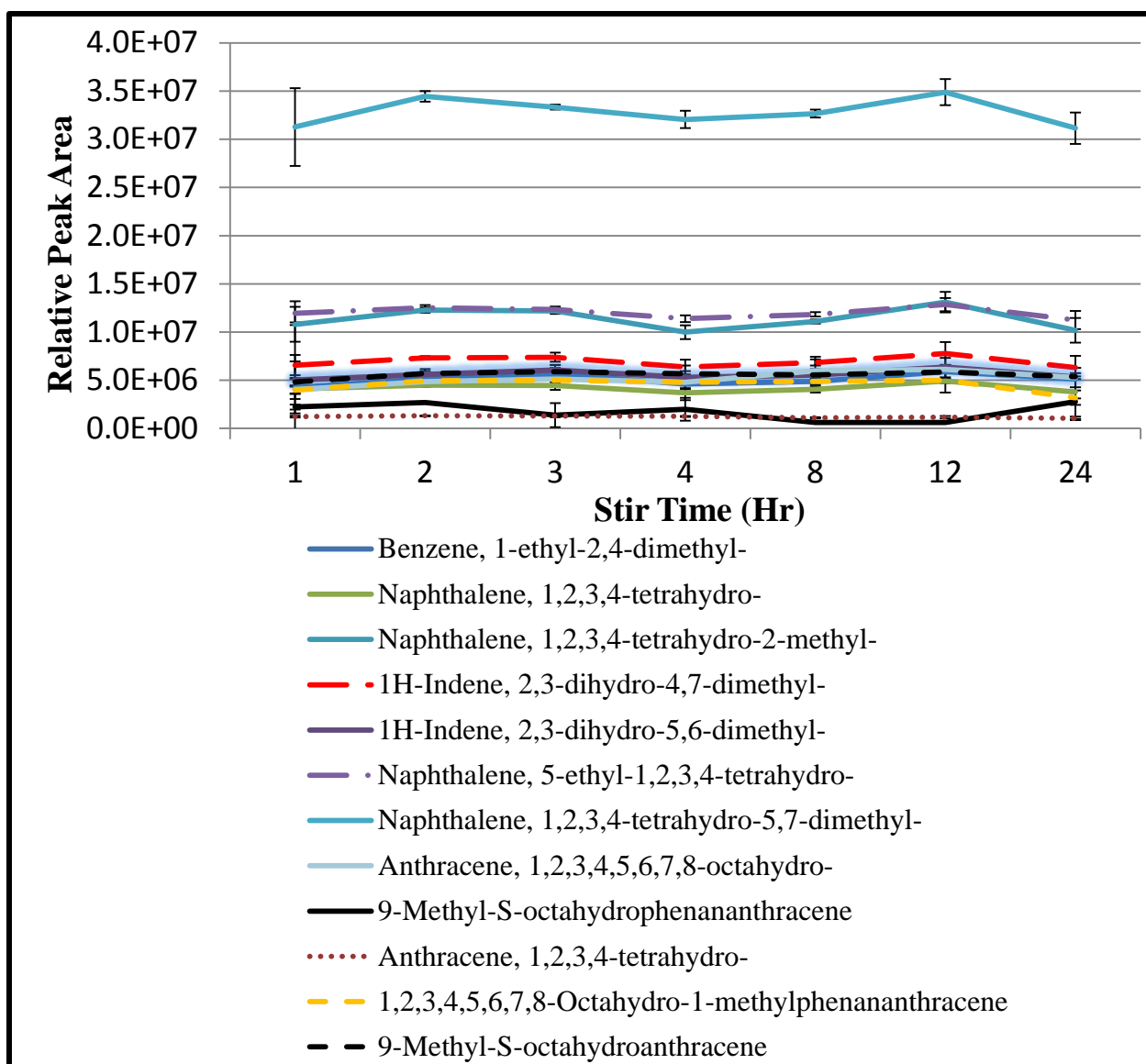


Figure 23: The relative target area of selected aromatic hydrocarbons from Diesel in MSW obtained from the GCMS after carrying out SBSE at different stir times. Samples were run in triplicates (n=3) for each treatment.

Figures 22 and 23 show the relative peak area of selected aromatic hydrocarbons in diesel at different stir times in both MFW and MSW. Unlike the trend observed in the relative peak area of n-alkanes at different stirring times, equilibrium of selected aromatic hydrocarbons is showing to be reached after 3 hours in MFW and 2 hours in MSW. After 2 and 3 hours, the stirring time did not seem to improve the recovery of these compounds. Looking at statistical

differences between stir times of these selected aromatic compounds in MFW and MSW—Table 19 and 20 (Appendix)—the recovery of 11 out of 13 aromatic compounds in MFW showed significant increase at 3 or 4 hour stirring; while the stirring time is 12 hours only affected the recovery of 1 out of 13 compounds in MSW.

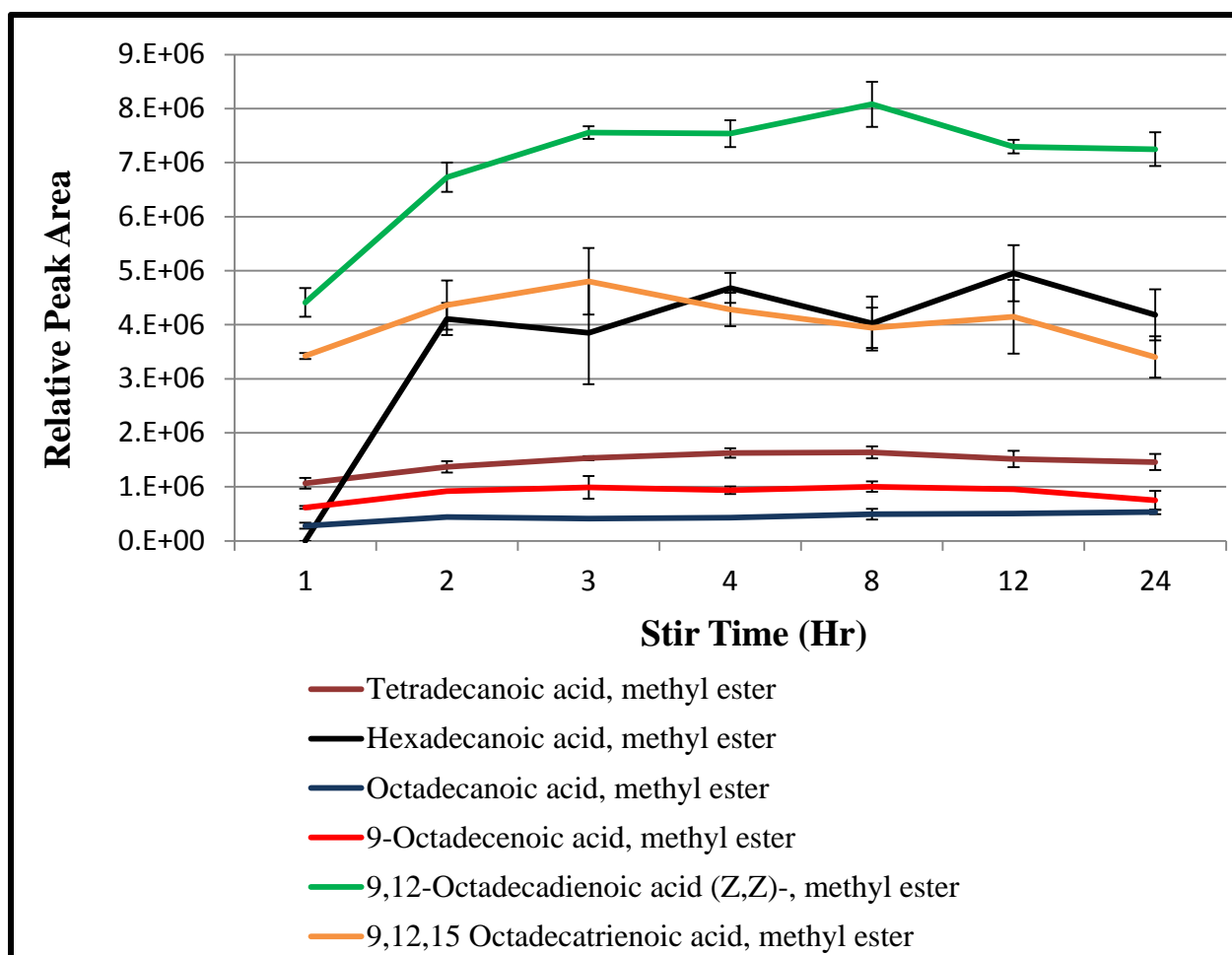


Figure 24: The relative target area of selected FAMES found in vegetable oil derived biodiesel (B100) in MFW obtained from the GCMS after carrying out SBSE at different stir times. Samples were run in triplicates (n=3) for each treatment.

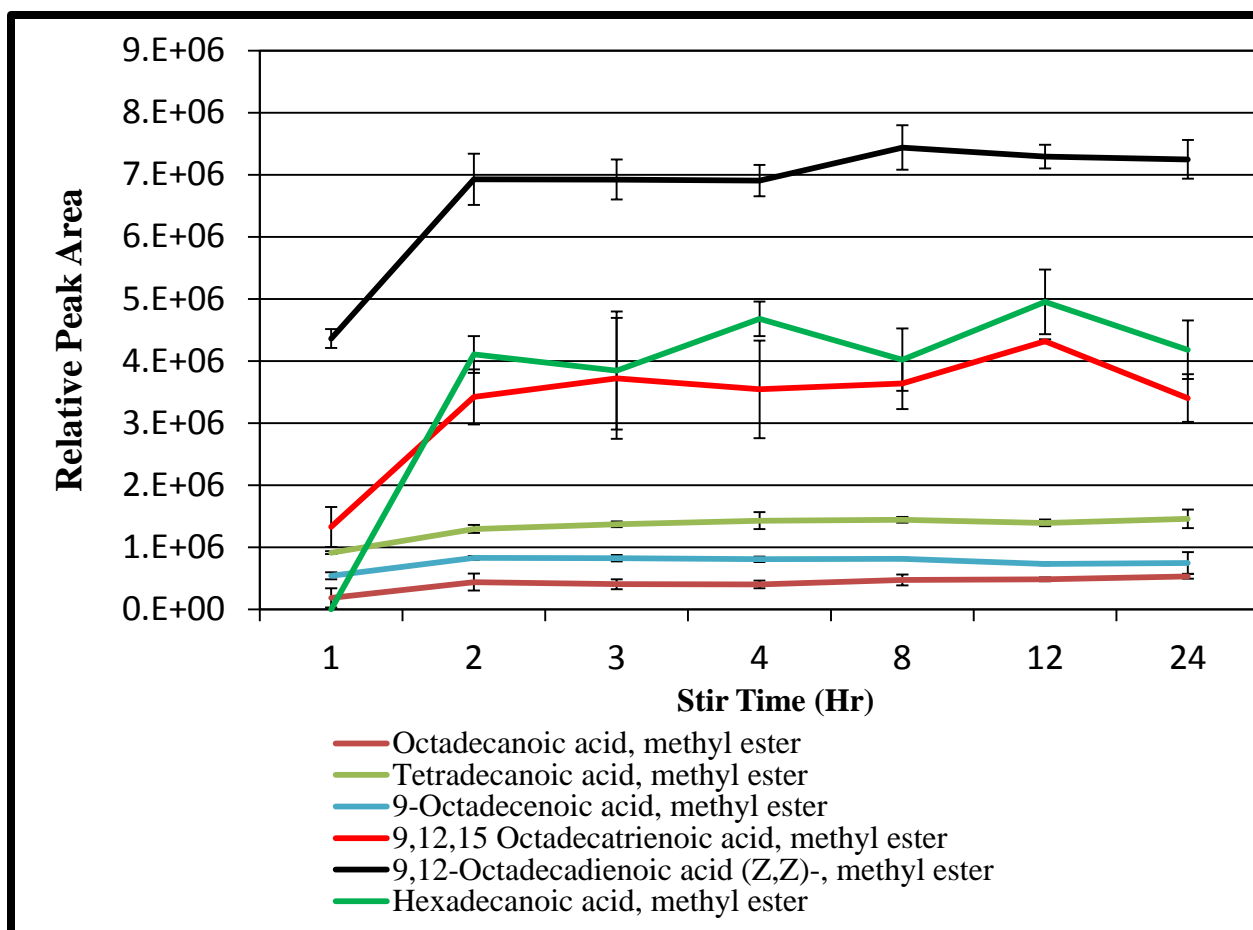


Figure 25: The relative target area of selected FAMES found in vegetable oil derived biodiesel (B100) in MSW obtained from the GCMS after carrying out SBSE at different stir times. Samples were run in triplicates (n=3) for each treatment.

Results for the SBSE stir time optimization of biodiesel in MFW and MSW are shown by Figures 24 and 25. The recovery for most FAMES in MFW have a significant increasing trend up until 2 hours, after which their extraction decreases or increases by small amounts (Table 21-22 in Appendix). Therefore, it is determined that 2 hours is adequate stirring time for equilibrium to be reached in the SBSE of biodiesel in MFW. For MSW, according to Figure 25, there is a similar pattern where, by 2 hours, equilibrium is reached.

### 3.1.3 pH

For the polydimethylsiloxane (PDMS) coated stir bar used for SBSE, specific pH ranges that are recommended for safe use that will not damage the polymer—is from 3 to 9. In this study, pH adjustments were done for Diesel and Biodiesel in MFW and MSW in ranges of 3, 7, and 9 approximately using hydrochloric acid and sodium hydroxide solutions. Without pH justification, labeled as “N”, the pH was 6.5 in MFW and for MSW the pH was initially 7.2.

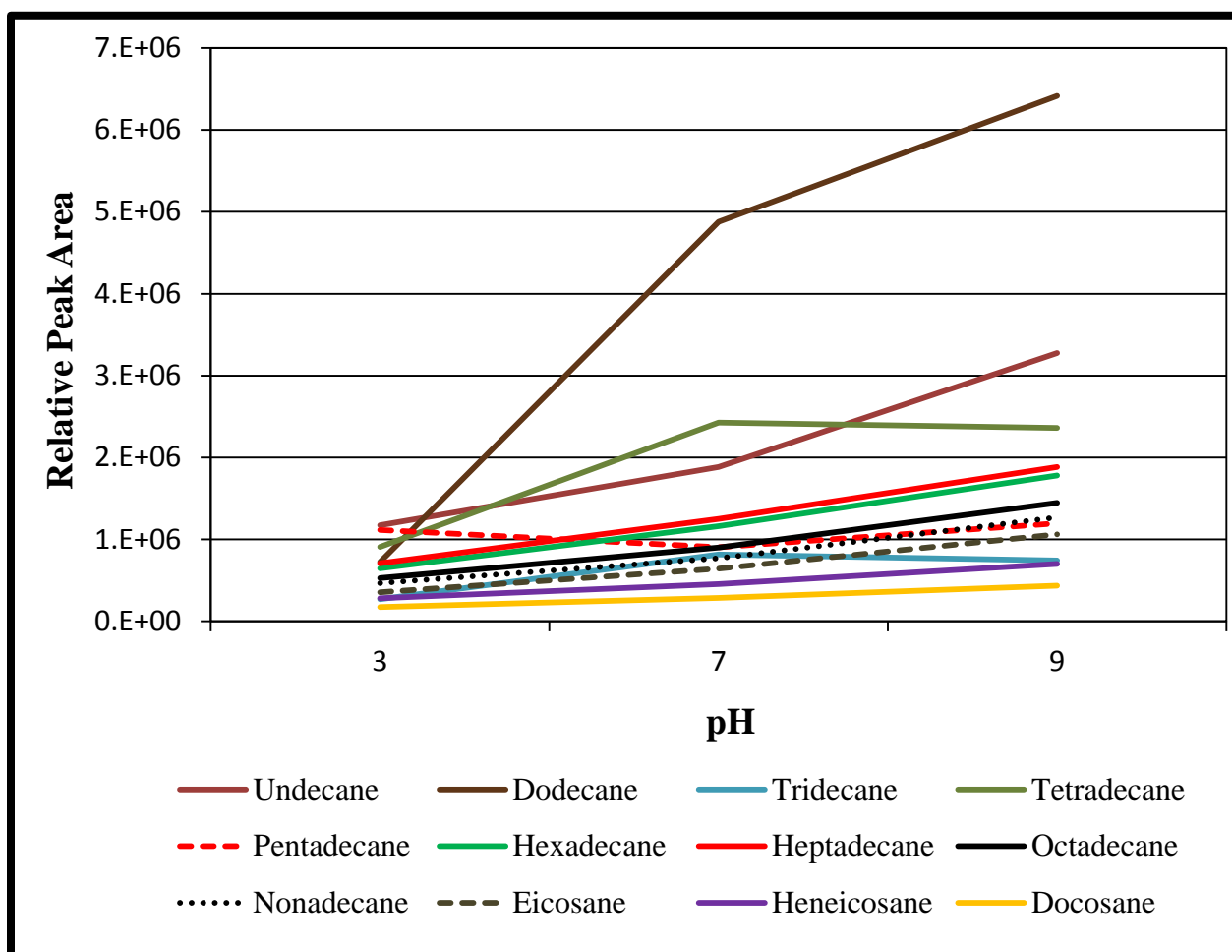


Figure 26: The relative target area of selected aliphatic hydrocarbons from Diesel in MFW obtained from the GCMS after carrying out SBSE at different pH. Samples were run in duplicates (n=2) for each treatment.

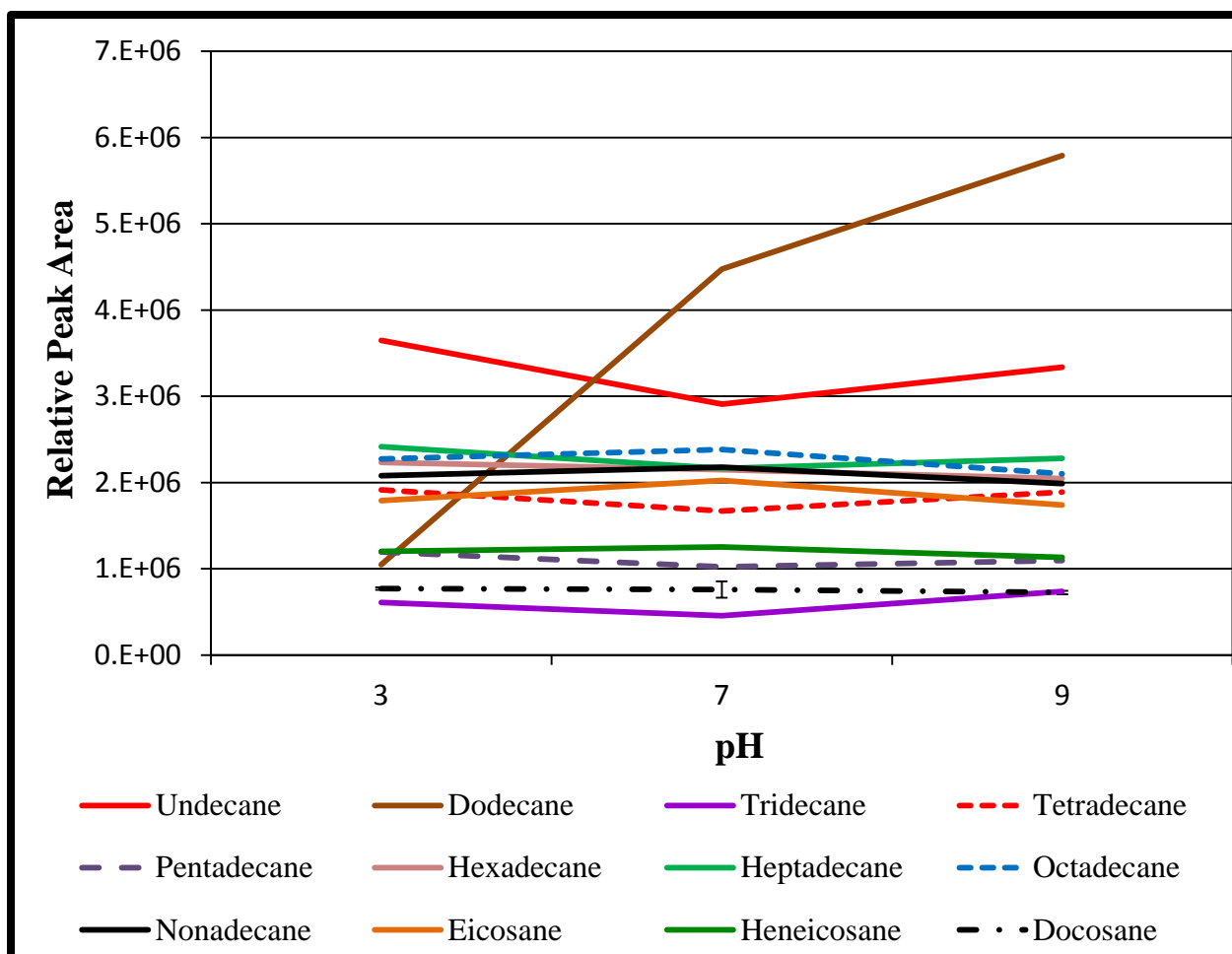


Figure 27: The relative target area of selected aliphatic hydrocarbons from Diesel in MSW obtained from the GCMS after carrying out SBSE at different pH. Samples were run in duplicates (n=2) for each treatment.

pH adjustment could be an important factor in increasing the extractability of analytes that are ionizable in water (43)(44) (45). As expected, the extraction recovery for most compounds in MFW and MSW was not significantly affected by the pH of the matrix. Nonetheless, as seen in Figure 26, there was a increase in recovery of alkanes in MFW as the pH increased. For the MSW (Figure 27) the relative peak area stays the same for tetradecane to docosane, while there is a slight increase with increasing pH for undecane and docosane in MFW. Since treatments in this case were done in duplicates it would be advisable to run triplicates in order to explore the reproducibility of the results. A possible reason for these



compounds having this odd trend in respect the others could be due to the coelution of a compounds that has similar target ions. Further studies are recommended to verify this and explore other potential possibilities.

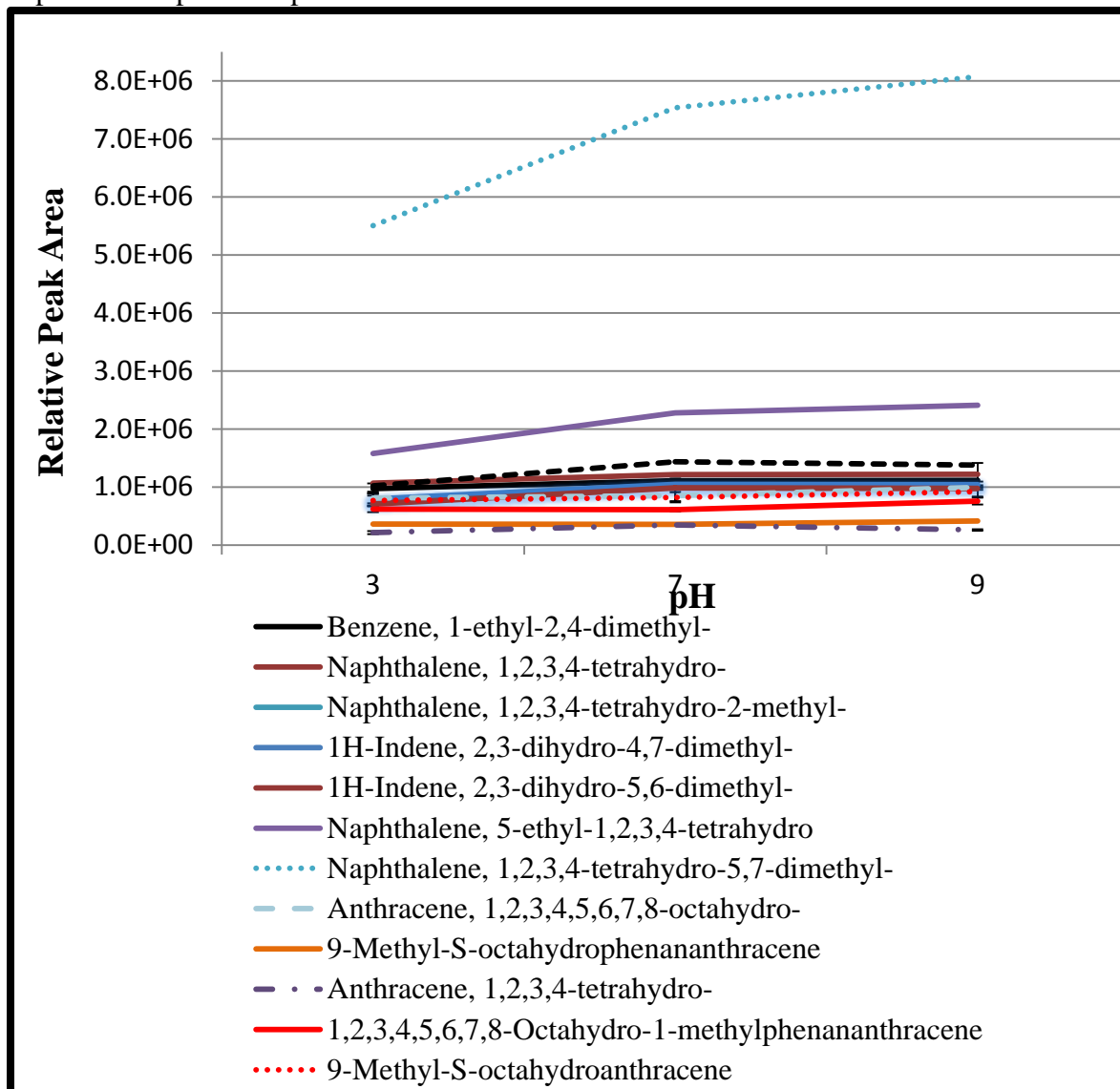


Figure 28: The relative target area of selected aromatic hydrocarbons from Diesel in MFW obtained from the GCMS after carrying out SBSE at different pH. Samples were run in duplicates (n=2) for each treatment.

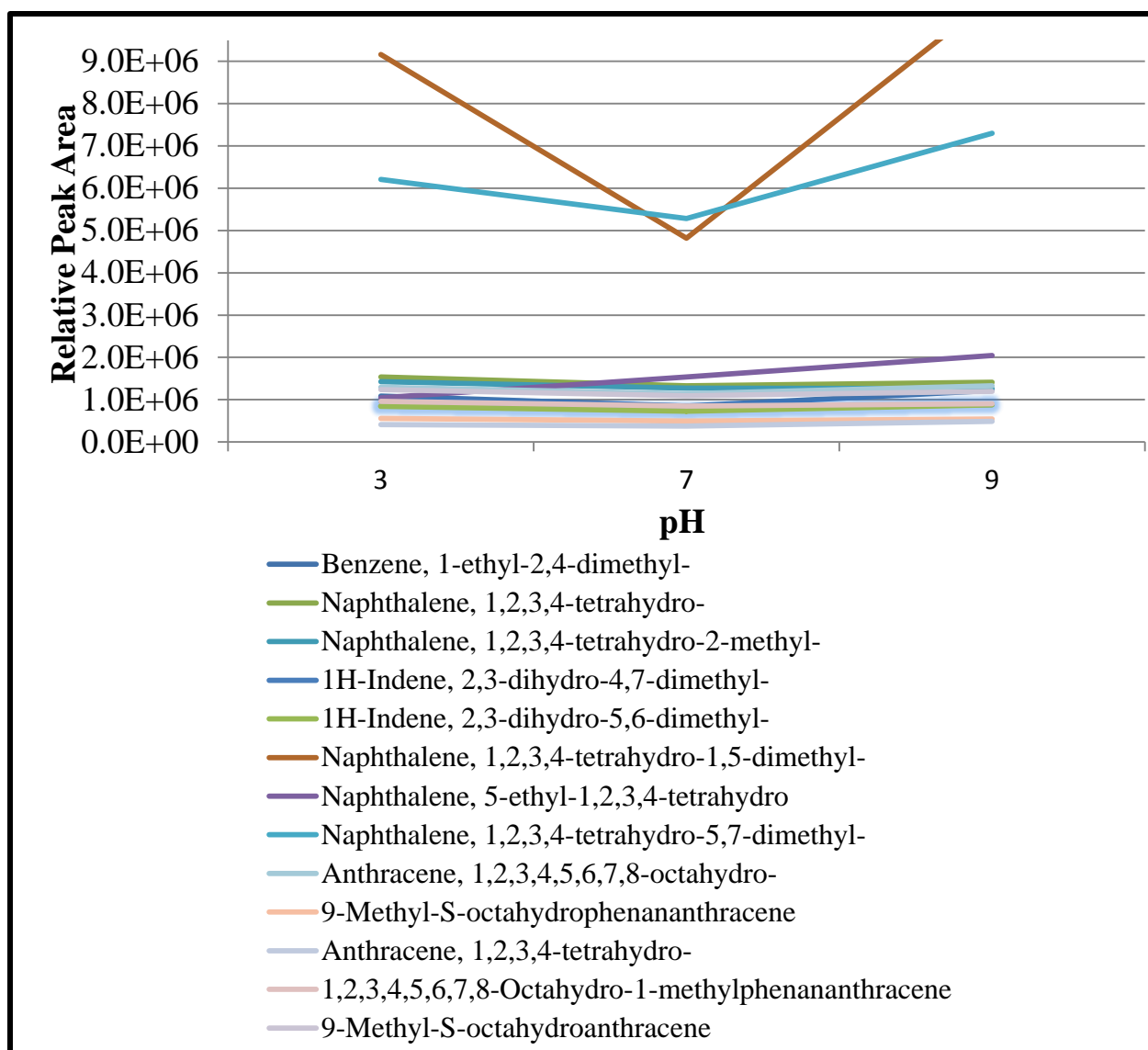


Figure 29: The relative target area of selected aromatic hydrocarbons from Diesel in MSW obtained from the GCMS after carrying out SBSE at different pH. Samples were run in duplicates (n=2) for each treatment.

The relative target response, which is an indication of the extraction recovery of aromatic hydrocarbons from diesel shows not particular preference for pH. Values stay similar for both MFW—Figure 28—and MSW—Figure 29. There is no significant difference between different pH treatments (Table 25 and 26 in Appendix).

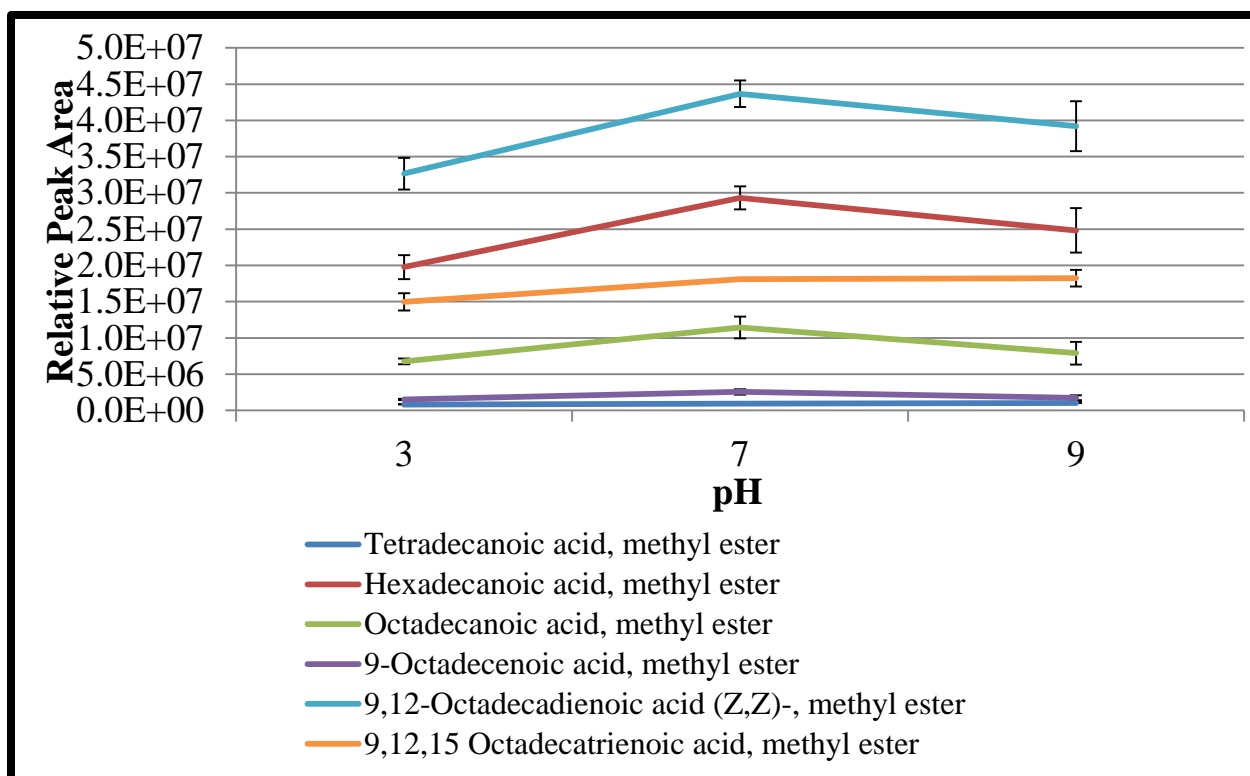


Figure 30: The relative target area of selected FAMES from vegetable oil derived biodiesel (B100) in MFW obtained from the GCMS after carrying out SBSE at different pH. Samples were run in triplicates (n=3) for each treatment.

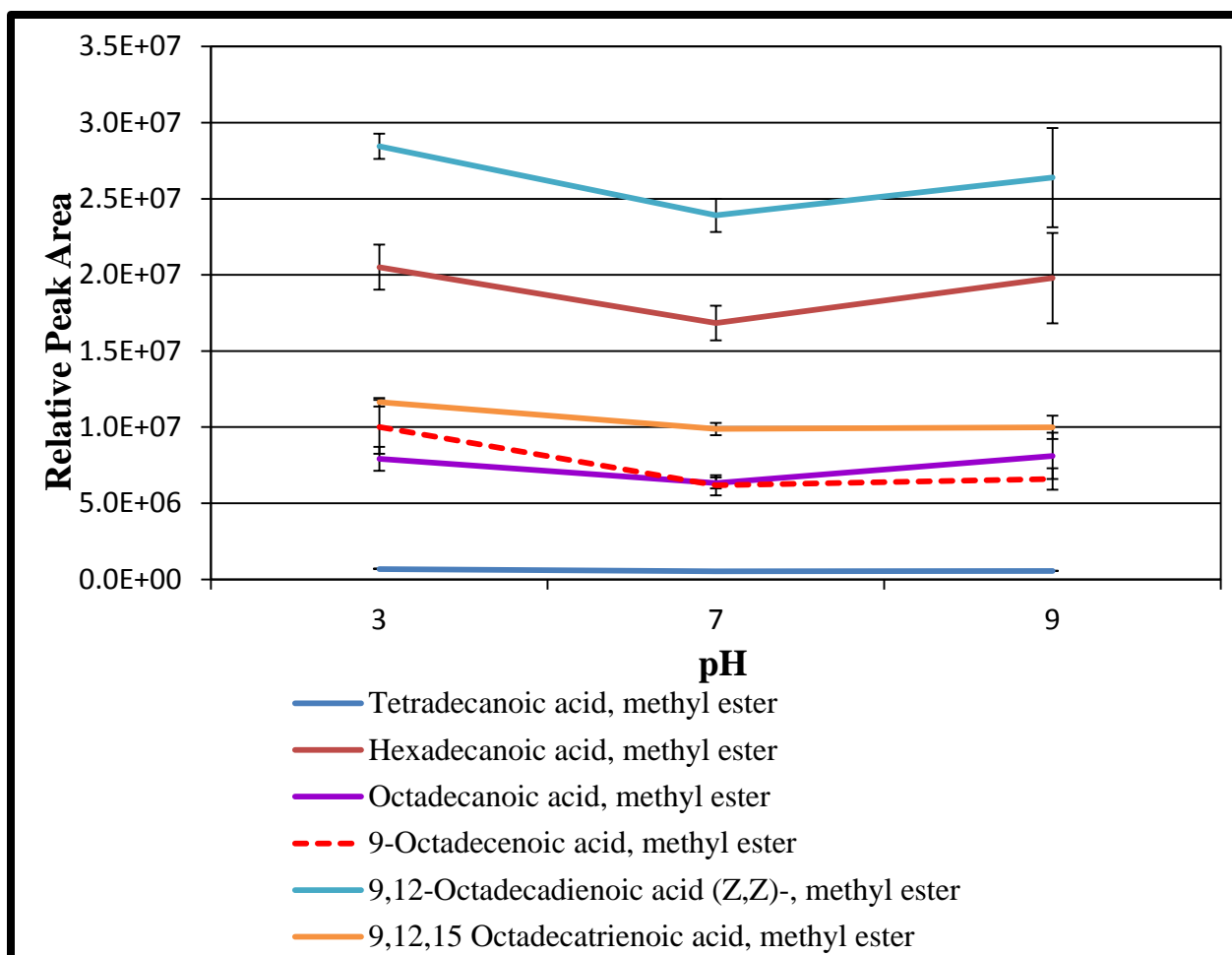


Figure 31: The relative target area of selected FAMES from vegetable oil derived biodiesel (B100) in MSW obtained from the GCMS after carrying out SBSE at different pH. Samples were run in triplicates (n=3) for each treatment.

Figures 30 and 31 illustrate the relative peak areas of Biodiesel (B100) FAMES at different pH for MFW and MSW. Figure 30—for MFW—shows no significant improvement for most compounds with the increase or decrease of pH in the sample. For Figure 31, there is an increase slight improvement in FAMES extracted in MSW at lower pH. Even though some degree of improvement through pH adjusting was expected in the recovery of FAMES as compared to the more nonpolar hydrocarbons of diesel, further investigation will be needed to understand the interactions between the solution, PDMS, and the analytes. It is possible that during the pH adjustment experiment, some hydrolysis of FAMES has occurred and therefore

reduced the FAMES in the solution. The results obtained from the experiment would not be reflecting the correct recovery of FAMES by SBSE.

### 3.1.4 Optimizations Summary

After varying methanol content, stir time, and pH in an effort to improve extraction efficiency of selected diesel hydrocarbons and biodiesel fatty acid methyl esters, the selected parameters can be found in the Table 6. In the case that all these compounds are mixed together in an actual biodiesel sample (B20), the parameters that benefit the overall extraction of all these compounds is 50 percent methanol, a 4 hours stir with no pH adjustment. This would be the case for both fresh and sea water.

Table 7: Summary of parameters that gave us the best overall results for respective fuels in for model fresh water and model sea water.

		Optimization Parameters		
		Methanol Content (%)	Stir Time (Hrs)	pH
<b>MFW</b>				
Diesel	Alkanes	50	4	N
	Aromatic	20	3	N
Biodiesel	FAMES	50	3	N
<b>MSW</b>				
Diesel	Alkanes	50	4	N
	Aromatic	10	2	N
Biodiesel	FAMES	40	4	N

## 3.2 WATER ACCOMMODATED FRACTIONS (WAFs)

Being able to effectively analyze the composition of water accommodated fractions of fuels instead of fuels as a whole is important since results can elucidate toxicity of fuels in aquatic systems more accurately. Various fuels have a wide range of compounds that vary in their octanol-water partitioning coefficient ( $K_{ow}$ ) depending on their molecular structures and

compositions. Consequently it is expected that the fuel composition in its initial form should be different from the fuel composition that accommodates itself in water. Utilizing the SBSE process in analyzing organic compounds in fuel, the difference in composition between WAFs of fuels and that of the pure fuel source were studied. Diesel and animal fat derived biodiesel (AB100) WAFs were prepared and their composition compared to that of their pure source is presented.

As Figure 32 and Figure 33 shows, for the WAFs in model fresh water (MFW), the abundance of n-alkanes in the WAF becomes the minority when compared to their presence in the pure fuel source, while aromatic compounds become relatively abundant. Aromatic compounds have chemical structures with high electron density which gives it slightly less hydrophobic character than that of alkanes. In addition, aromatic compounds have functional groups that also facilitate the interacting with other polar molecules, and increase their solubility in water. The same kind of behavior—where aromatic hydrocarbons become more abundant in the WAF—can be seen in the sea water model (Figure 34 and 35). Similar behavior has been noted where various PAHs increase in WAFs in actual spills in the North Sea, Gulf of Mexico and the coast of Canada (43).

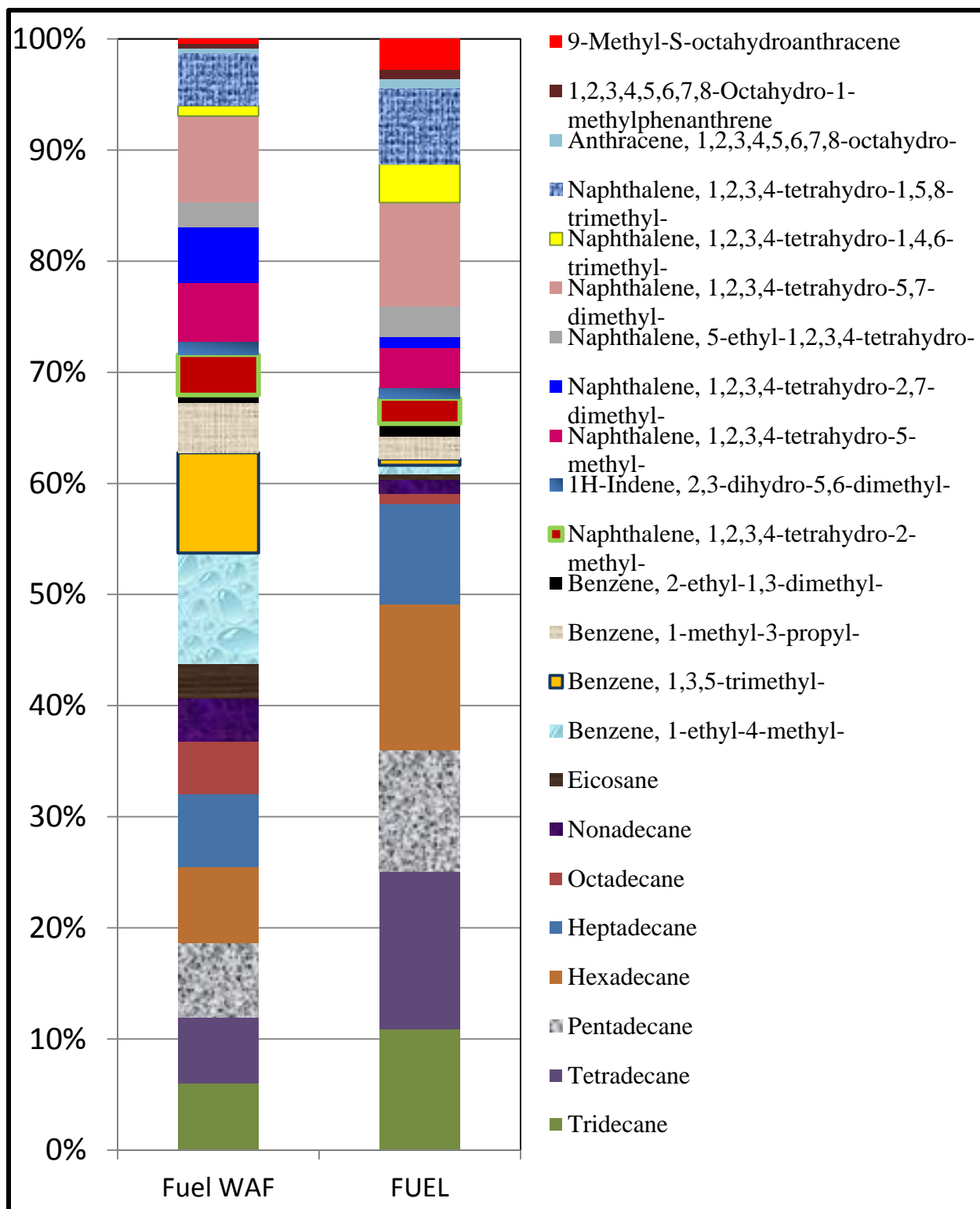


Figure 32: Percent composition of selected hydrocarbons between diesel spiked in MFW and diesel water accommodated fraction.

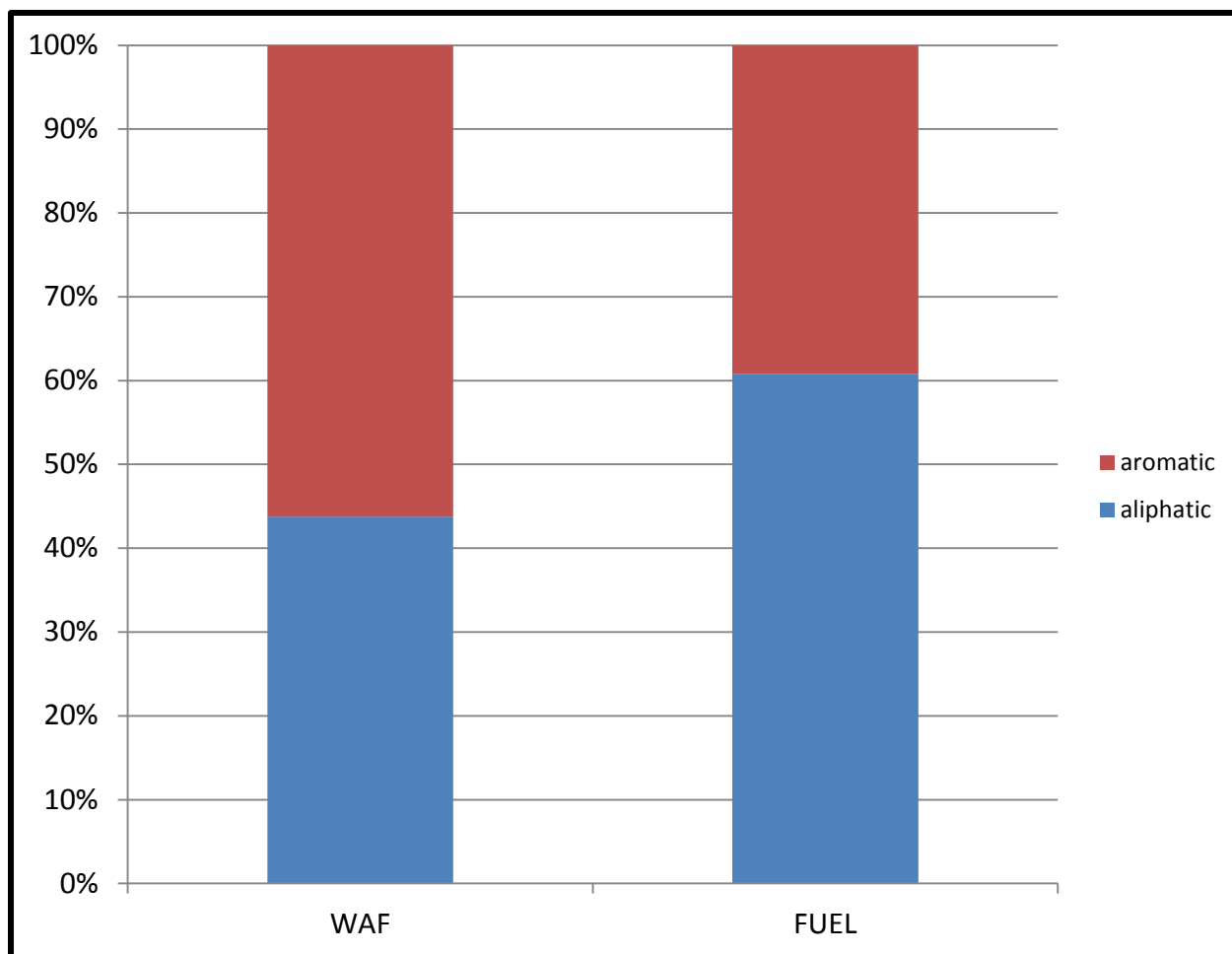


Figure 33: Percent composition of overall aromatic and aliphatic hydrocarbons of diesel, between spiked diesel in MFW and diesel's WAF.



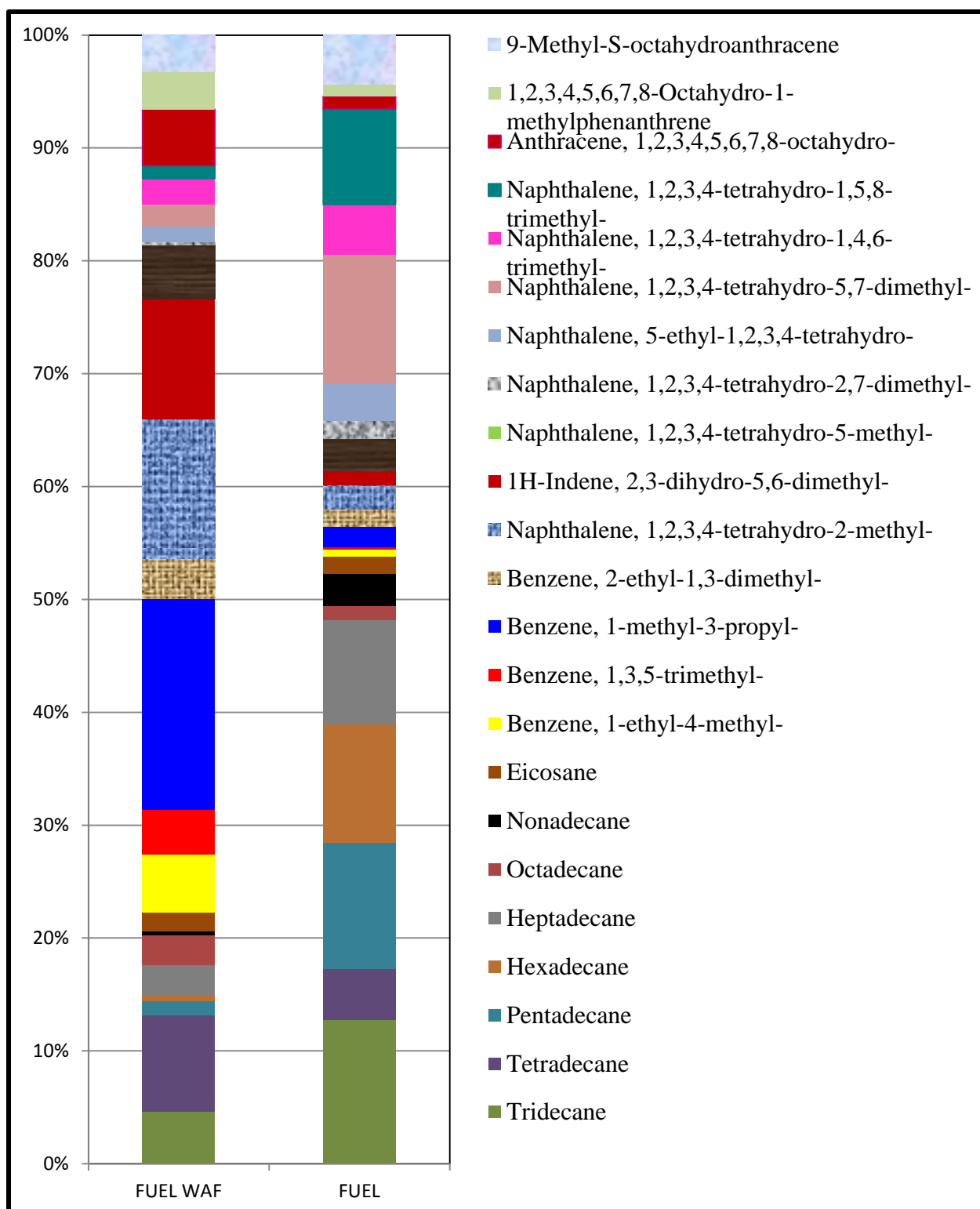


Figure 34: Percent composition of selected hydrocarbons between diesel spiked in MSW and diesel water accommodated fraction.

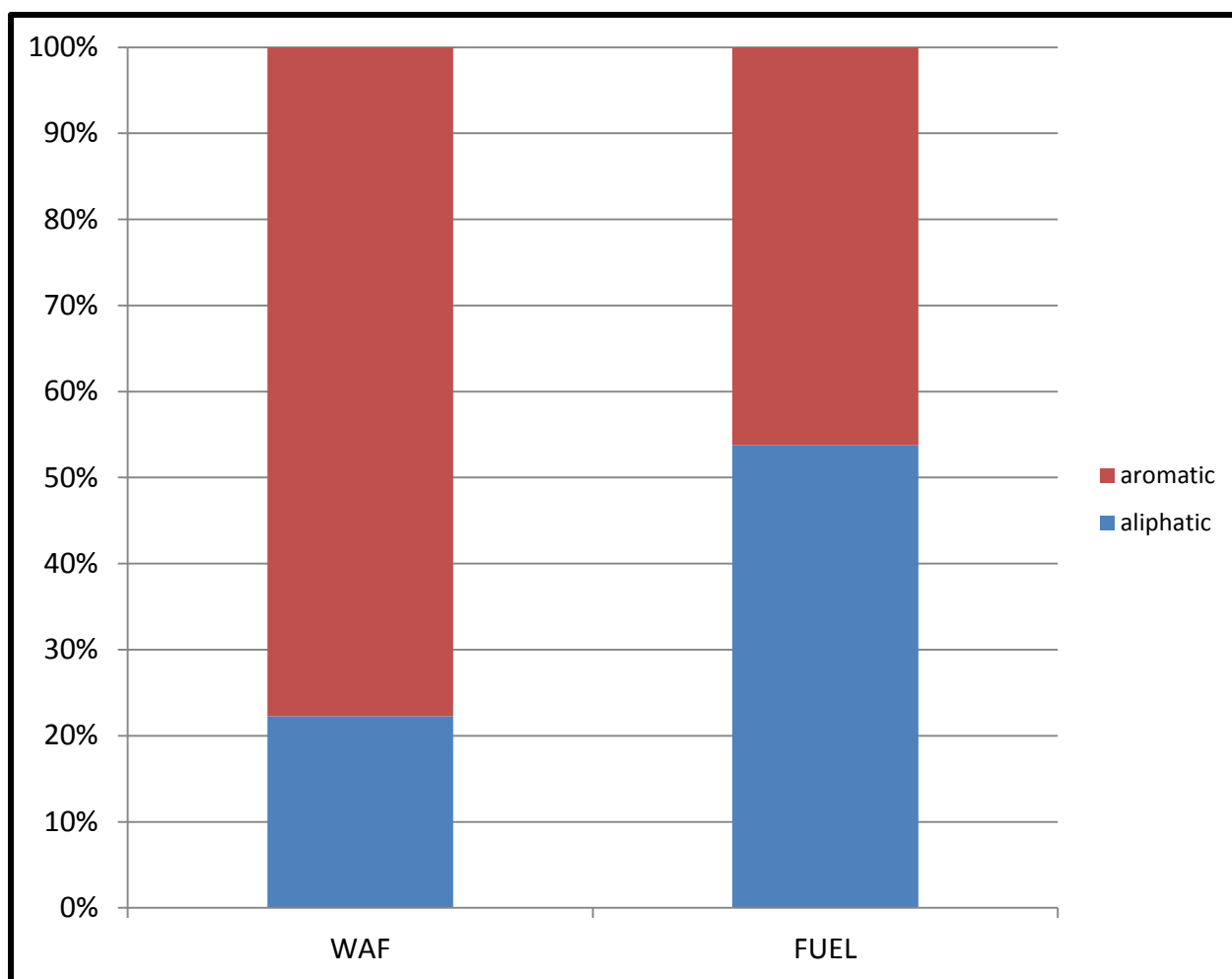


Figure 35: Percent composition of aromatic and aliphatic hydrocarbons of diesel, between spiked diesel in MSW and diesel's WAF.

Unlike the fossil fuels containing aromatic compounds that are persistent in the environment, biodiesel is commonly composed of various more readily biodegradable saturated and unsaturated esters (FAMES) of various lengths. Given that the structures of FAMES in biodiesel are less diverse than the hydrocarbons in diesel, similar compositions were expected between the WAF and the source in both our MFW and MSW model. As shown in Figures 36 through 39, there is no significant difference between the composition of the WAF and the pure source. Therefore, by studying the toxicity of the pure biodiesel source one may be able to obtain insight on the toxicity of the biodiesel accommodated in fresh or sea water.

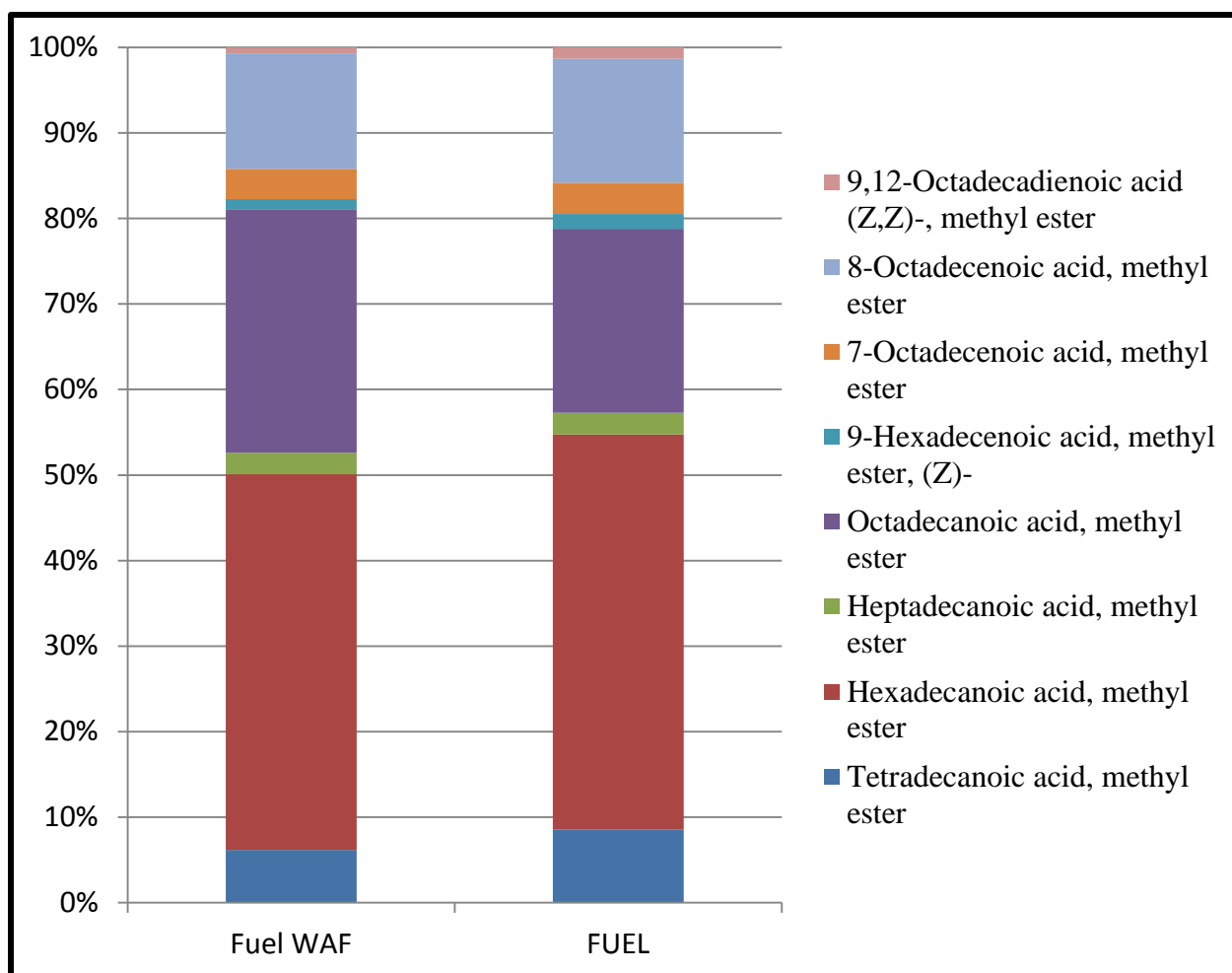


Figure 36: Percent composition of selected FAMES between animal derived biodiesel (AB100) spiked in MFW and AB100 water accommodated fraction.

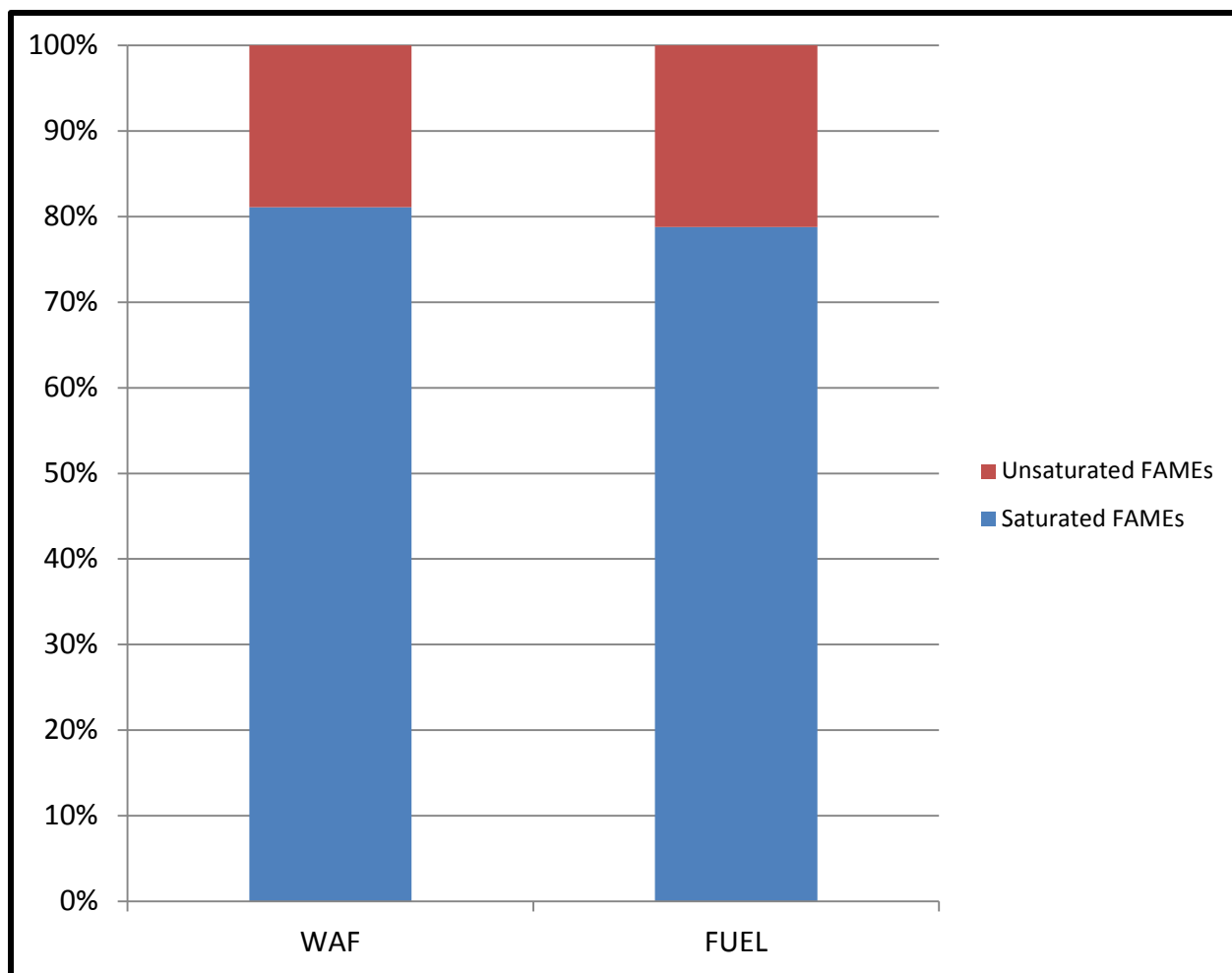


Figure 37: Percent composition of unsaturated and saturated FAMES in biodiesel, between spiked biodiesel in MFW and biodiesel's WAF.

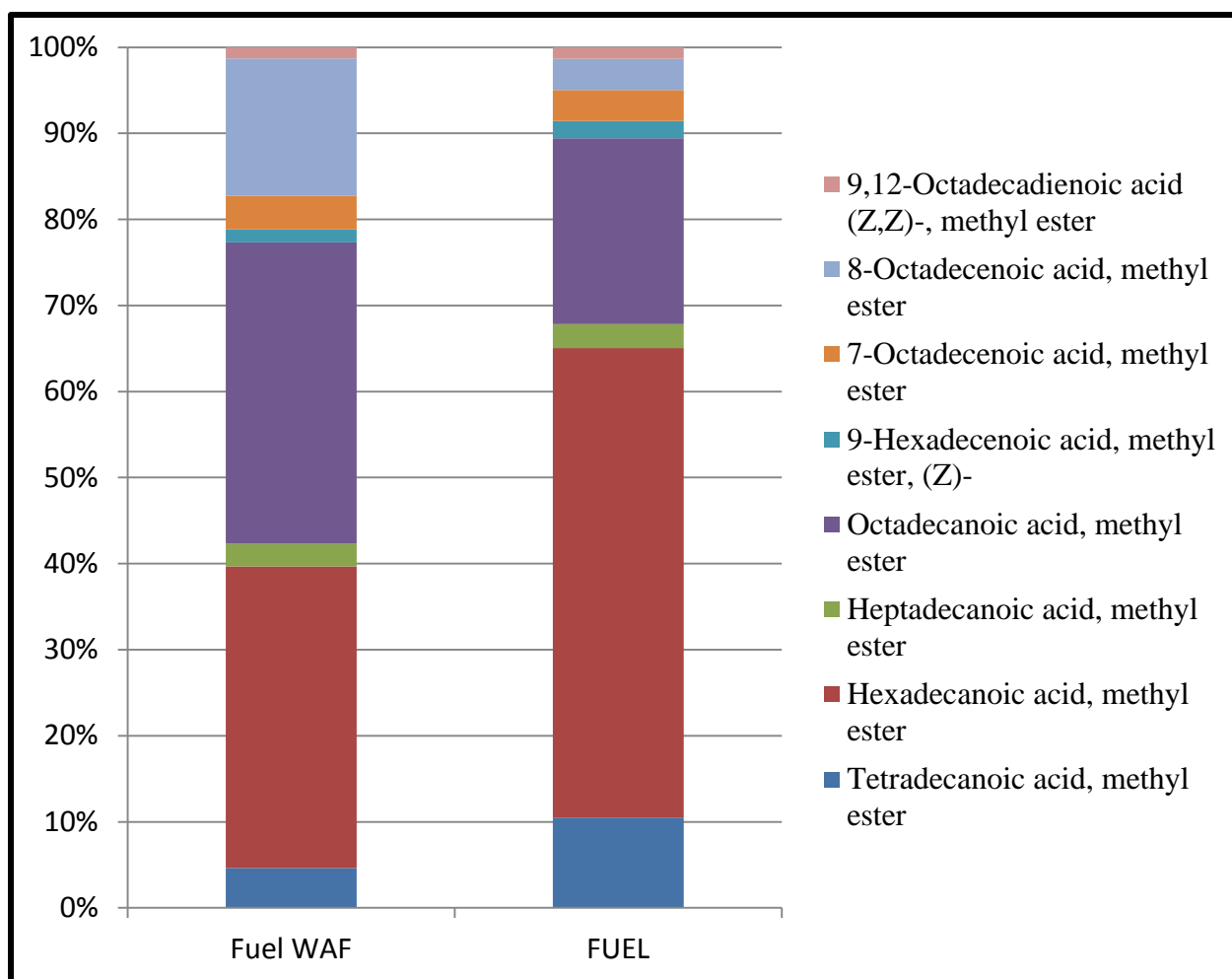


Figure 38: Percent composition of selected FAMES between animal derived biodiesel (AB100) spiked in MSW and AB100 water accommodated fraction.

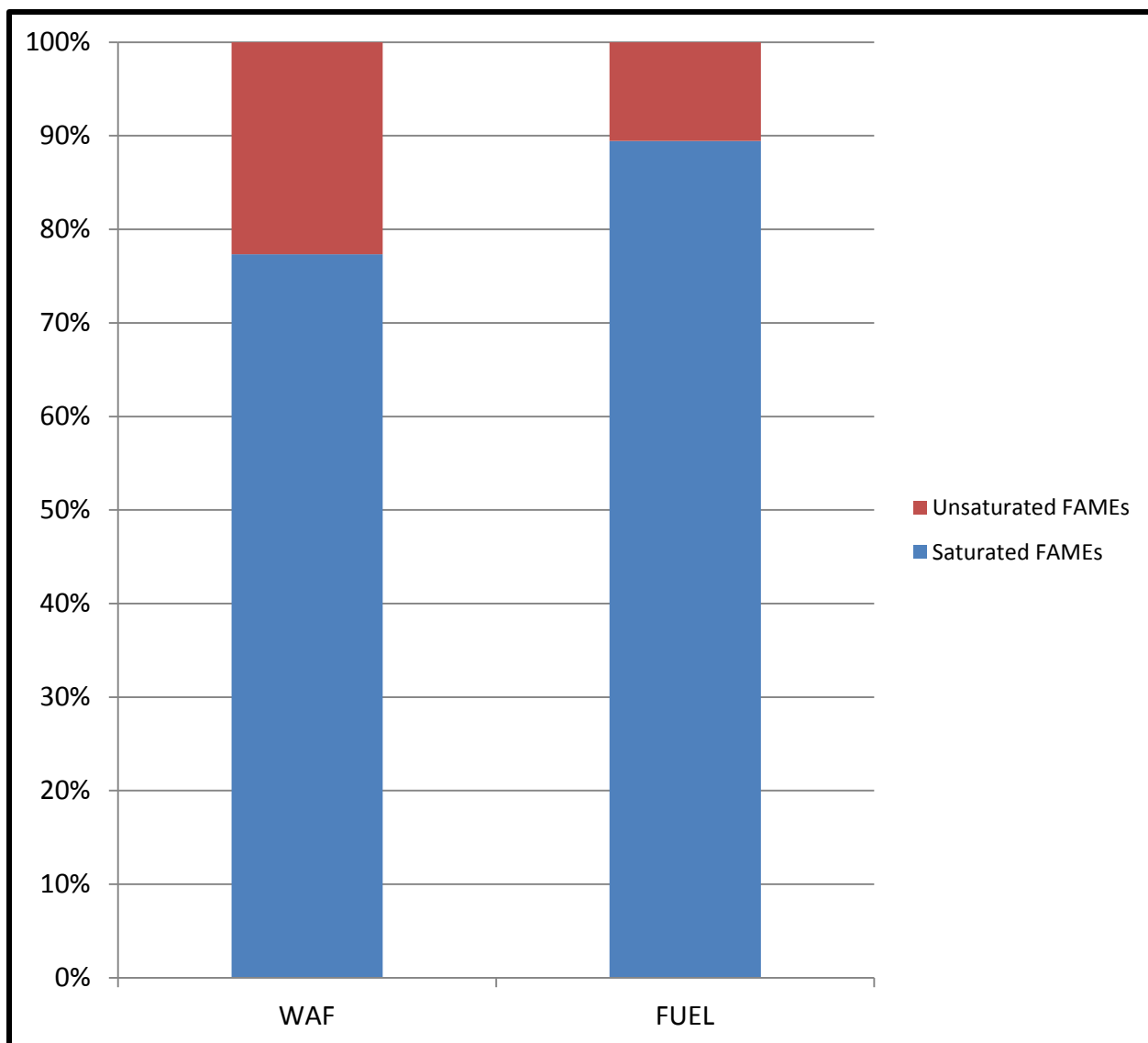


Figure 39: Percent composition of unsaturated and saturated FAMES in biodiesel, between spiked biodiesel in MSW and biodiesel's WAF.

### 3.3 CALIBRATION CURVE

To study the linearity of the optimized SBSE-TD-GC/MS method, target responses to nine different concentrations were explored for selected compounds found in diesel and biodiesel at concentration ranging from 0.005 ppb to 100 ppb. The parameters for SBSE were 4 hour stirring at 1000 rpm in MSW, 50 percent methanol, and no pH adjustment. Responses to particular compounds at various concentrations are shown in Table 7 and calibration curves for

target compounds are demonstrated in Figures 47-68 (Appendix)—with Figure 40 and 41 shown below as examples. The Method Detection Limit (MDL) were determined and Limit of Quantification (LOQ) for selected compounds were estimated by observing identifiable responses to selected concentrations and by seeing how target response fit in the equation of the line for respective calibration curves. The values obtained in our method were lower than various studies when it comes targeted alkanes. In a study using head space solid phase micro-extraction-flame ionization detector, alkanes were targeted using optimized parameters where LOQ ranged from 7.1 to 6.1 ppb and MDL ranged from 2 to 12 ppb (44). For aromatic compounds, such as the ones that were targeted in this study, LOQ and LOD values have been acquired at lower concentrations in other studies than concentrations found here. In a study done by Rianawati et al., for example, headspace SPME was optimized in order to extract and analyze various poly aromatic hydrocarbons in rainwater and storm water using GC-MS (48). Using their optimized method, limits of quantification ranged from 0.014 ppb to 0.081 ppb, while Detection limits ranged from 0.001 ppb to 0.039 ppb (48). For fatty acid methyl esters (FAMES), research such as that done by Meng et al., were able to obtain LOD ranging from 0.4 to 0.6 ppm, which are values that are higher than those done with our method (49).

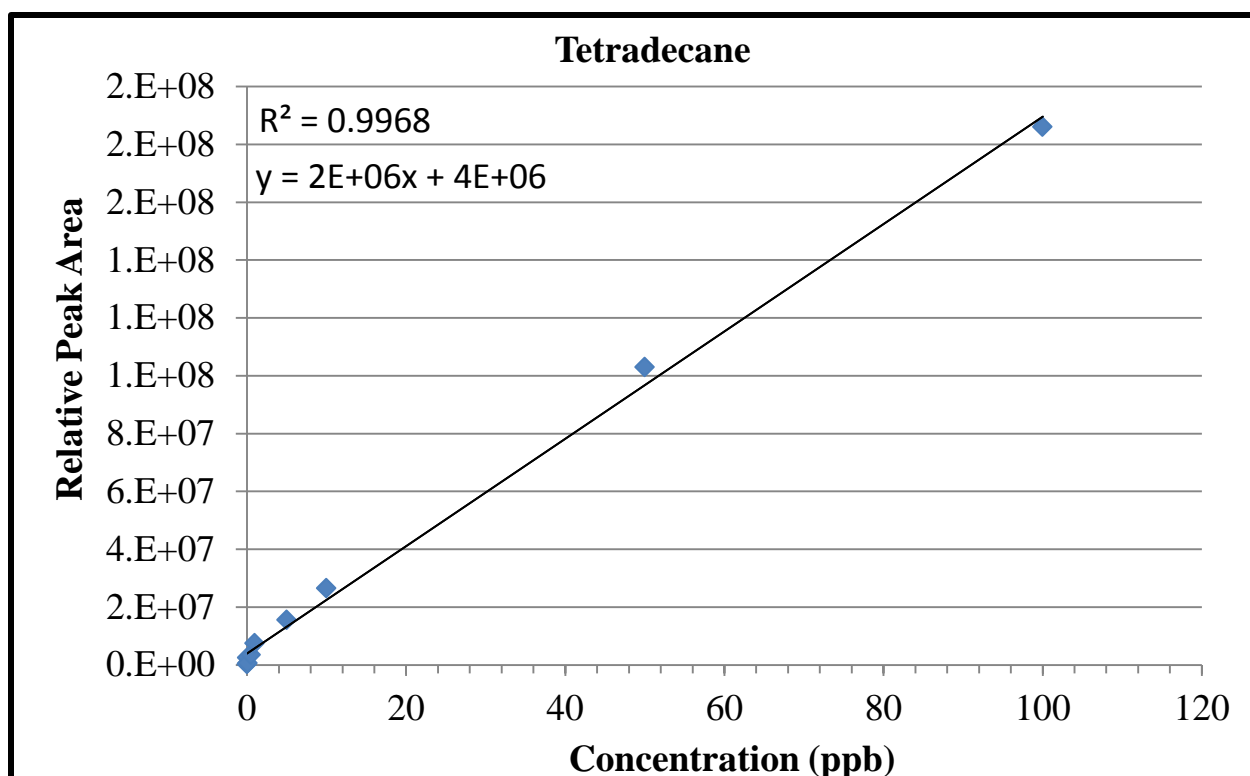


Figure 40: Calibration curve for Tetradecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.



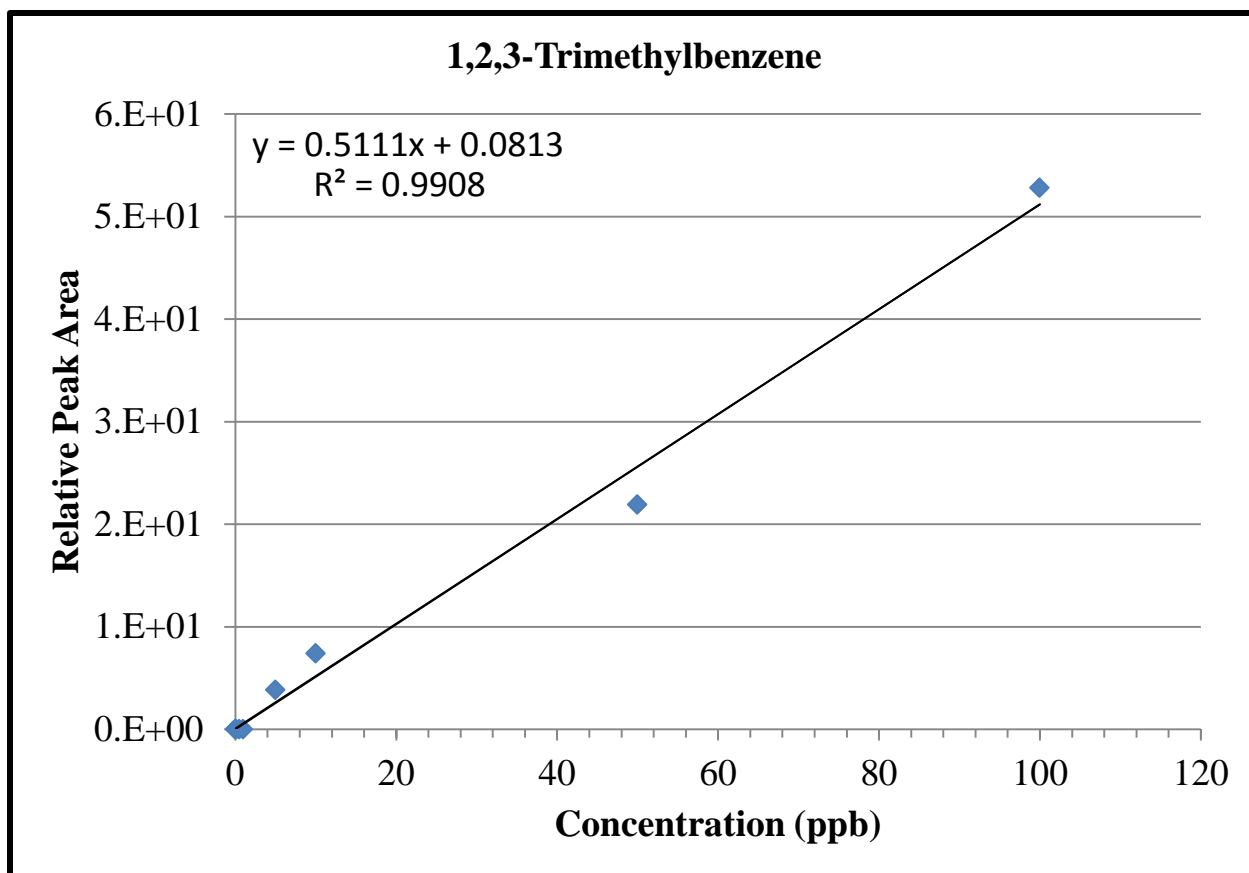


Figure 41: Calibration curve for 1,2,3-Trimethylbenzene at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

Table 8: Correlation Coefficients and Limit of Detection approximations for selected standards extracted in 50 percent methanol in MSW for during four hours.

Compound	Target Ion (m/Z)	Correlation Coefficient (R^2)	~LOD (ppb)	~LOQ (ppb)	Compound	Target Ion (m/Z)	Correlation Coefficient (R^2)	~LOD (ppb)	~LOQ (ppb)
1,2,3-Trimethylbenzene	105	0.9908	5	5	Dodecane	57	0.9851	0.005	0.05
Acenaphthylene	152	0.9805	5	5	Tridecane	57	0.9904	0.005	0.05
Acenaphthene	153	0.9794	5	5	Tetradecane	57	0.9968	0.005	0.05
Fluorene	166	0.9318	5	5	Pentadecane	57	0.9946	0.005	0.05
Anthracene	178	0.9267	5	5	Hexadecane	57	0.9858	0.005	0.05
Phenanthrene	178	0.9891	5	5	Heptadecane	57	0.9848	0.005	0.05
Tetradecanoic acid, methyl ester	74	0.968	0.005	0.05	Octadecane	57	0.986	0.005	0.05
Hexadecanoic acid, methyl ester	74	0.9783	0.005	0.05	Nonadecane	57	0.9912	0.005	0.05
Octadecanoic acid, methyl ester	74	0.968	0.005	0.05	Eicosane	57	0.9942	0.005	0.05
9-Octadecanoic acid, methyl ester	69	0.9828	0.1	0.5					
9, 12-Octadecadienoic acid methyl ester	67	0.9821	0.1	0.5					
9, 12,15-Octadecatrienoic acid, methyl ester	79	0.9708	0.5	0.5					

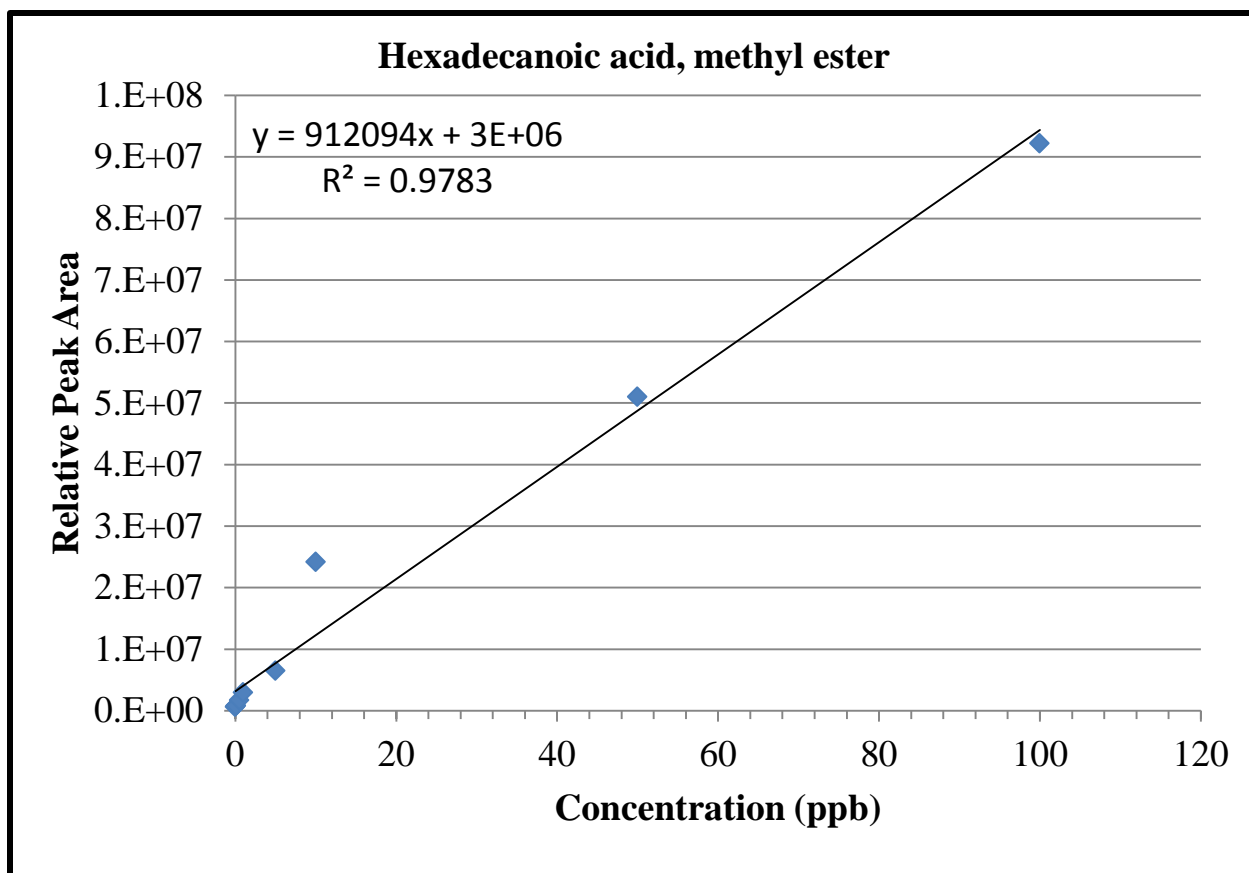


Figure 42: Calibration curve for Hexadecanoic acid, methyl ester at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

### 3.4 ACTUAL WATER SAMPLES

Water samples collected from Long Beach, California and the Louisiana Coast—after the Gulf Oil Spill of April 2010—were tested using the optimized SBSE method. Ten milliliters of water samples were used along with 10 mL of methanol and appropriate amount of internal standard solution. Water samples were taken through the SBSE process for 4 hours at 1000 rpm.

No targeted hydrocarbons were found in the water samples in Long Beach. Figure 43 shows a chromatogram obtained from the Gulf Coast water samples. Water samples collected from the Gulf Coast showed the presence of some alkanes—Tridecane, Pentadecane,

Heptadecane, Octadecane, Nonadecane, and Eicosane. The levels of compounds were unquantifiable using respective plotted calibration curves.

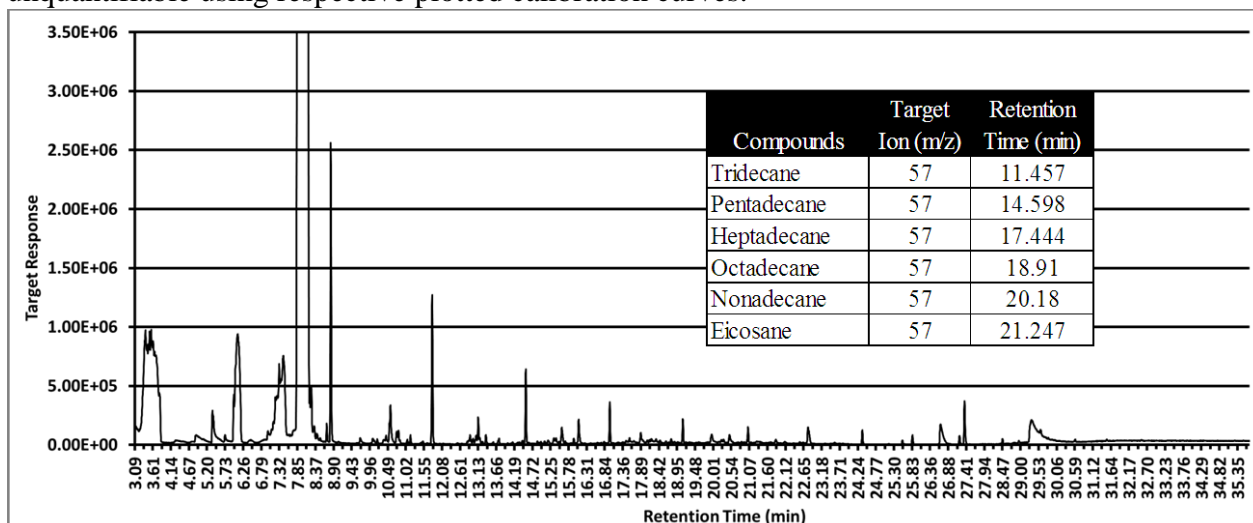


Figure 43: Chromatogram of water sample from Gulf Oil spill including a small table with identifiable compounds.

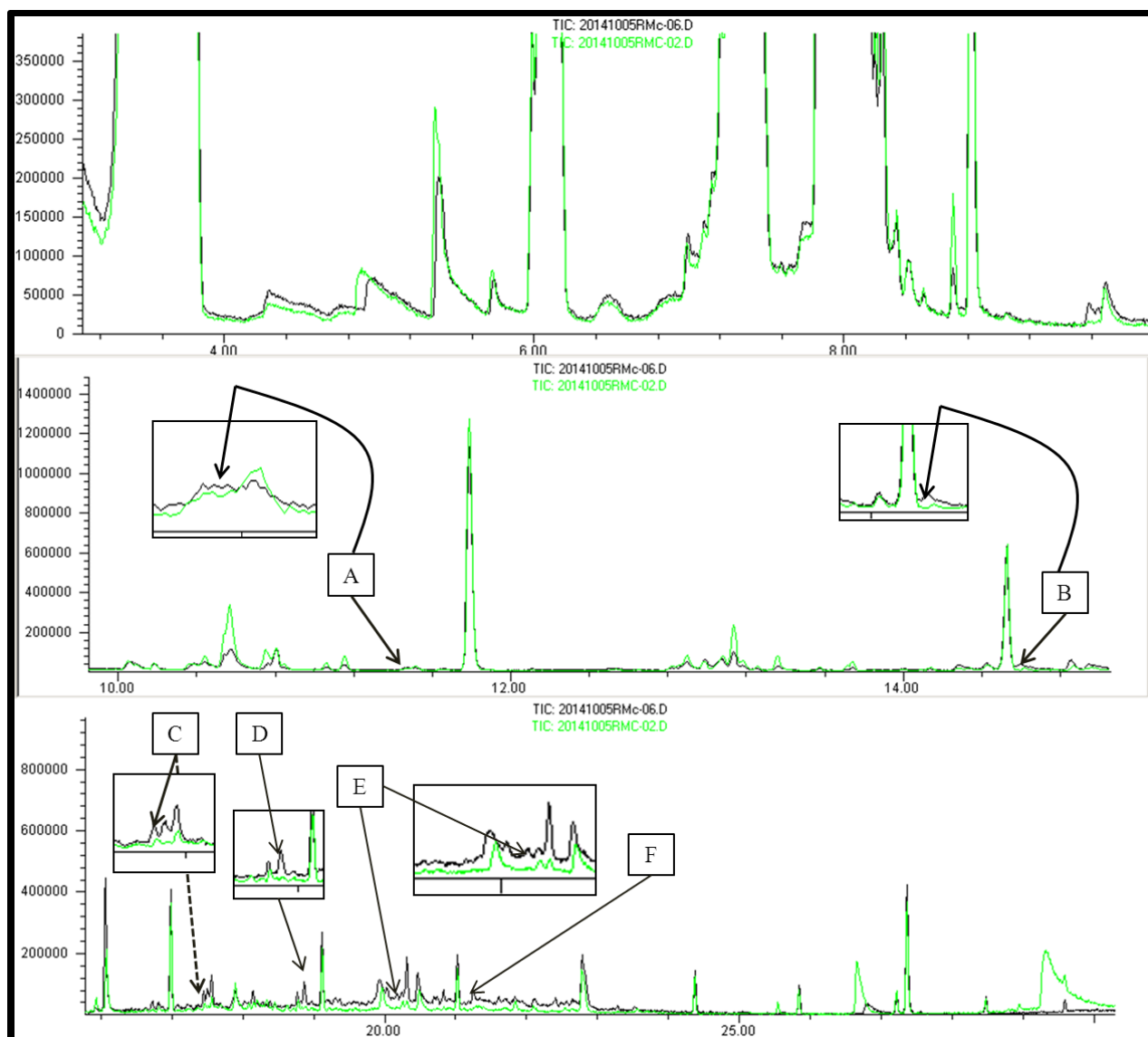


Figure 44: Overlaid chromatogram of two different samples: (black) sample from Gulf Oil Spill in 50 percent methanol; (green) blank sample run of model sea water in 50 percent methanol. Denoted letters represent the following compounds: A-Tridecane; B-Pentadecane; C-Heptadecane D-Octadecane E-Nonadecane F-Eicosane

## Chapter 4: Conclusion

SBSE-TD-GCMS continues to show potential as a viable technique for extracting hydrocarbons from fuel—more specifically, n-alkanes and aromatic compounds from diesel, and FAMES from biodiesel. Parameters, such as methanol addition, stir time, and pH for improved extraction, were explored for the extraction of hydrocarbon in fresh water (i.e. DI water in this study) and sea water (i.e. model sea water in this study). For better recovery n-alkanes from MFW and MSW by SBSE, 50 percent methanol content generally provided the best or satisfactory recovery for overall hydrocarbons of interest. A 4 hour stir time seemed to be more universally sufficient for most of the diesel n-alkanes and aromatic hydrocarbons. As for the factor of pH on extraction recovery of selected analytes altering the pH proved no significant improvement.

For biodiesel FAMES, 40 percent methanol content for both MFW and MSW was sufficient. Fifty percent methanol could have been used as well. For stir times, MFW and MSW also shared a 2 hour stir time as the best—after which, further extracting for more time does not significantly decrease the amount stirred. For the pH optimization stage, the results showed that pH adjustment is not necessary in MFW. In MSW, however, lower pH seemed to render better extraction for some compounds FAMES like Hexadecanoic acid, methyl ester and 9,12 Octadecanoic acid methyl ester, but statistically there is no significant difference with target responses obtained at neutral pH. Optimized SBSE in MSE were able to show good detection limits as low as 0.005 ppb for alkanes and saturated FAMES, while aromatic hydrocarbons and unsaturated FAMES had detection limits around 5 ppb.

Water accommodated fractions (WAFs) of diesel and biodiesel were prepared in both MFW and MSW to study the composition of fuel in aqueous environment. Using 50 percent methanol content for SBSE with 4 hours of stirring, the compositions of target compounds in WAFs were analyzed and compared to the composition of pure diesel and biodiesel in fresh water and sea water. In both MFW and MSW, the percent composition of n-alkanes decreases

in the WAF by about 20 percent and 30 percent, respectively, in comparison to the percentage found in the pure fuel source. This illustrates the increase in abundance of aromatic compounds in the water during oil spills when compared to aliphatic hydrocarbons. This is important since many aromatic hydrocarbons are considered both carcinogenic and stable in the environment. The composition of FAMES in biodiesel (B100) is not as diverse as that found within diesel; thus, it was no surprise that WAFs of biodiesel showed no pronounced difference in composition from that of the pure source.

To further test the applicability of the SBSE method using selected optimized parameters, actual water samples from Long Beach, California, and the Louisiana Gulf Coast were analyzed. Of the samples run, only a sample belonging to the Louisiana Gulf Coast showed the presence of several aliphatic alkanes even though, they were unquantifiable. Even though just a few selected hydrocarbons were found in one of the water, this technique shows promise when it comes to determining the presence of fuel related hydrocarbons in fresh and sea water.

## Appendix

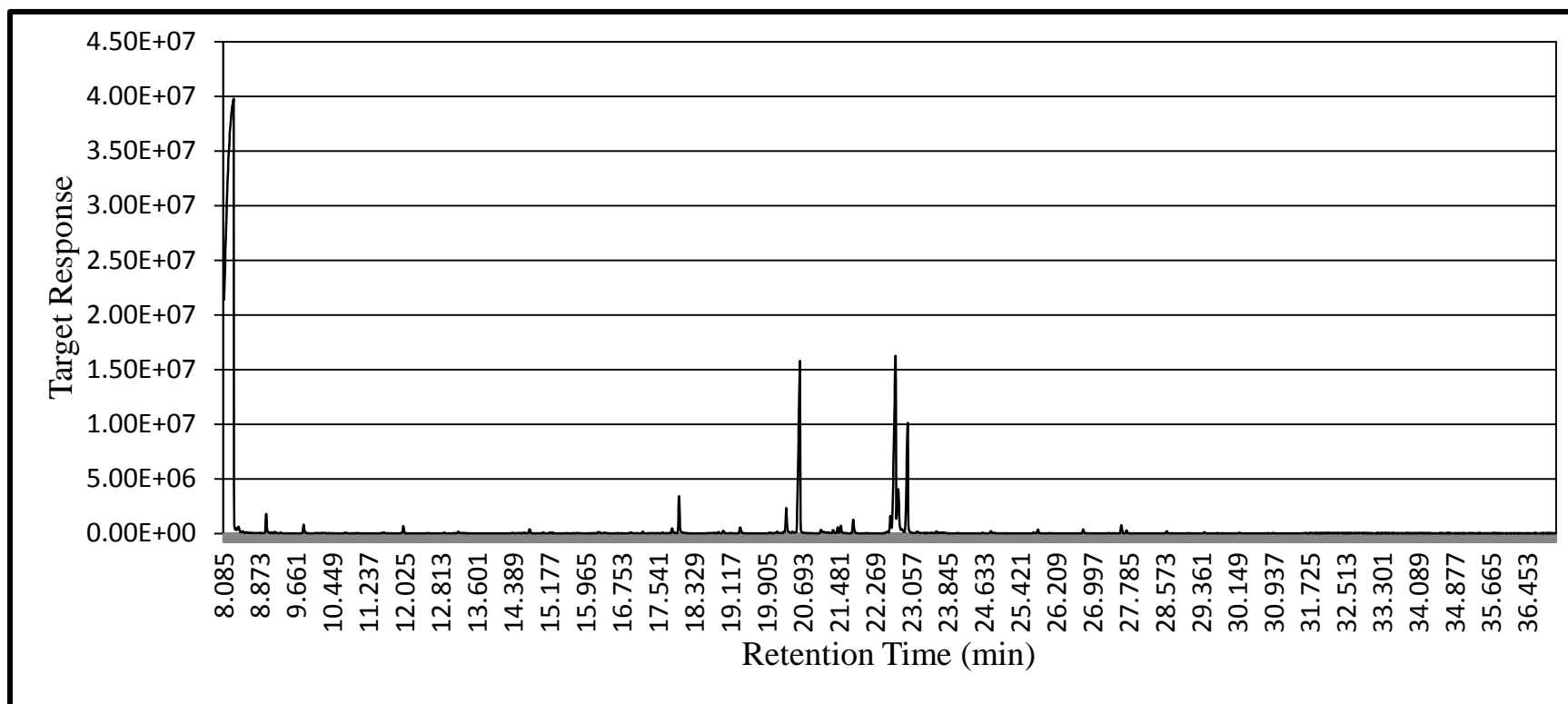


Figure 45: Chromatogram of diesel spiked in MFW with a spike of internal standard after SBSE-TD-GCMS.

Table 9: Compounds identified in the chromatogram in Figure 44 using NIST library.

Compounds	Retention Time (min)	Compounds	Retention Time (min)
o-xylene	4.21	Tetradecane	13.15
p-xylene	4.52	Naphthalene, 1,2,3,4-tetrahydro-1,4,6-trimethyl	13.95
Benzene, 1-ethyl-4-methyl-	5.69	Naphthalene, 1,2,3,4-tetrahydro-1,5,8-trimethyl	14.02
Benzene, 1,3,5-trimethyl-	6.71	2,5,8-Trimethyl-1,2,3,4-tetrahydronaphthene	14.37
Benzene, 1-methyl-3-propyl-	7.25	1,1'-Biphenyl, 4-methyl-	14.65
Benzene, 2-ethyl-1,3-dimethyl-	7.34	Pentadecane	14.49
Benzene, 1-ethyl-2,4-dimethyl-	7.69	Naphthalene, 1,6,7-trimethyl-	15.37
Undecane	7.98	Naphthalene, 1,4,5-trimethyl-	15.37
Naphthalene, 1,2,3,4-tetrahydro-	9.2	Hexadecane	16.18
Dodecane	9.77	Heptadecane	17.58
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	10.15	4,4'-Dimethylbiphenyl	17.87
Naphthalene, 1,2,3,4-tetrahydro-1-methyl-	10.31	Anthracene, 1,2,3,4,5,6,7,8-octahydro-	18.01
1H-Indene, 2,3-dihydro-4,7-dimethyl-	10.75	9-Methyl-S-octahydrophenanthracene	18.35
Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	11.01	Anthracene, 1,2,3,4-tetrahydro-	18.58
1H-Indene, 2,3-dihydro-5,6-dimethyl-	11.31	1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthrene	18.8
Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	11.49	Octadecane	18.91
Tridecane	11.5	9-Methyl-S-octahydroanthracene	19.74
Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-	11.91	Nonadecane	20.18
Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl-	12.35	Eicosane	21.4
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	12.51	Heneicosane	22.55
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro	12.57	Docosane	23.66
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	13.13	Mirex	27.57



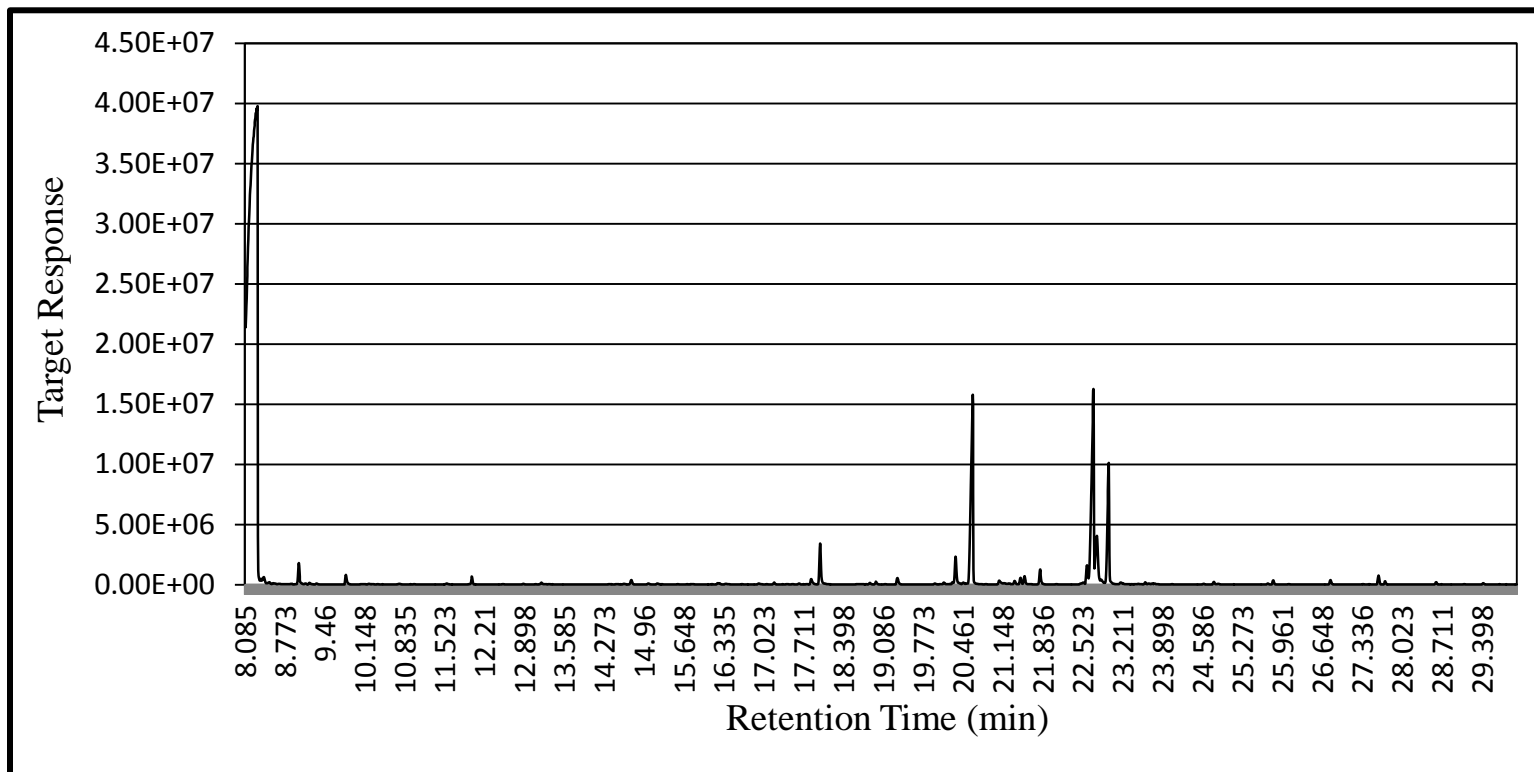


Figure 46 Chromatogram of vegetable based biodiesel spiked in MFW with a spike of internal standard after SBSE-TD-GCMS.

Table 10: Compounds identified in the chromatogram in Figure 45 using NIST library.

Compounds	Retention Time (min)
Cyclopentasiloxane, decamethyl-	8.936
Cycloptetrasiloxane, octamethyl-	10.163
Cyclohexasiloxane, dodecamethyl-	11.935
Diethyl Phthalate	16.399
Cyclononasiloxane, octadecamethyl-	19.27
Dibutyl phthalate	19.879
Hexadecanoic acid, methyl ester	20.513
9, 12-Octadecadienoic acid, methyl ester	22.512
9-Octadecanoic acid, methyl ester	22.56
9, 12,15-Octadecatrienoic acid, methyl ester	22.877
Octadecanoic acid, methyl ester	22.883
Mirex	27.521

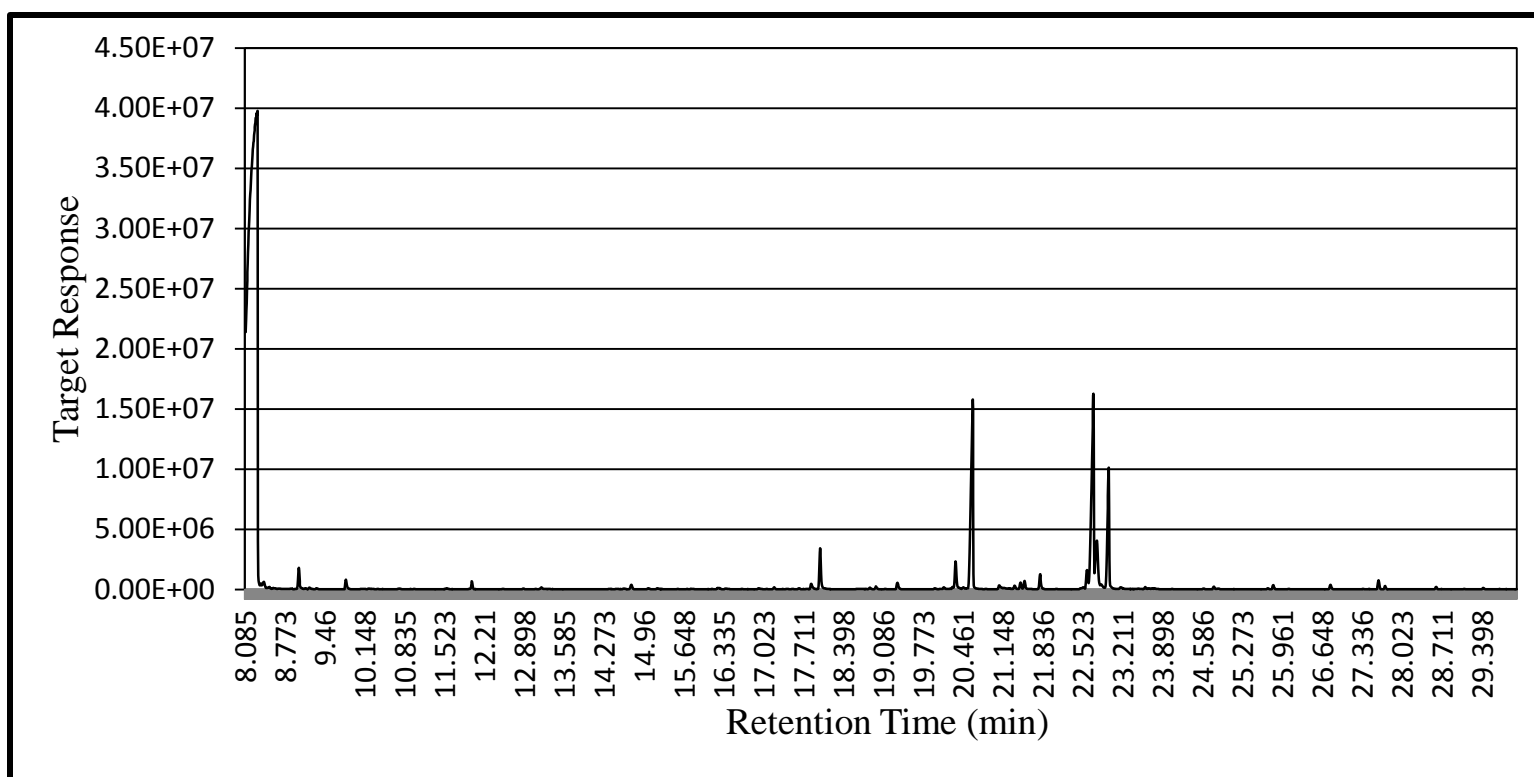


Figure 47: Chromatogram of animal fat based biodiesel spiked in MFW with a spike of internal standard after SBSE-TD-GCMS.

Table 11: Compounds identified in a chromatogram shown in Figure 45 using NIST library.

Compounds	Retention Time (min)
Undecane	8.265
Cyclopentasiloxane, decamethyl-	9.011
Dodecane	9.83
Tetradecanoic acid, methyl ester	17.996
Pentadecanoic acid, methyl ester	19.329
9-Hexadecenoic acid, methyl ester, (Z)-	20.328
Hexadecanoic acid, methyl ester	20.609
Heptadecanoic acid, methyl ester	21.783
9,12-Octadecadienoic acid, methyl ester	22.592
9-Octadecenoic acid, methyl ester, (E)-	22.682
8-Octadecenoic acid, methyl ester, (E)-	22.766
Octadecanoic acid, methyl ester	22.957
Mirex	27.621

Table 12: Target Responses for n-alkanes from diesel fuel extracted using SBSE in MFW during the methanol optimization stage.

Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	Methanol Content (%)					
	0		10		20	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	1543231 +/- 1647879 a	107%	2292810 +/- 1400763 ab	61%	3534399 +/- 1970899 ab	56%
Dodecane	5762355 +/- 1449595 a	25%	3841483 +/- 1625733 ab	42%	6307412 +/- 1181967 ab	19%
Tridecane	548943 +/- 141712 a	26%	2658831 +/- 2253227 a	85%	6157253 +/- 689896 b	11%
Tetradecane	1992223 +/- 269449 a	14%	2601108 +/- 989832 a	38%	3941274 +/- 295848 a	8%
Pentadecane	4049766 +/- 16276 a	0%	2820607 +/- 1275361 a	45%	2820997 +/- 1420709 a	50%
Hexadecane	1825276 +/- 882502 a	48%	1380772 +/- 194867 ab	14%	763223 +/- 179351 ab	23%
Heptadecane	1850383 +/- 934118 a	50%	1408624 +/- 195016 a	14%	446052 +/- 107803 a	24%
Octadecane	1571059 +/- 806545 a	51%	1176109 +/- 220430 a	19%	523833 +/- 297923 a	57%
Nonadecane	1268701 +/- 603406 a	48%	984513 +/- 208052 ab	21%	483189 +/- 228102 ab	47%
Eicosane	886014 +/- 407616 a	46%	695347 +/- 150275 a	22%	3896550 +/- 6054165 a	155%
Heneicosane	517279 +/- 224800 a	43%	387757 +/- 65717 ab	17%	214288 +/- 86470 ab	40%
Docosane	426042 +/- 129364 a	30%	217236 +/- 38190 a	18%	688165 +/- 556940a	81%
Mirex	354982 +/- 13665 a	4%	259001 +/- 25580 a	10%	570715 +/- 39495 a	7%
Compounds	Methanol Content (%)					
	30		40		50	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	5543103 +/- 1462984 bc	26%	8765246 +/- 199880 cd	2%	10397017 +/- 489466 d	5%
Dodecane	8860522 +/- 1552525 b	18%	13014327 +/- 245954 c	2%	16065622 +/- 102559 c	1%
Tridecane	8796886 +/- 1059497 b	12%	14401636 +/- 604026 c	4%	17967888 +/- 570313 d	3%
Tetradecane	6712138 +/- 391746 b	6%	11992563 +/- 786147 c	7%	17026290 +/- 1155152 d	7%
Pentadecane	4422843 +/- 317754 a	7%	11089848 +/- 732002 b	7%	17899236 +/- 1144461 c	6%
Hexadecane	2969878 +/- 185149 b	6%	8930830 +/- 497956 c	6%	16970056 +/- 1093457 d	6%
Heptadecane	1355591 +/- 139195 a	10%	6420392 +/- 586504 b	9%	14601572 +/- 996439 c	7%
Octadecane	465920 +/- 62034 a	13%	4125732 +/- 400014 b	10%	10812201 +/- 881679 c	8%
Nonadecane	216099 +/- 42442 b	20%	2312758 +/- 160552 c	7%	6231310 +/- 559252d	9%
Eicosane	8504222 +/- 1684684 ab	20%	1036652 +/- 10004 ab	1%	3688846 +/- 310537 b	8%
Heneicosane	65412 +/- 10251 ab	16%	334624 +/- 3882 b	1%	1810354 +/- 198125 c	11%
Docosane	656772 +/- 192294 a	29%	360114 +/- 314578 a	87%	925177 +/- 104306 a	11%
Mirex	1193159 +/- 76534 b	6%	1535218 +/- 4096 c	0%	1690294 +/- 134277 c	8%

Table 13: Target Responses for n-alkanes from diesel fuel extracted using SBSE in MSW during the methanol optimization stage. Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	Methanol Content (%)					
	0		10		20	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	2002975 +/- 2241924 a	112%	1007444 +/- 596385 a	59%	835992 +/- 477404 a	57%
Dodecane	2269949 +/- 1255250 ab	55%	3343528 +/- 2147700 ab	64%	1569993 +/- 517989 a	33%
Tridecane	287524 +/- 80120 a	28%	377376 +/- 48429 a	13%	2042985 +/- 416535 b	20%
Tetradecane	1309502 +/- 22692 a	2%	1303996 +/- 57929 a	4%	1504285 +/- 333905 a	22%
Pentadecane	2266251 +/- 697191 a	31%	2027746 +/- 1360420 a	67%	1227818 +/- 89815 a	7%
Hexadecane	975767 +/- 346572 a	36%	988754 +/- 162926 a	16%	922086 +/- 231470 a	25%
Heptadecane	980753 +/- 378650 a	39%	984747 +/- 167275 a	17%	690765 +/- 90892 a	13%
Octadecane	870608 +/- 312007 ab	36%	771572 +/- 334671 ab	43%	599310 +/- 87313 a	15%
Nonadecane	821190 +/- 288234 a	35%	711813 +/- 294709 a	41%	527066 +/- 85693 a	16%
Eicosane	653776 +/- 202995 a	31%	539103 +/- 239647 a	44%	407826 +/- 64336 a	16%
Heneicosane	409163 +/- 129471 a	32%	360202 +/- 161059 a	45%	308436 +/- 113786 a	37%
Docosane	221913 +/- 71292 ab	32%	193331 +/- 86232 a	45%	169758 +/- 59206 a	35%
Mirex	306292 +/- 32899 a	11%	278715 +/- 33476 a	12%	475901 +/- 45843 a	10%
Compounds	Methanol Content (%)					
	30		40		50	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	1386922 +/- 489879 a	35%	1449842 +/- 172210 a	12%	876818 +/- 234289 a	27%
Dodecane	3003776 +/- 164768 ab	5%	5053908 +/- 752302 b	15%	5411891 +/- 159637 b	3%
Tridecane	3511731 +/- 161636 c	5%	6184552 +/- 701269 d	11%	7265128 +/- 322789 d	4%
Tetradecane	2851287 +/- 76135 a	3%	4997169 +/- 455295 a	9%	771598 +/- 41253 a	5%
Pentadecane	1818121 +/- 44889 a	2%	4016705 +/- 330494 b	8%	6337030 +/- 187420 c	3%
Hexadecane	1261274 +/- 39371 a	3%	3105394 +/- 219017 b	7%	6013147 +/- 63888 c	1%
Heptadecane	832585 +/- 21696 a	3%	2281933 +/- 183119 b	8%	5237058 +/- 263169 c	5%
Octadecane	595614 +/- 23072 a	4%	1547416 +/- 155827 b	10%	3964804 +/- 723009 c	18%
Nonadecane	497993 +/- 10459 a	2%	931283 +/- 102130 a	11%	2520120 +/- 582899 a	23%
Eicosane	369502 +/- 16714 a	5%	508327 +/- 51360 a	10%	1604931 +/- 331438 b	21%
Heneicosane	236943 +/- 8861 a	4%	244696 +/- 21789 a	9%	849863 +/- 99664 b	12%
Docosane	244582 +/- 177484 ab	73%	129665 +/- 16574 a	13%	450756 +/- 33574 b	7%
Mirex	874695 +/- 83496 b	10%	1323854 +/- 131669 c	10%	1520376 +/- 70025 d	5%

Table 14: Target Responses for selected diesel compounds extracted using SBSE in MFW during the methanol content optimization stage. Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	Methanol Content (%)					
	0		10		20	
	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV
Benzene, 1-ethyl-2,4-dimethyl-	1190080 +/- 211748 a	18%	1916808 +/- 578626 ab	30%	2923321 +/- 292878 d	10%
Naphthalene, 1,2,3,4-tetrahydro-	1501055 +/- 194541 a	13%	1656001 +/- 278712 abc	17%	1795049 +/- 50206 c	3%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	1922493 +/- 238021 a	12%	3019339 +/- 1050940 abc	35%	3857062 +/- 194274 c	5%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	1389374 +/- 165465 a	12%	1919265 +/- 512830 ab	27%	2496906 +/- 93668 b	4%
1H-Indene, 2,3-dihydro-5,6-dimethyl-	1181807 +/- 137984 ab	12%	1599802 +/- 337475 bc	21%	1891796 +/- 32859 c	2%
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	3685208 +/- 3775726 a	102%	1637695 +/- 612335 a	37%	2385956 +/- 33362 a	1%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	2478790 +/- 368115 a	15%	3103467 +/- 1138172 ab	37%	4408277 +/- 45565 b	1%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	9393261 +/- 1007033 ab	11%	10648123 +/- 2954256 abc	28%	13639636 +/- 204506 c	1%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	976175 +/- 32350 a	3%	947451 +/- 58394 b	6%	1017723 +/- 39464 b	4%
9-Methyl-S-octahydrophenanthracene	442990 +/- 18206 a	4%	436474 +/- 30615 a	7%	480757 +/- 9566 ab	2%
Anthracene, 1,2,3,4-tetrahydro-	328026 +/- 10000 b	3%	336788 +/- 51903 b	15%	340016 +/- 3247 b	1%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	731416 +/- 27487 a	4%	733563 +/- 37777 a	5%	809165 +/- 17368 ab	2%
9-Methyl-S-octahydroanthracene	868226 +/- 47906 ab	6%	875548 +/- 55718 ab	6%	957085 +/- 27181 abc	3%
Mirex	354982 +/- 13665 a	4%	259001 +/- 25580 a	10%	570715 +/- 39495 a	7%
Compounds	Methanol Content (%)					
	30		40		50	
	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV
Benzene, 1-ethyl-2,4-dimethyl-	2400945 +/- 76406 bcd	3%	2732108 +/- 91851 cd	3%	1944302 +/- 74302 ab	4%
Naphthalene, 1,2,3,4-tetrahydro-	1604075 +/- 60082 c	4%	1505138 +/- 62653 bc	4%	921220 +/- 18806 ab	2%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	3433697 +/- 216273 c	6%	3403670 +/- 182227 bc	5%	2244884 +/- 25859 ab	1%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	2313064 +/- 101776 b	4%	2281672 +/- 8060 b	0%	1556343 +/- 61328 a	4%
1H-Indene, 2,3-dihydro-5,6-dimethyl-	1748367 +/- 71610 c	4%	1630168 +/- 2562 bc	0%	1164248 +/- 111907 a	10%
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	2318274 +/- 104401 a	5%	2279495 +/- 55421 a	2%	1282689 +/- 544686 a	42%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	4233649 +/- 241492 b	6%	4182483 +/- 52903 b	1%	3178473 +/- 40396 ab	1%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	13191560 +/- 601519 c	5%	12510815 +/- 280123 bc	2%	8782093 +/- 17213 a	0%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	1068523 +/- 9338 b	1%	1049355 +/- 30600 b	3%	843189 +/- 8734 b	1%
9-Methyl-S-octahydrophenanthracene	488498 +/- 29352 ab	6%	537861 +/- 10091 b	2%	497038 +/- 11721 ab	2%
Anthracene, 1,2,3,4-tetrahydro-	351984 +/- 15879 b	5%	302852 +/- 4873 b	2%	204483 +/- 34891 a	17%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	855226 +/- 19069 b	2%	906240 +/- 7943 a	1%	810034 +/- 21324 ab	3%
9-Methyl-S-octahydroanthracene	1010685 +/- 9164 bc	1%	1043516 +/- 7172 c	1%	894628 +/- 44739 ab	5%
Mirex	1193159 +/- 76534 b	6%	1535218 +/- 4096 c	0%	1690294 +/- 134277 c	8%

Table 15: Target Responses for selected diesel compounds extracted using SBSE in MSW during the methanol content optimization stage. Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	Methanol Content (%)					
	0		10		20	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Benzene, 1-ethyl-2,4-dimethyl-	739476 +/- 180758 a	24%	1634024 +/- 109604 c	7%	1405197 +/- 292949 bc	21%
Naphthalene, 1,2,3,4-tetrahydro-	945416 +/- 323568 a	34%	1529517 +/- 7399 b	0%	925065 +/- 76548 a	8%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	986366 +/- 307124 a	31%	1900911 +/- 61925 c	3%	1477467 +/- 47717 b	3%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	794183 +/- 223412 a	28%	1346211 +/- 36106 c	3%	1123020 +/- 75873 ab	7%
1H-Indene, 2,3-dihydro-5,6-dimethyl-	751053 +/- 213076 a	28%	1162508 +/- 129492 b	11%	959847 +/- 38584 ab	4%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	1388360 +/- 887168 a	64%	2786803 +/- 153041 b	5%	2269449 +/- 91431 ab	4%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	7774112 +/- 1060744 abc	14%	9187507 +/- 455418 c	5%	7111175 +/- 122456 ab	2%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	941260 +/- 175543 bc	19%	1010179 +/- 157726c	16%	701105 +/- 34039 ab	5%
9-Methyl-S-octahydrophenanthracene	433366 +/- 70422 a	16%	473679 +/- 101995 a	22%	331568 +/- 16873 a	5%
Anthracene, 1,2,3,4-tetrahydro-	302319 +/- 50934 b	17%	349997 +/- 95799 bc	27%	215236 +/- 15703 ab	7%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	667950 +/- 115868 a	17%	758528 +/- 136422 a	18%	554613 +/- 30637 a	6%
9-Methyl-S-octahydroanthracene	863933 +/- 137374 a	16%	957485 +/- 176384 a	18%	692471 +/- 40605 a	6%
Mirex	306292 +/- 32899 a	11%	278715 +/- 33476 a	12%	475901 +/- 45843 a	10%
Compounds	Methanol Content (%)					
	30		40		50	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Benzene, 1-ethyl-2,4-dimethyl-	1534719 +/- 119794 bc	8%	1408975 +/- 9937 bc	1%	1132295 +/- 31463 ab	3%
Naphthalene, 1,2,3,4-tetrahydro-	899798 +/- 119670 a	13%	771303 +/- 3179 a	0%	571336 +/- 9365 a	2%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	1545635 +/- 182075 b	12%	1471244 +/- 36025 b	2%	1144286 +/- 51793 ab	5%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	1206657 +/- 130928 bc	11%	1182417 +/- 70778 bc	6%	899087 +/- 35460 ab	4%
1H-Indene, 2,3-dihydro-5,6-dimethyl-	999550 +/- 81446 ab	8%	1000831 +/- 34580 ab	3%	679383 +/- 120527 a	18%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	2321763 +/- 226559 ab	10%	2433433 +/- 24010 b	1%	1855430 +/- 214554 ab	12%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	7880475 +/- 583390 bc	7%	8153843 +/- 129634 bc	2%	6371100 +/- 297457 a	5%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	717538 +/- 68434 ab	10%	752216 +/- 3928 abc	1%	619016 +/- 22418 a	4%
9-Methyl-S-octahydrophenanthracene	352353 +/- 27245 a	8%	362517 +/- 43267 a	12%	317982 +/- 33978 a	11%
Anthracene, 1,2,3,4-tetrahydro-	219609 +/- 22207 ab	10%	200614 +/- 12728 ab	6%	126962 +/- 707 a	1%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	580298 +/- 57133 a	10%	652167 +/- 22896 a	4%	580658 +/- 33370 a	6%
9-Methyl-S-octahydroanthracene	716890 +/- 66273 a	9%	782043 +/- 14543 a	2%	723485 +/- 19527 a	3%
Mirex	874695 +/- 83496 b	10%	1323854 +/- 131669 c	10%	1520376 +/- 70025 d	5%



Table 16: Target Responses for selected FAMES in biodiesel extracted by SBSE in MFW during methanol content optimization. Target responses represent their triplicates averages. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	Methanol Content (%)					
	0		10		20	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Tetradecanoic acid, methyl ester	94695 +/- 9366 a	10%	95135 +/- 14881 ab	16%	153015 +/- 6680 b	4%
Hexadecanoic acid, methyl ester	922969 +/- 119934 a	13%	927781 +/- 133440 a	14%	1187003 +/- 49783 bc	4%
Octadecanoic acid, methyl ester	415558 +/- 45001 a	11%	403010 +/- 50532 a	13%	438837 +/- 53734 a	12%
9-Octadecenoic acid, methyl ester	376742 +/- 51224 a	14%	436921 +/- 44155 a	10%	460871 +/- 42539 ab	9%
9,12-Octadecadienoic acid (Z,Z), methyl ester	1026591 +/- 307874 a	30%	1694064 +/- 50054 ab	3%	2331402 +/- 181417 bc	8%
9,12,15 Octadecatrienoic acid, methyl ester	350054 +/- 14997 a	4%	546971 +/- 28322 a	5%	599425 +/- 49371 ab	8%
Mirex	1275263 +/- 77305 a	6%	1211976 +/- 187727 a	15%	1938196 +/- 15122 ab	1%

Compounds	Methanol Content (%)					
	30		40		50	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Tetradecanoic acid, methyl ester	167248 +/- 9084 bc	5%	226980 +/- 38162 c	17%	200446 +/- 5849 c	3%
Hexadecanoic acid, methyl ester	2409488 +/- 171086 b	7%	3368740 +/- 235543 c	7%	3384459 +/- 245015 c	7%
Octadecanoic acid, methyl ester	844362 +/- 64649 a	8%	1329426 +/- 92358 b	7%	1531105 +/- 62107 b	4%
9-Octadecenoic acid, methyl ester	818626 +/- 84432 b	10%	1028650 +/- 98879 c	10%	1066173 +/- 82624 c	8%
9,12-Octadecadienoic acid (Z,Z), methyl ester	3517704 +/- 352268 cd	10%	4013944 +/- 424747 d	11%	3893318 +/- 272600 d	7%
9,12,15 Octadecatrienoic acid, methyl ester	901672 +/- 61925 bc	7%	975254 +/- 130025 c	13%	891030 +/- 58095 c	7%
Mirex	2980726 +/- 343301 b	12%	3208792 +/- 371158 b	12%	3046485 +/- 407326.224	13%

Table 17: Target Responses for selected FAMES in biodiesel extracted by SBSE in MSW during methanol content optimization. Target responses represent their triplicate averages. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compound	Methanol Content (%)					
	0		10		20	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Tetradecanoic acid, methyl ester	32229 +/- 45578 b	141%	247916 +/- 154091 a	62%	263957 +/- 204248 a	77%
Hexadecanoic acid, methyl ester	2072708 +/- 120213 a	6%	618120 +/- 73976 a	12%	1911858 +/- 499892 a	26%
Octadecanoic acid, methyl ester	179072 +/- 26449 a	15%	110327 +/- 35147 a	32%	192396 +/- 19993 a	10%
8-Octadecenoic acid, methyl ester	587439 +/- 44273 a	8%	436324 +/- 55905 a	13%	966125 +/- 220367 a	23%
9-Octadecenoic acid, methyl ester	586176 +/- 17995 a	3%	436324 +/- 55905 a	13%	966125 +/- 220367 a	23%
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	937577 +/- 3274 a	0%	1628850 +/- 304100 a	19%	3368373 +/- 604354 b	18%
9,12,15 Octadecatrienoic acid, methyl ester	390200 +/- 509 a	0%	543438 +/- 48776 a	9%	858605 +/- 86991 b	10%
Mirex	616024 +/- 41371 a	7%	1328090 +/- 169714 b	13%	1624480 +/- 122761 bc	8%
Compound	Methanol Content (%)					
	30		40		50	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Tetradecanoic acid, methyl ester	404803 +/- 123724 a	31%	707149 +/- 253212 a	36%	600906 +/- 48197 ab	8%
Hexadecanoic acid, methyl ester	5788365 +/- 531491 b	9%	10109191 +/- 1062671 c	11%	9477308 +/- 179971 c	2%
Octadecanoic acid, methyl ester	803246 +/- 153629 b	19%	1887934 +/- 96863 c	5%	1893265 +/- 290240 c	15%
8-Octadecenoic acid, methyl ester	2674853 +/- 390125 b	15%	3913251 +/- 119116 c	3%	3432004 +/- 35985 bc	1%
9-Octadecenoic acid, methyl ester	2674853 +/- 390125 b	15%	3913251 +/- 119116 c	3%	3432004 +/- 35985 bc	1%
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	8347966 +/- 694387 c	8%	10247256 +/- 195233 d	2%	8895426 +/- 268918 cd	3%
9,12,15 Octadecatrienoic acid, methyl ester	2013772 +/- 11572 c	1%	2343911 +/- 12375 c	1%	1958485 +/- 108773 c	6%
Mirex	2035809 +/- 66037 c	3%	2062871 +/- 117470 c	6%	1894555 +/- 300296 c	16%

Table 18: Target Responses for selected diesel compounds extracted using SBSE in MFW during the stir time optimization stage.

Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	STIR TIME (hr)							
	1		2		3		4	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	2790230 +/- 362781 a	13%	4106089 +/- 296252 ab	7%	3847051 +/- 949512 ab	25%	4680051 +/- 277897 b	6%
Dodecane	4080335 +/- 537659 a	13%	6247516 +/- 507442 bc	8%	5508500 +/- 1003161 ab	18%	7109586 +/- 478525 bc	7%
Tridecane	5853886 +/- 595811 a	10%	8299727 +/- 322605 bc	4%	7428899 +/- 607793 ab	8%	9110436 +/- 527579 bc	6%
Tetradecane	5368515 +/- 509673 a	9%	7288431 +/- 420535 a	6%	6843237 +/- 720454 a	11%	8317414 +/- 512653 a	6%
Pentadecane	5554844 +/- 316261 a	6%	7295643 +/- 263567 bc	4%	6886140 +/- 359131 b	5%	8159796 +/- 407532 cd	5%
Hexadecane	5703853 +/- 292685 a	5%	7137983 +/- 378227 b	5%	7166843 +/- 131599 b	2%	8184588 +/- 283513 c	3%
Heptadecane	5324224 +/- 225520 a	4%	6394844 +/- 371847 b	6%	6864881 +/- 299713 bc	4%	7486031 +/- 266649 cd	4%
Octadecane	4170332 +/- 204145 a	5%	4914795 +/- 160630 ab	3%	5671455 +/- 469715 bc	8%	5921796 +/- 479826 c	8%
Nonadecane	2942928 +/- 122335 ab	4%	3229372 +/- 74941 ab	2%	3745011 +/- 367745 b	10%	3800858 +/- 327877 b	9%
Eicosane	2033499 +/- 83664 a	4%	2182913 +/- 71787 a	3%	2371827 +/- 227670 a	10%	2425481 +/- 199788 a	8%
Heneicosane	1100567 +/- 16014 a	1%	1234435 +/- 52304 ab	4%	1271088 +/- 120987 ab	10%	1277618 +/- 95316 ab	7%
Docosane	494930 +/- 7727 a	2%	665081.2 +/- 34910 b	5%	678367 +/- 45164 b	7%	658756 +/- 51744 b	8%
Mirex	1090397 +/- 14633 a	1%	1530607 +/- 64607 b	4%	1716275 +/- 63188 bc	4%	1739724 +/- 54314 bc	3%

Compounds	STIR TIME (hr)					
	8		12		24	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	4022059 +/- 501926 ab	12%	4953195 +/- 519380 b	10%	4181232 +/- 472098 ab	11%
Dodecane	6302599 +/- 897037 bc	14%	7682140 +/- 771958 c	10%	6691965 +/- 704704 bc	11%
Tridecane	8765376 +/- 1023339 bc	12%	9822549 +/- 869027 c	9%	9001067 +/- 737839 bc	8%
Tetradecane	7883222 +/- 884142 a	11%	9021631 +/- 779068 a	9%	8254676 +/- 505185 a	6%
Pentadecane	8198599 +/- 461658 cd	6%	8882243 +/- 763876 d	9%	8781938 +/- 228801 d	3%
Hexadecane	8706434 +/- 449182 cd	5%	8989402 +/- 257299 cd	3%	9131281 +/- 273038 d	3%
Heptadecane	8640768 +/- 113728 d	1%	8423841 +/- 42831 d	1%	9217183 +/- 203883 d	2%
Octadecane	7728370 +/- 152941 d	2%	7601622 +/- 215110 d	3%	8815882 +/- 221906 d	3%
Nonadecane	841826 +/- 65473 ab	8%	1030967 +/- 69071 a	7%	1322749 +/- 47241 ab	4%
Eicosane	3149057 +/- 217354 b	7%	3620801 +/- 101633 c	3%	4752774 +/- 112045 d	2%
Heneicosane	1484939 +/- 67470 bc	5%	1655067 +/- 40468 c	2%	2209847 +/- 149576 d	7%
Docosane	695854 +/- 1452 b	0%	765886 +/- 27851 bc	4%	946108 +/- 103183 c	11%
Mirex	1610963 +/- 59538 bc	4%	1717504 +/- 2047 bc	0%	1867791 +/- 294336 c	16%

Table 19: Target Responses for selected diesel compounds extracted using SBSE in MSW during the stir time optimization stage.

Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	STIR TIME							
	1		2		3		4	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	26,734,623 +/- 13412688 a	50%	32,117,310 +/- 1473073 a	5%	35,330,010 +/- 898324 a	3%	30,791,239 +/- 4642397 a	15%
Dodecane	31,588,482 +/- 4763199 a	15%	37,028,987 +/- 663716 a	2%	41,998,367 +/- 4454039 a	11%	35,673,911 +/- 2326188 a	7%
Tridecane	47,425,877 +/- 5071768 a	11%	45,071,464 +/- 1062704 a	2%	35,056,690 +/- 29001626 a	83%	50,743,926 +/- 4358044 a	9%
Tetradecane	33,430,629 +/- 7900652 a	24%	44,194,257 +/- 3563319 ab	8%	47,853,690 +/- 1469975 ab	3%	48,733,539 +/- 5915451 b	12%
Pentadecane	27,498,003 +/- 3795931 a	14%	40,889,356 +/- 3024739 ab	7%	49,493,927 +/- 1364620 ab	3%	51,153,833 +/- 1958120 ab	4%
Hexadecane	18,605,917 +/- 2453492 ab	13%	27,923,950 +/- 966970 b	3%	5,956,603 +/- 653443 a	11%	16,095,657 +/- 15929952 ab	99%
Heptadecane	12,636,351 +/- 1502042 a	12%	20,179,623 +/- 563777 ab	3%	28,252,182 +/- 1754303 c	6%	27,880,225 +/- 2031993 bc	7%
Octadecane	9,160,984 +/- 1299348 a	14%	15,337,319 +/- 362658 ab	2%	8,061,655 +/- 10792369 a	134%	7,627,186 +/- 10008098 a	131%
Nonadecane	939,129 +/- 206244 a	22%	1,384,924 +/- 517949 ab	37%	1,467,955 +/- 106206 ab	7%	1,585,547 +/- 187309 ab	12%
Eicosane	4,519,902 +/- 1213138 a	27%	8,043,142 +/- 939099 ab	12%	10,246,750 +/- 1413630 bc	14%	12,342,573 +/- 2419900 cd	20%
Heneicosane	2,696,454 +/- 820438 a	30%	4,945,831 +/- 861160 ab	17%	6,255,750 +/- 1025628 ab	16%	7,963,697 +/- 1936260 b	24%
Docosane	1,594,519 +/- 532918 a	33%	2,148,465 +/- 1071037 a	50%	3,673,637 +/- 762167 a	21%	3,026,368 +/- 3087400 a	102%
Mirex	914,642 +/- 119048 a	13%	1,307,105 +/- 70231 b	5%	1,361,973 +/- 68652 b	5%	1,249,908 +/- 132685 b	11%

Compounds	STIR TIME					
	8		12		24	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Undecane	33,982,773 +/- 1316597 a	4%	34,804,272 +/- 2791447 a	8%	32,627,802 +/- 5417882 a	17%
Dodecane	38,918,323 +/- 803502 a	2%	39,750,867 +/- 1760233 a	4%	38,139,934 +/- 7187037 a	19%
Tridecane	51,375,310 +/- 309721 a	1%	1,495,720 +/- 226968 a	15%	19,480,099 +/- 30521022 a	157%
Tetradecane	56,463,093 +/- 4927739 b	9%	55,255,755 +/- 3518088 b	6%	53,806,704 +/- 8704700 b	16%
Pentadecane	57,275,619 +/- 2396610 ab	4%	58,007,416 +/- 770017 ab	1%	63,031,613 +/- 1819468 b	3%
Hexadecane	8,166,754 +/- 448740 a	5%	8,285,588 +/- 244248 a	3%	9,131,898 +/- 575742 a	6%
Heptadecane	35,128,199 +/- 3460715 cd	10%	36,340,042 +/- 1520100 d	4%	45,758,764 +/- 5678123 d	12%
Octadecane	24,127,841 +/- 2670662 ab	11%	2,471,615,051 +/- 44516033 b	2%	31,236,768 +/- 2977335 b	10%
Nonadecane	1,826,979 +/- 170744 ab	9%	242,286,586 +/- 90022273 ab	37%	2,824,399 +/- 1259986 b	45%
Eicosane	13,889,519 +/- 406448 cd	3%	1,419,904,322 +/- 47804641 d	3%	14,629,856 +/- 1325612 d	9%
Heneicosane	8,663,393 +/- 355783 b	4%	5,275,713 +/- 457203281. a	87%	2,156,170 +/- 204784 a	9%
Docosane	4,965,570 +/- 255945 a	5%	5,234,874 +/- 44362594 a	8%	4,427,090 +/- 1926011 a	44%
Mirex	1,335,952 +/- 19417 b	1%	1,310,438 +/- 7721808 b	6%	1,309,029 +/- 9683 b	1%

Table 20: Target Responses for selected diesel compounds extracted using SBSE in MFW during the stir time optimization stage.

Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	STIR TIME (hr)							
	1		2		3		4	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Benzene, 1-ethyl-2,4-dimethyl-	1207151 +/- 149788 a	12%	1191389 +/- 78905 a	7%	1363456 +/- 119216 a	9%	1446560 +/- 78038 a	5%
Naphthalene, 1,2,3,4-tetrahydro-	644478 +/- 73160 a	11%	633319 +/- 33239 a	5%	704769 +/- 30119 a	4%	713424.5 +/- 20830 a	3%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	1248234 +/- 76919 a	6%	1364358 +/- 45626 ab	3%	1445459 +/- 117040 ab	8%	1444507 +/- 18080 ab	1%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	857255 +/- 89664 a	10%	973468 +/- 68457 ab	7%	1079937 +/- 95101 b	9%	1080691 +/- 25818 b	2%
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	868838 +/- 242393 a	28%	1166155 +/- 47881 ab	4%	1339713 +/- 93909 b	7%	1370925 +/- 104091 b	8%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro	1914928 +/- 144002 a	8%	2232187 +/- 69473 b	3%	2450950 +/- 136728 bc	6%	2512219 +/- 70278 c	3%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	5961214 +/- 490128 a	8%	6777646 +/- 196060 a	3%	7749136 +/- 358944 b	5%	7801072 +/- 256507 b	3%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	539877 +/- 16247 a	3%	666666 +/- 10138 b	2%	717949 +/- 32096 bc	4%	755014.6 +/- 26075 cd	3%
9-Methyl-S-octahydrophenananthracene	292864 +/- 20030 a	7%	360610 +/- 13281 ab	4%	388071 +/- 48281 bc	12%	431675.7 +/- 3313 bc	1%
Anthracene, 1,2,3,4-tetrahydro-	124679 +/- 18805 a	15%	148638 +/- 5165 ab	3%	179859 +/- 25793 b	14%	164968.6 +/- 7710 ab	5%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenananthracene	469335 +/- 21081 a	4%	610525 +/- 6558 b	1%	670592 +/- 32563 bc	5%	710372.7 +/- 10703 c	2%
9-Methyl-S-octahydroanthracene	552283 +/- 26018 a	5%	727031 +/- 10583 a	1%	799635 +/- 38830 bc	5%	825016.5 +/- 10880 c	1%
Mirex	1090397 +/- 14633 a	1%	1530607 +/- 64607 b	4%	1716275 +/- 63188 bc	4%	1739724 +/- 54314 bc	3%
Compounds	STIR TIME (hr)							
	8		12		24			
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Benzene, 1-ethyl-2,4-dimethyl-	1483571 +/- 19174 a	1%	1458027 +/- 218250 a	15%	1447773 +/- 161659 a	11%		
Naphthalene, 1,2,3,4-tetrahydro-	704573 +/- 52983 a	8%	735883 +/- 86854 a	12%	724447 +/- 62637 a	9%		
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	1509059 +/- 69601 b	5%	1467917 +/- 186492 b	13%	1460908 +/- 23881 ab	2%		
1H-Indene, 2,3-dihydro-4,7-dimethyl-	1152610 +/- 52808 b	5%	1113475 +/- 151510 b	14%	1088978 +/- 38485 b	4%		
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	1381974 +/- 12818 b	1%	1352862 +/- 103245 b	8%	1390525 +/- 71738 b	5%		
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	2606974 +/- 63132 c	2%	2516335 +/- 64795 c	3%	2618250 +/- 108620 c	4%		
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	8118608 +/- 352081 b	4%	8061862 +/- 399074 b	5%	7996197 +/- 207441 b	3%		
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	760949 +/- 9145 cd	1%	814069 +/- 25416 d	3%	788720 +/- 45453 cd	6%		
9-Methyl-S-octahydrophenananthracene	405356 +/- 43221 bc	11%	456109 +/- 22225 c	5%	453710 +/- 22691 c	5%		
Anthracene, 1,2,3,4-tetrahydro-	198213 +/- 37404 b	19%	176559 +/- 9638 b	5%	186534 +/- 10466 b	6%		
1,2,3,4,5,6,7,8-Octahydro-1-methylphenananthracene	728668 +/- 23764 c	3%	775643 +/- 10268 c	1%	742291 +/- 51303 c	7%		
9-Methyl-S-octahydroanthracene	859544 +/- 26640 c	3%	881274 +/- 36870 c	4%	873439 +/- 66103 c	8%		
Mirex	1610963 +/- 59538 bc	4%	1717504 +/- 2047 bc	0%	1867791 +/- 294336 c	16%		

Table 21: Target Responses for selected biodiesel compounds extracted using SBSE in MSW during the stir time optimization stage.

Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	STIR TIME							
	1		2		3		4	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Benzene, 1-ethyl-2,4-dimethyl-	4244421 +/- 2705112 a	64%	5128816 +/- 225829 a	4%	5648461 +/- 937900 a	17%	4587246 +/- 406496 a	9%
Naphthalene, 1,2,3,4-tetrahydro-	4089691 +/- 1111640 a	27%	4472679 +/- 133767 a	3%	4440613 +/- 172550 a	4%	3680989 +/- 421765 a	11%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	10796005 +/- 2947870 a	27%	12271970 +/- 414290 a	3%	12172109 +/- 493806 a	4%	9980392 +/- 536329 a	5%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	6560299 +/- 1409095 a	21%	7312952 +/- 209005 a	3%	7381611 +/- 320749 a	4%	6358302 +/- 523014 a	8%
1H-Indene, 2,3-dihydro-5,6-dimethyl-	4989837 +/- 1041721 a	21%	5575129 +/- 186190 a	3%	6028317 +/- 465396 a	8%	5278088 +/- 760160 a	14%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro	11953623 +/- 1223840 a	10%	12506141 +/- 273366 a	2%	12336569 +/- 295995 a	2%	11382285 +/- 358074 a	3%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	31278712 +/- 4045960 a	13%	34458215 +/- 558456 a	2%	33343291 +/- 264361 a	1%	32059405 +/- 893764 a	3%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	4030765 +/- 399433 a	10%	4827682 +/- 77804 ab	2%	5126358 +/- 228310 ab	4%	4792556 +/- 158994 ab	3%
9-Methyl-S-octahydrophenanthracene	2216491 +/- 262623 a	12%	2668558 +/- 100210 a	4%	1363149 +/- 1252472 a	92%	1988029 +/- 1186037 a	60%
Anthracene, 1,2,3,4-tetrahydro-	1213525 +/- 102391 a	8%	1294783 +/- 37490 a	3%	1271104 +/- 110558a	9%	1235069 +/- 41842 a	3%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	3947122 +/- 375393 a	10%	4945345 +/- 141384 a	3%	4996106 +/- 158543 a	3%	4773255 +/- 182332 a	4%
9-Methyl-S-octahydroanthracene	4815343 +/- 434407 a	9%	5705031 +/- 431591 a	8%	5865192 +/- 405260 a	7%	5674814 +/- 250110 a	4%
Mirex	914641.7 +/- 119048 a	13%	1307105 +/- 70231 b	5%	1361973 +/- 68652 b	5%	1249908 +/- 132685 b	11%

Compounds	STIR TIME					
	8		12		24	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Benzene, 1-ethyl-2,4-dimethyl-	4858151 +/- 73377 a	2%	5863458 +/- 712932 a	12%	5100658 +/- 1181631 a	23%
Naphthalene, 1,2,3,4-tetrahydro-	4043290 +/- 108828 a	3%	4893342 +/- 653102 a	13%	3771667 +/- 705737 a	19%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	11090415 +/- 204474 a	2%	13098646 +/- 1607535 a	12%	10171257 +/- 1769529 a	17%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	6825720 +/- 115572 a	2%	7767803 +/- 860945 a	11%	6315514 +/- 906092 a	14%
1H-Indene, 2,3-dihydro-5,6-dimethyl-	5524014 +/- 322932 a	6%	6326516 +/- 1176035 a	19%	5297764 +/- 1207922 a	23%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro	11827644 +/- 232066 a	2%	12851522 +/- 688036 a	5%	11241027 +/- 952806 a	8%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	32670571 +/- 415605 a	1%	34892671 +/- 1350036 a	4%	31155068 +/- 1632613 a	5%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	5975320 +/- 1469710 ab	25%	6108111 +/- 1209070 b	20%	5266947 +/- 1003634 ab	19%
9-Methyl-S-octahydrophenanthracene	595757.3 +/- 46280 a	8%	599079 +/- 43619 a	7%	2762110 +/- 334271 a	12%
Anthracene, 1,2,3,4-tetrahydro-	1099445 +/- 52597 a	5%	1159610 +/- 125971 a	11%	1028712 +/- 171065 a	17%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	4864939 +/- 152117 a	3%	4996303 +/- 293757 a	6%	3167897 +/- 2210846 a	70%
9-Methyl-S-octahydroanthracene	5543748 +/- 617402 a	11%	5851507 +/- 377800 a	6%	5369399 +/- 348148 a	6%
Mirex	1335952 +/- 19417 b	1%	1310438 +/- 77218 b	6%	1309029 +/- 9683 b	1%

Table 22: Target Responses for selected biodiesel compounds extracted using SBSE in MFW during the stir time optimization stage.

Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	STIR TIME					
	1		2		3	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Tetradecanoic acid, methyl ester	279677.8 +/- 57423 a	21%	442598.5 +/- 13087 a	3%	409632.9 +/- 17663 a	4%
Hexadecanoic acid, methyl ester	4411698 +/- 266590 a	6%	6730375 +/- 271207 b	4%	7557940 +/- 117510 b	2%
Octadecanoic acid, methyl ester	1111762 +/- 80985 a	7%	1582784 +/- 103438 b	7%	1876755 +/- 106983 b	6%
9-Octadecenoic acid, methyl ester	1467630 +/- 108790 a	7%	2070930 +/- 161510 b	8%	2104266 +/- 228981 b	11%
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	3422815 +/- 56215 a	2%	4363105 +/- 456849 ab	10%	4803384 +/- 614696 b	13%
9,12,15 Octadecatrienoic acid, methyl ester	618826.7 +/- 28761 a	5%	920481 +/- 16492 b	2%	989802.2 +/- 211403 b	21%
Mirex	1066222 +/- 98258 a	9%	1368312 +/- 103615 ab	8%	1530074 +/- 36980 b	2%

Compounds	STIR TIME					
	8		12		24	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Tetradecanoic acid, methyl ester	492496.3 +/- 101054 a	21%	503508.5 +/- 9940 a	2%	533690.4 +/- 38682 a	7%
Hexadecanoic acid, methyl ester	8080755 +/- 417116 b	5%	7295715 +/- 126345 b	2%	7247511 +/- 312187 b	4%
Octadecanoic acid, methyl ester	1886720 +/- 37760 b	2%	1615541 +/- 20886 b	1%	1682568 +/- 115685 b	7%
9-Octadecenoic acid, methyl ester	2482311 +/- 72112 b	3%	2105117 +/- 432875 b	21%	2186802 +/- 295304 b	14%
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	3944179 +/- 373563 a	9%	4146445 +/- 683598 ab	16%	3403115 +/- 383681 a	11%
9,12,15 Octadecatrienoic acid, methyl ester	1003629 +/- 97993 b	10%	956306 +/- 3066 b	0%	748811 +/- 176434 ab	24%
Mirex	1636418 +/- 110485 b	7%	1515489 +/- 151992 b	10%	1458655 +/- 148803 b	10%

Table 23: Target Responses for selected biodiesel compounds extracted using SBSE in MSW during the stir time optimization stage.

Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	STIR TIME (hr)							
	1		2		3		4	
	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV
Tetradecanoic acid, methyl ester	437962 +/- 25916 a	6%	599527 +/- 137194 b	23%	1363755 +/- 941078 b	69%	739711 +/- 59265 b	8%
Hexadecanoic acid, methyl ester	14728572 +/- 4472541 a	30%	25937915 +/- 2935131 b	11%	31033882 +/- 4171206 bc	13%	28412884 +/- 1096909 c	4%
Octadecanoic acid, methyl ester	1629345 +/- 919772 a	56%	2760576 +/- 119378 b	4%	5058431 +/- 2315308 b	46%	4033311 +/- 450318 b	11%
9-Octadecenoic acid, methyl ester	6263645 +/- 2615338 a	42%	15452975 +/- 565040 a	4%	18911993 +/- 4573662 b	24%	17904730 +/- 1229436 b	7%
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	17799240 +/- 3989358 a	22%	27550808 +/- 949346 ab	3%	33554026 +/- 8156440 b	24%	31898351 +/- 2178680 b	7%
9,12,15 Octadecatrienoic acid, methyl ester	4716605 +/- 791990 a	17%	6796381 +/- 354516 ab	5%	12558907 +/- 8158978 bc	65%	11558834 +/- 5727753 bc	50%
Mirex	651631 +/- 140683 a	22%	1058194 +/- 61973 a	6%	1385681 +/- 23060 a	2%	1529501 +/- 67695 a	4%
Compounds	STIR TIME (hr)							
	8		12		24			
	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV		
Tetradecanoic acid, methyl ester	847805 +/- 22208 b	3%	921173 +/- 15574 b	2%	1052558 +/- 75071 b	7%		
Hexadecanoic acid, methyl ester	41324056 +/- 3243317 c	8%	40343632 +/- 1536739 c	4%	42914631 +/- 4463437 c	10%		
Octadecanoic acid, methyl ester	6845210 +/- 499602 b	7%	6279411 +/- 35353 b	1%	7538238 +/- 1621095 b	22%		
9-Octadecenoic acid, methyl ester	26412439 +/- 3494360 b	13%	25642957 +/- 11657 b	0%	27221736 +/- 3892109 b	14%		
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	47194819 +/- 6214809 b	13%	45349535 +/- 97258 b	0%	48684052 +/- 6950485 b	14%		
9,12,15 Octadecatrienoic acid, methyl ester	22322654 +/- 2895565 c	13%	21514762 +/- 66967 c	0%	22921961 +/- 3293440 c	14%		
Mirex	1027804 +/- 2395 a	0%	1040832 +/- 19768 a	2%	1083536 +/- 39933 a	4%		



Table 24: Target Responses for selected diesel compounds extracted using SBSE in MFW during the pH optimization. Target responses represent an average of duplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	pH									
	3				N				9	
	Target Response			%STDEV	Target Response			%STDEV	Target Response	
Undecane	1172232	+/-	166798 a	14%	1883515	+/-	2314 a	0%	3277007	+/- 664309 a
Dodecane	724899	+/-	301525 a	42%	4879507	+/-	554360 b	11%	6415343	+/- 1054888 b
Tridecane	268843	+/-	129959 a	48%	814638	+/-	54798 a	7%	743091	+/- 271852 a
Tetradecane	908657	+/-	350314 a	39%	2426789	+/-	46609 a	2%	2360495	+/- 850098 a
Pentadecane	1117021	+/-	934561 a	84%	905157	+/-	154949 a	17%	1197311	+/- 551217 a
Hexadecane	645967	+/-	3822 a	1%	1162022	+/-	148509 a	13%	1781199	+/- 645280 a
Heptadecane	709991	+/-	116469 a	16%	1249506	+/-	118244 a	9%	1882972	+/- 589276 a
Octadecane	528210	+/-	87891 a	17%	900365	+/-	119452 a	13%	1445173	+/- 562984 a
Nonadecane	467842	+/-	80359 a	17%	770733	+/-	92461 a	12%	1269630	+/- 390832 a
Eicosane	356712	+/-	63234 a	18%	643406	+/-	144369 a	22%	1063686	+/- 374217 a
Heneicosane	283682	+/-	22302 a	8%	456860	+/-	118469 a	26%	701059	+/- 258982 a
Docosane	176469	+/-	2819 a	2%	285015	+/-	80176 a	28%	437472	+/- 187856 a
Mirex	334575	+/-	17994 a	5%	380604	+/-	7969 a	2%	483142	+/- 86134 a

Table 25: Target Responses for selected diesel compounds extracted using SBSE in MSW during the pH optimization. Target responses represent an average duplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	Target Response						
	3		N		9		
	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV	
Undecane	3649448 +/- 483398 a	13%	2908005 +/- 95570 a	3%	3335573 +/- 267923 a	8%	
Dodecane	1048904 +/- 1013153 a	97%	4472267 +/- 341253 b	8%	5788745 +/- 537562 b	9%	
Tridecane	610981 +/- 25594 a	4%	454306 +/- 216555 a	48%	738040 +/- 26560 a	4%	
Tetradecane	1914688 +/- 74882 a	4%	1668281 +/- 300672 a	18%	1888779 +/- 17526 a	1%	
Pentadecane	1192402 +/- 202525 a	17%	1023451 +/- 265775 a	26%	1093768 +/- 39244 a	4%	
Hexadecane	2233475 +/- 150650 a	7%	2149194 +/- 404041 a	19%	2047395 +/- 19759 a	1%	
Heptadecane	2417190 +/- 152296 a	6%	2164498 +/- 801263 a	37%	2280875 +/- 4192 a	0%	
Octadecane	2272670 +/- 89061 a	4%	2384207 +/- 345567 a	14%	2100496 +/- 112186 a	5%	
Nonadecane	2077613 +/- 119210 a	6%	2178254 +/- 289781 a	13%	1986768 +/- 15270 a	1%	
Eicosane	1790260 +/- 154248 a	9%	2023919 +/- 16194 a	1%	1739936 +/- 27343 a	2%	
Heneicosane	1203335 +/- 56418 a	5%	1252648 +/- 138739 a	11%	1132918 +/- 39535 a	3%	
Docosane	769536 +/- 15222 a	2%	758915 +/- 94692 a	12%	725321 +/- 20561 a	3%	
Mirex	544544 +/- 16770 a	3%	502357 +/- 55360 a	11%	623400 +/- 4105 a	1%	

Table 26: Target Responses for selected diesel compounds extracted using SBSE in MFW during the pH optimization. Target responses represent an average duplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	pH					
	3		N		9	
	Target Response	%STDEV	Target Response	%STDEV	Target Response	%STDEV
Benzene, 1-ethyl-2,4-dimethyl-	974593 +/- 87842 a	9%	1110867 +/- 32778 a	3%	1115402 +/- 297642 a	27%
Naphthalene, 1,2,3,4-tetrahydro-	1067584 +/- 91954 b	9%	1214516 +/- 45228 ab	4%	1221337 +/- 114603 a	9%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	1021276 +/- 90546 a	9%	1432784 +/- 168774 a	12%	1379255 +/- 775 a	0%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	795561 +/- 98173 a	12%	1048326 +/- 65035 a	6%	1038525 +/- 35510 a	3%
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	3410342 +/- 4006434 a	117%	747237 +/- 478232 a	64%	833104 +/- 474623 a	57%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	1579206 +/- 538025 a	34%	2276341 +/- 92658 a	4%	2409864 +/- 3182 a	0%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	5507484 +/- 1752663 a	32%	7535636 +/- 239403 a	3%	8073489 +/- 81327 a	1%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	807471 +/- 87829 a	11%	850817 +/- 95047 a	11%	991220 +/- 40613 a	4%
9-Methyl-S-octahydrophenanthracene	362082 +/- 19407 a	5%	353902 +/- 77686 a	22%	415288 +/- 95947 a	23%
Anthracene, 1,2,3,4-tetrahydro-	212853 +/- 27993 a	13%	345635 +/- 15233 a	4%	258757 +/- 14988 a	6%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	617959 +/- 50059 a	8%	607018 +/- 29566 a	5%	758470 +/- 59092 a	8%
9-Methyl-S-octahydroanthracene	768300 +/- 81073 a	11%	818701 +/- 88718 a	11%	920521 +/- 84479 a	9%
Mirex	334575 +/- 17994 a	5%	380604 +/- 7969 a	2%	483142 +/- 86134 a	18%

Table 27: Target Responses for selected diesel compounds extracted using SBSE in MSW during the pH optimization. Target responses represent an average duplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	Target Response					
	3		N		9	
	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV
Benzene, 1-ethyl-2,4-dimethyl-	1,083,502 +/- 169863 a	16%	849,390 +/- 135272 a	16%	1,214,947 +/- 86288 a	7%
Naphthalene, 1,2,3,4-tetrahydro-	1,533,552 +/- 47219 a	3%	1,327,477 +/- 28412 ab	2%	1,412,540 +/- 46626 b	3%
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	1,422,266 +/- 71022 a	5%	1,270,337 +/- 36479 a	3%	1,257,296 +/- 231539 a	18%
1H-Indene, 2,3-dihydro-4,7-dimethyl-	958,369 +/- 48934 a	5%	851,889 +/- 29673 a	3%	884,875 +/- 156948 a	18%
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	9,160,192 +/- 49940 a	1%	4,819,741 +/- 5902475 a	122%	10,499,740 +/- 72196 a	1%
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro	1,046,346 +/- 917225 a	88%	1,535,969 +/- 181699 a	12%	2,047,651 +/- 171075 a	8%
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	6,205,129 +/- 628020 a	10%	5,285,597 +/- 744456 a	14%	7,296,963 +/- 428264 a	6%
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	1,290,763 +/- 138696 a	11%	1,137,188 +/- 93744 a	8%	1,327,103 +/- 28493 a	2%
9-Methyl-S-octahydrophenanthracene	558,058 +/- 45457 a	8%	491,916 +/- 30500 a	6%	545,892 +/- 30797 a	6%
Anthracene, 1,2,3,4-tetrahydro-	413,446 +/- 61637 a	15%	372,902 +/- 46749 a	13%	490,625 +/- 103848 a	21%
1,2,3,4,5,6,7,8-Octahydro-1-methylphenanthracene	957,930 +/- 124925 a	13%	848,456 +/- 68515 a	8%	903,737 +/- 22845 a	3%
9-Methyl-S-octahydroanthracene	1,240,899 +/- 121613 a	10%	1,093,584 +/- 66277 a	6%	1,194,222 +/- 44774 a	4%
Mirex	544,544 +/- 16770 a	3%	502,357 +/- 55360 a	11%	623,400 +/- 4105 a	1%

Table 28: Target Responses for selected biodiesel compounds extracted using SBSE in MFW during the pH optimization. Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	pH					
	3		N		9	
	Target Response	% STDEV	Target Response	% STDEV	Target Response	% STDEV
Tetradecanoic acid, methyl ester	820911 +/- 73380 a	9%	925900 +/- 107144 a	12%	1051494 +/- 182482 a	17%
Hexadecanoic acid, methyl ester	19768232 +/- 1660465 a	8%	29304185 +/- 1593565 ab	5%	24829534 +/- 3076405 b	12%
Octadecanoic acid, methyl ester	6769908 +/- 385066 a	6%	11440511 +/- 1485490 a	13%	7895632 +/- 1585348 b	20%
9-Octadecenoic acid, methyl ester	1518387 +/- 76642 a	5%	2558947 +/- 361607 a	14%	1758738 +/- 327563 b	19%
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	32652499 +/- 2192667 a	7%	43676522 +/- 1826146 b	4%	39202916 +/- 3457912 b	9%
9,12,15 Octadecatrienoic acid, methyl ester	14990307 +/- 1193663 a	8%	18089975 +/- 126382 b	1%	18248576 +/- 1159192 b	6%
Mirex	2757934 +/- 120451 a	4%	2724007 +/- 453623 a	17%	3027483 +/- 193218 a	6%

Table 29: Target Responses for selected biodiesel compounds extracted using SBSE in MSW during the pH optimization. Target responses represent an average of triplicates. Averages with the same letter between different treatments and the same compound represent no significant difference at Tukey's test ( $p \leq 0.05$ ).

Compounds	pH									
	3				N				9	
	Target Response		%STDEV		Target Response		%STDEV		Target Response	
Tetradecanoic acid, methyl ester	675,178	+/- 45589 a	7%		531,246	+/- 4686465 a	9%		553,489	+/- 2988712 b
Hexadecanoic acid, methyl ester	20,506,787	+/- 1476004 a	7%		16,837,343	+/- 1131281 a	7%		19,787,656	+/- 2965398 a
Octadecanoic acid, methyl ester	7,914,201	+/- 788643 a	10%		6,336,171	+/- 371003 a	6%		8,110,636	+/- 1521398 a
9-Octadecenoic acid, methyl ester	10,019,155	+/- 1766532 a	18%		6,179,642	+/- 666862 a	11%		6,591,101	+/- 704279 b
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	28,440,860	+/- 822809 a	3%		23,909,407	+/- 1088813 a	5%		26,387,804	+/- 3255103 a
9,12,15 Octadecatrienoic acid, methyl ester	11,635,682	+/- 284844 a	2%		9,881,962	+/- 406475 a	4%		9,988,321	+/- 762940 b
Mirex	2,329,832	+/- 281692 a	12%		2,342,862	+/- 138115 a	6%		2,445,591	+/- 281445 a

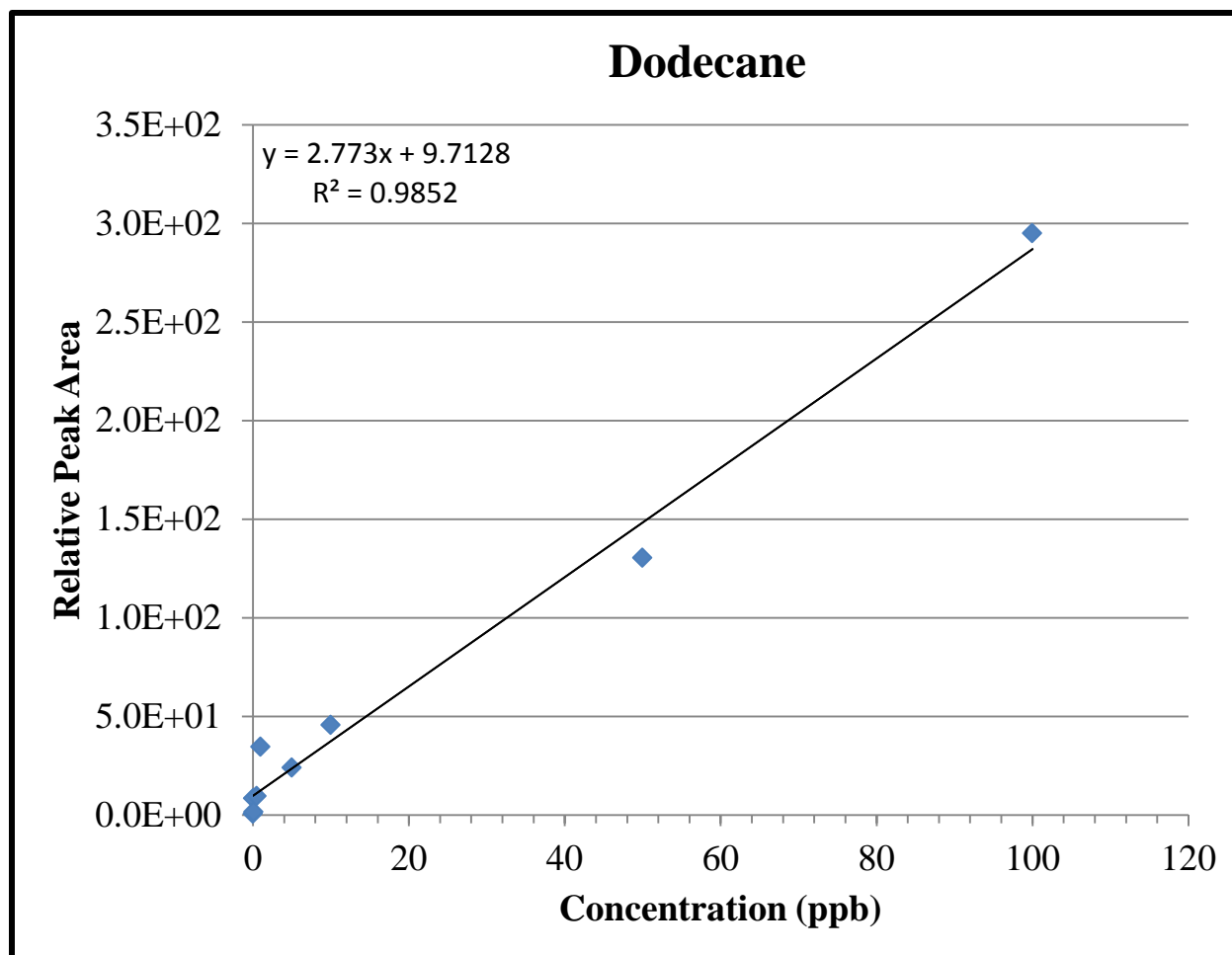


Figure 48: Calibration curve for Dodecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

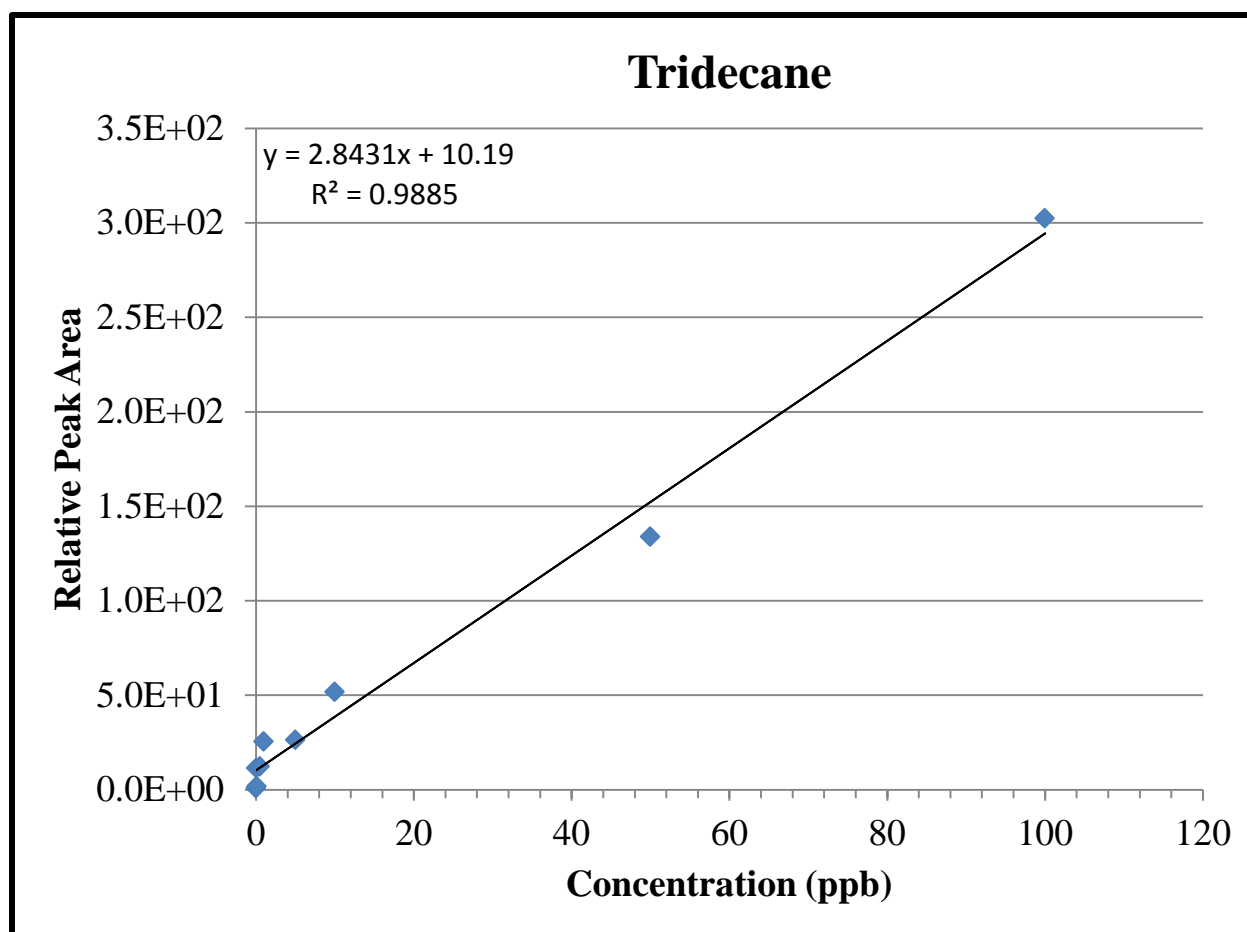


Figure 49: Calibration curve for Tridecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

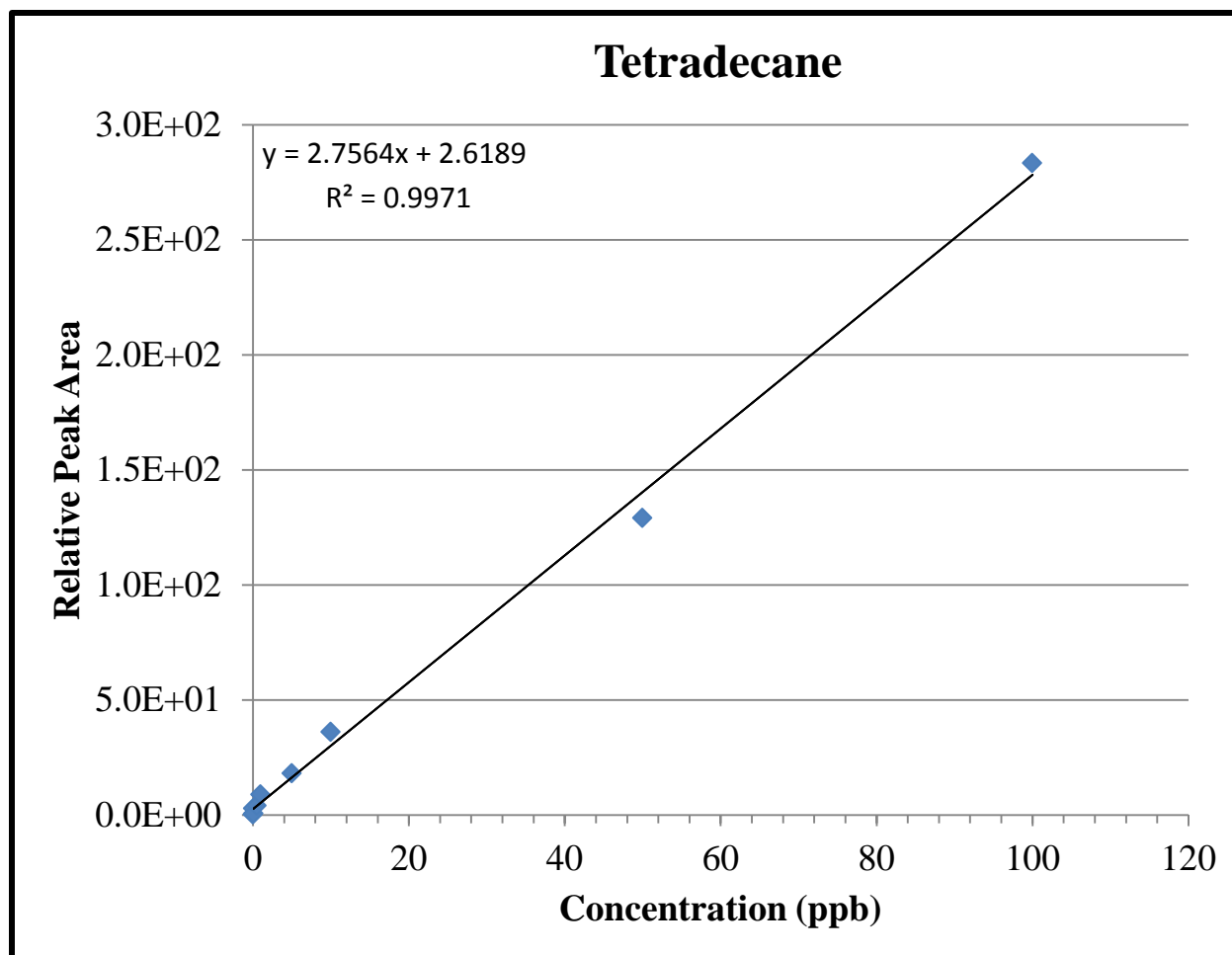


Figure 50: Calibration curve for Tetradecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.



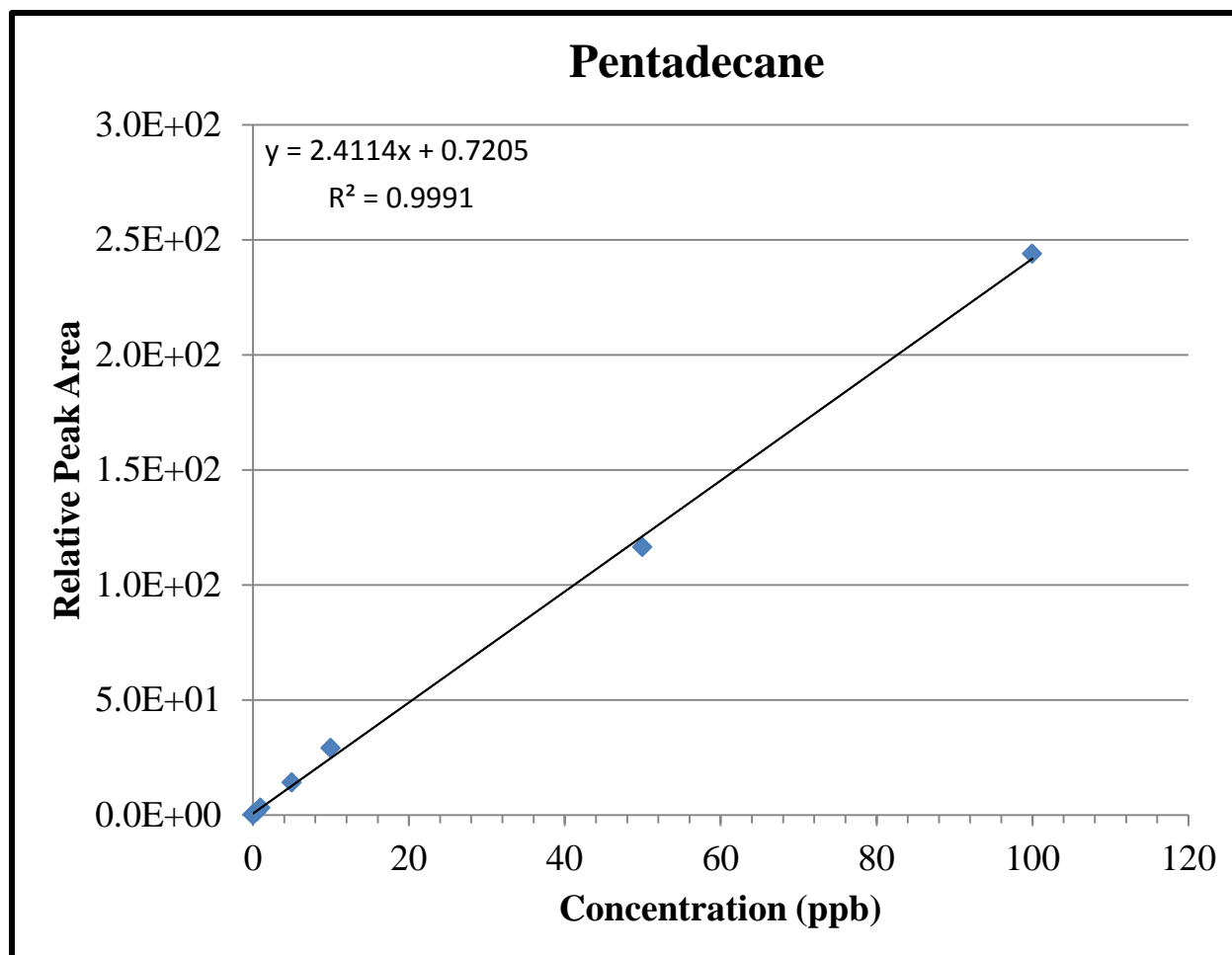


Figure 51: Calibration curve for Pentadecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

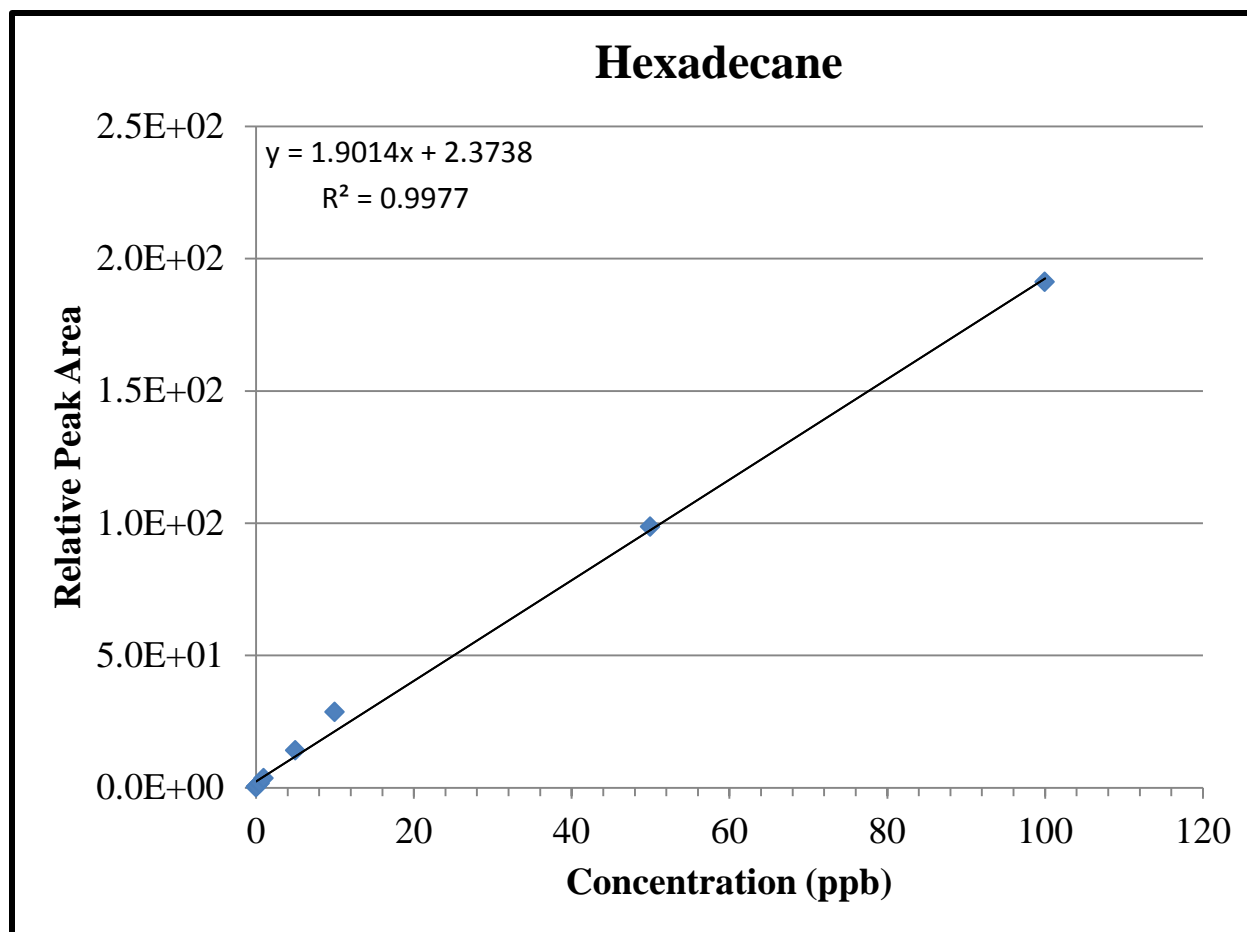


Figure 52: Calibration curve for Hexadecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

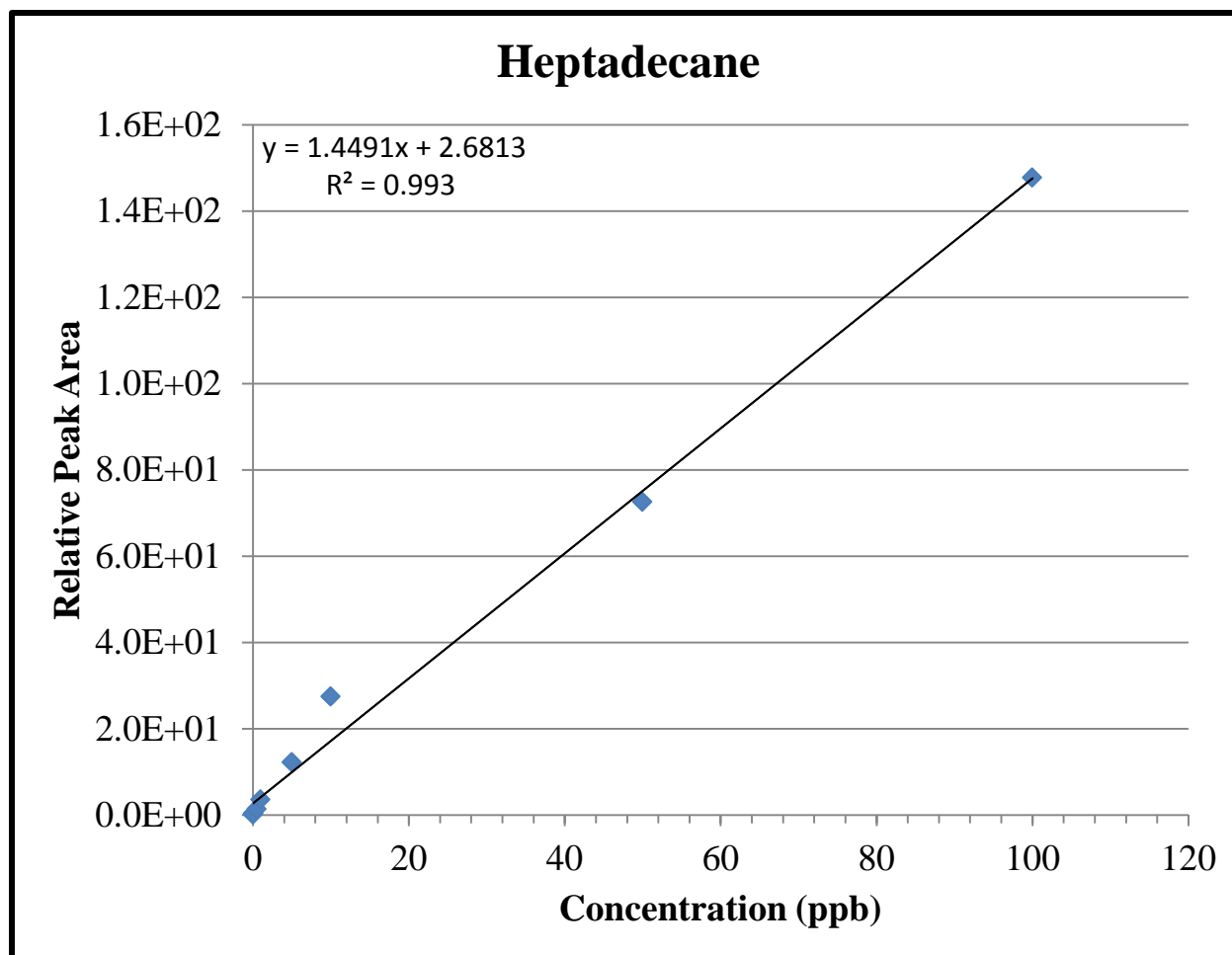


Figure 53: Calibration curve for Heptadecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

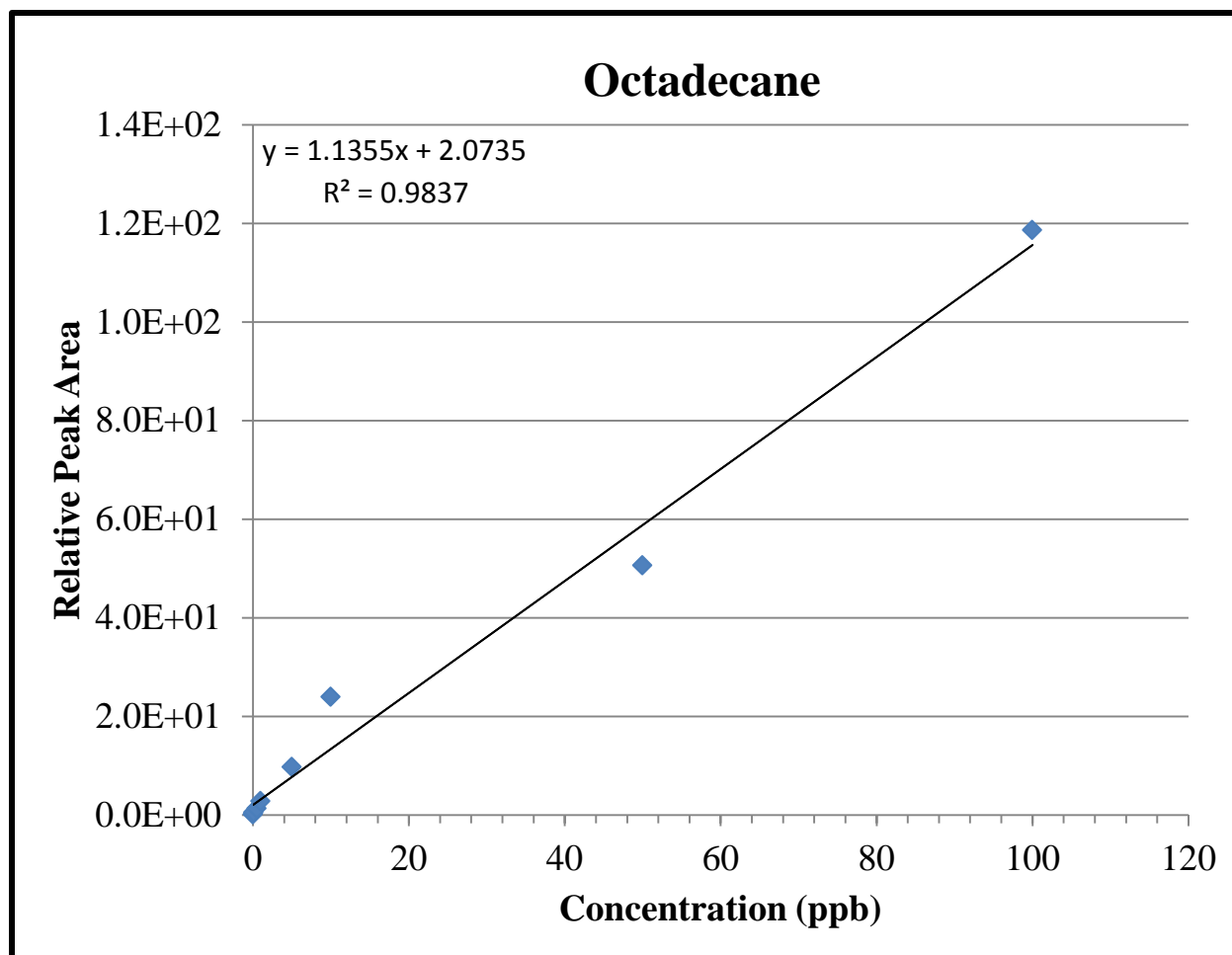


Figure 54: Calibration curve for Octadecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

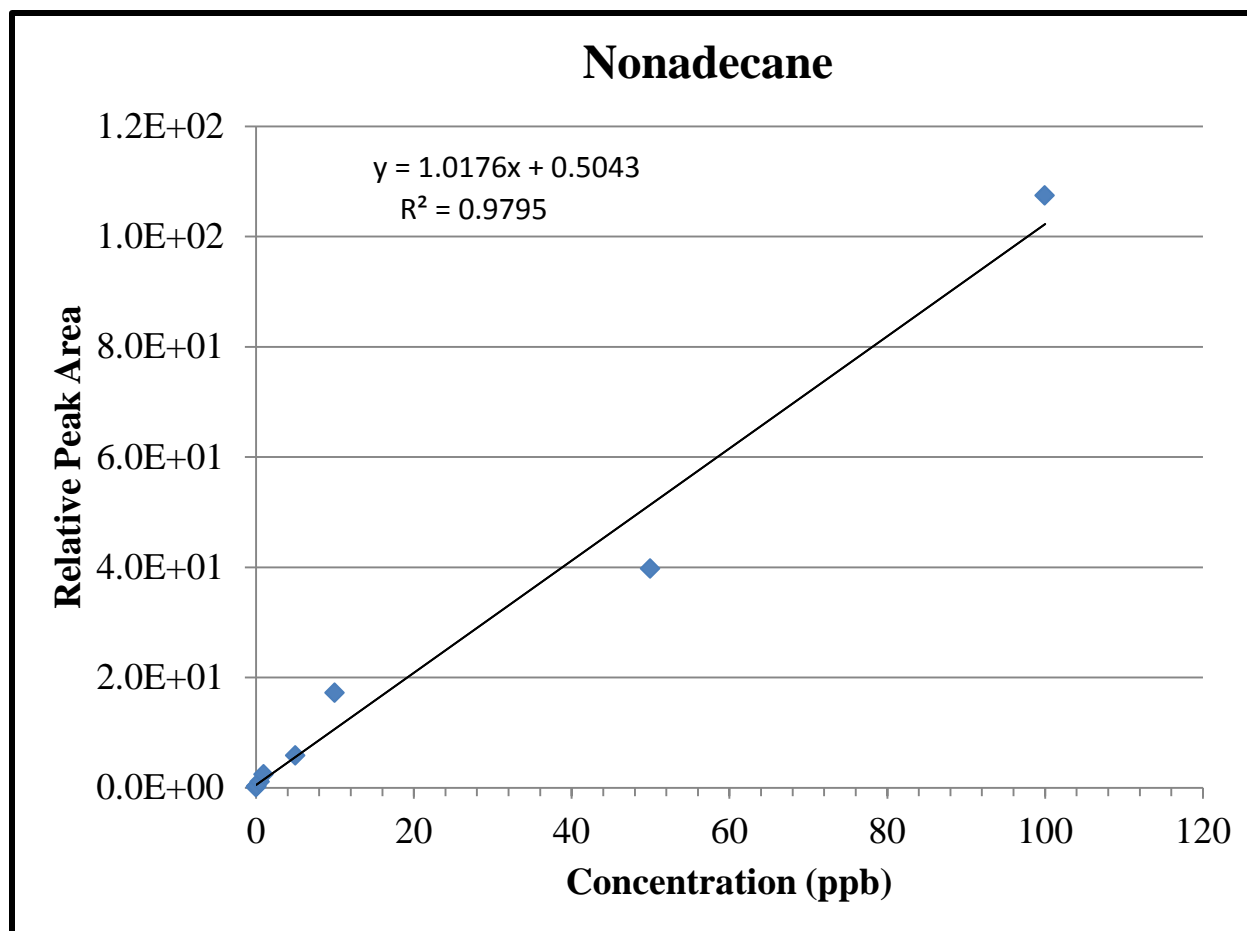


Figure 55: Calibration curve for Nonadecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

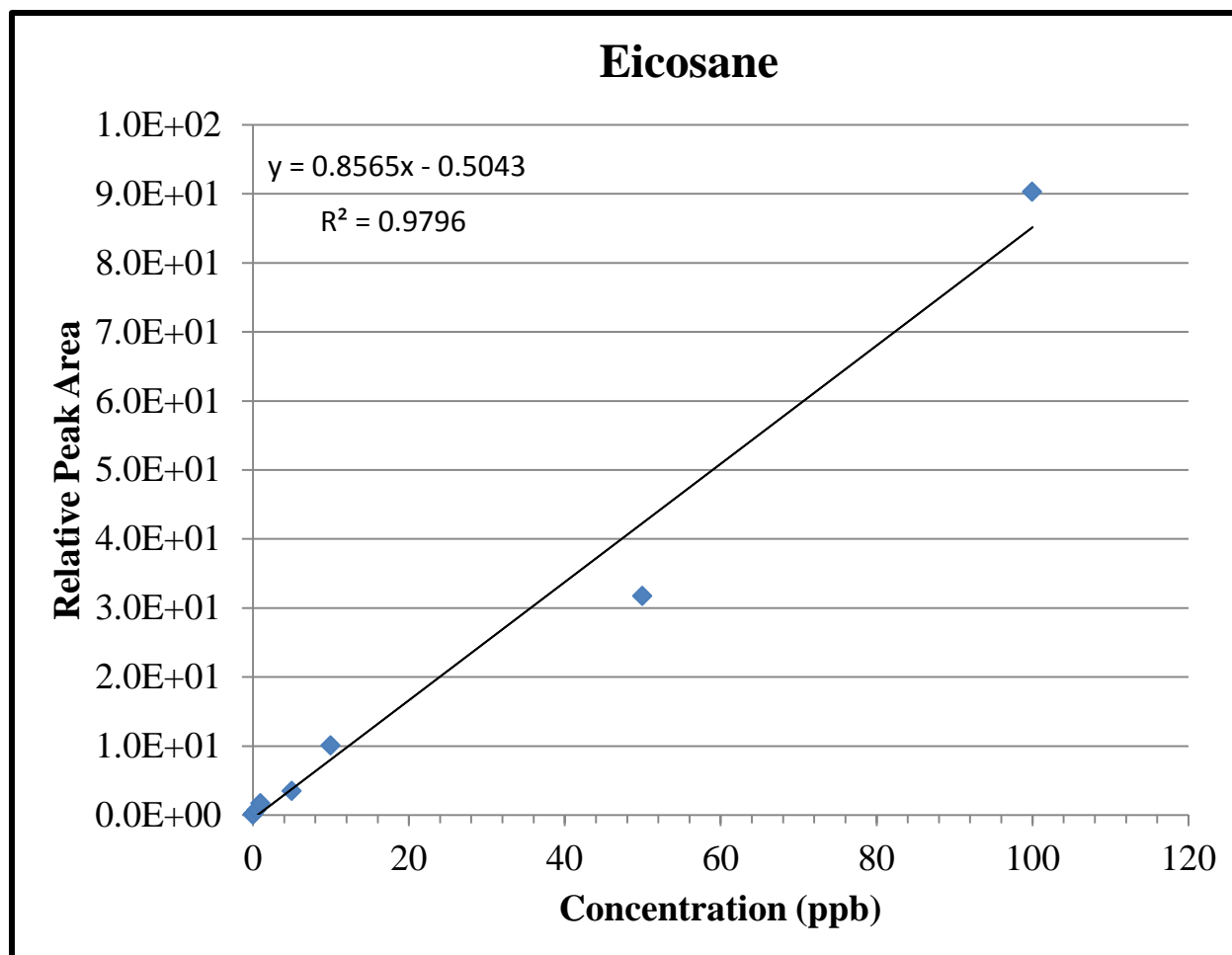


Figure 56: Calibration curve for Eicosane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

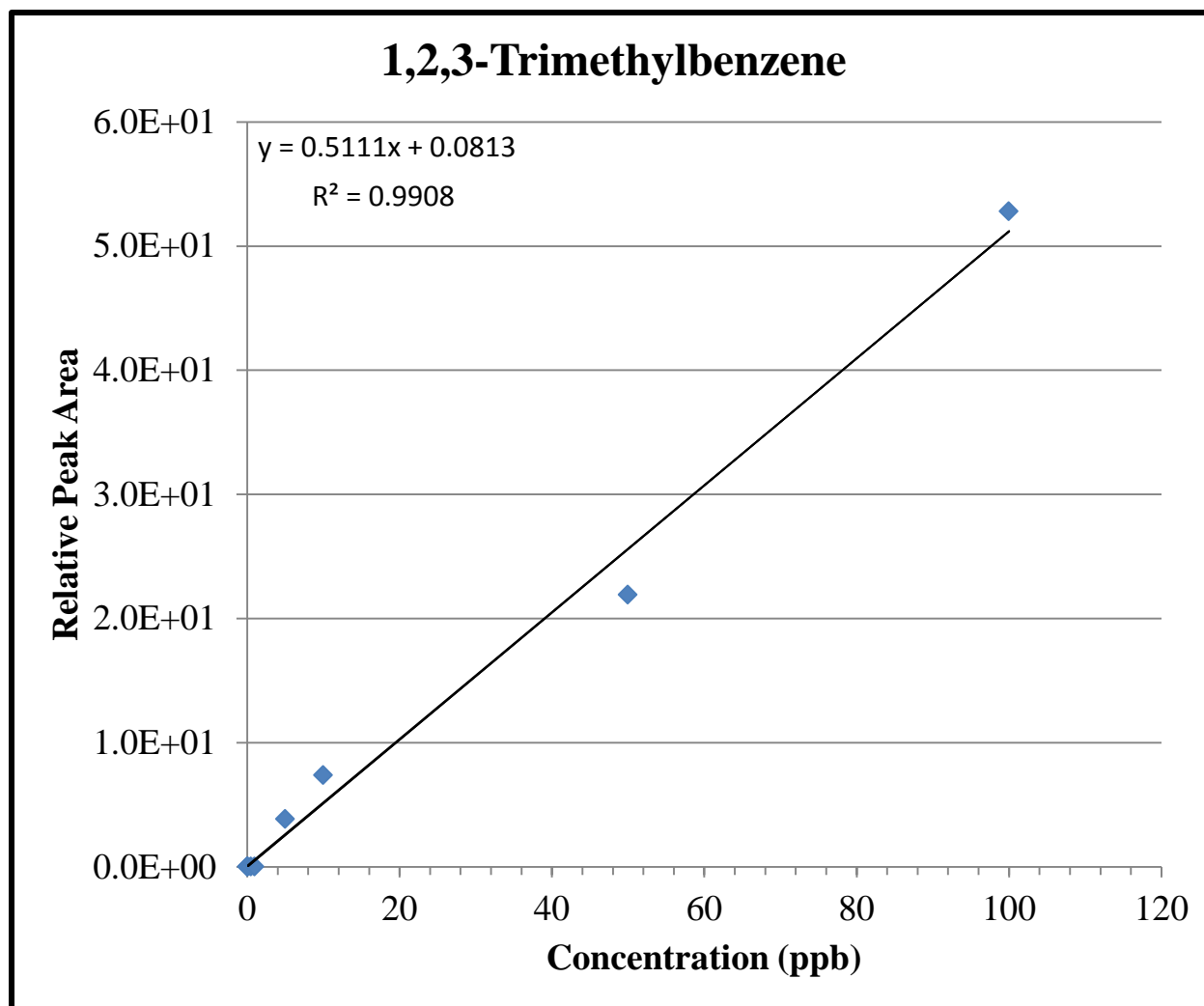


Figure 57: Calibration curve for Tetradecane at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

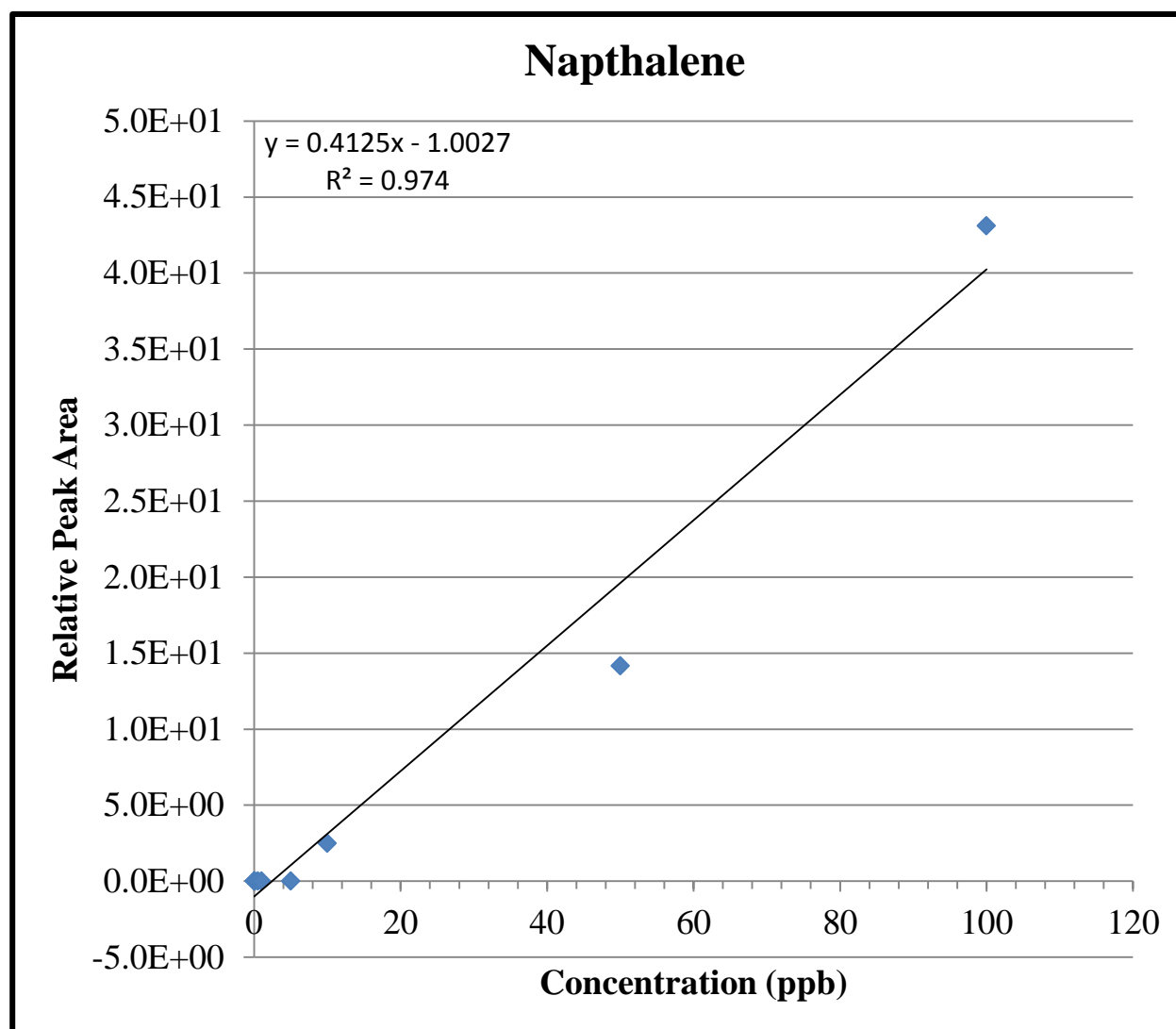


Figure 58: Calibration curve for Napthalene at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.



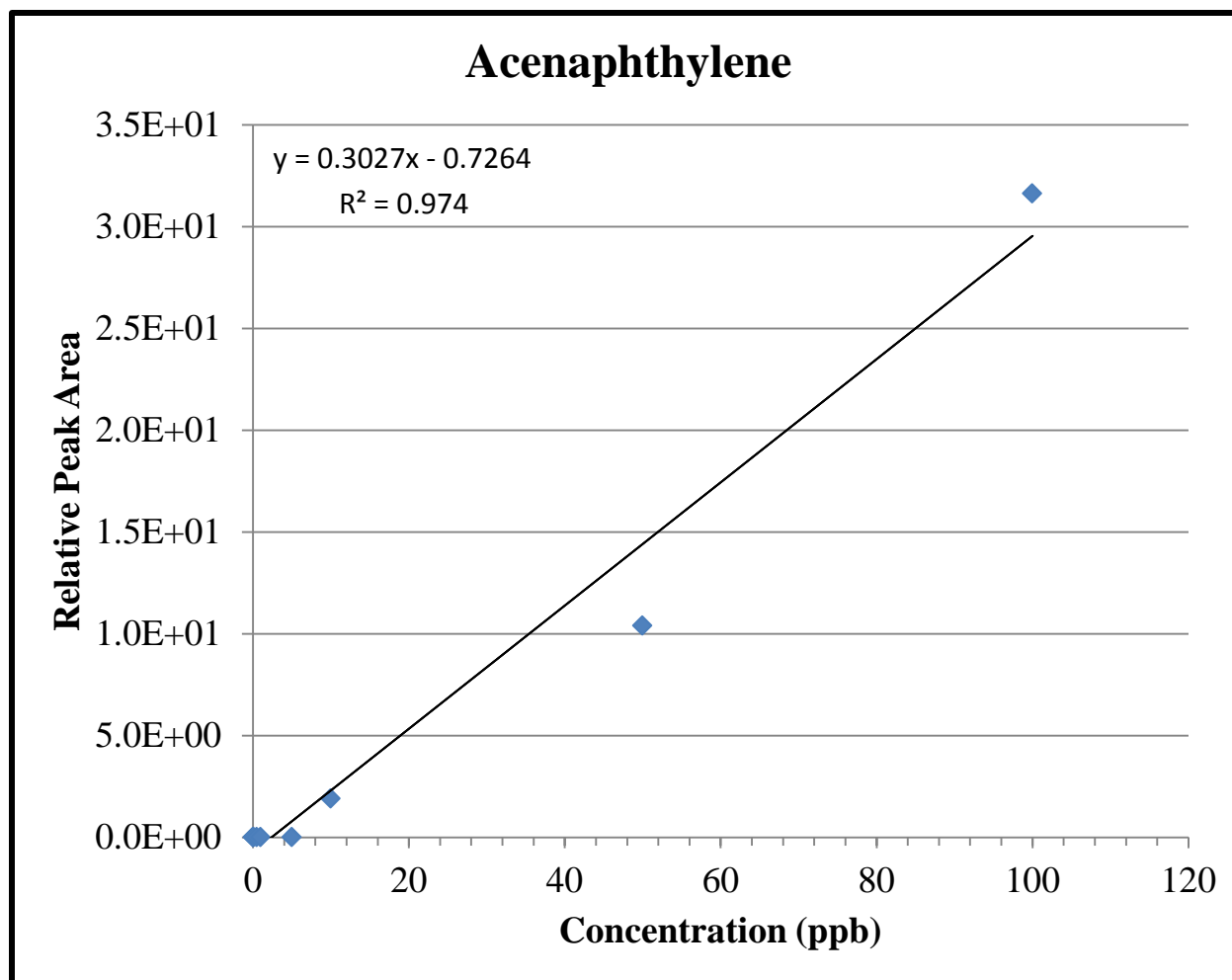


Figure 59: Calibration curve for Acenaphthylene at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

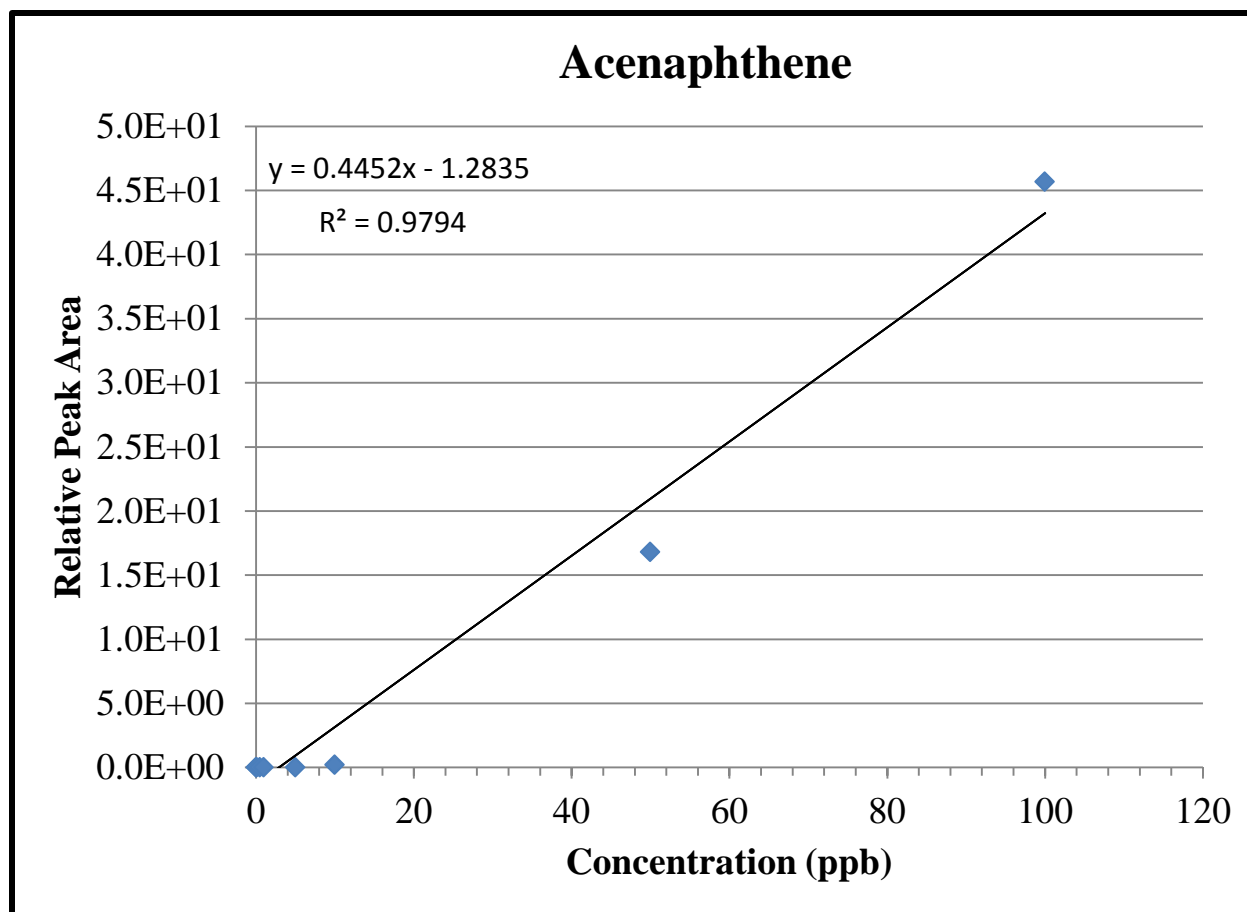


Figure 60: Calibration curve for Acenaphthene at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

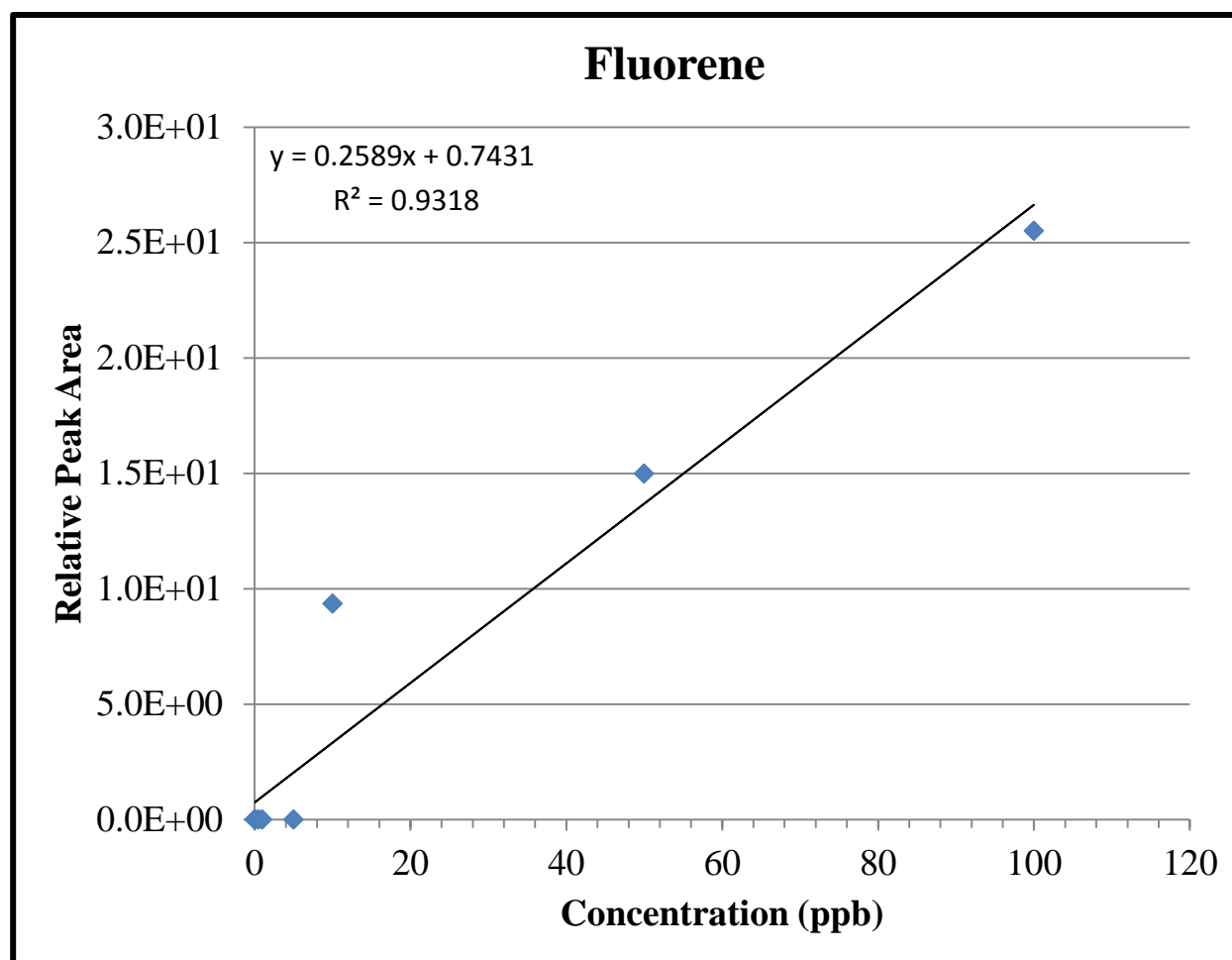


Figure 61: Calibration curve for Fluorene at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

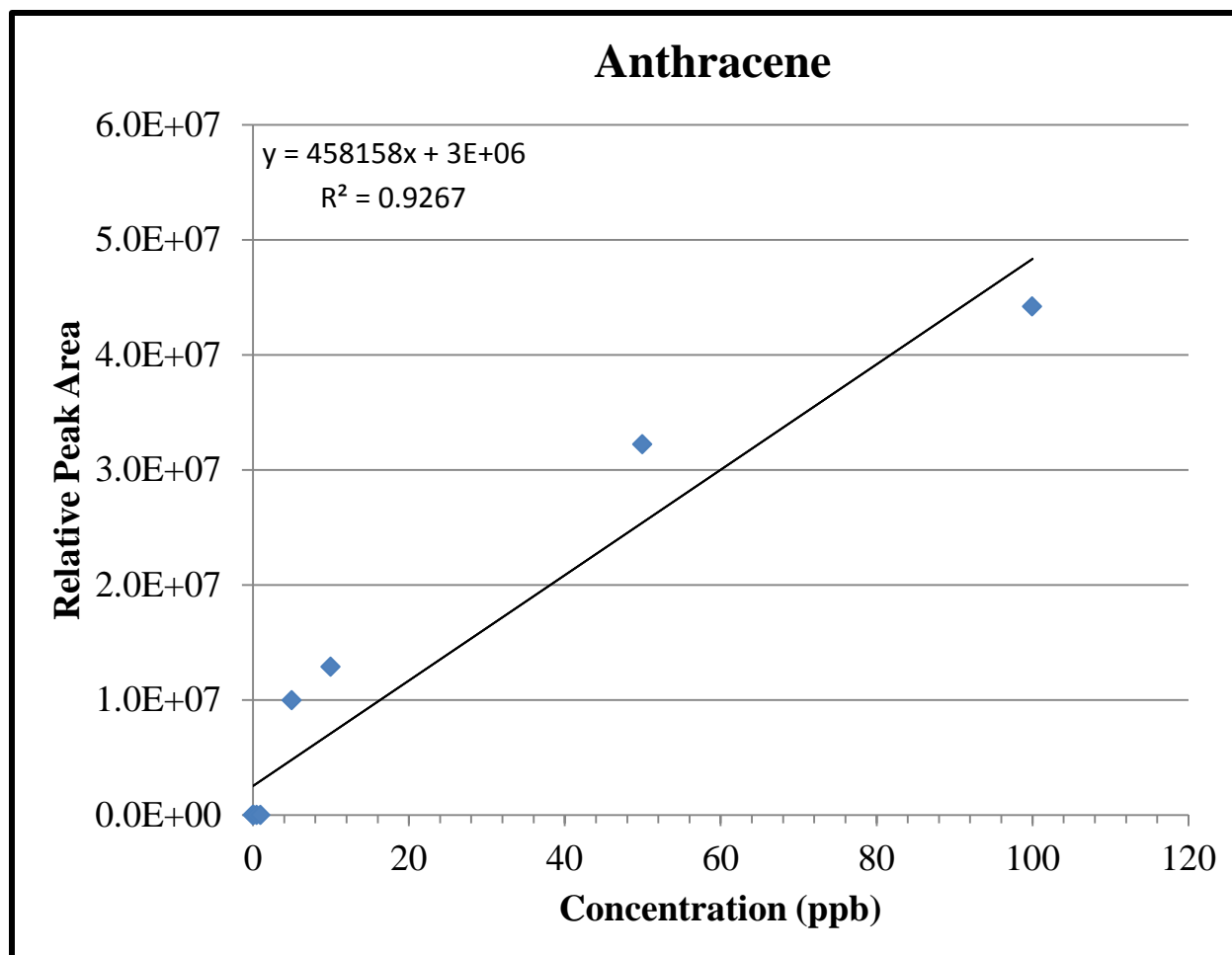


Figure 62: Calibration curve for Anthracene at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

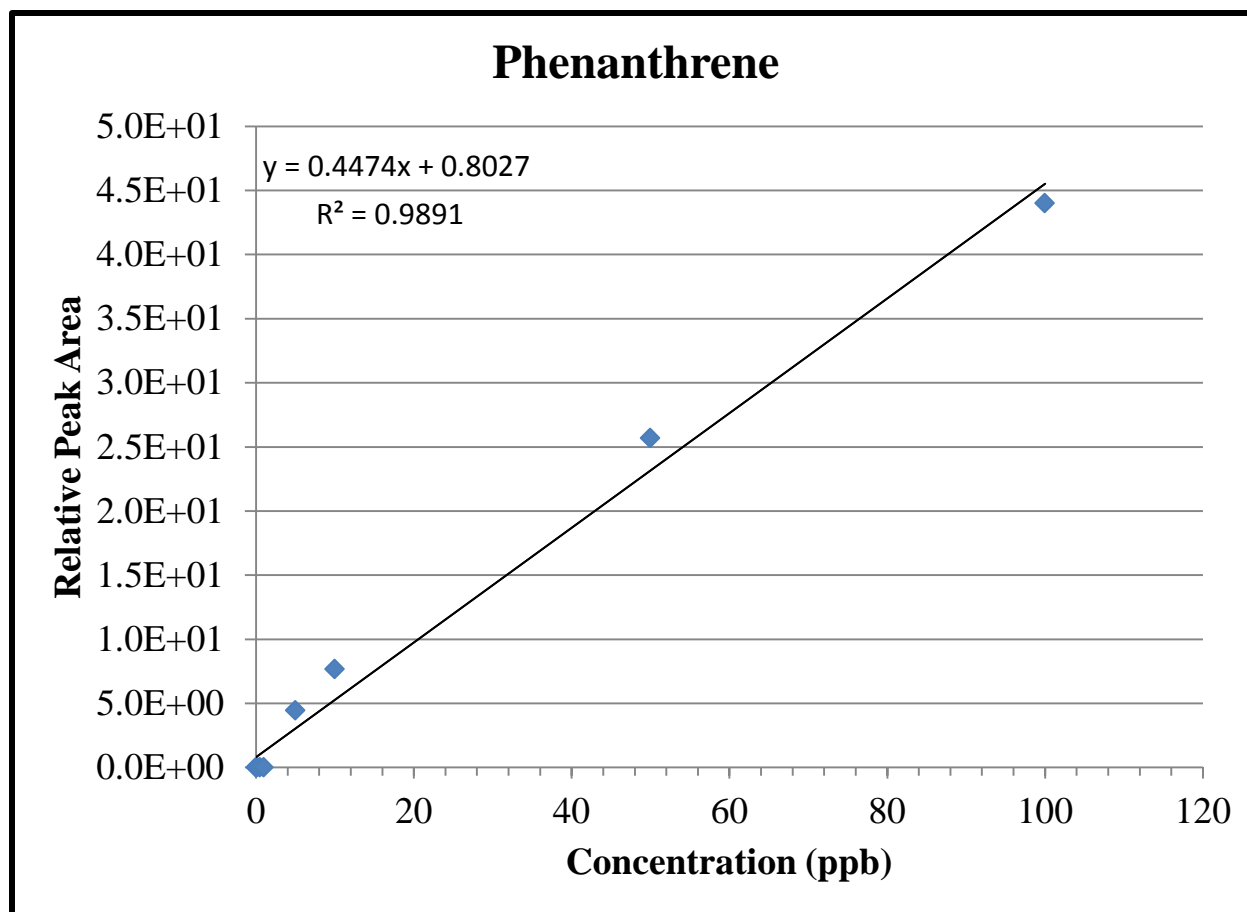


Figure 63: Calibration curve for Phenanthrene at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

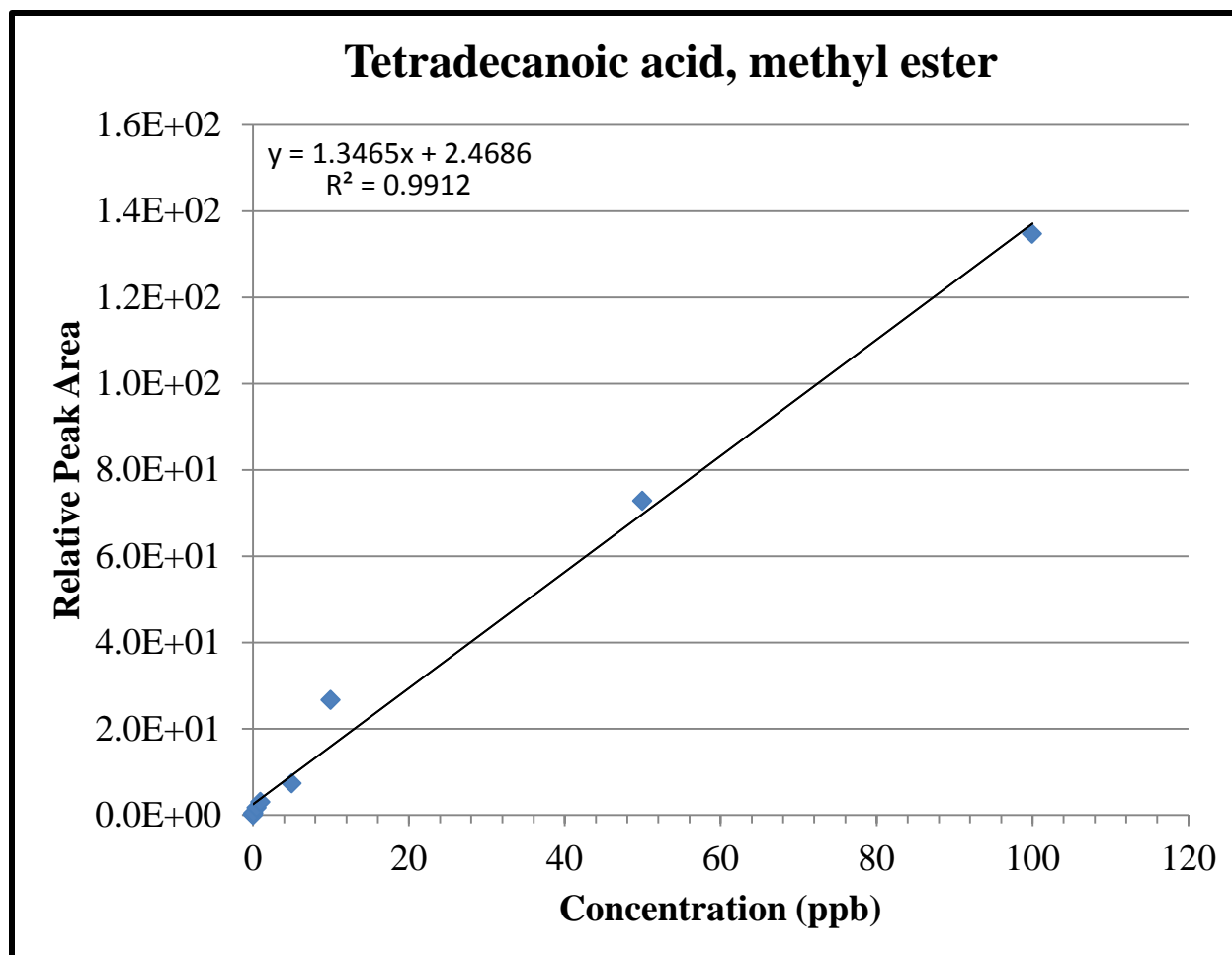


Figure 64: Calibration curve for Tetradecanoic acid, methyl ester at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

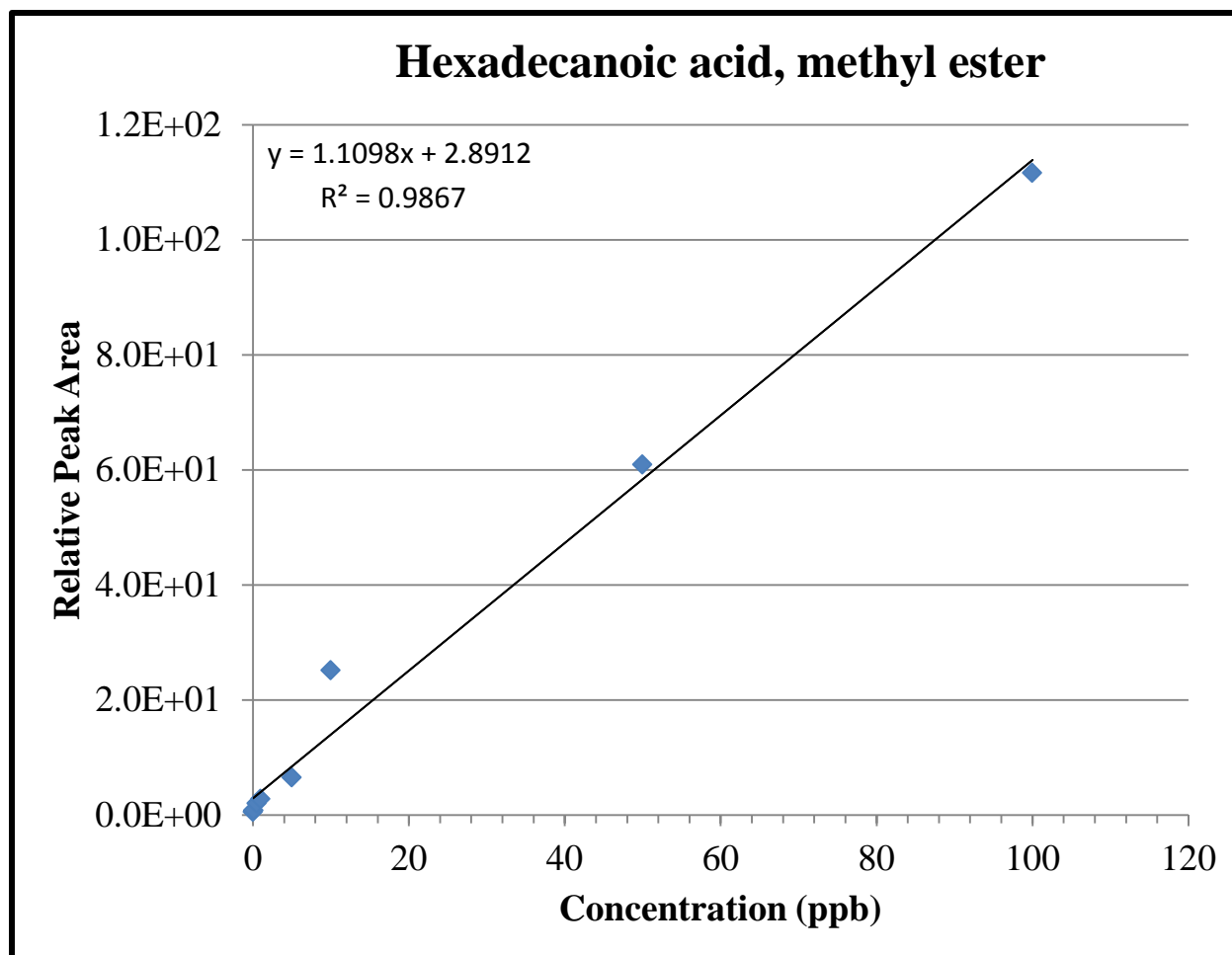


Figure 65: Calibration curve for Hexadecanoic acid, methyl ester at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

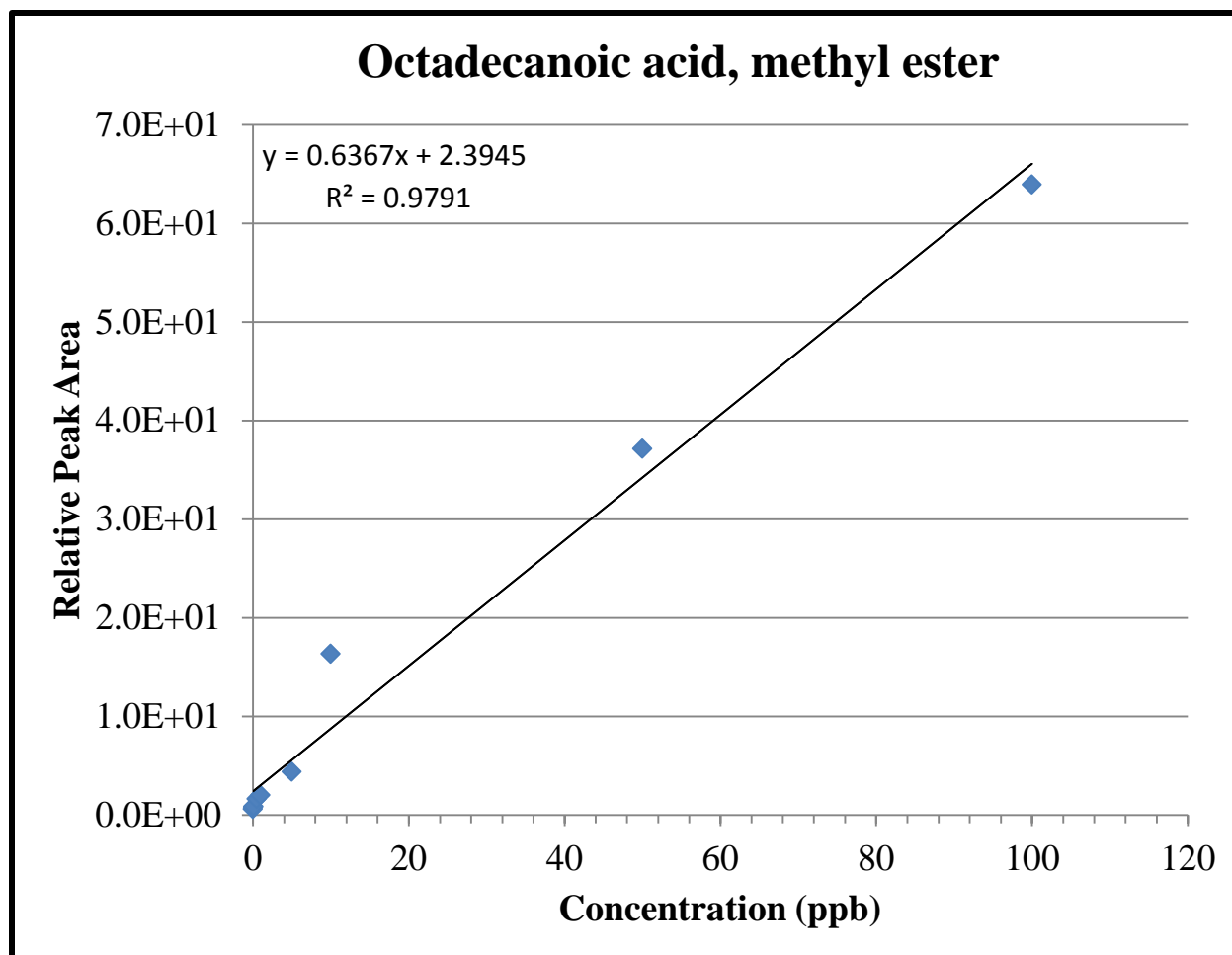


Figure 66: Calibration curve for Octadecanoic acid, methyl ester at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.



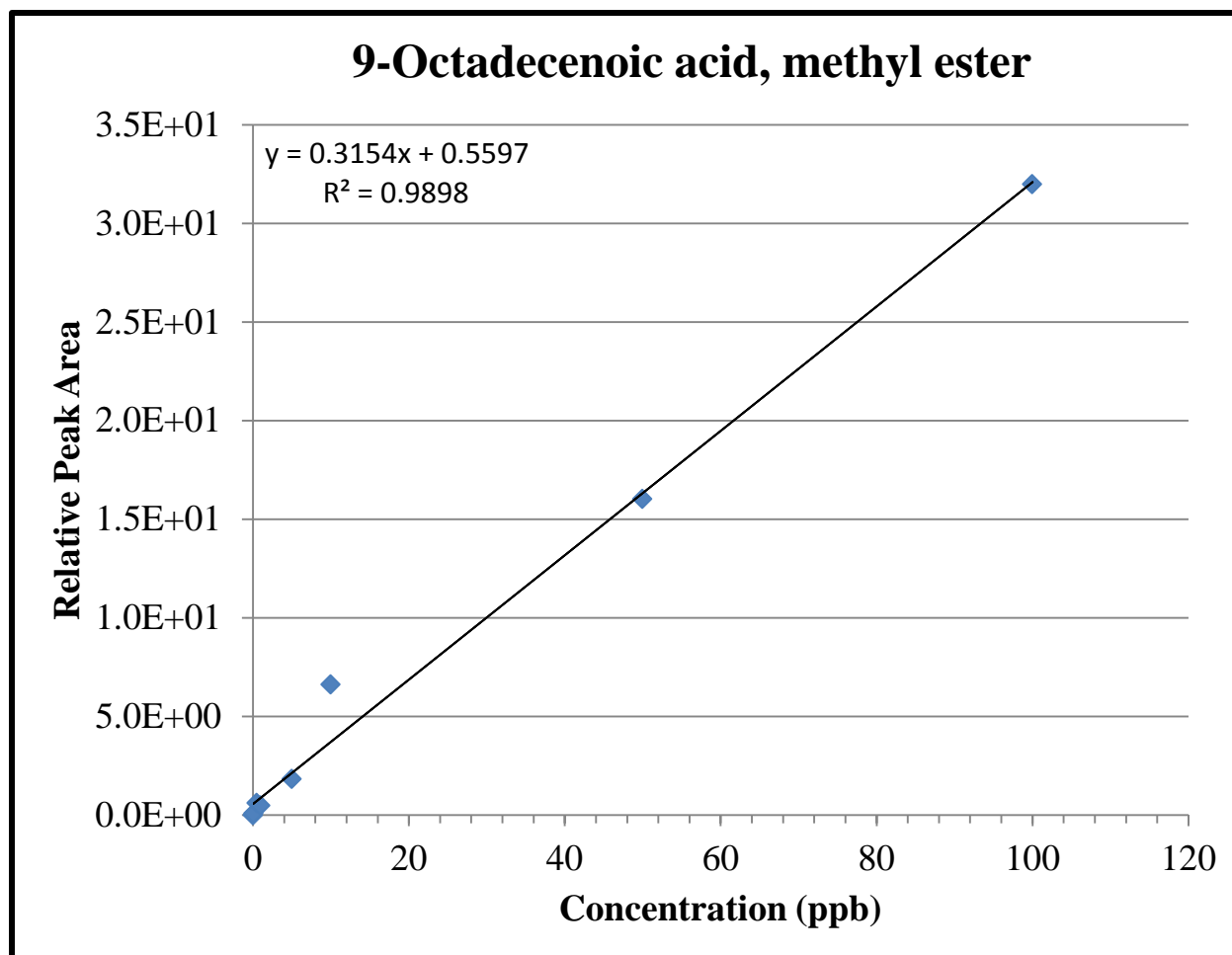


Figure 67: Calibration curve for 9-Octadecenoic acid, methyl ester at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

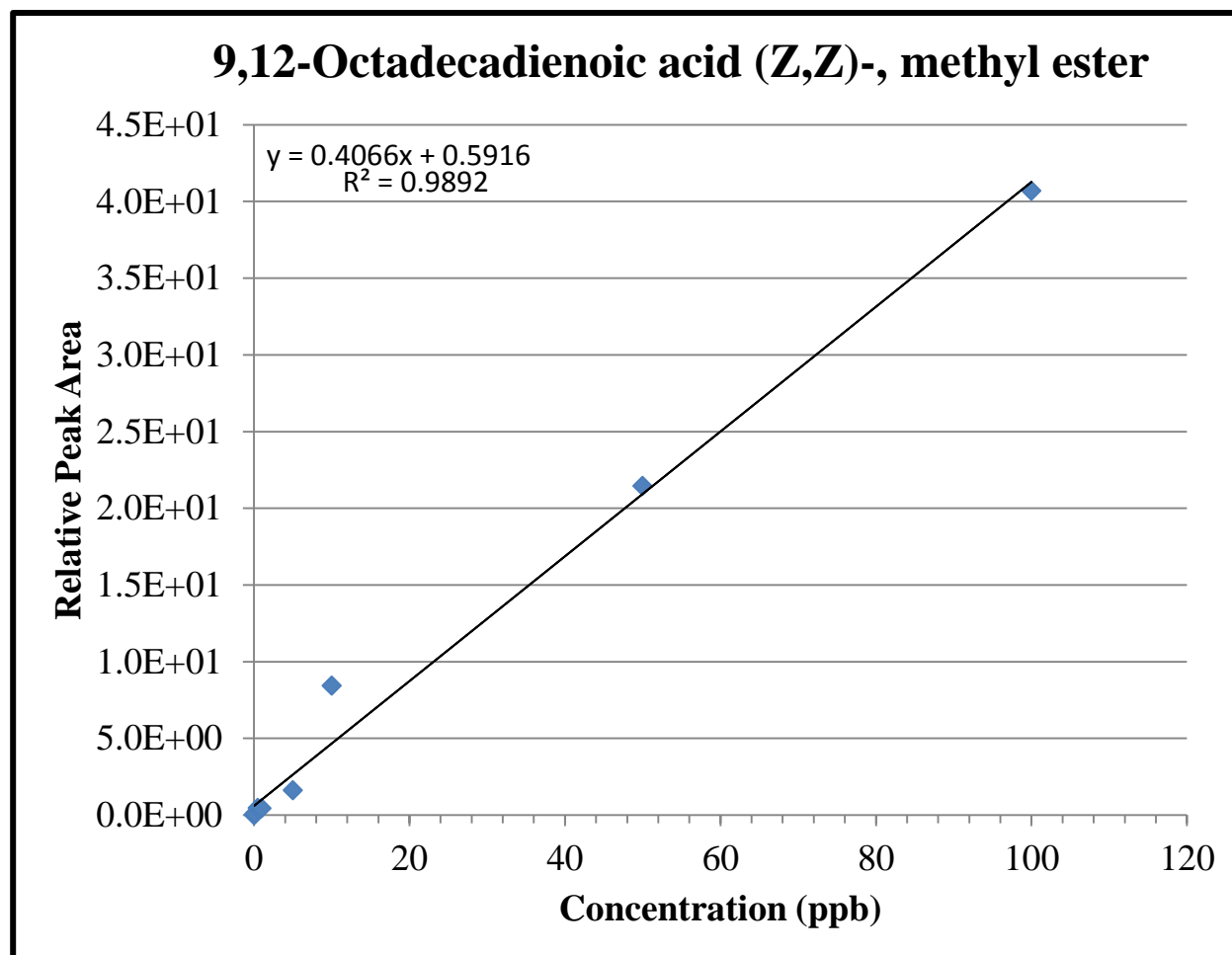


Figure 68: Calibration curve for 9,12-Octadecadienoic acid, methyl ester at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

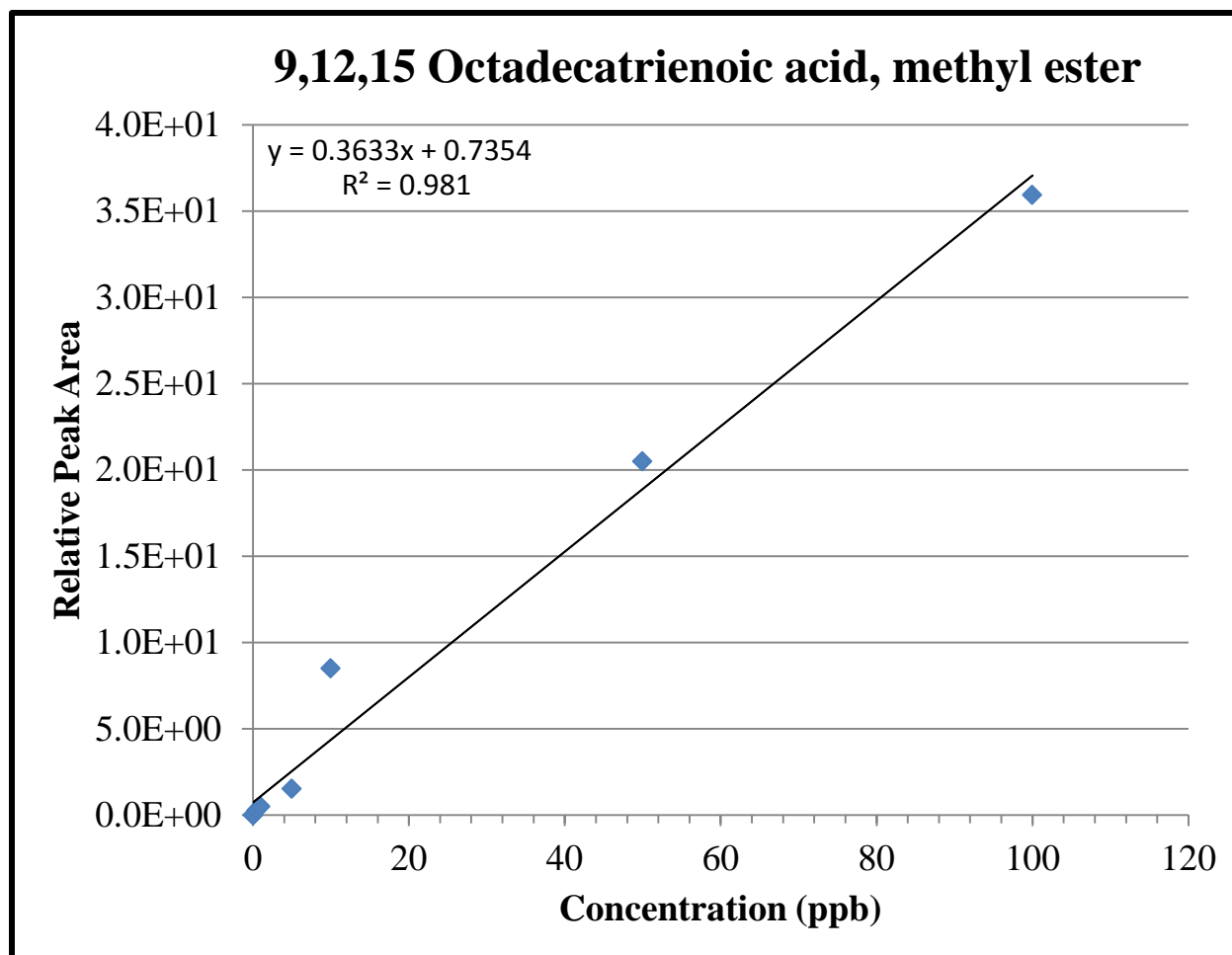


Figure 69: Calibration curve for 9,12,15 Octadecatrienoic acid, methyl ester at concentrations of 0.005ppb, 0.05ppb, 0.1ppb, 0.5ppb, 1ppb, 2.5ppb, 10ppb, 50ppb, and 100ppb after SBSE in 50 percent methanol in MSW and 4 hour stirring time at 1000 rpm.

Table 30: Summary of target responses obtained for selected analyte for the calibration curve. Actual plotted points on calibration curve are a ratio between the analyte of interest and the internal standard, Mirex.

Compound Name	Concentration (ppb)								
	0.005	0.05	0.10	0.50	1.00	5.00	10.00	50.00	100.00
Undecane	736,369,046	505,943,969	644,303,627	593,303,070	474,817,451	343,074,953	375,782,686	412,955,869	501,111,352
Dodecane	684,511	7,325,316	1,520,286	8,327,372	28,849,559	20,472,837	33,397,126	103,944,416	193,691,272
Tridecane	839,860	9,892,932	1,808,953	10,589,638	21,213,726	22,416,818	37,914,022	106,700,478	198,455,365
Tetradecane	249,029	2,456,584	589,779	3,478,656	7,378,326	15,455,084	26,433,662	102,961,427	185,964,356
Pentadecane	89,384	244,489	235,545	1,123,743	2,568,357	12,092,464	21,298,472	92,792,463	160,104,539
Hexadecane	133,001	341,401	367,322	1,348,848	2,896,396	12,004,989	20,974,977	78,584,810	125,512,859
Heptadecane	97,350	201,732	414,459	1,184,619	2,941,708	10,447,283	20,136,783	57,886,075	97,003,204
Octadecane	95,731	258,115	569,794	1,119,371	2,333,633	8,295,469	17,565,030	40,352,862	77,882,685
Nonadecane	53,579	112,001	303,373	935,267	2,002,164	4,960,337	12,624,685	31,688,669	70,528,482
Eicosane	46,230	112,724	174,230	621,203	1,380,574	2,972,004	7,368,264	25,287,523	59,253,535
Mirex	1,117,164	872,218	1,018,686	864,950	833,646	855,920	733,043	797,446	656,598
1,2,3-Trimethylbenzene	-	-	-	-	-	2,879,521	5,631,214	14,477,413	31,210,601
Napthalene	-	-	-	-	-	-	1,890,414	9,356,212	25,477,666
Acenaphthylene	-	-	-	-	-	1,423,398	7,923,466	20,901,512	31,738,116
Acenaphthene	-	-	-	-	-	144,159	12,811,763	30,175,352	44,132,569
Fluorene	-	-	-	-	-	7,020,765	11,428,783	16,851,402	39,932,123
Anthracene	-	-	-	-	-	9,948,872	12,868,622	32,198,673	44,197,493
Phenanthrene	-	-	-	-	-	3,335,688	5,848,568	16,966,735	26,015,783
Mirex	794,173	853,321	903,310	863,579	722,773	750,956	762,749	660,889	591,290
Compound Name	Concentration (ppb)								
	0.005	0.05	0.10	0.50	1.00	2.50	10.00	50.00	100.00
Octadecanoic acid, ME	729,515	806,549	795,431	1,351,545	2,136,755	4,363,535	15,701,199	31,103,400	52,791,393
Tetradecanoic acid, ME	180,546	285,803	410,863	1,407,598	3,131,579	7,255,641	25,595,773	60,981,361	111,187,109
Mirex	1,194,200	1,038,212	940,518	831,759	1,062,654	995,407	960,871	837,570	825,713
9-Octadecenoic acid, ME	-	-	76,016	506,385	501,105	1,807,006	6,359,600	13,414,574	26,408,340
9,12,15 Octadecatrienoic acid, ME	-	-	-	221,556	516,802	1,502,318	8,164,437	17,150,792	29,661,991
9,12-Octadecadienoic acid (Z,Z)-, ME	-	-	70,498	378,126	461,846	1,587,939	8,081,778	17,959,045	33,591,433
Hexadecanoic acid, ME	603,549	735,103	778,964	1,655,640	2,942,261	6,490,268	24,160,185	50,997,524	92,167,366

Table 31: Estimated Limit of Detections, Limit of Quantification, and Estimated Linear Ranges of target aliphatic hydrocarbons, polyaromatic hydrocarbons, and fatty acid methyl esters.

Compound	Target Ion (m/Z)	Correlation Coefficient (R <sup>2</sup> )	~LOD (ppb)	~LOQ (ppb)	Estimated Linear Range ppb (ug/L)
1,2,3-Trimethylbenzene	105	0.9908	5	5	5-100
Acenaphthylene	152	0.9805	5	5	5-100
Acenaphthene	153	0.9794	5	5	5-100
Fluorene	166	0.9318	5	5	5-100
Anthracene	178	0.9267	5	5	5-100
Phenanthrene	178	0.9891	5	5	5-100
Tetradecanoic acid, methyl ester	74	0.968	0.005	0.05	0.05-100
Hexadecanoic acid, methyl ester	74	0.9783	0.005	0.05	0.05-100
Octadecanoic acid, methyl ester	74	0.968	0.005	0.05	0.05-100
9-Octadecanoic acid, methyl ester	69	0.9828	0.1	0.5	0.5-100
9, 12-Octadecadienoic acid methyl ester	67	0.9821	0.1	0.5	0.5-100
9, 12,15-Octadecatrienoic acid, methyl ester	79	0.9708	0.5	0.5	0.5-100
Dodecane	57	0.9851	0.005	0.05	0.05-100
Tridecane	57	0.9904	0.005	0.05	0.05-100
Tetradecane	57	0.9968	0.005	0.05	0.05-100
Pentadecane	57	0.9946	0.005	0.05	0.05-100
Hexadecane	57	0.9858	0.005	0.05	0.05-100
Heptadecane	57	0.9848	0.005	0.05	0.05-100
Octadecane	57	0.986	0.005	0.05	0.05-100
Nonadecane	57	0.9912	0.005	0.05	0.05-100
Eicosane	57	0.9942	0.005	0.05	0.05-100

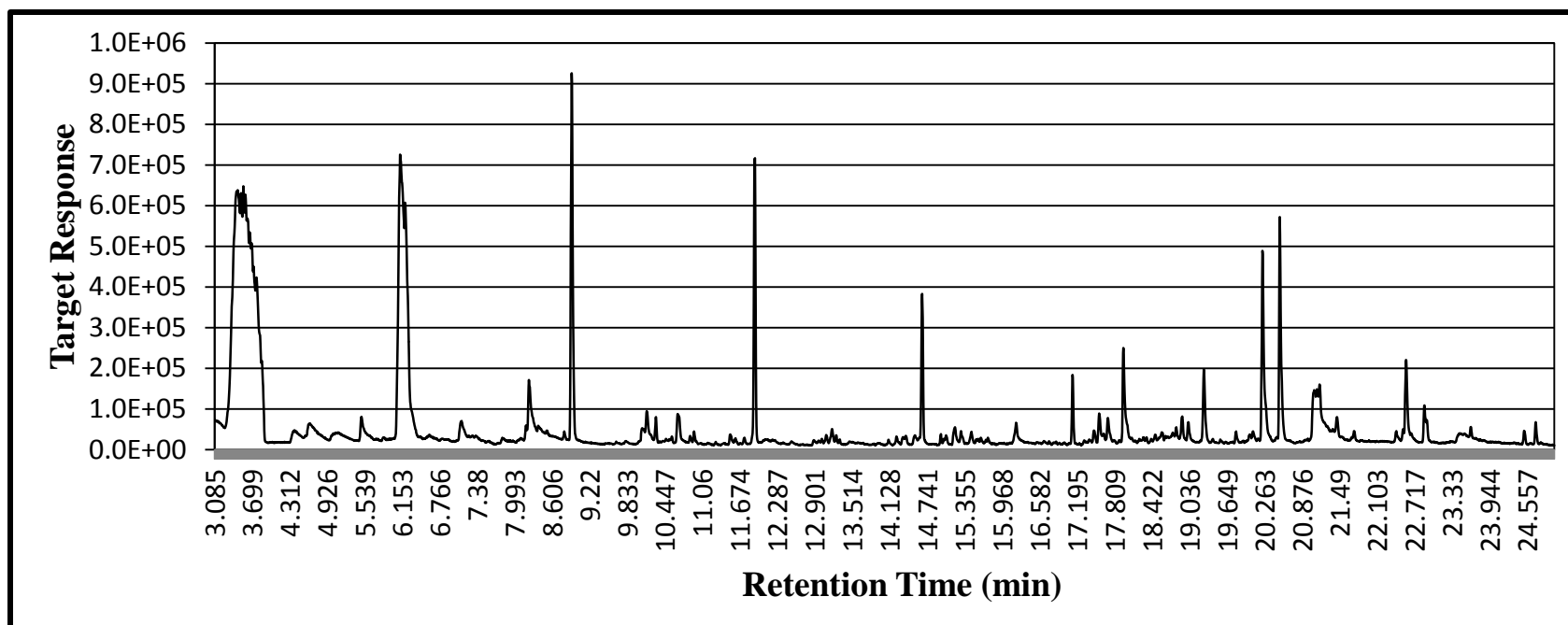


Figure 70: Sample chromatogram belonging to a sample from the Gulf Coast after SBSE-TD-GCMS.

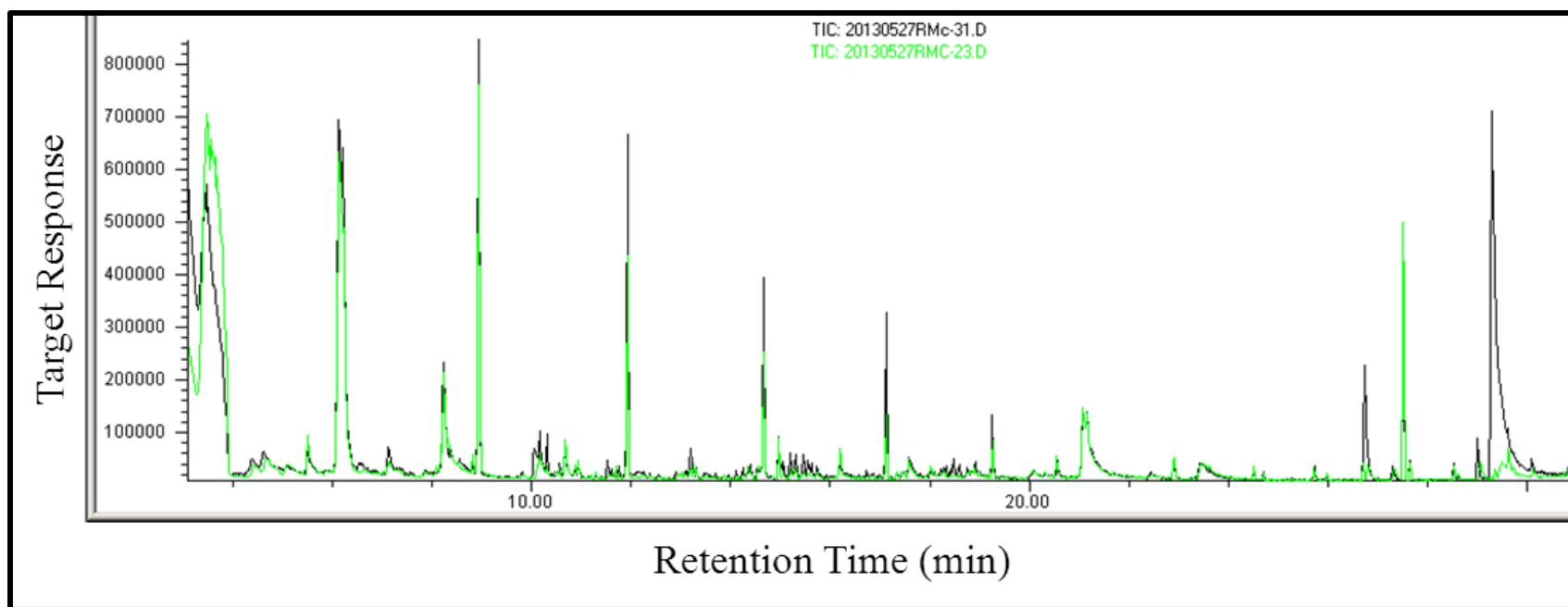


Figure 71: Overlaid chromatograms of a field blank (black) containing DI water and a sample from Long Beach after SBSE-TD-GCMS.

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## **Vita**

Ricardo McCreary Jr. was born on September 15<sup>th</sup>, 1987 in El Paso, Texas. The oldest of his siblings, he received his High School Diploma in 3 years from Captain John L. Chapin High School on June 2<sup>nd</sup> of 2005. Providing much needed monetary support at home through scholarships he would later obtain a Bachelors of Science degree from the University of Texas at El Paso (UTEP) December 12<sup>th</sup>, 2009. Later, through his involvement in the Honors Program at UTEP, he would acquire undergraduate research experience his last year and decide to pursue graduate school after attending a national scientific conference. The following year, January 2010, he decided to become involved with the graduate program at that same university to obtain his M.S. degree in Chemistry under the mentorship of Dr. Wen-Yee Lee. Parts of his research have been presented at the 2011 and 2012 Society for Advancement of Chicanos and Native Americans in Science (SACNAS) National Conferences and Society of Environment Toxicology and Chemistry (SETAC) North America Annual Meeting. After obtaining his M.S. degree in chemistry, Ricardo McCreary Jr. plans to pursue future research opportunities in a variety of areas.

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