A STUDY OF METHODS USED TO ANALYZE TOTAL OIL AND POLYCYCLIC AROMATIC HYDROCARBONS IN PRODUCED WATER: STEPS TOWARDS THE VALIDATION OF MOLECULARLY IMPRINTED POLYMERS FOR USE IN MARINE ENVIRONMENTS

by

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Abstract

Produced water is a by-product of offshore oil and gas production, and is released in large volumes when platforms are actively processing crude oil. Some pollutants are not typically removed by conventional oil/water separation methods and are discharged with produced water. Oil and grease can be found dispersed in produced water in the form of tiny droplets, and polycyclic aromatic hydrocarbons (PAHs) are commonly found dissolved in produced water. Both can have acute and chronic toxic effects in marine environments even at low exposure levels. The analysis of the dissolved and dispersed phases are a priority, but effort is required to meet the necessary detection limits.

There are several methods for the analysis of produced water for dispersed oil and dissolved PAHs, all of which have advantages and disadvantages. In this work, EPA Method 1664 and APHA Method 5520 C for the determination of oil and grease will be examined and compared. For the detection of PAHs, EPA Method 525 and PAH MIPs will be compared, and results evaluated.

APHA Method 5520 C Partition-Infrared Method is a liquid-liquid extraction procedure with IR determination of oil and grease. For analysis on spiked samples of artificial seawater, extraction efficiency ranged from 85 – 97%. Linearity was achieved in the range of 5 – 500mg/L. This is a single-wavelength method and is unsuitable for quantification of aromatics and other compounds that lack sp^3-hybridized carbon atoms. EPA Method 1664 is the liquid-liquid extraction of oil and grease from water samples followed by gravimetric determination. When distilled water spiked with reference oil

was extracted by this procedure, extraction efficiency ranged from 28.4 – 86.2%, and %RSD ranged from 7.68 – 38.0%.

EPA Method 525 uses solid phase extraction with analysis by GC-MS, and was performed on distilled water and water from St. John's Harbour, all spiked with naphthalene, fluorene, phenanthrene, and pyrene. The limits of detection in harbour water were 0.144, 3.82, 0.119, and 0.153 μg/L respectively. Linearity was obtained in the range of 0.5-10 μg/L, and %RSD ranged from 0.36% (fluorene) to 46% (pyrene).

Molecularly imprinted polymers (MIPs) are sorbent materials made selective by polymerizing functional monomers and crosslinkers in the presence of a template molecule, usually the analytes of interest or related compounds. They can adsorb and concentrate PAHs from aqueous environments and are combined with methods of analysis including GC-MS, LC-UV-Vis, and desorption electrospray ionization (DESI)-MS. This work examines MIP-based methods as well as those methods previously mentioned which are currently used by the oil and gas industry and government environmental agencies. MIPs are shown to give results consistent with other methods, and are a low-cost alternative improving ease, throughput, and sensitivity. PAH MIPs were used to determine naphthalene spiked into ASTM artificial seawater, as well as produced water from an offshore oil and gas operation. Linearity was achieved in the range studied (0.5 – 5 mg/L) for both matrices, with $R^2 = 0.936$ for seawater and $R^2 = 0.819$ for produced water. The %RSD for seawater ranged from 6.58 – 50.5% and for produced water, from 8.19 – 79.6%.

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Abbreviations

4-VP – 4-vinyl pyridine

APHA – American Public Health Association

ASTM – American Standard Test Methods

BTEX – benzene, toluene, ethylbenzene, and o, m, and p isomers of xylene

CNLOPB – Canada-Newfoundland and Labrador Offshore Petroleum Board

DCM – dichloromethane (methylene chloride)

DMPA – 2,2-dimethoxy-2-phenylacetophenone

EGDMA – ethylene glycol dimethacrylate

EPA – Environmental Protection Agency (United States)

GC-FID – gas chromatography flame ionization detection

GC-MS – gas chromatography mass spectrometer/spectrometry

HCl – hydrochloric acid

HEM – *n*-hexane extractable material

IR – infrared

mg/L – milligram per litre

MIP – molecularly imprinted polymer

m/z – mass-to-charge ratio

NIP – non-imprinted polymer

NPD – naphthalene, phenanthrene, and dibenzothiophene

OSPAR – Oslo-Paris convention

PA – peak area

PAH – polycyclic aromatic hydrocarbon

PCE – tetrachloroethylene (perchloroethylene)

PTFE – polytetrafluoroethylene (Teflon)

PW – produced water

PWRI – produced water re-injection

SGT-HEM – silica gel treatable *n*-hexane extractable material

SPE – solid phase extraction

SW – seawater (ASTM artificial seawater)

TGA – thermogravimetric analysis

μg/L – microgram per litre

1. Introduction and literature review

1.1 Produced water

1.1.1 Source

Produced water is a byproduct of offshore oil and gas production. It includes both formation and injected water. Formation water, trapped for millions of years between layers of impenetrable rock along with oil and natural gas, may be found within a reservoir. When a well reaches an undersea reservoir, this formation water may be released into the surrounding ocean [1]. Water and production chemicals are often injected into a reservoir to enhance recovery of oil and gas, and this mixture is usually recovered with extracted oil and gas [2]. Recovered produced water is sometimes re-injected into the reservoir, or discharged into the ocean following treatment [2] at offshore oil and gas platforms. Combined, injected water and formation water together are referred to as produced water, and make up the largest waste stream associated with oil and gas production [3].

The amount of produced water that is generated from oil and gas fields tends to increase over the life of the reservoir and increases as the amount of oil and gas in the reservoir decreases. For example, produced water discharges from the Hibernia platform increased from 17,000 m^3/day to 20,300 m^3/day from July to September in 2007 [1]. In the early stages of oil production, the formation water content of a reservoir is low, but these amounts can rise to as much as 80% of total extracted materials as a reservoir is depleted [4]. Once the volume of produced water extracted with petroleum products becomes too large for economically viable oil production, the reservoir has essentially

reached the end of its life [5]. Oil and gas reservoirs are generally made up of porous rock such as sandstone or carbonates, which contain void spaces where petroleum may be found. There are three modes of recovery employed in the extraction of petroleum from reservoirs: primary, secondary, and tertiary. Primary recovery uses the natural energy of the reservoir, such as buoyancy and reservoir pressure, to drive oil to the surface of the production well. Secondary recovery relies on artificial pressure maintenance, which uses fluid injection to maintain pressure. In most oilfields, secondary recovery accounts for the largest proportion of oil extraction. Water is the most common fluid used in fluid injection at this stage, as it is higher density than most petroleum fluids, which can be forced to the surface by water collecting below them. This water flooding gives a constant downhole pressure, increasing the extraction efficiency of the well as the reservoir is depleted. Depletion results in decreased reservoir pressure gradient, so as the amount of petroleum in the reservoir decreases, the amount of water needed for injection increases, eventually causing injected fluids to break through and mix with the oil. Combined, primary and secondary recovery generally extract between 30-50% of the oil in a reservoir. Tertiary recovery is more complex and expensive, using thermal, chemical, miscible, or microbial methods to lower the viscosity of oil and enhance recovery. However, due to the high cost and complexity of this method, it is only feasible if a large amount of oil remains in the reservoir after primary and secondary extraction. In 2010, only 1.5% of global oil production came from tertiary recovery [6]. In 2009, non-renewable fossil fuels provided 81% of the global primary energy supply, with oil accounting for 33% of the world's energy needs [6].

1.1.2 Composition

Generally, produced water is composed of seawater, formation water, and contaminants including aromatic hydrocarbons, organic acids, phenols, inorganic compounds, and other chemicals used in the production and separation of petroleum products. The specific composition, however, can vary depending on the geology of the reservoir and can change throughout the production lifetime of a reservoir [7]. Produced water contains hydrocarbons either in the dissolved phase or dispersed oil phase depending on the solubility of the components in water. The dissolved portion cannot typically be removed by conventional oil/water separation methods, and is therefore discharged with produced water [8]. Mainly lighter, more volatile hydrocarbons are found in the dissolved fraction, such as BTEX (benzene, toluene, ethylbenzene, and xylenes) and NPD (naphthalene, phenanthrene, and dibenzothiophene) and their C1-C3 homologues, as well as some higher molecular weight compounds such as chrysene and benzo[a]pyrene. The concentrations of BTEX and NPD are not typically dependent on the efficiency of oil and water separation, unlike higher molecular weight PAHs, which tend to stay dissolved in oil droplets [7]. The concentration and distribution of BTEX and alkylphenols in waters surrounding oilfields depends primarily on the partition equilibrium between oil and water [9]. Phenols dissolved in the aqueous phase of produced water can have alkyl chains with up to seven carbon atoms, and organic acids in this phase generally contain chains with up to six carbon atoms. Metals found dissolved in produced water can vary, but barium and iron are the most common [2]. The concentrations of dissolved and particulate barium, iron, and manganese in water discharged from the Hibernia platform off the coast of Newfoundland are markedly

higher than in samples of clean seawater [1]. Injected water contains many different types of oilfield chemicals, the exact composition of which, due to commercial confidentiality, is not made public. Generally, only the legally required health and safety information is available, referring only to the relevant classes of compounds. Oilfield chemicals include scale inhibitors, which serve to prevent mineral deposition on pipes, corrosion inhibitors, which keep salt water and dissolved gases from degrading pipework, chemicals to prevent the growth of bacteria that can degrade oil, and demulsifiers added to facilitate the separation of oil and water [4]. Salinity is also a factor in the composition of produced water. In the early stages of oil and gas production, produced water is mostly fresh, originating predominantly from water that condenses on tubing. As production goes on and produced water is recovered and re-injected, it becomes increasingly more saline [7].

Table 1.1 Concentration range of major components of produced water in the North Sea and North Atlantic Ocean [1, 2, 7]

Compound class	Concentration range (μg/L)
BTEX	$10 - 2.244 \times 10^6$
NPD	1 – 10439
PAHs	0.4 – 4125
Phenols	$3.6 \times 10^2 – 1.68 \times 10^4$
Metal ions	2311.91 - 4412.26
Organic acids	$<1 - 1.0 \times 10^7$

Table 1.2 Concentration range for individual components of produced water in the North Sea and North Atlantic Ocean [1, 2, 7]

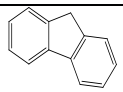
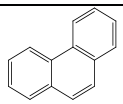
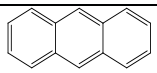
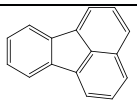
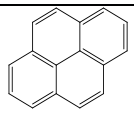
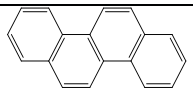
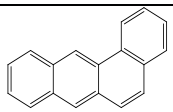
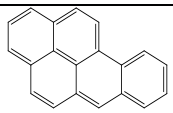
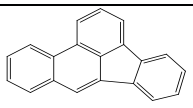
Compound	Concentration range (μg/L)
Benzene	32-14966
Toluene	58-5855
Ethylbenzene	86-565
Xylenes (o, m, p)	553-2684
Naphthalene	194-841
C1-C3 naphthalenes	510-8190
Phenanthrene	1.3-111
C1-C3 phenanthrenes	40-961
Dibenzothiophene	1-23
C1-C3 dibenzothiophenes	13-312
Acenaphthene	0.37-15.3
Acenaphthylene	1.3-6.1
Anthracene	0.26
Fluorene	2.6-66.7
Pyrene	0.03-7.7
Fluoranthene	0.01-1.1
Benz[a]anthracene	0.01-0.74
Chrysene	0.02-15.2
Benzo[b]fluoranthene	0.01-3.4
Benzo[k]fluoranthene	0.006-0.6
Benzo[a]pyrene	0.01-1.1

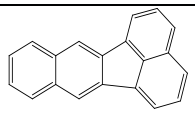
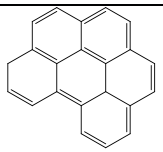
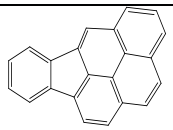
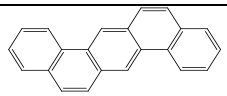
Indeno[1,2,3-cd]pyrene	0.022-0.4
Dibenz[a,h]anthracene	0.012-1.2
Benzo[g,h,i]perylene	0.01-2.7

PAHs are hydrocarbons composed of two or more fused aromatic rings. They can enter the environment through both natural and anthropogenic sources. Found naturally as components of oil and gas, they are released into the environment through natural petroleum seeps [10] and in the process of oil and gas exploration and extraction. They are also often the products of incomplete combustion of hydrocarbons [11]. These hydrocarbons are found in gasoline, diesel, and engine exhaust, cigarette and wood smoke, and emissions from the burning of other fossil fuels [12, 13], and variations in configuration can give different properties [11]. It is estimated that about 90% of PAHs are of anthropogenic origin [12, 14], meaning that they are a result of human activity. The toxicity of aromatic hydrocarbons has a tendency to increase with increasing molecular weight and hydrophobicity [7]. Many publications refer to "16 Priority PAHs" as designated by the US EPA based on their toxicity, possibility of human exposure, and prevalence at industrial waste sites [15, 16, 17, 18], however the current incarnation of the priority chemical list, first published by the US EPA in 1998, contains only eight individual PAHs [19], with the addition of benzo[a]pyrene upon development of the Persistent, Bioaccumulative, and Toxic Chemicals List [20]. The first instance of referral to the 16 PAHs was in 1978 by Ogan *et al.*, which specifically mentions "16 PAHs on the EPA Consent Decree List" [21], and in 1979, Ogan *et al.* published a paper that refers to

the 16 PAHs on the EPA's Priority Pollutant List [22]. The complete 16 are outlined in Table 1.3:

Table 1.3 16 PAHs and their relevant physical properties

Compound (molecular weight – g/mol)	Structure	$\log K_{ow}$	Solubility in H_2O (mg/L)	Vapour Pressure (kPa)	Carcinogen classification[c]
Naphthalene (128.17)		3.37[a]	31	1.19×10^{-2}	2B
Acenaphthylene (152.20)		4.07[a]	16.1	3.87×10^{-3}	nd
Acenaphthene (154.21)		3.92[b]	3.8	5.00×10^{-4}	3
Fluorene (166.22)		4.18[a]	1.9	4.32×10^{-4}	3
Phenanthrene (178.23)		4.57[a]	1.1	9.07×10^{-5}	3
Anthracene (178.23)		4.54[a]	0.045	3.40×10^{-6}	3
Fluoranthene (202.26)		5.22[a]	0.26	1.08×10^{-6}	3
Pyrene (202.26)		5.18[a]	0.132	5.67×10^{-7}	3
Chrysene (228.29)		5.86[a]	0.0015	1.04×10^{-9}	2B
Benz[a]anthracene (228.29)		5.91[a]	0.011	2.05×10^{-8}	2B
*Benzo[a]pyrene** (252.32)		6.04[a]	0.0038	6.52×10^{-10}	1
Benzo[b]fluoranthene (252.32)		5.8[a]	0.0015	1.07×10^{-8}	2B

Benzo[k]fluoranthene (252.32)		6.0[a]	0.0008	1.28×10^{-11}	2B
Benzo[g,h,i]perylene (276.34)		6.5[a]	0.00026	1.33×10^{-11}	3
Indeno[1,2,3-cd]pyrene (276.34)		nd	0.00019[b]	1.87×10^{-11}	2B
Dibenz[a,h]anthracene (278.35)		6.75[b]	0.0005	2.80×10^{-12}	2A

[a][7]
[b][23]
[c][24]

1: Carcinogenic to humans
2A: Probably carcinogenic to humans
2B: Possibly carcinogenic to humans
3: Not classifiable as to its carcinogenicity to humans
nd: No data available

Compounds in italics indicate those currently found on the EPA Priority Chemical List
*Benzo[a]pyrene is found on the US EPA's PBT List[20]

The nonpolar nature of PAHs and their low solubility in water means that their concentration in salt and fresh water is typically very low, and tends to decrease with increasing molecular weight [25]. The dilution of discharged produced water by the surrounding ocean lowers the concentration of PAHs to near background levels even a short distance from the discharge point. Evaporation, sedimentation, adsorption, chemical and photo-oxidation, and biodegradation can also contribute to lowering PAH concentrations in seawater [26]. Thus, analysis at these low concentrations can be difficult and necessitates extraction and preconcentration steps [12, 26]. These steps increase analysis time, cost, and amounts of reagents; and moreover, analyte losses can seriously impact quantitation [12], which is a significant problem in trace analysis.

Alkylphenols are organic compounds, generally used industrially as surfactants and lubricants. The degradation products of these surfactants are often found in discharged wastewater as well as effluent from sewage treatment plants [27]. Alkylphenols tend to accumulate in organisms due to their amphiphilic nature, which can concentrate them in lipid-based tissues [28]. These compounds are also thought to be estrogen mimics. At the levels they are commonly found in the environment, they can disrupt endocrine functions in humans, as well as many species of wildlife and fish [27]. The most toxic and strongest estrogen mimics are alkylphenols with C8 or C9 alkyl substituents; these compounds are found mainly in the dispersed oil phase of produced water, and are rarely found in the dissolved phase. Smaller alkylphenols (those with C4 or C5 alkyl substitutions) are less toxic and weaker estrogen mimics, but are much more abundant in produced water and are therefore a greater concern [8].

Thiophenes are aromatic heterocyclic compounds based on a five-membered ring containing one sulfur atom. These compounds occur naturally in petroleum and are a by-product of the industrial production of benzene from petroleum [29]. Along with sulfides, disulfides, and mercaptans, thiophenes make up a large portion of the sulfur compounds found in petroleum [30]. Dibenzothiophene, which has two benzene rings fused to a thiophene ring, is typically discharged in high concentrations relative to seawater concentrations [28].

1.1.3 Environmental effects

There is no one component of produced water that can be implicated in causing the toxic effects observed in the ecosystems surrounding oilfields [31]. The environment to which produced water is being discharged is also a factor. For example, Arctic environments tend to contain relatively few species, and those species tend to be more highly specialized than in ecosystems farther south [31]. Food chains found in the Arctic are more easily disrupted if key species are affected, causing major impacts to many other species [32]. Factors such as ice cover, low light levels, and low temperatures constrain the degradation and evaporation of the dissolved fraction of produced water, resulting in longer exposure periods for organisms in the area, which can still be harmful even at low concentrations [31]. The toxic effects of produced water as a whole are due largely to the absorption of water-soluble components through the gills or permeable body surface, and through the ingestion of particulates. Both the dissolved fraction and the dispersed fraction, which may include particulate matter in the form of precipitated solids or tiny droplets of oil, are found in the water column and sediment in the immediate discharge area, and are therefore available to the entire ecosystem [5].

Organic compounds, heavy metals, the ions responsible for salinity, and the osmotic properties of water have all been shown to have varying effects on the organisms living in close proximity to produced water discharge points [5]. Following discharge, produced water is diluted by the surrounding ocean, and evaporation and biodegradation may change the concentration of components and overall composition [2, 5]. At a distance of 3-4 km from the discharge location, dilution lowers the concentration of produced water in seawater to approximately 0.1% of the original concentration, at which

point the concentration of potentially harmful components is too low for acute effects to be easily observed and measured [5]. BTEX, and to a lesser extent, NPD, are able to evaporate from discharged produced water as long as it is near the ocean surface, and low molecular weight PAHs are more readily degradable with half-lives of several hours. Larger PAHs, however, can have longer residence times, with half-lives as high as several months [7].

As previously noted, low molecular weight PAHs tend to be less toxic than higher molecular weight PAHs, as bioaccumulation potential increases with increasing molecular weight, but only up to a point. PAHs with six rings are generally too large to pass through cell membranes [7]. Toxic effects brought about by exposure to PAHs are varied and depend on factors such as the compound, exposure level (acute vs. chronic), the species of exposure, and environmental parameters such as ocean temperature or salinity. PAHs are linked to effects such as non-polar narcosis, and can be photo-oxidized or biochemically activated leading to the production of compounds that can have mutagenic, carcinogenic, and teratogenic effects. Biochemical activation occurs mainly during chronic, prolonged exposure to low concentrations of PAHs. Some may even function as endocrine disruptors, influencing hormone regulation in some organisms [7]. The degradation of some PAHs may also produce reactive oxygen species (free-radicals), which on their own do not have adverse effects on most species, however exposure to pollution can damage the antioxidant systems of organisms, which exist in order to prevent oxidative damage. Diminished capacity to deal with free-radicals coupled with increased exposure to them can result in oxidative stress and damage to proteins, lipids,

and DNA. This damage is expressed as decreased cell functionality, malformations, mutations, and cancer cell growth [31].

In a study by Strømgren and coworkers [5], four organisms (Skeletonema costatum – a type of algae, Mytilus edulis – juvenile mussels, Abra alba – a sediment reworking bivalve, and Crassostrea gigas – oyster embryos) commonly found in ocean waters in the North Sea were used to examine the toxicity of raw and biodegraded produced water at varying concentrations in uncontaminated seawater. The organisms examined exhibit different body structures and different physiological mechanisms, and all were exposed to produced water sampled from three different oilfields, having different compositions and concentrations of pollutants. They found that acute toxic effects are related to the chemical composition of the discharged water, as well as levels of biodegradation, volatilization, dispersion, and dilution. As the discharged produced water is dispersed and diluted in the surrounding ocean, and as some of the organic components are volatilized, the toxicity typically decreases, however in some cases, biodegradation results in an increase in toxicity due to the production of toxic, more bioavailable compounds from larger hydrocarbons. Larger, more hydrophobic compounds are less soluble in water, but they are broken down into smaller fragments which may be more soluble in water [5]. Tests were performed using raw produced water and samples of produced water that had been biodegraded over the course of 28 days. Fitness or health parameters examined included shell growth and fecal pellet production. Mytilus edulis and Abra alba were able to ingest any particle less than 100 μm in size, which means that

these and likely other similar species are exposed to the dissolved and dispersed phase of produced water, and contaminated particulate [5].

In raw produced water, the EC_{50}, which is the concentration of produced water in seawater which causes a 50% reduction in performance of a species, was found to be in a range from 0.2-30% by volume of raw produced water in seawater, with the lower values indicating a higher toxicity. One of the oilfields was found to have a much higher toxicity than the other two. Biodegraded water from the three wells, however, was found to have similar levels of toxicity for the organisms studied. Biodegraded samples of produced water were found to have EC_{50} values of 0.4% (v/v) for juvenile mussels, to 2.6% (v/v) for bivalves [5].

It was found that the concentration of hydrocarbons in produced water samples correlates to toxicity in some species, but not in others. The total concentration of hydrocarbons measured in single samples from each oilfield was between about 6-30 mg/L, which includes both the dissolved and dispersed phases. It was also determined that organic compounds may be degraded or volatilized, and that biodegradation can change the toxicity of produced water by changing the ratio of dispersed to dissolved hydrocarbons, and by making some compounds more bioavailable [5].

Another study by Hatlen and coworkers examined the long-term effects of the water-soluble fraction of crude oil on the Arctic sea ice amphipod *Gammarus wilkitzkii*. Specimens were exposed over periods of 36 or 113 days to water containing 28 PAHs at varying concentrations. While mortality was not observed, there were signs of oxidative stress detected through increased respiration and increased concentration of malondialdehyde, an end product of lipid oxidation [31].

Biomarkers—most often metabolites of one or more of the ingested toxic compounds—may be used in the detection of produced water exposure in some organisms. Sundt and coworkers performed experiments on Atlantic cod, measuring PAH and alkylphenol metabolites in bile, and found that these are good indicators of prolonged produced water exposure, even when diluted to 0.125% produced water in seawater [33].

The aforementioned are only a few examples of toxicity studies of produced water on organisms living in Arctic ecosystems. As previously discussed, because there is no single type of toxic action of the components of produced water, and because there are so many variables in this type of experiment (composition and concentration of produced water in seawater, species and stage of development, ocean current and depth affecting dispersion and dilution, exposure level and time [1, 2, 5, 31, 33], among others), it is difficult to give a concise summary of results. Generally, due to predicted dispersion and biodegradation rates of discharged produced water, acute toxicity is less likely to occur beyond the immediate discharge area. However, continued chronic exposure may cause changes in the ecosystem which, though non-lethal, can be serious. Decreased community and genetic diversity, lower reproductive success, decreased growth, endocrine disruption, respiratory problems, behavioural and physiological disorders, and decreased developmental success [1].

1.1.4 Regulatory guidelines

The US EPA regulates produced water discharge and total oil and grease in offshore wells. For offshore platforms, total oil and grease may not exceed 42 mg/L per

day, or a monthly average of 29 mg/L [34]. A grab sample must be taken from the produced water after its final treatment and before it is combined with any other wastewater. At least one sample must be taken per month, but if only one sample is taken in a month, it must meet both the daily and monthly average limits. Otherwise, the daily average may be obtained from four samples collected in a 24-hour period. Additionally, samples must be collected for analysis within two hours of an oil sheen being observed on the surface of the water. A sheen is defined by the US EPA as "a silvery or metallic sheen, gloss, or increased reflectivity; visual colour; iridescence; or oil slick on the surface." Regulations are also in place governing the locations where produced water may be discharged and how it must be sampled for regular monitoring of its quality. No discharge is permitted from facilities located within 1000 m of an area of biological concern, or within 1000 m of a federally designated dredged material ocean disposal site [35]. These requirements also apply to platforms and coastal locations in the Gulf of Mexico, but due to the low temperatures and sensitive ecosystems of northern climates, monitoring effluent water discharge is especially important in those regions.

In Canada, discharged produced water can have a rolling daily average of no more than 44 mg/L oil and grease (recalculated at each sample interval), and a monthly average of 30 mg/L. These limits are based on total petroleum hydrocarbon concentration as measured by *Standard Methods for the Examination of Water and Wastewater, 20th edition* (or as amended or updated) 5520 Oil and Grease, 5520 C Partition-Infrared Method, 5520 F Hydrocarbons [36]. Produced water discharge limits are the same for offshore platforms in Newfoundland and Labrador [36].

According to the Canada-Newfoundland and Labrador Offshore Petroleum Board (CNLOPB), discharged produced water should be sampled at least every 12 hours in order to calculate the 24-hour average, and analysis of samples is performed using Method 5520 Oil and Grease, 5520 C Partition-Infrared Method, and 5520 F Hydrocarbons from the American Public Health Association *Standard Methods for the Examination of Water and Wastewater, 20th edition* [36, 37]. Samples taken for the purpose of compliance monitoring should be collected upstream of the discharge point and downstream of the last water treatment unit. Additionally, the sampling port must be designed such that a representative sample can be easily collected. Results of these analyses are reported monthly to the CNLOPB, as well as amounts of any additives that have been used to prevent the formation of ice or hydrates. Regular toxicity testing must also be carried out, and chemical characterization of discharged water must be reported annually [36]. It is important to note that the routine analysis of produced water are based on infrared absorption methods which determine total oil, because legislation on the composition of discharged produced water is generally limited to the "total oil" defined by the method, and is primarily concerned with monitoring the efficacy of oil and water separations [2].

Oil and water separations traditionally rely on the differences in specific gravity of oil and water, but without activated carbon or some other method of adsorbing dissolved materials, these methods cannot remove dissolved components from the aqueous phase [7]. A hydrocyclone or hydraulic cyclone uses rotational energy due to fluid pressure to create rotational fluid motion. It is this motion that causes the components of produced water with different densities and viscosities to experience different relative motion. This

allows heavy components to be separated from lighter ones with ease and little energy input. Unlike centrifuges, which are more powerful, hydrocyclones have no moving parts—the vessel itself does not spin. Instead, rotation is produced by tangential fluid injection into the cylindrical or conical cyclone vessel [38]. These physical separation methods are only able to remove dispersed oil from produced water, but no appreciable amount of the compounds found in the dissolved phase. Further separation is possible using mechanical coalescing systems and chemical flocculation and coagulation, and to reduce oil content even further, centrifuges, absorbents, membranes, and biological treatment may be employed. It is only some of these newer methods that are able to remove significant amounts of BTEX, NPD, and PAHs from produced water, but they tend to rely on larger capacity and holding time for treatment, chemical additives, and additional energy, which makes removal of dissolved aromatics expensive, and causes a significant environmental impact, especially at the high volumes associated with offshore oil and gas production. Use of these specialized techniques is therefore limited by throughput, weight, space, and cost [7]. Wastewater treatment plants at onshore refineries are able to use biological treatment in which microorganisms break down and remove dissolved hydrocarbons, but offshore installations do not have this capability. Most offshore water treatment facilities are able to achieve a discharge level of <40 mg/L oil in water utilizing hydrocyclone technology and simple polishing steps, in which a degasser vessel removes dissolved gases. By these methods, operators can generally achieve a 15-30 mg/L discharge. Another technique to reduce the amount of oil and grease discharged from platforms is produced water re-injection (PWRI). In this method, produced water can be re-injected into a disposal well, or into the reservoir where it originated. This

technique reduces the discharge of produced water, but requires a suitable injection zone as well as the high amounts of energy needed to achieve the high pump pressure required for re-injection. The high energy use associated with PWRI increases greenhouse gas emissions, and this technique simply reduces the amount of produced water that is discharged, but does not actually reduce the amount of total oil in discharged produced water. The complexity, risk, and high cost of these treatments can significantly impact the viability of mature reservoirs [7].

1.2 Oil and grease

1.2.1 Definition

Oil and grease is a term that is dependent on the method that is used to measure it. OSPAR differentiates between total oil and the dispersed phase of produced water. Total oil refers to total hydrocarbons, and dispersed phase is the total concentration of compounds that are extractable in *n*-pentane that are not adsorbed by florisil and which, when analyzed by GC-FID, have retention times that fall between those of *n*-heptane (C_7H_{16}) and *n*-tetracontane ($C_{40}H_{82}$), excluding toluene, ethylbenzene, and the three isomers of xylene [39]. The United States refers to oil in produced water as "oil and grease" and defines it as materials that are extractable in *n*-hexane that are not evaporated at 70 °C and that are capable of being weighed. While there is an international standard method available for the measurement of oil in produced water (ISO 9377-2), there is no single unified method [40].

1.2.2 Current methods

There are three main strategies for measuring total oil in water: gravimetric determination, infrared (IR) absorption, and analysis by GC-FID.

Gravimetric methods measure any substances that are extractable in a specified organic solvent, which are not lost in the process of solvent removal and can be weighed [40]. Some examples of gravimetric methods include ASTM D4281-95, APHA 5520 B, US EPA 413.1, and US EPA 1664 (Revision A). Of these, APHA 5520 B and US EPA 1664 are still in use. In the US EPA 1664 method, produced water samples are acidified and extracted three times with *n*-hexane, then dried over sodium sulfate. The solvent is removed from the extract by distillation and the residue is desiccated and the dried residue is weighed. This is one of the ways to measure the total oil and grease in a sample, referred to as HEM or *n*-hexane extractable materials, which can include non-volatile hydrocarbons, waxes, greases, and other similar materials. The residue can then be re-dissolved in *n*-hexane and treated with silica gel to remove polar compounds, filtered to remove the silica gel, distilled to remove the solvent, and desiccated once more. The resulting mass gives the total non-polar material in the sample, referred to as SGT-HEM or silica gel treatable *n*-hexane extractable materials. These methods are applicable for oil-in-water in the range of 5-1000 mg/L with a detection limit of 1.4 mg/L and a limit of quantitation of 5.0 mg/L [41]. It is worth noting, however, that components of produced water are not measured if they are not extractable in *n*-hexane [42], or if they have boiling points below that of *n*-hexane. This method is widely used in the United States and HEM is treated as synonymous with oil and grease, and this operational definition is used to assess compliance with discharge limits in the US [40].

IR absorption methods are based on the principle of the Beer-Lambert law, represented by the equation

$$A = log\frac{I_o}{I} = ELc$$

where A is the absorbance at the specified wavelength, I_o is the incident light intensity, I is the transmitted light intensity, E is a constant, L is the cell path length, and c is the concentration of hydrocarbons in the sample [40]. Total petroleum hydrocarbons (TPHs) in aqueous samples can be analyzed by repeated extraction with a fluorocarbon solvent in a separatory funnel. After extraction and drying with anhydrous Na_2SO_4, samples are measured directly by IR at a wavelength of 2930 cm^{-1}. Nonaqueous samples are first dried with Na_2SO_4 and Soxhlet extracted with Freon-113 for 3-4 hours before IR analysis. Silica gel can be used to remove any discolouration in the samples, which represents polar compounds such as organic acids [27]. However, since the use of Freon-113 is restricted by the Montreal Protocol [43], tetrachloroethylene may be used in its place [43]. Supercritical fluid extraction may be used in place of Soxhlet extraction [27], but equipment for this method may not be available. TPHs can also be analyzed by GC, using the purge and trap method of extraction for gasoline range organics, methylene chloride extraction for diesel range organics, and separate FID determination for each segment. The results of the GC-FID analyses are added to determine the total petroleum hydrocarbons in the sample [27].

A major problem with measuring total oil in produced water is that different methods may produce different results that are not easily comparable. While the US EPA Method 1664 directly measures the mass of non-volatile oil in produced water, other

methods measure only specific fractions of oil. Additionally, the composition of oil in water can vary greatly depending on changes in the produced water source and treatment chemicals added to it [42]. Changing the detection method can also influence the results, since methods such as colourimetry, IR, fluorescence, and UV spectroscopy all give analytical signals for different components of oil [27]. For this reason, it is the method of detection that in practice defines the amount of oil in water. Most detection methods ignore the components of oil that are not soluble in the extraction solvent or below its boiling point [42].

One set of methods currently in use, and mandated by the Canada-Newfoundland and Labrador Offshore Petroleum Board (CNLOPB) is the 5520 Methods in the American Public Health Association's *Standard Methods for the Examination of Water and Wastewater, 20th edition*. This set consists of five separate methods in parts B – F, with part C (Partition-Infrared) and F (Hydrocarbons) used by the CNLOPB. In this determination of oil and grease, the exact quantity of specific components of produced water is not measured, but groups of substances having similar physical characteristics are quantified based on their solubility in the organic extraction solvent. This method defines "oil and grease" as "any material recovered as a substance soluble in the solvent", and includes other substances that are extractable from an acidified sample and not volatilized during the procedure, such as elemental sulfur, complex aromatic compounds, hydrocarbons containing chlorine, sulfur, and nitrogen, and some organic dyes. Not included in this definition are volatile hydrocarbons that may be lost during analysis, or compounds found in heavier residues of petroleum that are not soluble in the extraction solvent but may be found suspended in water in small amounts if emulsions are formed in

the treatment and discharge process. In the 12th edition of *Standard Methods*, petroleum ether is recommended as the extraction solvent for natural and treated water samples, and *n*-hexane for polluted water samples. The 13th edition added trichlorotrifluoroethane (Freon-113) as an optional solvent for either water type. The 14th – 17th editions specify only Freon-113, but due to environmental problems associated with chlorofluorocarbons, an alternative mixture of 80% *n*-hexane with 20% methyl-*tert*-butyl ether was suggested for gravimetric methods in the 19th edition. The 20th edition only uses Freon-113 for part C, and suggests *n*-hexane for the other procedures. Sampling procedures are carefully outlined in Method 5520 to minimize variations in sample handling. A grab sample must be taken into a clean, dry, solvent-rinsed glass bottle with a PTFE-lined cap. Samples are normally 1 L unless more than 1000 mg of extractable material is expected in 1 L. In this case, smaller sample volumes can be used. Grab samples must not be subdivided in the laboratory, instead multiple samples should be obtained, in rapid succession, or in parallel if possible. This is to prevent variations in composition due to uneven dispersion of oil and particulates in the sample. Samples must be acidified to pH 2 and refrigerated if they are not analyzed immediately [37]. These requirements can add a significant cost in both time spent sampling and in space for storage of multiple large sample volumes.

Method 5520 C Partition-Infrared Method — specifies the use of Freon-113 as the extraction solvent, but in recent years, tetrachloroethylene or S-316 have been substituted due to the restriction of Freon-113 by the Montreal Protocol [43]. The use of a fully chlorinated and/or fluorinated solvent allows C–H absorbance, at 2930 cm^{-1}, of the extractable components of produced water to quantify oil and grease in a sample. Since there is no evaporation step, volatilization is kept to a minimum, and as little as 0.2 mg of

oil and grease can be measured in a 1 L sample, with adequate instrumentation. A stock solution should be prepared using a small portion of a known oil where possible, specific to the location from which the water samples were obtained. If this is not possible, a reference oil with a known composition may be used. A set of standards are used to form a calibration curve against which to compare results from real samples. Wastewater samples tested by a single lab gave oil and grease concentrations of 17.5 mg/L oil and grease in water. When samples of this wastewater were spiked with 14.0 mg of a mixture of No. 2 fuel oil and Wesson oil, 99% recovery was achieved with a standard deviation of 1.4 mg. [37], or a relative standard deviation of 10%. This is one of the few examples that have been published of this method in use.

Method 5520 F Hydrocarbons — uses silica gel to adsorb polar compounds from the extracts obtained using any of the 5520 methods B – E. According to this method, compounds remaining after silica gel adsorption are considered hydrocarbons. This method is designed to target non-polar, sp^3-hybridized carbon-containing components of oil and grease extracted from samples of produced water. For IR determination, the extract can be analyzed directly after treatment with silica gel. In a test of this method, using reagent water spiked with approximately 20 mg/L each of hexadecane and stearic acid, the recovery of hexadecane was 83 – 116% with a relative standard deviation of 13%. In lab-fortified matrices, recoveries of 66 – 114% were obtained, with a relative standard deviation of 24%. The average recovery for 10 synthetic solvent extracts containing known amounts of various petroleum products was 97.2%, compared with extracts of olive oil, Crisco, and butter which gave 0.0% recoveries. This demonstrates

that this method removes polar compounds such as fatty acids and triglycerides, leaving non-polar compounds behind [37].

1.3 Current methods for dissolved components of produced water

1.3.1 PAHs

PAHs in aqueous samples are often treated similarly to total oil. They are extracted with an organic solvent such as methylene chloride in a separatory funnel and concentrated to 1 mL for analysis by GC-MS. For HPLC analysis, the solvent extract is mixed with acetonitrile and the resulting azeotrope is co-evaporated and made up to 1 mL. Any suspected impurities in the sample may be removed by treatment with silica gel before the final workup [27].

Another accepted method for extracting PAHs from water samples involves their extraction from the aqueous medium by solid phase extraction (SPE) using a reversed phase C-18 stationary phase column, which has been conditioned with 10:1 toluene and methanol, followed by methanol, then deionized water. PAH analytes are eluted using 10:1 toluene and methanol [27]. A similar method based on SPE is currently used by the US EPA for analysis of organic compounds in drinking water. In US EPA Method 525, a 1 L water sample is passed through a C-18 SPE cartridge containing 200 mg of the stationary phase. The organic compounds are then eluted using small, equal volumes (no more than 1-5 column volumes) of first ethyl acetate and then dichloromethane, and this extract is dried over sodium sulfate and concentrated down under nitrogen gas for analysis by GC/MS [44].

Liquid-liquid extraction (LLE) is another effective method for the separation and analysis of PAHs from water, but the procedure is tedious, time-consuming, and uses large volumes of organic solvents [45]. These solvents are often toxic or flammable, which can lead to problems in handling, storage, and disposal. LLE can also be subject to emulsion formation, making efficient separation difficult. While the apparatus for LLE is inexpensive, it is difficult to ensure that contamination or analyte loss does not occur from samples coming into contact with glassware to which many organic compounds can adsorb [25]. Solid phase extraction (SPE) uses less solvent, but recovery and reproducibility can be problematic, especially in complex matrices such as seawater or wastewater [45]. Selectivity is limited by this technique, since all classes of compounds that can adsorb to the solid phase will be isolated, which can be a problem in complex environmental samples. Samples containing particulate matter can pose a problem for SPE methods, and may be treated by preliminary filtering, but this may result in loss of analyte through adsorption to suspended particles that are removed during filtration [25]. Solid phase micro-extraction (SPME) is a technique that is solvent-free, sensitive, and uses small sample volumes. Sensitivity is especially important, since upon entering the environment, PAHs can distribute into various phases: water, suspended dispersed colloidal organic phase droplets of organic matter, suspended particulate, or sediments. PAHs can associate strongly with dissolved organic matter, which can make them less available to the water or sediment phases. SPME measures only the freely dissolved PAHs, which are also the most readily available for bio-uptake, however, because SPME is an equilibrium-based extraction method, it is critical to maintain the same experimental conditions in all extractions, since any variation can cause variation in results [45].

Salinity can influence the extraction efficiency of PAHs. For example, extraction efficiency of light PAHs is improved in seawater over fresh water, but is worse for heavy PAHs. Further increasing the salinity beyond that of seawater lowers the extraction efficiency for all PAHs except naphthalene. In SPME, the effect on extraction efficiency can sometimes correlate with the solubility and polarity of the compound, where a high degree of salinity can enhance the hydrophobic interactions between the analyte and the solid phase, but only up to a point, after which the extraction efficiency is lowered with increasing salinity [45].

1.3.2 Phenol and alkylphenols

Phenol and alkylphenols are generally determined using an extraction step followed by GC-MS or LC-MS. They can also be analyzed by HPLC-fluorescence, HPLC-UV, and GC-FID. The preferred method is usually LC-MS due to the complexity of the sample, which can contain many different isomers and oligomers, which are molecules consisting of only a few monomer units. Solid phase extraction is often used to extract the compounds of interest from aqueous samples [27]. The Norwegian Oil Industry Association outlines a procedure which involves liquid-liquid extraction with dichloromethane at a pH of 2, followed by gel permeation chromatography to purify the extract and remove interfering compounds before the sample is analyzed by GC-MS [46]. It is important to note, however, that smaller phenols and alkylphenols are volatile compounds and may present problems due to evaporation during analysis.

1.4 MIPs

Molecularly imprinted polymers (MIPs) are polymeric sorbent materials that are made selective by the use of a template molecule to form a complementary binding site in a solid polymer matrix [47]. They can be produced in several formats, including bulk monolithic phase, particulate phase (made by crushing monoliths), spherical beads, membranes, or thin films. Bulk phase MIPs are useful in solid phase extraction (SPE or MISPE—molecularly imprinted solid phase extraction) or chromatographic applications. Spherical beads may also be used for chromatography. MIP membranes can be utilized in selective filtration [48] and chemical sensors [49], and thin films are optimal for use in chemical sensors [48].

1.4.1 Advantages

MIPs have many advantages over traditional sorbent materials, as their high degree of selectivity helps to minimize matrix interferences from complex samples such as wastewater and sediments, which often have multistep cleanup procedures to achieve selectivity, remove interferences, and increase concentration. In addition, only small amounts of polymer are necessary for analysis, due to the high sorption capacity of MIPs [12]. These polymers have high mechanical and thermal stabilities [12, 50], high degrees of selectivity [12], and are cheap and easy to produce [50]. Their uptake mechanism and selectivity is similar to that of antibodies [51], but their binding properties can often exceed those of antibodies and enzymes, which are also much less tolerant to changes in

experimental conditions such as pH and temperature, and much less physically robust [48].

1.4.2 Composition

MIPs are usually composed of a functional monomer, crosslinker, template molecule, thermo- or photo-initiator, and porogenic solvent. They are synthesized through the co-polymerization of the crosslinking agent with a complex that is made up of the template molecule and polymerizable monomers having functional groups that interact with the template molecule through covalent and non-covalent bonds [52]. The template molecule must be able to bind with the monomer prior to polymerization through one or more of these bond modes. Non-covalent bonding can include hydrogen bonding, van der Waals forces, and π-π interactions. Non-covalent bonding mechanisms are useful because they are relatively easy to engineer, facilitate straightforward template removal, and analyte uptake is favoured by fast mass transfer [53]. Polymerization occurs through free radical polymerization, which can be accomplished using a thermal or UV radical initiator [54]. This can be seen in Figure 1.1. Once the solid polymer has been synthesized, the template is generally removed through extraction with organic solvent. This leaves behind pores that are selective for the template, and through structural and chemical similarities between the template and target analytes, the pores are also selective towards the target analytes. The overarching porous structure is created during the phase separation process in which the growing polymer becomes insoluble in the porogen [55].

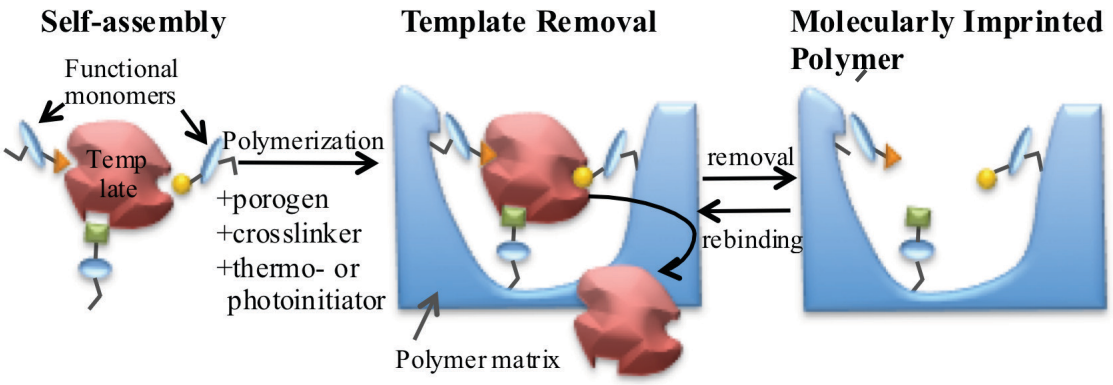


Figure 1.1 MIP synthesis

1.4.3 Template selection and removal

The binding affinity and imprinting factor of an MIP towards its template molecule depends heavily on the interaction between the template and the monomer [52]. The template molecule has historically been one or more of the analytes of interest, and many MIPs have been developed with multiple templates for the uptake of multiple analytes. This can raise the issue of template bleeding, however, which can occur when the template removal step is incomplete, resulting in artificially elevated results upon sample analysis. Various template removal methods are possible, such as solvent extraction, Soxhlet extraction [56, 57], sonication, and supercritical fluid extraction [57]. However, the stability of imprinted pores can be compromised by the use of aggressive template removal methods [56, 57]. Some solutions have been suggested, including isotope molecular imprinting, parallel extraction of blank samples [58], and pseudo-template imprinting [58, 59]. The use of a pseudo-template has been shown to help

combat this problem, without the use of expensive isotopically-labeled reagents or time-consuming parallel extraction methods [51, 60]. Pseudo-templates are molecules that are selected based on their structural or functional similarity to the analyte of interest. The first use of pseudo-templates was published in 1997 by Andersson *et al*. using bulk polymers for SPE, synthesized to bind selectively to sameridine, a compound with local anesthetic and analgesic properties, with structural analogs as the template molecule [59]. In a study by Egli *et al,* toluene was successfully used as a pseudo-template for the uptake of light PAHs from seawater [51]

Table 1.4 Previous research on the use of MIPs for the analysis of PAHs in aqueous media

Reference	Analytes	Template	Polymer format	MDL	Detection method
[61]	PAHs	Combinations of two of the following: benzanthracene, chrysene, perylene, acenaphthene, pyrene, naphthalene	Thin-film	~30 ng/L	Fluorescence
[62]	Benzo[a]pyrene	Benzo[a]pyrene	Bulk (for SPE), microspheres (for HPLC)	NR	SPE-fluorescence, HPLC-fluorescence
[12]	Benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, chrysene, dibenzo[a,h]pyrene, indeno[1,2,3-cd]pyrene	Benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, chrysene, dibenzo[a,h]pyrene, indeno[1,2,3-cd]pyrene	Bulk monolith, ground to 2-10 μm particles in ball mill	0.3-1.5 μg/L	Fluorescence
[50]	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene benzo[g,h,i]perylene	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene benzo[g,h,i]perylene	Sol-gel polymerized MIP-coated silica gel beads (400-600 mesh)	5.2-12.6 ng/L	MISPE-GC-MS

1.5 Principles, advantages, and limitations of key analytical methods

1.5.1 Gas chromatography - mass spectrometry

Gas chromatography separates complex mixtures of analytes on the basis of their interaction with a stationary phase contained within a capillary column. The analyte mixture is vapourized and moved through the column using a carrier gas, typically helium, nitrogen, or hydrogen [63]. As each analyte interacts with the stationary phase, the rate at which they move through the column changes, separating individual components and causing them to elute from the column at different times. These retention times help with the identification of each compound in the mixture. The internal diameter of the column normally ranges from 0.10-0.53 mm, and column length from 15-100 m, with the most common length being 30 m [63]. Factors such as injection volume, carrier gas flow rate, and oven temperature programming also influence the retention time of analytes. After leaving the column, the now separated analytes enter the detector.

The mass spectrometer is made up of five principal components: the sample inlet, ion source, mass analyzer, detector, and data system. The mass analyzer separates sample ions based on their differing mass-to-charge (m/z) ratios. In order to obtain a mass spectrum, the gaseous species is desorbed from a condensed phase and ionized by a variety of possible methods. For example, electron ionization (EI) [64], chemical ionization (CI) [65], and atmospheric pressure chemical ionization (APCI) [66] are a few of the methods [67] commonly used for small, relatively volatile molecules such as PAHs. The produced ions are accelerated into the mass analyzer by an electric field and separated according to their mass-to-charge (m/z) ratio [68], which is equal to the mass of

the ion if the charge on the ion is equal to +1 [63]. The most commonly used mass analyzer for small organic molecules is the linear quadrupole mass filter, in which a radio frequency (RF) potential is applied to two parallel sets of metal rods arranged around a central axis [67]. The high selectivity and resolution associated with MS, its reliable accuracy and precision, wide dynamic range, and high sensitivity have made GC-MS methods of analysis for many types of organic compounds. Gas chromatography coupled with MS (GC-MS) has been used to analyze PAHs since the early 1960s, and is now one of the standard methods for their detection. Complex mixtures of PAHs can be separated, although PAHs having more than 24 carbon atoms cannot be analyzed by GC-MS, due to their lack of volatility [69]. PAHs and volatile compounds such as BTEX can be quantified at the low levels found in environmental samples by extraction and preconcentration procedures such as liquid-liquid extraction (LLE), solid phase extraction (SPE) [70], or closed-system purge-and-trap methods [71]. Mass spectrometry holds the advantage over flame ionization detection in terms of selectivity and sensitivity, due in part to the use of selected ion monitoring (SIM) mode, which enables trace analysis of specific compounds in complex mixtures [69]. Selectivity and sensitivity are increased by the use of SIM mode over scan mode because only a few specific ions are selected for transmission through the mass analyzer to the detector. These ions are generally selected based on their abundance and should be structurally characteristic of the target analyte [67].

1.5.2 Infrared spectroscopy

Nearly all compounds absorb in the infrared region of the electromagnetic spectrum. For the purposes of IR spectroscopy, the vibrational range of the IR region which encompasses radiation with wavelengths of 2.5 – 25 μm. Wavelength (λ) is inversely proportional to the frequency (ν) according to the equation

$$\nu = \frac{c}{\lambda}$$

where c = the speed of light. In IR spectroscopy, this radiation is referred to as *wavenumber* ($\bar{\nu}$) which is expressed in units of cm^{-1}. The absorptions of each type of bond are found in specific areas of the IR region. For example, the stretching of the alkane C–H bond absorbs in the range of 3000 – 2850 cm^{-1}.

In the detection of oil and grease in produced water, IR methods are more sensitive than gravimetric methods [72] which are prone to error due to volatilization of analytes and accidental inclusion of compounds that dissolve in the extraction solvent but are not considered oil and grease. However, IR methods, particularly single-wavelength methods, are very limited in the information they can provide about the actual concentration of oil and grease in a water sample. Since so many components of produced water are aromatics, and many of these may be unsubstituted, single-wavelength IR methods are unsuitable for detecting them. Triple-wavelength methods provide more comprehensive analysis of oil and grease components of produced water, but even these methods are not without their problems. Specifically, the large sample volumes and large amounts of organic solvents required for these methods are not ideal. Furthermore, tetrachloroethylene and carbon tetrachloride, two commonly used solvents for IR, are

classified by the International Agency for Research on Cancer as 2A (probably carcinogenic to humans) and 2B (possibly carcinogenic to humans), respectively [24] and carbon tetrachloride causes stratospheric ozone depletion. The alternative, solvent S-316 by Horiba, may be prohibitively expensive for some laboratories.

1.5.3 Gas chromatography with flame ionization detection

GC-FID is a commonly used for analysis of hydrocarbon samples. It is currently used as part of international standard methods for the determination of dispersed oil in water, ISO 9377-2, as well as the OSPAR Agreement 2005 and TNRCC Method 1005 [40]. After a sample is treated, commonly by liquid-liquid extraction, it is dried, purified, and concentrated before injection into the GC-FID. Hydrocarbons are separated based on their volatility and affinity for the column, and the FID response in a specific carbon range or retention time is compared to standards of known concentrations [40]. In the flame ionization detector, the analyte mixture eluted from the GC column is burned in a mixture of hydrogen gas and air. The ions produced during the combustion of the hydrocarbons induce a current between the two electrodes. The current is then amplified and converted to a digital signal. The response of the detector to organic compounds is proportional to the concentration of carbon content and therefore analyte concentration injected over seven orders of magnitude [63]. For the determination of total hydrocarbons in a sample that fall within a certain mass range, these methods are effective, but they do not provide information on the specific composition of the hydrocarbon mixture, or about components of a sample that are not ionized. Interferences can be an issue if the samples

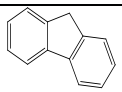
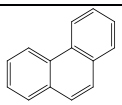
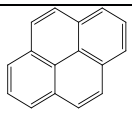
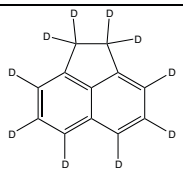
are contaminated in the course of preparation, or if the raw sample contains chemicals used in the drilling or extraction process, which can have complex compositions and may obscure the obtained spectrum. GC-FID is also unable to resolve between some pairs of compounds that have the same volatility and affinity for the column. EPA Method 8100 for the determination of PAHs by GC-FID cannot resolve anthracene/phenanthrene, chrysene/benzo[a]anthracene, benzo[b]fluoranthene/benzo[k]fluoranthene, or dibenzo[a,h]anthracene/indeno[1,2,3-cd]pyrene [73]. GC-FID is less useful for trace analysis of pollutants in complex samples than is GC-MS due to its inability to function in selected ion monitoring (SIM) mode, resulting in more complex spectra and poor resolution of individual compounds. This can severely impact quantitation.

1.6 Research goals

The purpose of this research has been to evaluate existing methods for the analysis of produced water for oil and grease as well as for PAHs and to apply and compare these methods to the results obtained using new materials developed for the determination of PAHs in water by Dr. Stefana Egli in the Bottaro Group at Memorial University of Newfoundland and Labrador [51]. The toxic effects of produced water and its components have been extensively examined. However, due to the sensitivity of harsh and Arctic environments, improved methods for trace analysis of the components of produced water are necessary. In recent years it has become more of a priority for the oil and gas industry to improve detection methods, due to increasing pressure from public concerns and the increase in more stringent government environmental regulations. Thin-

film molecularly imprinted polymers have been found to be effective in the selective uptake of PAHs from produced water. PAH MIPs developed by Dr. Stefana Egli have been shown to have a linear response in PAH-spiked wastewater samples over a range of 10-100 μg/L. Linearity was obtained in naphthalene-spiked seawater samples in the range of 0.5-5 μg/L, and a detection limit of 18 ng/L has been achieved for naphthalene using these MIPs [51]. New materials and new methods must be validated before they may be confirmed as suitable replacements for those already in use. This study aims to show that PAH MIPs are a reliable material for the determination of PAHs in water, particularly at the low levels commonly found in the environment near produced water discharge sites. A comparison of the performance of PAH MIPs with an existing method for the analysis of PAHs in water will be made, and two methods for the analysis of oil and grease in water will be examined. All of the methods will also be assessed in terms of their suitability for use with total oil and grease as well as PAHs. The PAHs that have been the focus of this study are shown in Table 1.5. One quantifier ion for each analyte is selected for use in determining the concentration of the analyte in the extract, and two qualifier ions for each analyte are selected for the purpose of verifying that the analyte in question is present in the solution.

Table 1.5 PAH analytes focused on in this work

Compound	Structure	Molecular Weight (g/mol)	Quantifier ion (m/z)	Qualifier ions (m/z)
Naphthalene		128.17	128	74, 127
Fluorene		166.22	166	139, 165
Phenanthrene		178.23	178	152, 179
Pyrene		202.26	202	101, 200
*Acenaphthene-d_{10}		164.17	164	158, 162

*internal standard used

2. Experimental methods for analysis of oil and grease and PAHs analysis

The analysis of bulk hydrocarbons in produced water may be performed in a number of different ways. The most common methods use infrared or gravimetric determination. APHA Method 5520 C Partition-Infrared Method relies on liquid-liquid extraction of oil and grease from water samples followed by IR determination. This single-wavelength method measures only the absorbance at 2930 cm^{-1}, corresponding to the CH_2 stretch vibration frequency. This method was performed on samples of artificial seawater spiked with a reference oil designed to mimic some of the components found in a sample of produced water. Results were compared with a calibration curve in order to determine the apparent concentration of the reference oil extracted from water. A calibration curve is necessary due to the complex nature and variability in composition of oil-in-water samples. The extraction solvent was optimized in order to overcome the problem of interferences in the IR detection method, and a study was performed on the efficacy and suitability of this method for detecting aromatic compounds.

EPA Method 1664A involves the liquid-liquid extraction of oil and grease from a water sample in *n*-hexane, followed by solvent removal by distillation and subsequent heating and cooling steps to completely remove all *n*-hexane from the residue until a stable mass is obtained. This residue is referred to as *n*-hexane extractable material (HEM), which includes non-volatile hydrocarbons, waxes, and greases. Any substance soluble in *n*-hexane that has a boiling point below that of *n*-hexane is measured by this method, while volatile components of produced water are removed in the solvent-removal steps, and substances insoluble in *n*-hexane are not extracted from the water sample. This method was used to perform extractions on 100 mL aliquots of distilled water spiked with

varying amounts of a synthetic reference oil designed to represent some of the components found in produced water. A volatility study was also conducted to examine the suitability of this method for measuring various aliphatic and aromatic hydrocarbons in a range of sizes.

2.1 APHA Method 5520 C partition-infrared method

2.1.1. Materials

Tetrachloroethylene (ACS reagent grade), hexadecane (anhydrous, ≥99% purity), and sodium sulfate (anhydrous, reagent grade) were purchased from Sigma-Aldrich (Oakville, ON). Benzene (ACS reagent grade, ≥99% purity) was obtained from ACP, 2,2,4-trimethylpentane (isooctane, HPLC grade) was purchased from J.T. Baker, and solvent S-316 was purchased from Horiba. Filter papers used were Whatman No. 40 (ashless, 90 mm dia.) and anhydrous sodium sulfate (ACS reagent grade), both purchased from Sigma-Aldrich (Oakville, ON).

2.1.2 Method

A 100 mL aqueous sample containing reference oil was transferred to a 250 mL separatory funnel and the sample bottle was rinsed with 30 mL of tetrachloroethylene (or "perchloroethylene" – PCE). The solvent washings were combined with the sample in the funnel. The separatory funnel was shaken vigorously for two minutes and layers were allowed to separate for ten minutes. All but a very small portion of the lower PCE layer

was drained through a glass funnel containing a filter paper and 10 g sodium sulfate, both rinsed with PCE prior to filtration, and drained into a clean 100 mL volumetric flask. This extraction was performed twice more with fresh 30 mL portions of solvent. Extracts were combined in the volumetric flask and the filter and sodium sulfate was rinsed with 10 mL of solvent. The volume was made up to 100 mL with PCE.

Stock solutions of known oil content were prepared using a reference oil (composition obtained from Method 5520 C Partition-Infrared Method in *Standard Methods for the Examination of Water and Wastewater, 20th ed.*) made up of 37.5% v/v isooctane, 37.5% v/v hexadecane, and 25.0% v/v benzene. This mixture was prepared using 37.5 mL isooctane, 37.5 mL hexadecane, and 25.0 mL benzene, and stored in a 125 mL sample bottle made from polytetrafluoroethylene (PTFE), sealed with Parafilm, covered in aluminum foil, and stored in the refrigerator at 3-4 °C. A portion of this reference oil was weighed into a 100 mL volumetric flask and made up to the mark with PCE to give a stock solution. From this stock solution, a set of standards was made with concentrations of 5, 10, 20, 30, 40, and 50 mg/L. These standards were analyzed by IR using a liquid cell with silica glass windows and a path length of 1 cm, 24 scans per run at a resolution of 4 cm^{-1} and a scan range of 3200-2700 cm^{-1}. Results using these standards were unsatisfactory, as will be discussed in section 2.1.2, so standards were prepared using Solvent S-316.

Solvent S-316 is often used industrially for this method. A 1 L bottle of S-316, a chlorotrifluoroethylene telomer, was purchased and used to make standard solutions of reference oil. A portion of reference oil was weighed into a 10 mL volumetric flask and

made up to the mark with S-316 to give a stock solution. This stock solution was used to make a set of standards with concentrations of 1, 5, 10, 20, 30, 40, 50, 100, 200, and 500 mg/L. These standards were analyzed by IR using a liquid cell with silica glass windows and a path length of 1 cm, 24 scans per run at a resolution of 4 cm^{-1} and a scan range of 3200-2700 cm^{-1}. Method 5520 C specifies the use of the absorbance at 2930 cm^{-1}, which corresponds to the stretching of sp^3-hybridized C–H bonds, so this was used to construct the calibration curve.

To examine the relationship between the composition of the reference oil or the dispersed phase of produced water and the response of this method, a study was conducted wherein a portion of benzene was dissolved in 10 mL S-316 to obtain a stock solution. This stock solution was used to make a solution with a concentration of 200 mg/L. This solution was analyzed by IR using parameters as outlined above.

2.1.3 Results and discussion

Method 5520 in *Standard Methods for the Examination of Water and Wastewater, 20st edition* recommends the use of trichlorotrifluoroethane, or Freon-113, as the extraction solvent for Method 5520 C Partition-Infrared Method, and *n*-hexane for the methods of analysis that do not use infrared spectroscopy [37]. However, due to restrictions by the Montreal Protocol, the use of Freon-113 is restricted [43]. Tetrachloroethylene (or "perchloroethylene" – PCE) has been suggested as a replacement solvent [8, 37], so this solvent was used in preliminary experiments.

A set of standards was prepared by weighing out 0.9946 g of reference oil into a 100 mL volumetric flask and making up to the mark with PCE to give a stock solution with a concentration of 9946 mg/L. This stock solution was used to make a set of standards with concentrations of 5, 10, 20, 30, 40, and 50 mg/L reference oil in PCE. These standards were analyzed by IR on a Bruker Tensor 27 FT-IR. Results are given in Figure 2.1 and Table 2.1, below:

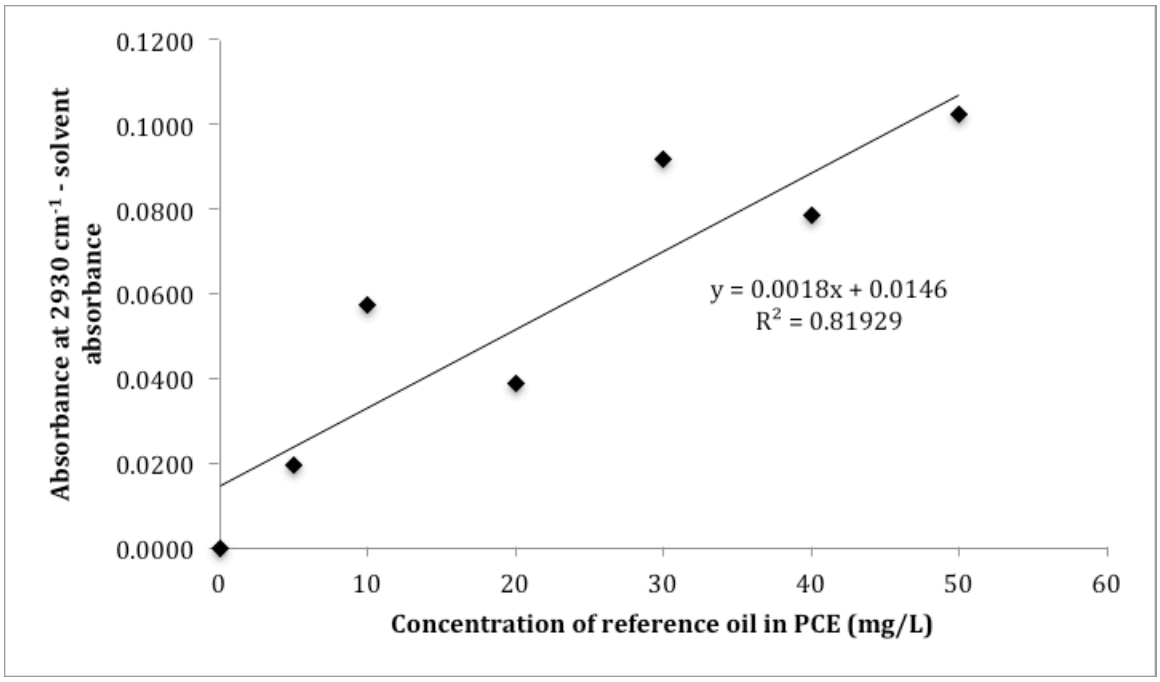


Figure 2.1 Calibration curve for reference oil in PCE by IR (n = 1)

Table 2.1 Absorbances of reference oil standards in PCE at 2930 cm^{-1}

Conc. of reference oil in PCE	Raw absorbance at 2930 cm^{-1}	Raw abs. – PCE abs.
0	0.6941	0.0000
5	0.7138	0.01966
10	0.7514	0.05728
20	0.7329	0.03876
30	0.7860	0.09189
40	0.7727	0.07857
50	0.7967	0.1026

IR results from preliminary work with PCE were unsatisfactory and gave inconsistent responses as the concentration of reference oil varied, as unexpected interferences were found in the pure solvent. Upon further investigation it was discovered that all grades of PCE currently available contain small amounts of hydrocarbon stabilizing agents that interfere with the response at the wavenumber where hydrocarbon C–H stretch is observed in this method; the basis upon which the quantification is made. This can be seen most obviously at 0 mg/L reference oil in PCE, where the absorbance is almost as high as at 5 mg/L, indicating that there are additives or impurities in what is intended to be a fully chlorinated solvent. PCE has also been classified as a category 2A carcinogen (probably carcinogenic to humans) by the IARC. The structure for PCE is shown in Figure 2.2.

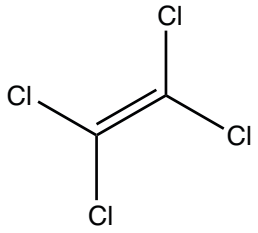
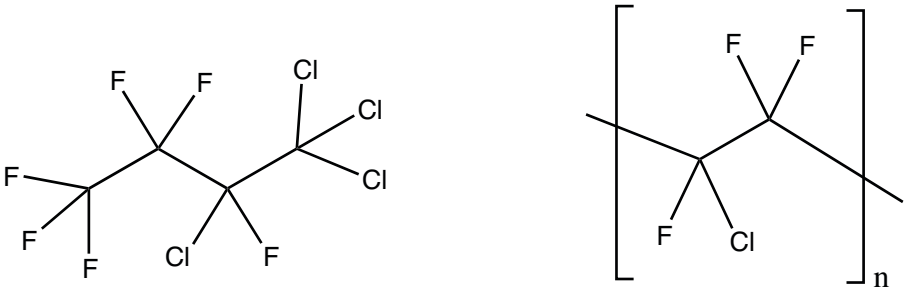


Figure 2.2 Tetrachloroethylene (PCE) structure

Solvent S-316, manufactured and sold exclusively by Horiba Instruments Inc., was presented as a possible alternative. S-316 is a telomer mixture made up of 65-75% tetrachlorohexafluorobutane and 25-35% chlorotrifluoroethylene trimer or tetramer [74]. Figure 2.3 shows the structures of these two components.



Tetrachlorohexafluorobutane Chlorotrifluoroethylene

Figure 2.3 Components of solvent S-316 and their structures

A new set of standards was prepared using reference oil in solvent S-316, with 0.1063 g of reference oil in 10 mL of S-316 to obtain a stock solution with a concentration of 10630 mg/L. This stock was further diluted in S-316 to give standards with concentrations of 5, 10, 20, 30, 40, 50, 100, 200, and 500 mg/L. These solutions

were analyzed by IR on a Bruker Tensor 27 FT-IR. Results are shown in Figure 2.4 and Table 2.2.

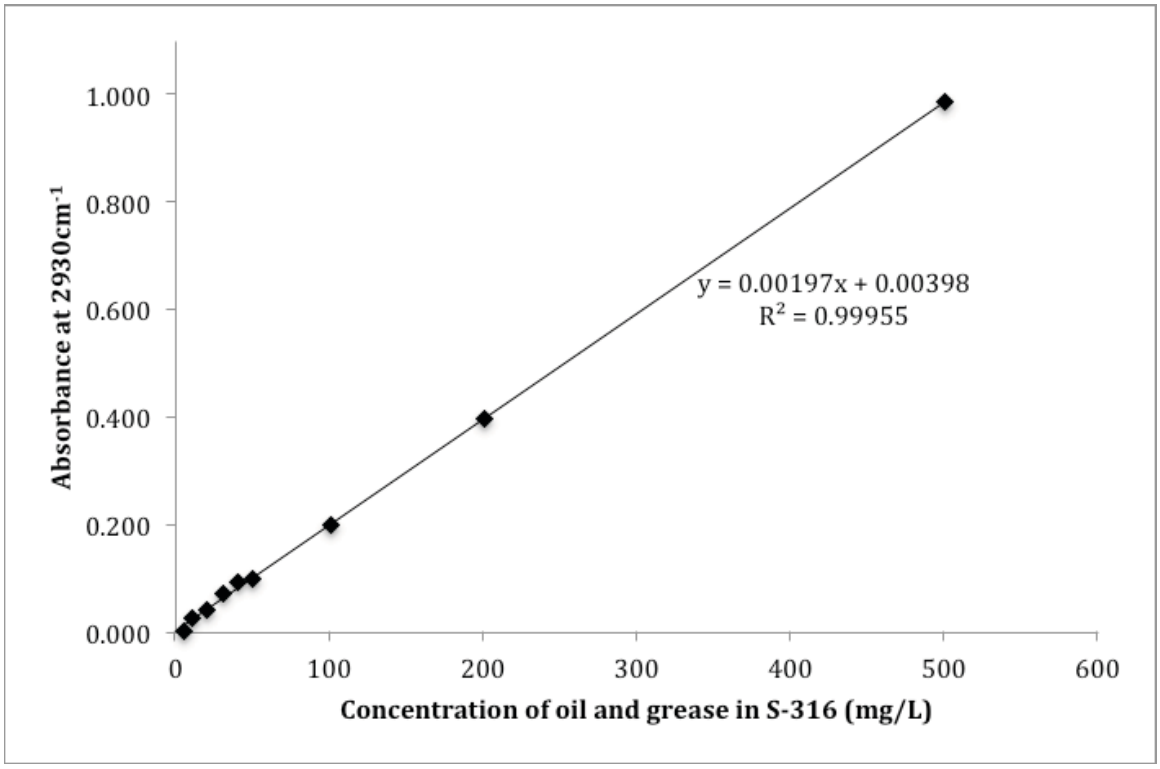


Figure 2.4 Calibration curve for reference oil in S-316 by IR

Table 2.2 Absorbances of reference oil standards in S-316 at 2930 cm^{-1}

Conc. of ref oil in S-316 (mg/L)	Raw absorbance at 2930 cm^{-1}	Corrected abs.*
0	0.1603	0.0000
5	0.1634	0.0032
10	0.1799	0.0259
20	0.1971	0.0431
30	0.2248	0.0645
40	0.2483	0.0942
50	0.2544	0.1004
100	0.3593	0.1991
200	0.5573	0.3971
500	1.1473	0.9870

*Raw absorbance – S-316 absorbance

The method states that a 1 cm path length is appropriate for a working range of approximately 4-40 mg/L [37], and this set of standards shows that linearity is achieved in the range of 0-500 mg/L under these conditions. In cases where the concentration is too high for a 1 cm path length to be suitable, the sample could be diluted accordingly.

Extractions were performed in triplicate on aliquots of reference oil in 100 mL of ASTM artificial seawater (for composition of and method of preparation for ASTM artificial seawater, see Appendix A) with concentrations of approximately 110 mg/L. The results for these extractions are shown in Table 2.3.

Table 2.3 Results of extractions of reference oil from artificial seawater using APHA Method 5520 C Partition-Infrared Method

Sample #	Spike conc. ref oil in seawater (mg/L)	Conc. of extract (mg/L)	% Recovery
1	119	101	85%
2	104	100	97%
3	111	98.4	89%

These results show that the method and solvent are suitable for the extraction of oil and grease from seawater samples, but that it is difficult to achieve consistently reproducible results. However, further examination into the suitability of the composition of the suggested reference oil was performed. The two alkane components, hexadecane and isooctane (2,2,4-trimethylpentane) have strong C–H absorbances at the wavenumber 2930 cm^{-1}, but the third component, benzene, has a strong C–H absorbance at 3030 cm^{-1}. To test the detectability of benzene under the recommended conditions, benzene was made up in S-316 at a concentration of 200 mg/L, it shows an apparent concentration of 0.512 mg/L, based on the calibration curve and the absorbance at 2930 cm^{-1} only. Although there is a clear difference in the IR spectra of the pure solvent and the solvent containing 200 mg/L of benzene, as can be seen in Figure 2.5, that difference is not observed using this method, which only records at the absorbance at 2930 cm^{-1}. Since the aromatic C–H bond stretches absorb at around 3030 cm^{-1}, benzene is not well represented at 2930 cm^{-1}.

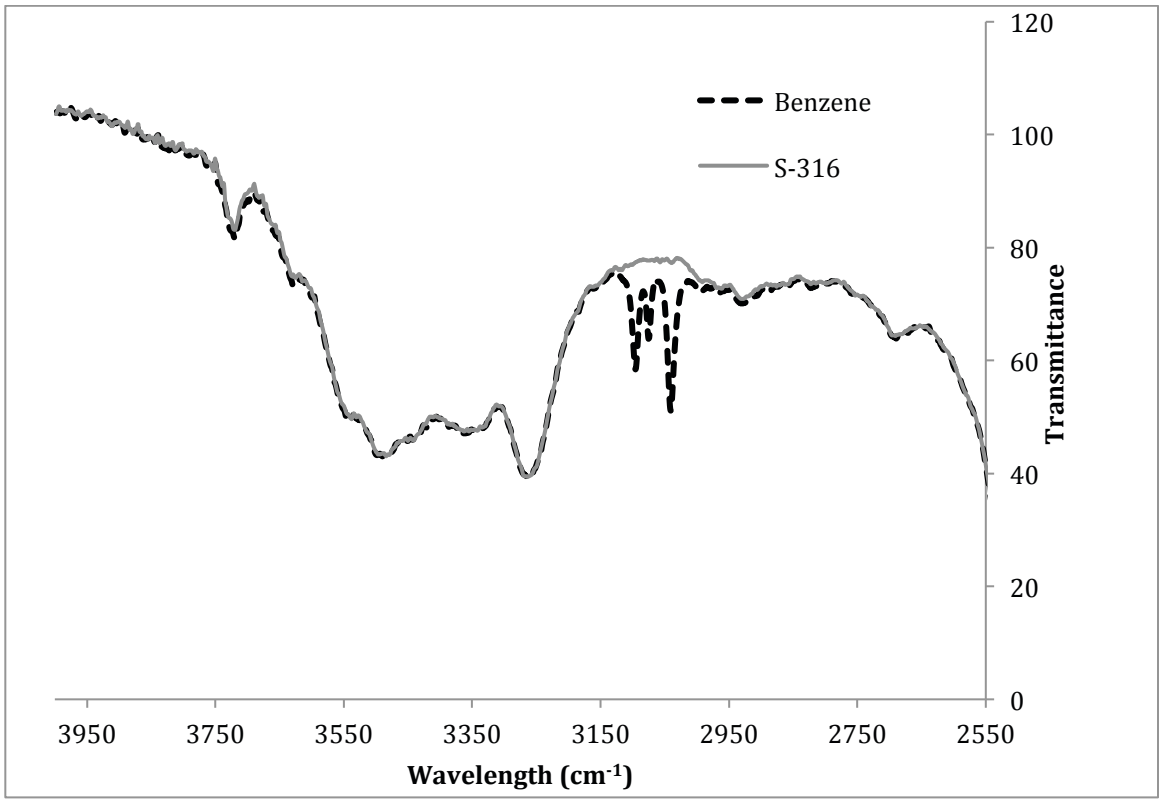


Figure 2.5 IR absorbance spectra of pure S-316 and 200 mg/L benzene in S-316

This means that a calibration curve constructed from standards made of this designated reference oil will give a response that appears to account for all extractable components of oil and grease, when in fact only those with alkyl C–H bonds will be counted. This is a clear flaw in the method and one that could be remedied by adapting it for the use of three wavelengths rather than only one. Triple peak or three wavelength methods take into account the absorbances at three different wavelengths (3030 cm^{-1}, 2960 cm^{-1}, 2930 cm^{-1}) corresponding to the stretch vibration frequency of aromatic C–H, methylene C–H, and methyl CH_2-H, respectively [40]. The single wavelength Method 5520 C was selected because of its use by the CNLOPB for analysis of oil and grease in produced water.

2.2 EPA Method 1664

2.2.1 Materials

Hexadecane (anhydrous, ≥99% purity), heptane (anhydrous, 99% purity), octanoic acid (≥99% purity), octadecane (99% purity), tetradecane (≥99% purity), fluorene (HPLC grade), naphthalene (99% purity), pyrene (≥99.0% purity), phenanthrene (≥99.5% purity), silica gel (high purity, Davisil Grade 923, pore size 30 Å, 100-200 mesh), Whatman filter papers (No. 40, ashless, 90 mm dia.), and sodium sulfate (anhydrous, granular, reagent grade) were purchased from Sigma-Aldrich (Oakville, ON). Boiling granules were purchased from Hengar Co. (Thorofare, NJ). Benzene (ACS reagent grade, ≥99% purity) was obtained from ACP, 2,2,4-trimethylpentane (isooctane, HPLC grade) was purchased from J.T. Baker. Octane (97% purity) was purchased from EM Science. Hydrochloric acid (ACS grade) was obtained from ACP. Hexanes (Optima grade) and acetone (ACS grade) were purchased from Fisher Scientific (Pittsburgh, PA).

2.2.2 Method

Sodium sulfate and silica gel were dried in an oven at 200-250 °C for 24 hours, removed, left to cool in a desiccator, and stored there until use. All glassware was washed in hot water with detergent, rinsed with tap water, distilled water, then acetone, and left to air dry. 250 mL round-bottom flasks used as boiling flasks were washed in this manner and then dried in an oven at 105-115 °C for a minimum of one hour and stored in a desiccator until needed. Boiling chips were also dried for at least one hour in the oven at 105-115 °C. The mass of the dried boiling flask plus the boiling chips was recorded.

Since a standard reference oil was not designated by the 1664 method, one was prepared based on the reference oil from APHA Method 5520 B Gravimetric Method, which is very similar to EPA Method 1664 in an attempt to give a reasonable representation of a sample of oil and grease. This reference oil was made up of 37.5% v/v isooctane, 37.5% v/v hexadecane, and 25.0% v/v benzene

n-Hexane extractable material (HEM) determination

Distilled water was spiked with varying masses of reference oil. The oil and water mixture was acidified with 6 M HCl to a pH of 2 (to replicate conditions required for real produced water samples—the purpose of acidification upon sampling is to prevent the growth of bacteria that can degrade the oil and grease content of the sample), and the mixture was extracted in *n*-hexane by shaking the separatory funnel vigorously with periodic venting of gas into the fume hood. The ratio of aqueous sample volume to the total volume of *n*-hexane used is approximately 10:1, so for a 1 L sample, three extractions are performed with 30 mL of *n*-hexane, plus approximately 10 mL *n*-hexane for rinsing, giving a total of 100 mL. The layers were allowed to separate for at least 10 minutes before the aqueous layer was drained into the original sample bottle and the organic layer was drained through a filter paper containing 10 g of anhydrous sodium sulfate, into the pre-weighed boiling flask. This extraction was performed a total of three times using fresh portions of *n*-hexane. The tip of the separatory funnel, the filter paper, and the glass funnel were rinsed with 2-3 small portions (3-5 mL) of hexanes and the rinsings were collected in the designated boiling flask. The extract was distilled by immersing the boiling flask in a water bath and distilling at 68.5 °C. When the

temperature of the system reached 70 °C, the distillation was stopped and the distillation flask was carefully removed and wiped to remove moisture and fingerprints. The flask containing the extract was heated in an oven maintained at 70 ± 2 °C for 30 minutes to evaporate the remaining solvent, then moved to a dessicator and cooled completely before weighing. This process of heating and cooling was repeated until the weight loss was <4% of the previous weight, or <0.5 mg, whichever is less. The solvent-free, dry extract residue is referred to as *n*-hexane extractable material, or HEM, and is determined by subtracting the weight of the empty flask and boiling chips from the total mass. This experiment was first carried out at full-scale, with 1 L of distilled water, but was later scaled down to volumes of 100 mL distilled water and varying amounts of reference oil added.

Silica gel treatable *n*-hexane extractable material (SGT-HEM) determination

The extract residue from the HEM measurement is treated with silica gel to remove polar compounds. The residue remaining after treatment is referred to as silica gel treatable *n*-hexane extractable material and is made up of non-polar components of oil and grease. A 50 mL volume of hexanes was added to the boiling flask to dissolve HEM, and this solution was transferred to a clean, dry, 125 mL Erlenmeyer flask. Assuming that 3 g of silica gel will adsorb 100 mg of polar materials from the extract [41], 3.0 ± 0.3 g of anhydrous silica gel was added to the boiling flask for every 100 mg of HEM, to a maximum of 30 g silica gel. A stir bar was added to the flask and the mixture was stirred for 15 minutes. The mixture was filtered through a filter paper pre-wetted with *n*-hexane,

into another dried, pre-weighed boiling flask with a few boiling chips, and glassware was rinsed with a few mL of *n*-hexane as before. The solvent was distilled and the residue dried as for HEM determination. The residue is referred to as silica-gel treatable *n*-hexane extractable material, and represents non-polar components of oil and grease.

Volatility study of reference oil components

Results from the HEM determination step indicated that the reference oil in use may have been too volatile to achieve reproducible results with each extraction and distillation. A sample of reference oil as well as its separate components, and a selection of other typical hydrocarbon components of produced water were subjected to thermal conditions similar to those in the final step of the method.

An aliquot of the reference oil was placed in a clean, dry, and tared 100 mL round-bottom flask and heated to 70 °C for 30 minutes, then cooled completely in a desiccator and weighed. This heating and cooling process was repeated twice more. The reference oil volatility was also measured by thermogravimetric analysis (TGA) on a TA Instruments Q500 TGA. In this experiment, an aliquot of reference oil was placed in a differential scanning calorimetry (DSC) pan with a small hole at the top and rapidly heated to 70 °C for a total of 90 minutes. This apparatus was configured in such a way as to allow even evaporation of the liquid inside but prevent "bumping" due to rapid boiling of the liquid. The purpose of performing TGA on liquid samples was to subject them to more controlled heating and weighing conditions than are possible using the oven and analytical balance. Additionally, because it is unsafe to evaporate large quantities of some

of the PAHs used, and very small quantities are difficult to weigh accurately on an analytical balance, the TGA was used for these substances.

Only compounds with boiling points higher than that of *n*-hexane were tested. A list of compounds examined and their boiling points is given in Table 2.4. Components of the reference oil and other liquid hydrocarbons tested were weighed into clean, dry beakers (beakers were used instead of round-bottom flasks in this experiment to enable many samples to be heated at once—limitations on glassware and cork flask holders were the main motivation for this change) and heated in an incubator at 70 °C for 30 minutes, cooled completely in a desiccator, and weighed. This process was carried out a total of three times and each substance was tested in replicates of four. Four PAHs were also examined for their volatility under similar conditions but using TGA for controlled heating and weighing. Each PAH was weighed into a TGA pan and heated in the TGA at an isotherm of 70 °C for 90 minutes.

Table 2.4 Organic compounds tested for volatility under experimental conditions of EPA Method 1664

Compound	Molar mass (g/mol)	Boiling point (°C)
Heptane	100.20	98.1
Octane	114.23	125.1
Isooctane	114.23	99.1
Octanoic acid	144.21	239.7
Tetradecane	198.39	253.7
Hexadecane	226.44	287
Octadecane	254.49	317
Naphthalene	128.17	218
Fluorene	166.22	298
Phenanthrene	178.23	340
Pyrene	202.25	404

2.2.3 Results and discussion

In order to test the method for extraction efficiency and reproducibility, extractions were performed on 100 mL volumes of distilled water spiked with aliquots of reference oil to determine HEM. Results of these extractions are presented in Table 2.5.

Table 2.5 EPA Method 1664 HEM determination results

Initial mass ref oil (mg)	Final mass ref oil (mg)	% Recovery	Standard Deviation* (mg)	%RSD*
Replicate 1 - 254.6	167.2	65.7	40.9	23.5
Replicate 2 - 256.6	137.3	53.5		
Replicate 3 - 253.1	218.1	86.2		
Replicate 4 - 615.0	174.5	28.4	97.6	38.0
Replicate 5 - 544.7	364.8	67.0		
Replicate 6 - 513.9	232.0	45.1		
Replicate 7 - 1001.0	375.9	37.6	29.6	7.68
Replicate 8 - 1006.1	418.1	41.6		
Replicate 9 - 1048.5	361.1	34.4		

*Statistics calculated based on final mass of reference oil extracted from water.

HEM determination for the reference oil in distilled water gave poor recoveries and reproducibility, which prompted the study of the volatilities of the components of reference oil and other possible components of produced water. Results for the examination of the complete reference oil show that at least some of the components are volatile and may be lost in the drying process. Results for the initial study carried out in the incubator are outlined in Table 2.6.

Table 2.6 Measuring volatility of reference oil at experimental conditions of EPA Method 1664 (70 °C for 30 minutes × 3)

Time (min)	Mass (g)	Mass lost (g)	% loss
0	1.0095	0	0
30	0.7933	0.2162	21.42%
60	0.4746	0.5349	52.99%
90	0.3661	0.6434	63.73%

Further examination of the reference oil was carried out by thermogravimetric analysis (TGA). A 2.5476 mg aliquot of reference oil was heated to 70 °C and held there for 90 minutes. The results of TGA analysis are shown in Figure 2.6.

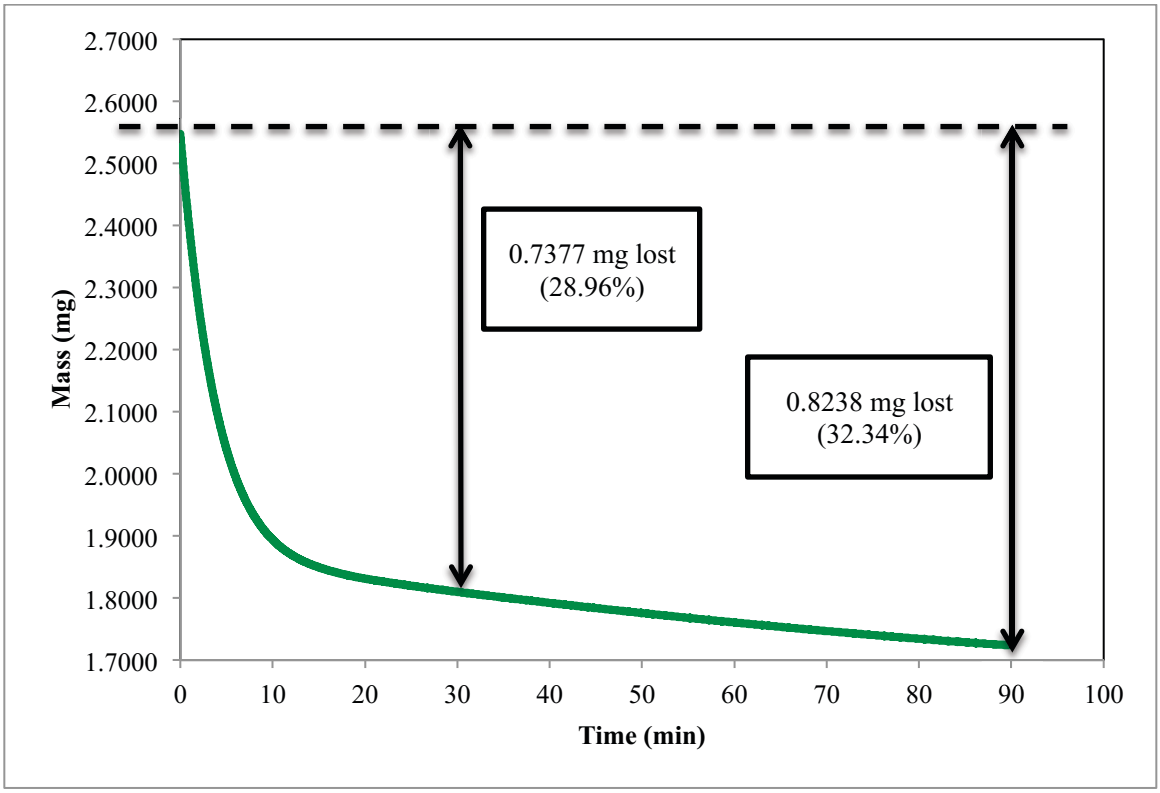


Figure 2.6 Thermogravimetric analysis of reference oil at 70 °C isotherm

Figure 2.6 shows that 28.96% of the initial mass was lost in the first 30 minutes of heating, and after 90 minutes, the total mass lost was 32.34%. Arrows indicate the 30- and 90-minute marks and the horizontal dotted line shows the initial mass of the reference oil. Since it was not logistically feasible to perform this analysis at three separate intervals of 30 minutes, a 90-minute trial was performed with mass analysis at 30 and 90 minutes. The reduction in mass loss from the incubator trial may be attributed to the much smaller initial mass in the TGA trial as well as the fact that the system was isolated in the TGA furnace and not open to the ambient environment, nor was it left to cool in a desiccator, which can take a great deal of time—time in which more of the mixture could potentially be lost. Additionally, the DSC pan used had a much smaller surface area, and the opening at the top was very small. These factors may have resulted in a reduction in the mass of the reference oil volatilized over that in the incubator experiment.

Volatilities of a range of aliphatic hydrocarbons were examined by heating to 70 °C at 30-minute intervals in an incubator. PAHs were examined by heating to 70 °C for 90 minutes in the TGA. Results are given in Table 2.7 and Figures 2.7 and 2.8.

Table 2.7 Volatility study results: mass loss % at 30, 60, and 90 minutes at 70 °C

Compound	Avg initial mass	Avg mass loss % (30 minutes)	Std Dev	Avg mass loss % (60 minutes)	Std Dev	Avg mass loss % (90 minutes)	Std Dev
Heptane	1.0061 g	100.03%	0.04%	0.00%	-	0.00%	-
Octane	1.0044 g	100.00%	0.03%	0.00%	-	0.00%	-
Isooctane	1.0063 g	46.40%	13.90%	80.14%	20.31%	96.20%	4.61%
Octanoic acid	1.0150 g	0.69%	0.26%	1.09%	0.32%	1.27%	0.33%
Tetradecane	1.0094 g	3.96%	0.24%	7.78%	0.66%	12.25%	0.80%
Hexadecane	1.0141 g	0.61%	0.08%	1.26%	0.15%	1.91%	0.24%
Octadecane	1.0087 g	0.03%	0.02%	0.13%	0.03%	0.16%	0.03%
Naphthalene	5.2420 mg	65.55%	5.24%	97.97%	2.48%	99.85%	0.29%
Fluorene	5.4330 mg	2.10%	0.14%	4.39%	0.29%	6.67%	0.45%
Phenanthrene	5.4958 mg	0.63%	0.13%	1.29%	0.16%	1.95%	0.20%
Pyrene	5.4205 mg	-0.46%	0.52%	-0.25%	0.19%	-0.28%	0.20%

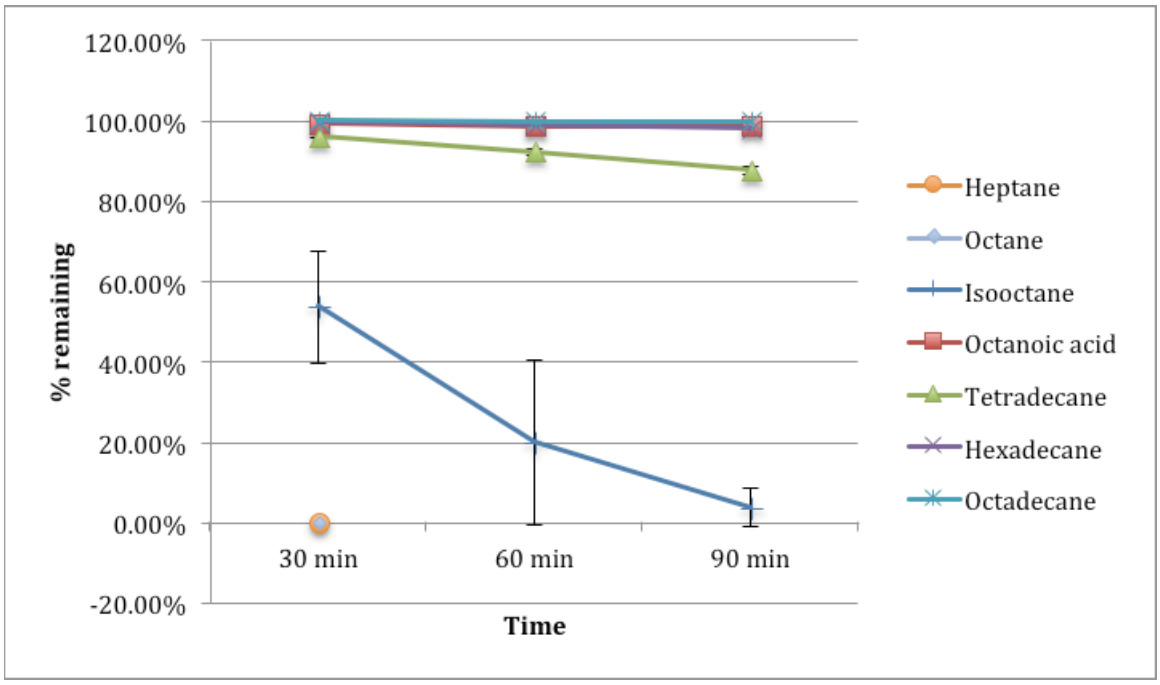


Figure 2.7 Volatility study results for aliphatic hydrocarbons: % remaining at 30, 60, and 90 minutes

Note: No lines seen for heptane and octane because they had completely evaporated by the 30-minute mark. Error bars represent standard deviation of the % remaining of each substance (n = 4).

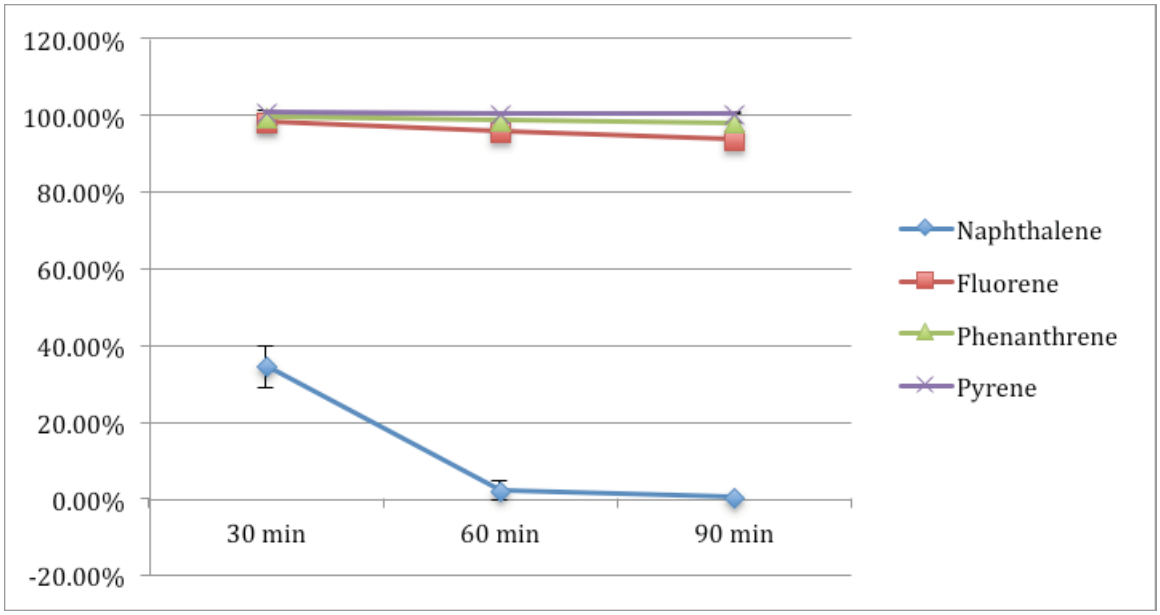


Figure 2.8 Volatility study results for PAHs: % remaining at 30, 60, and 90 minutes

Note: Error bars represent standard deviation of the % remaining of each substance (n = 4).

The results of this study tell us that the more volatile components of oil and grease extracted from produced water samples are not likely to remain in the residue long enough to be accurately measured using this Method 1664. This means that this and other gravimetric methods ignore components of produced water that could be harmful to ecosystems in harsh and Arctic environments, particularly since lighter hydrocarbons are less volatile at lower temperatures and are therefore more likely to remain dissolved in water under these conditions. It is these light hydrocarbons that would be excluded using gravimetric methods of analysis, giving an artificially low result for total oil and grease or HEM in a sample.

3. Experimental methods for PAH analysis

Small PAHs are of interest due in part to their higher degree of solubility in water than their larger counterparts, as well as their complex mechanisms of toxicity. Even at the low concentrations typically found in the environment surrounding oil and gas reservoirs, PAHs can have acute and chronic toxic effects. Although larger PAHs such as benzo(a)pyrene are of interest due to their carcinogenicity, they are found more in the dispersed phase of produced water than the dissolved phase. As previous experiments have shown, measuring trace levels of PAHs in oil and grease can be difficult. Measuring smaller PAHs in aqueous samples can therefore potentially serve as a proxy for other harmful PAHs found in produced water. However, at the low concentrations at which most PAHs are found in the water surrounding produced water discharge points, it is necessary to extract and concentrate the analytes of interest prior to analysis. Two methods of achieving this are solid phase extraction (SPE) via EPA Method 525, and by the use of molecularly imprinted polymers (MIPs) specifically designed to target small PAHs.

EPA Method 525 relies on the binding of a wide variety of neutral and aromatic compounds to a polymeric reversed phase. The extract from this method is concentrated to a smaller volume under nitrogen for analysis by GC-MS. This method was performed first on standard solutions of PAHs in distilled water, then on spiked samples of water from St. John's Harbour, and finally on samples of produced water. A great deal of optimization was required before this method could be applied to real samples.

PAH MIPs were used to measure PAHs in spiked samples of ASTM artificial seawater and spiked samples of produced water. The MIP was first immersed in the

aqueous sample and stirred for 90 minutes, then rinsed, and extraction of the analytes were performed by stirring in 15 mL of ethyl ether for 60 minutes. This extract was concentrated under nitrogen for analysis by GC-MS. These experiments were performed in parallel to measure the efficacy of the method on real samples as well as to attempt to quantify any PAHs already in the produced water samples.

3.1 EPA Method 525

3.1.1 Materials

Strata-X 33u, polymeric reversed phase, 200 mg/6 mL SPE cartridges were purchased from Phenomenex (Torrance, CA). Filter papers used were Whatman No. 40 (ashless, 90 mm dia.). Dichloromethane (certified ACS stabilized) was purchased from Fisher Scientific (Pittsburgh, PA), ethyl acetate (ACS reagent grade) was purchased from ACP, and methanol (ACS grade) was purchased from Fisher Scientific (Pittsburgh, PA). Naphthalene (99% purity), fluorene (HPLC grade), phenanthrene (≥99.5% purity), and pyrene (≥99.0% purity) were all obtained from Sigma-Aldrich (Oakville, ON). Acenaphthene-d_{10} (99 atom % D) was purchased from Isotec (Canton, GA). Anhydrous sodium sulfate (ACS reagent grade) was obtained from Sigma-Aldrich (Oakville, ON). Reagent grade acetonitrile was purchased from Caledon (Georgetown, ON). Acetone (ACS grade) used to clean glassware was obtained from Fischer Scientific (Pittsburgh, PA). GC used in all experiments is model 6890N interfaced to a single quadrupole 5973 inert MSD, model number G2578A, both from Agilent (Mississauga, ON).

3.1.2 GC-MS methods and modification for EPA Method 525

Development of GC-MS method

A PAH multi-standard containing naphthalene, fluorene, phenanthrene, and pyrene, with acenaphthene-d_{10} as internal standard (chosen due to its structural similarity to other PAH analytes and unlikelihood of being found naturally in samples), was prepared in dichloromethane and diluted to an approximate concentration of 100 μg/L with ethyl acetate, which is a good representation of the composition of extracts obtained by US EPA method 525. This method originally allows for the separation of many more compounds than was necessary for the purposes of this experiment, and the run time for the entire method was around 60 minutes. Since only a small number of these compounds were to be resolved, shortening the run time significantly became necessary to avoid wasting time during analysis. It should be noted that in the case of very complex samples, the method may need to be altered again in order to resolve all components. Two different GC-MS methods were set up according to the parameters outlined by the US EPA in guidelines for method 525, and they are as follows:

a) Program A - multi-ramp temperature program:

A 1 μL aliquot of sample is injected onto a 30 m DB-5 column with an internal diameter of 0.250 mm and film thickness of 0.25 μm, in splitless mode with helium as the carrier gas, with a flow rate of 33 cm/s and an inlet temperature of 45 °C, and held for 1 minute. Oven temperature is increased rapidly from 45 °C to 130 °C at 25 °C/minute. At the 3-minute mark, the temperature is raised from 130-180 °C at 12 °C/minute, then from

180-240 °C at 7 °C/minute, and finally from 240-320 °C at 12 °C/minute. Data acquisition is begun at the 4-minute mark. The range of data collection is m/z 45-450. This method is henceforth referred to as PAHMULTIRAMP.

b) Program B - single-ramp linear temperature program:

As with program A - PAHMULTIRAMP, a 1 μL aliquot of sample is injected onto a DB-5 column in splitless mode, He carrier gas, at a flow rate of 33 cm/s. The inlet was at 40 °C, held there for 1 minute. The temperature was rapidly increased to 160 °C at a rate of 25 °C/minute. At the 3-minute mark, the temperature program is begun, from 160-320 °C at a rate of 6 °C/minute, and held at 320 °C for a further 2 minutes. Data acquisition begins at 3 minutes, and the range of collection is m/z 45-450. This method is henceforth referred to as PAHSINGLERAMP.

When the PAH multi-standard was run in scan mode to determine analyte retention times using each of the above sets of parameters, the resulting chromatograms showed no PAHs. It was later determined that the inlet temperature specified for the method (45 °C) was well below the boiling point of ethyl acetate (77.1 °C), causing a large amount of ethyl acetate to elute with the analytes. This causes problems with chromatography such as analytes appearing to “stick” on the column. These analytes eluted upon a DCM blank being run on the instrument, and as DCM is also used in conjunction with ethyl acetate in EPA Method 525 and because its boiling point is 39.6 °C, DCM was chosen as the solvent with which to make up the extracts to volume for analysis by GC-MS.

A new PAH multi-standard solution was made up using DCM in place of ethyl acetate as the solvent. The concentration was increased to 10 mg/L to ensure that peaks would be clearly visible. The temperature programming of PAHMULTIRAMP was changed as follows: 45-130 °C at 30 °C/minute, then 130-180 °C at 12 °C/minute, 180-240 °C at 10 °C/minute, and 240-320 °C at 12 °C/minute. The temperature programming of PAHSINGLERAMP was modified to 45-160 °C at 30 °C/minute, followed by 160-320 °C at 8 °C/minute. For both modified methods based on PAHMULTIRAMP and PAHSINGLERAMP, all peaks were widely separated, so the temperature programming could be sped up even further. A modified program based on PAHMULTIRAMP was developed, changing the temperature ramping to 45-130 °C at 30 °C/minute, 130-180 °C at 14 °C/minute, 180-240 °C at 12 °C/minute, and 240-300 °C at 14 °C/minute. PAHSINGLERAMP was changed to 45-160 °C at 30 °C/minute, and 160-300 °C at 25 °C/minute.

All methods were run in scan mode at 3.58 scans/second with m/z scan range of 45-450 amu until retention times were finalized. It was determined that PAHMULTIRAMP would be used for all further analysis, with selected ion monitoring (SIM) parameters as outlined in Table 3.1. Under SIM mode, primary (quantifier) and secondary (qualifier) ions were selected based on the three most abundant peaks when separate standards were previously run in scan mode on GC-MS.

Table 3.1 PAH analytes and internal standard GC-MS SIM parameters

Analyte	Primary ion (m/z)	Secondary ions (m/z)	Start time (min)
Naphthalene	128 [M+]	74 [M-54], 127 [M-H]	4.00
Acenaphthene-d_{10}	164 [M+]	158 [M-6], 162 [M-D]	9.50
Fluorene	166 [M+]	139 [M-27], 165 [M-H]	10.90
Phenanthrene	178 [M+]	152 [M-26], 179 [M+H]	12.90
Pyrene	202 [M+]	101 [M-101], 200 [M-2]	15.50

Note: [M+] represents the molecular ion peak, and [M±x] indicates a fragment.

SPE for PAHs from distilled water

A PAH multi-standard stock solution was prepared using approximately 10 mg each of naphthalene, fluorene, phenanthrene, and pyrene in 100 mL acetonitrile, to give an average concentration of approximately 100 mg/L. All solutions used to construct calibration curves were prepared from this stock by serial dilution in distilled, deionized water. An internal standard was prepared by dissolving approximately 10 mg of acenaphthene-d_{10} in 100 mL acetonitrile, followed by serial dilutions in dichloromethane to reach the desired concentration. Extracts were spiked with acenaphthene-d_{10} internal standard to give a concentration in 1 mL of 500 μg/L.

Strata-X 33u polymeric reversed phase SPE cartridges with a 200 mg bed mass and 6 mL reservoir volume were conditioned with 5 mL ethyl acetate followed by 5 mL dichloromethane. The cartridge was drained dry after each of these two flushes and 10 mL methanol was passed through. From this point onward the solvent level was not allowed to drain past the top of the packing and the cartridge was not allowed to drain dry. Prior to sample loading, the cartridge was rinsed with 10 mL of distilled, deionized

water, followed immediately by the sample. Each 100 mL sample was loaded onto the cartridge under a vacuum of 135-170 mbar, taking about 30 minutes to pass the entire sample through. Once the entire sample had been added, air was aspirated through the cartridge for 10 minutes. Each sample was then eluted using 5 mL ethyl acetate followed by 5 mL dichloromethane. The extracts were combined and dried over 5-7 g ACS grade anhydrous sodium sulfate and filtered through a fluted filter paper in a glass funnel to remove the drying agent. The sodium sulfate and filter paper were rinsed with 2-3 mL of DCM and this rinsing was added to the filtered extract. Solvent volume was reduced by placing the extract in a water bath heated to approximately 30 °C and under a stream of $N_{2(g)}$ to a volume of no less than 0.5 mL. An internal standard of acenaphthene-d_{10} was added and the volume of the spiked extract was made up to 1 mL with DCM for analysis by GC-MS. A solvent blank was run during each analysis, and the method used was PAHMULTIRAMP.

Calibration curves for each PAH were constructed by applying the SPE method to multi-standard solutions having concentrations of 0, 0.5, 1, 3, 5, and 10 μg/L. All standard extracts were prepared in replicates of four.

3.1.3 Results and discussion

The full SPE/GC-MS method was performed on distilled water spiked with a PAH multi-standard to test the method on a simple sample, then on spiked water samples from St. John's Harbour, and finally on produced water samples obtained from an oil and gas operator (unnamed). A great deal of optimization was necessary before acceptable results

were obtained. The solvent specified for making up extracts for analysis by GC-MS, ethyl acetate, proved unsuitable for the method due to problems in the chromatography caused by the high boiling point of ethyl acetate, so DCM was used in its place, as it was already used as a part of the extraction preparation and provided reproducible and accurate results. GC-MS parameters and retention times given in the method were optimized for the instrument and conditions, and the GC-MS method was shortened significantly. All samples were run using GC-MS method PAHMULTIRAMP.

Results for the distilled water studies are presented in Table 3.2 and Figure 3.1. Data was collected for this set of experiments with the assistance of Stephanie Collins, undergraduate summer lab assistant.

Table 3.2 EPA Method 525 - PAHs in distilled water

PAH	Upload conc. (μg/L)	Average peak area (PA) of analyte	Average PA of internal standard	$PA_{analyte}/PA_{internal\ standard}$	Standard Deviation of PA ratio	%RSD
Naph	0	168051	1010535	0.1663	0.0022	1.3
	0.53	164227	944806	0.1738	0.0047	2.7
	1.07	224906	906069	0.2482	0.0094	3.8
	3.15	508122	990359	0.5131	0.027	5.3
	5.65	1737714	1955419	0.8887	0.028	3.2
	10.7	2042063	1459356	1.3993	0.086	6.2
Fluo	0	14645	948015	0.0154	0.00016	1.0
	0.52	106974	944806	0.1132	0.0020	1.8
	1.02	168854	906069	0.1864	0.0056	3.0
	3.12	1040774	990359	1.0509	0.049	4.6

	5.25	2890047	1955419	1.4780	0.71	48
	10.2	3822048	1459356	2.6190	0.038	1.4
Phen	0	7493	965087	0.0078	0.0016	20
	0.51	81528	944806	0.0863	0.0027	3.2
	1.09	125892	891210	0.1413	0.000022	0.020
	3.36	514001	990359	0.5190	0.10	19
	5.15	1853318	1955419	0.9478	0.058	6.2
	11.4	3219721	1459356	2.2063	0.087	3.9
Pyr	0	8667	965087	0.0090	0.0025	28
	0.52	259658	944806	0.2748	0.32	1.2×10^2
	1.02	228625	906069	0.2523	0.070	28
	3.18	700024	990359	0.7068	0.24	34
	5.3	2381541	1955419	1.2179	0.097	7.9
	10.2	3575667	1459356	2.4502	0.12	5.1

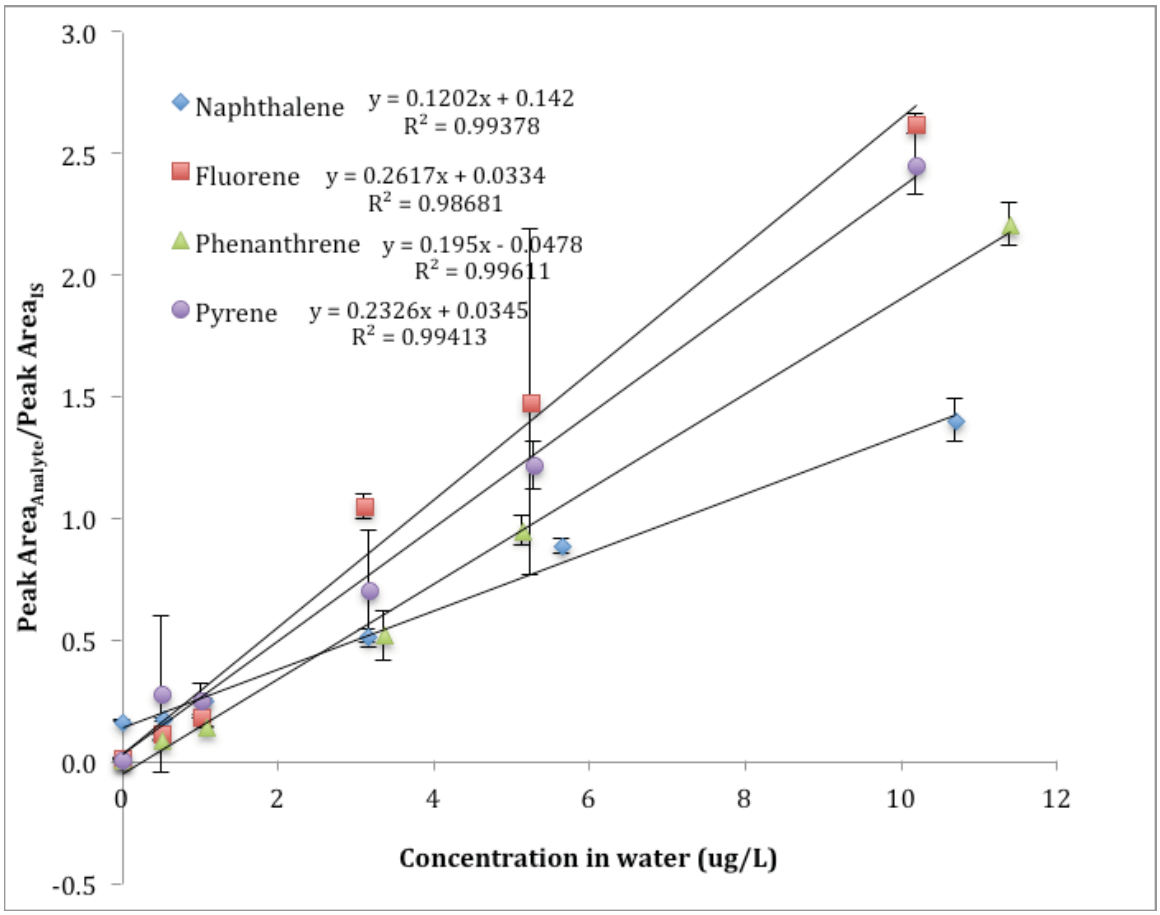


Figure 3.1 EPA Method 525 - PAHs in distilled water by SPE-GC-MS

Error bars represent standard deviation (n = 4)

Because it was not practical to perform the required number of blank determinations needed to calculate limit of detection (LOD) for this method under these conditions, LOD was estimated using the regression line and least squares analysis. The equation of the regression line is given in the form:

$$y = mx + b$$

where y is the ratio of analyte peak area to internal standard peak area, m is the slope of the line, x is the concentration of the analyte spike, and b is the y-intercept. The

instrument detection limit in terms of the standard error of the regression (LOD_y) is given by the equation:

$$LOD_y = 3s_m + b$$

where s_m is the standard deviation of the slope. The LOD_c (the concentration limit of detection) is calculated from the regression line:

$$x = LOD_c = \frac{(LOD_y - b)}{m}$$

and the equations are then combined to give:

$$LOD_c = \frac{3s_m}{m}$$

Limits of detection for each analyte in the two water types used are given in Table 3.3

Table 3.3 Concentration limit of detection (LOD_c) for PAHs in aqueous media calculated from linear regression

	Naphthalene	Fluorene	Phenanthrene	Pyrene
LOD_c (μg/L) in distilled water	0.118	0.173	0.0938	0.115
LOD_c (μg/L) in harbour water	0.144	3.82	0.119	0.153

The limits of detection for all analytes in this trial show that this method is appropriate for analysis of low concentrations of PAHs, although in future work, more extractions should be performed in the low concentration range to further examine the response between 0-0.5 μg/L PAHs in water. The extremely high %RSD associated with some data points (particularly fluorene at 5.25 μg/L and pyrene at 3.18 μg/L) are likely the result of human error. The non-zero intercepts for all four PAHs are the result of noise present in the response from the GC-MS.

Harbour water

Trials of EPA Method 525 were carried out using water collected from St. John's Harbour to examine matrix effects and to determine how effective the method is in very complex water samples. Water was collected in PTFE bottles and acidified to pH 2 with concentrated HCl. A 100 mL aliquot of harbour water was spiked with a PAH multi-standard to give individual PAH concentrations of approximately 0, 0.5, 1, 3, 5, and 10 μg/L in water, and spiked with acenaphthene-d_{10} internal standard to give a concentration of 5 μg/L in water. The real concentrations of each PAH are shown in Table 3.4. Initial trials of internal standard in harbour water samples indicate that lack of selectivity in the Strata-X polymeric reversed phase SPE cartridges allows too many interfering compounds through, obscuring the internal standard peak. The internal standard was not visible in GC-MS chromatograms at this concentration. It was found to be necessary to add an additional step following loading; all SPE cartridges were cleaned using 5 mL of distilled water prior to sample elution. Results from EPA Method 525 on samples of harbour water spiked with PAHs are given in Table 3.4 and Figure 3.2. Limits of detection are given in Table 3.3.

Table 3.4 EPA Method 525 - PAHs in raw seawater from St. John's Harbour

PAH	Upload conc. (μg/L)	Average PA analyte	Average PA internal standard	$PA_{analyte}/PA_{internal\ standard}$	Standard Deviation PA ratio	%RSD
Naph	0	64877	492585	0.1317	0.0088	6.7
	0.58	359898	1172522	0.3069	0.0070	2.3
	1.16	439011	1125923	0.3899	0.0072	1.9
	3.09	632778	778899	0.8124	0.026	3.3

	5.4	412673	391194	1.0549	0.083	7.9
	10.8	1315179	575350	2.2859	0.11	4.8
Fluo	0	0	492585	0	0	0
	0.515	1348400	1172522	1.1500	0.0041	0.36
	1.03	872026	758283	1.1500	0.038	3.3
	3.06	802266	778899	1.0300	0.022	2.1
	5.45	422490	391194	1.0800	0.065	6.0
	10.9	621378	575350	1.0800	0.059	5.5
Phen	0	0	492585	0	0	0
	0.57	36627	1172522	0.0312	0.0022	7.0
	1.14	77105	758283	0.1017	0.047	46
	3.24	473143	778899	0.6075	0.021	3.5
	5.05	450730	391194	1.1522	0.10	8.9
	11	1604855	575350	2.7894	0.17	5.9
Pyr	0	0	492585	0	0	0
	0.5	34687	1172522	0.0296	0.0068	23
	1	68461	758283	0.0903	0.036	39
	3.21	466265	752462	0.6197	0.010	1.6
	5.45	614571	391194	1.5710	0.17	11
	10.4	1759317	575350	3.0578	0.23	7.4

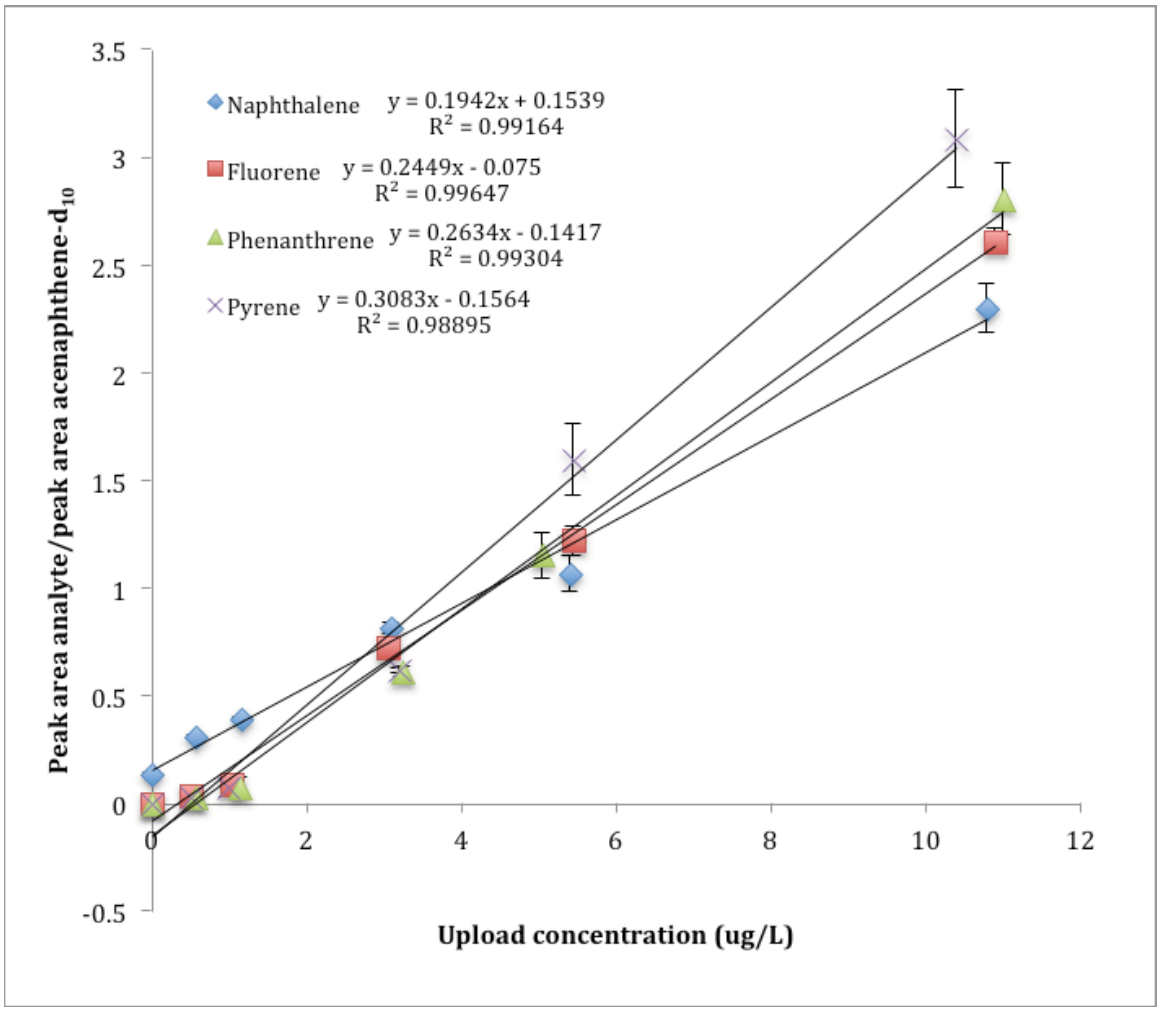


Figure 3.2 EPA Method 525 - PAHs in raw seawater from St. John's Harbour by SPE-GC-MS

Error bars represent standard deviation (n = 4)

The response shown for naphthalene at 0 µg/L spike concentration indicates that there is naphthalene present in the raw harbour water sample. All four PAHs show good linearity using this method, with R^2 values of 0.98 or better. The average recoveries of each PAH at spike concentrations 0-10 µg/L were as follows: 119.9-346.4% naphthalene, 96.1-114.9% fluorene, 67.7-119.9% phenanthrene, and 78.6-141.4% pyrene. The extremely high recovery for naphthalene is indicative of its presence in the matrix, and

the slightly high values for the other PAHs could suggest the presence of interfering compounds; as well the error associated with each data point obtained may also account for this variation. No PAHs other than naphthalene were conclusively found in the blank harbour water extracts. Based on instrument calibration, the amount of naphthalene found in the blank harbour water samples was 90.6-102.3 μg/L. An increase in error associated with this method can likely be attributed to the complexity of the matrix, but these trials show that EPA Method 525 is adaptable for use with samples in highly polluted matrices.

The non-zero intercepts for all analytes are primarily products of noise present in the spectra obtained from the GC-MS. Also, the linear regression may alter the intercept if a measured data point has high error associated with it. Even at zero concentration, there is a non-zero response from the instrument. As well, the extremely high estimated limit of detection for fluorene in this trial (3.82 μg/L) is almost certainly a result of human error coupled with the fact that this method of calculating limit of detection is merely an estimate based on the standard deviations of the data points. The other limits of detection are comparable with those obtained through extraction of PAHs from distilled water as in the previous trial. The slopes of the lines for all analytes other than fluorene are higher than in the distilled water trial, indicating that the extraction in harbour water was more sensitive. This could be due to the complex "salting out" effect, which can increase extraction efficiency in some cases, but this theory should be examined further in future work.

Produced water

Samples of raw produced water were obtained from an offshore oil platform, stored in 2 × 2.5 L amber glass bottles, stored in a refrigerator at 3-4 °C. and these samples were analyzed by EPA Method 525, with some adaptations. Initially, because the concentration of hydrocarbons in the sample was unknown, a full-scale experiment was attempted, with 1 L of produced water spiked with acenaphthene-d_{10} internal standard at a concentration of 0.5 μg/L. The capacity of the SPE cartridge was clearly overloaded, however. This could be visually observed in the water sample after extraction, as it was still coloured yellow and slightly cloudy, indicating that not all organic compounds had been removed. This is clear evidence of breakthrough. Additionally, the solid phase within the cartridge was coloured brown and the eluted extract, once reduced to the requisite 1 mL, was coloured dark brown. This can be seen in Figure 3.3.

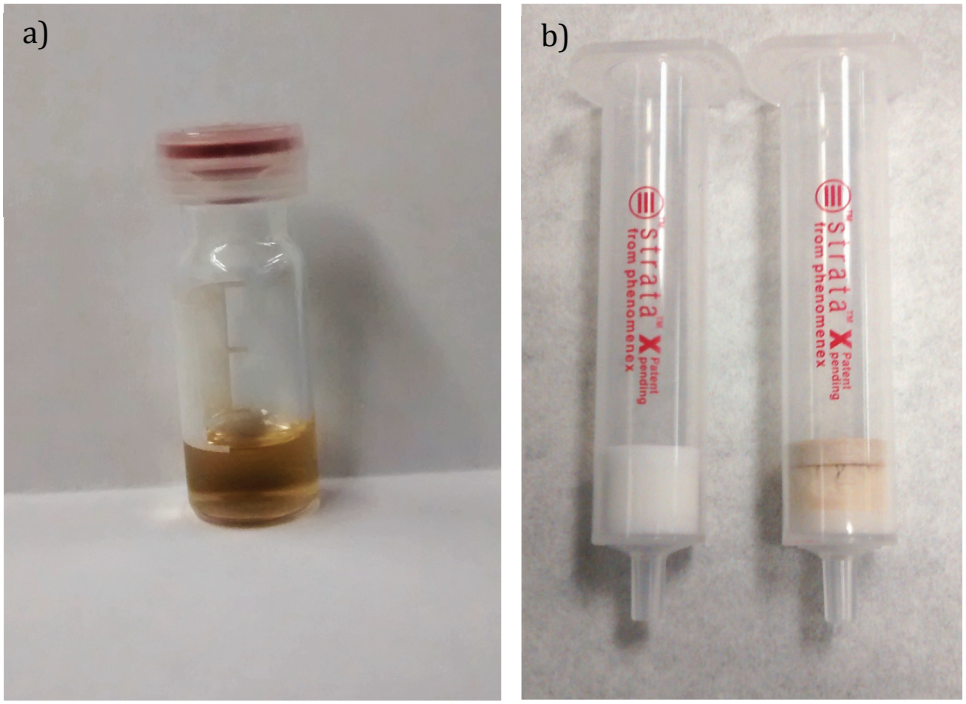


Figure 3.3 First extraction attempt on produced water sample

a) 1 mL extract from a 1 L sample of produced water treated by SPE as per EPA Method 525.
b) Comparison of an unused SPE cartridge (left) and the cartridge after elution of the first sample of produced water (right).

The volume of produced water was reduced to 10, 20, and 50 mL aliquots, spiked with acenaphthene-d_{10}, made up to 100 mL in ASTM artificial seawater, and extracted by EPA Method 525. The average recovery of naphthalene from each trial is shown in Table 3.5.

Table 3.5 Naphthalene concentration in produced water as determined by EPA Method 525

Trial	Average conc. (µg/L) in 100 mL	Std. Dev. (n = 4)	%RSD
1 (50 mL in 100 mL)	82.01	2.2682	2.766
2 (20 mL in 100 mL)	130.45	5.5369	4.244
3 (10 mL in 100 mL)	119.94	5.2829	4.404

The low concentration measured in Trial 1 may be attributed to the volume of produced water being too large and the organic contaminants overloading the solid phase of the SPE cartridge. Even at volumes of 10 mL produced water in 100 mL ASTM artificial seawater, the extracts retained a faint yellow colour, which indicates the presence of compounds other than the target analytes. Produced water is known to contain compounds with conjugated π-electrons that can impart colour to the mixture.

3.2 PAH molecularly imprinted polymers

3.2.1 Materials

Naphthalene (99% purity), fluorene (HPLC grade), phenanthrene (≥99.5% purity), and pyrene (≥99.0% purity) were all obtained from Sigma-Aldrich (Oakville, ON). The internal standard, isotopically-labeled acenaphthene-d_{10} (99 atom % D) was purchased from Isotec (Canton, GA). 3-(Trimethoxysylil)propyl methacrylate for derivatizing glass, 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator, ethylene glycol dimethacrylate (EGDMA) crosslinker, 4-vinyl pyridine (4-VP) functional monomer, and 1-octanol (≥99% purity) porogen were purchased from Sigma-Aldrich (Oakville, ON). Toluene, the template, and derivatizing solvent (ACS grade, ≥99.5% purity), was purchased from ACP (Montreal, QC), as was ethyl ether (ACS reagent grade), and concentrated hydrochloric acid (ACS grade). Dichloromethane (ACS reagent grade) and methanol (ACS reagent grade) were obtained from Fisher Scientific (Pittsburgh, PA), as was acetone (ACS grade). 95% ethanol was purchased from Commercial Alcohols

(Brampton, ON), and acetonitrile (reagent grade) was obtained from Caledon (Georgetown, ON).

3.2.2 Method

Glass microscope slides were cut into approximately 1-inch squares and numbered with a diamond pen. Slides were cleaned with soap and water, rinsed with distilled water, dried, and immersed in a 1:1 solution of concentrated HCl and methanol for 30 minutes. They were then rinsed with distilled water and ethanol, dried under $N_{2(g)}$ and immersed in derivatizing solution, a 2% (v/v) solution of 3-(trimethoxysilyl)propyl methacrylate in toluene, covered in aluminum foil, and left overnight. The next day they were removed from the derivatizing solution and rinsed with 95% ethanol and dried under $N_{2(g)}$. Slides were stored in the dark until used for the preparation of MIPs and NIPs.

The toluene-octanol pre-polymerization solutions for molecularly imprinted polymers and non-imprinted polymers (MIPs and NIPs) were prepared according to the composition developed by Stefana Egli [51], with the amounts shown in Table 3.6.

Table 3.6 Composition of toluene-octanol MIP and NIP pre-polymerization solutions

Compound	MIP	NIP
Toluene (template)	21.25 μL	-
4-VP (monomer)	85 μL	85 μL
EGDMA (crosslinker)	755 μL	755 μL
DMPA (initiator)	0.016 g	0.016 g
1-octanol (porogen)	1000 μL	1020 μL

Each solution was prepared and sonicated for 15 minutes to fully dissolve the components and degas the mixture.

MIPs and NIPs were prepared by pipetting 8 μL of the pre-polymerization solution onto the derivatized glass slide, and carefully covering with a 1 cm^2 glass microscope cover slide to prevent exposure to oxygen. The polymer was cured for 30 minutes under UV light, and the cover slide was removed.

To remove the template, MIPs were immersed in separate petri dishes containing ethyl ether and stirred for 90 minutes. The ethyl ether was replaced with fresh solvent and stirred for a further 90 minutes. NIPs were treated in the same way for consistency and to remove any unreacted components.

After template removal, MIPs and NIPs are ready for sample upload. One MIP or NIP was immersed in a beaker containing a solution of water spiked with PAHs and stirred for 90 minutes, covered with aluminum foil. After upload was complete, each slide was removed, rinsed with distilled water and carefully dried, taking care not to touch the surface of the polymer. To extract the analytes, the MIP was placed in a new beaker with

a small magnetic stir bar and 15 mL of ethyl ether. Each beaker was covered with plastic wrap and aluminum foil and stirred for 60 minutes. Then the MIP and stir bar were carefully removed and rinsed with a small amount of ethyl ether into the beaker. The extract was reduced in volume under $N_{2(g)}$ to less than 0.5 mL, spiked with internal standard, and made up to 1 mL in DCM for analysis by GC-MS. All extracts were analyzed using method PAHMULTIRAMP in SIM mode (for SIM parameters, see Table 3.1).

3.2.2 Results and discussion

In order to examine the efficacy of the toluene-octanol MIPs in real produced water samples, experiments were performed on spiked, diluted produced water in parallel with spiked ASTM artificial seawater. Naphthalene was chosen over larger PAHs because it was determined to be present in produced water samples in high abundance by previous experiments using EPA Method 525. It also tends to be the most difficult of the PAHs to recover with high efficiency using SPE. Acenaphthene-d_{10} was used as the internal standard as in previous experiments. Solutions of naphthalene in produced water and naphthalene in artificial seawater were made having concentrations of 0, 0.5, 1, 3, and 5 mg/L. MIPs were uploaded with 25.0 mL of each solution in replicates of four, with one MIP per beaker. A set of four NIPs for each matrix was uploaded with the corresponding 5 mg/L solution. Results for these preliminary experiments are shown in Table 3.7 and Figures 3.4 and 3.5.

Table 3.7 Results of standard addition upload of naphthalene in produced water and ASTM artificial seawater to toluene-octanol MIPs/NIPs

Water type	Polymer type	Spike conc. (mg/L)	Average peak area naph	Average peak area internal standard	$PA_{analyte}/PA_{internal\ standard}$	Standard deviation PA ratio	%RSD
SW	MIP	0	0	8512829	0	0	0
		0.5	4772539	9764744	0.489	0.247	50.49
		1	9113425	8980303	1.015	0.123	12.12
		3	16321740	9176515	1.779	0.117	6.58
		5	41425716	8582706	4.827	1.962	40.65
	NIP	5	47267059	8949915	5.281	2.615	49.52
PW	MIP	0	6937909	9648886	0.719	0.151	21.04
		0.5	12474949	10368579	1.203	0.099	8.19
		1	16309183	9815638	1.662	0.155	9.32
		3	20103049	10009310	2.008	1.598	79.56
		5	74449390	9252416	8.046	0.770	9.57
	NIP	5	84972267	9251446	9.185	1.589	17.30

PW = produced water
SW = ASTM artificial seawater

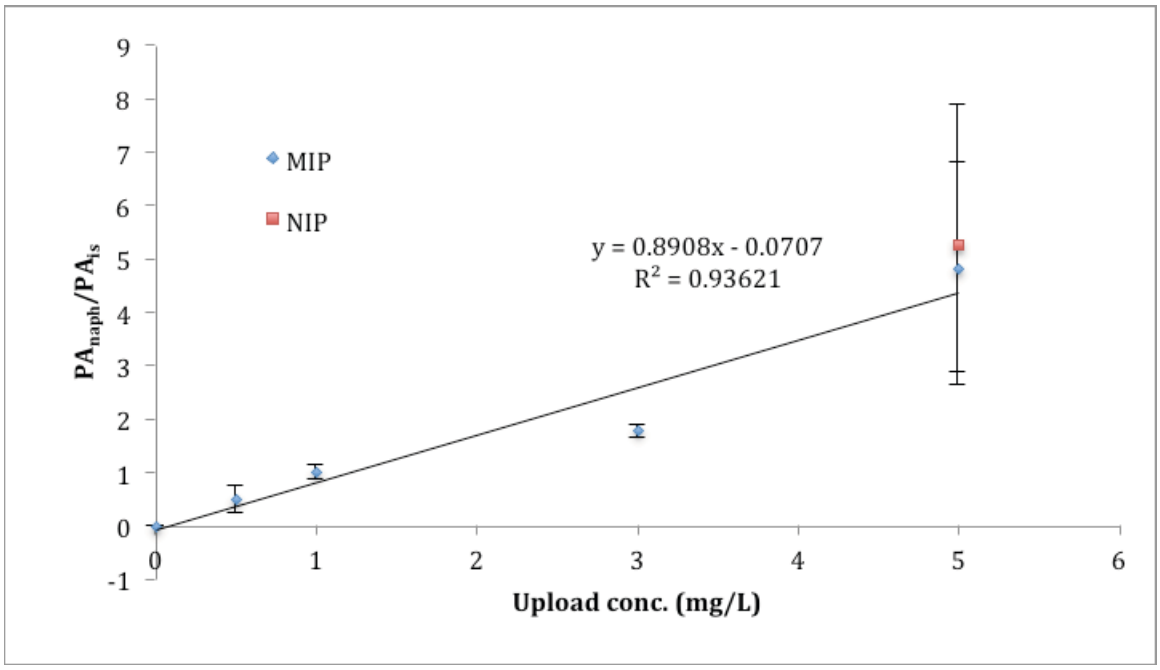


Figure 3.4 Standard addition curve for upload of naphthalene in ASTM artificial seawater to toluene-octanol MIPs/NIPs

Note: Error bars represents standard deviation (n = 4)

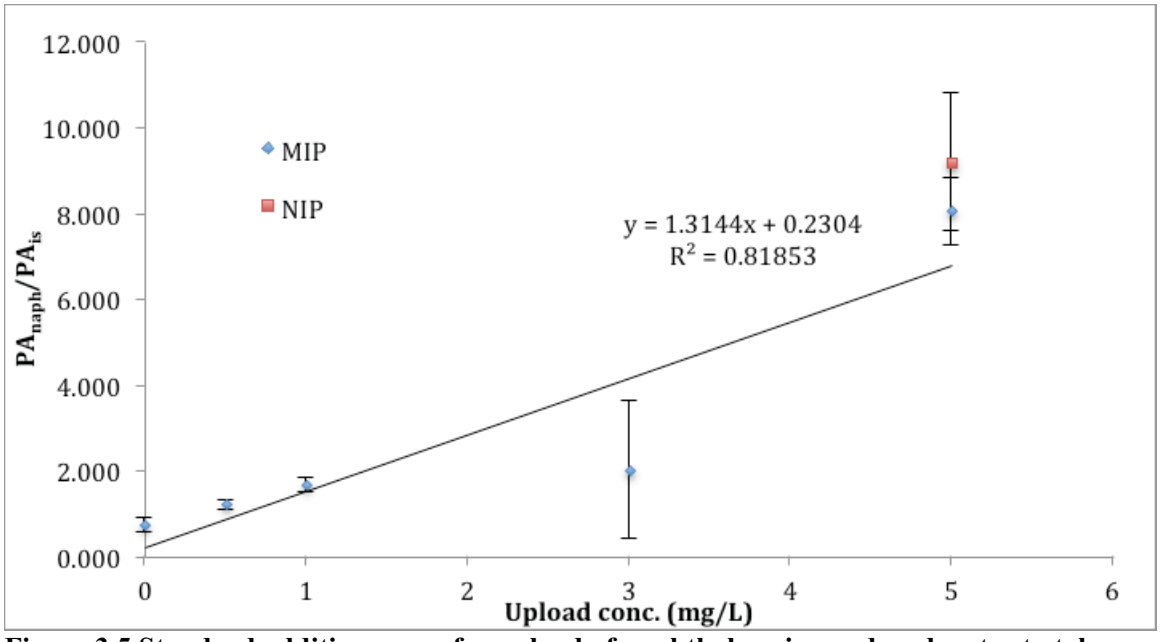


Figure 3.5 Standard addition curve for upload of naphthalene in produced water to toluene-octanol MIPs/NIPs

Note: Error bars represent standard deviation (n = 4)

A comparison between the experiments performed in artificial seawater and produced water indicate that a linear response is possible using toluene-octanol MIPs, but as these results are only preliminary, there are some issues.

The high %RSD values for some data points may indicate human error, but when comparing the results for the 3 mg/L upload solution in either matrix, it is clear that more uncertainty is present in the produced water samples.

The produced water used in these experiments was not treated or cleaned up in any way to remove residual oil, and there were issues with a film of oil adhering to the surface of the MIP after it was removed from the upload solution. This could have a few different effects: the film of oil may introduce interferences and competition for selective pores between naphthalene and other components of produced water, or it may have introduced contaminants into the final extract solution which could interfere with the GC-MS analysis by obscuring the desired peak or suppressing ionization of the target analyte. Further experiments are necessary in order to refine this method.

4. Conclusions and future work

The goal of this research was to evaluate existing methods for the analysis of produced water and some of the compounds found therein. Specifically, two methods for analysis of oil and grease were looked at, as well as a method for determining PAHs in water.

The two methods for the determination of oil and grease examined were found to have many flaws that are inherent in the methods themselves. It is problematic that the definition of oil and grease is operational and depends on the method used to measure it, because both EPA Method 1664 and APHA Method 5520 C ignore significant components of produced water that can pose a risk to the environment, particularly sensitive Arctic ecosystems. Since these methods are insufficient for the determination of many of the more harmful components of produced water, improvements should be made and other methods could be used to supplement their results.

EPA Method 1664 and other gravimetric methods suffer from the volatility of some of their extractable components, and the fact that many harmful compounds found in produced water may not be extractable in the extraction solvent, or may be removed with the solvent during the distillation process. At best, the method is easy to perform, but it provides poor reproducibility and no information as to the composition of produced water.

APHA Method 5520 C is another method that measures oil and grease in produced water and relies on liquid-liquid extraction to remove oil and grease components from water samples. Where this method falls short is in the single wavelength IR analysis, which excludes components of produced water with no aliphatic

C–H bonds, such as unsubstituted aromatics. It also makes use of very large sample volumes and large volumes of solvents that are probable human carcinogens, e.g. tetrachloroethylene or CFCs such as S-316, which can be prohibitively expensive and may be ozone-depleting.

EPA Method 525 was optimized for use with produced water and other highly polluted samples and determined to be a suitable method for measuring PAHs in produced water, but lacks selectivity which can cause problems when attempting to quantify specific analytes in a complex mixture. Because any compound that is hydrophobic will end up in the final extract, the resulting chromatogram may be overly complicated and specific analytes may be obscured.

Molecularly imprinted polymers have been developed by Dr. Stefana Egli in the Bottaro research group for the selective analysis of PAHs in water, and have been determined to be effective for use in produced water. While there is some error in the results for this thesis, these results are only preliminary and the use of these MIPs in real samples of produced water had not been previously attempted. Improvement should be possible if samples are pretreated before upload, to remove suspended oil that might adhere to the surface of the glass slides and polymer. This could be accomplished simply by placing a sample of produced water in a separatory funnel and removing only the desired aqueous layer from the bottom, however online analysis is not feasible using these methods. Additionally, it is difficult to predict the composition of produced water, so some work may have to be done to examine the behavior of toluene-octanol MIPs in varying compositions of produced water.

In order to validate the suitability of PAH MIPs for use in place of existing methods for the analysis of PAHs in water, more steps must be taken. The limits of detection and quantitation of the method, as well as the limit of linearity must be obtained and thoroughly compared with those of EPA Method 525, which has been found to be appropriate for measuring PAHs in water. A triple-wavelength IR analysis method may also be optimized for comparison to MIP results, if it could be proven to be more accurate at measuring aromatic compounds than currently used single-wavelength methods such as APHA Method 5520 C.

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Appendix A: Preparation of ASTM artificial seawater

A.1 Materials

Sodium sulfate, boric acid, strontium chloride hexahydrate, and magnesium chloride hexahydrate were obtained from Sigma-Aldrich (Oakville, ON), and sodium bicarbonate was purchased from ACP. Potassium bromide and potassium chloride were purchased from BDH. Calcium chloride was obtained from Anachemia, and sodium fluoride was purchased from Alfa Division. All chemicals were ACS reagent grade.

A.2 Method

4 L of ASTM artificial seawater were prepared according to the following procedure:

Stock solution 1 was prepared using 555.6 g $MgCl_2 \cdot 6H_2O$, 57.9 g $CaCl_2$ (anhydrous), and 2.1 g $SrCl_2 \cdot 6H_2O$ dissolved in 1 L distilled water. Stock solution 2 was prepared by dissolving 69.5 g KCl, 20.1 g $NaHCO_3$, 10.0 g KBr, 2.7 g H_3BO_3, and 0.3 g NaF in 1 L of distilled water.

98.14 g NaCl, 16.38 g Na_2SO_4, 80 mL of stock solution 1, and 40 mL of stock solution 2 were dissolved in 4 L of distilled water and stored in an amber glass bottle.

Appendix B: Characterization of harbour water and produced water samples

An attempt was made to characterize some of the components found in samples of water from St. John's Harbour and produced water. A 100 mL aliquot of seawater from St. John's Harbour was extracted using EPA Method 525 and analyzed by GC-MS using method PAHMULTIRAMP in scan mode. Peaks were identified using the most probable match in the NIST database. Characterization results are shown in Figure B.1.

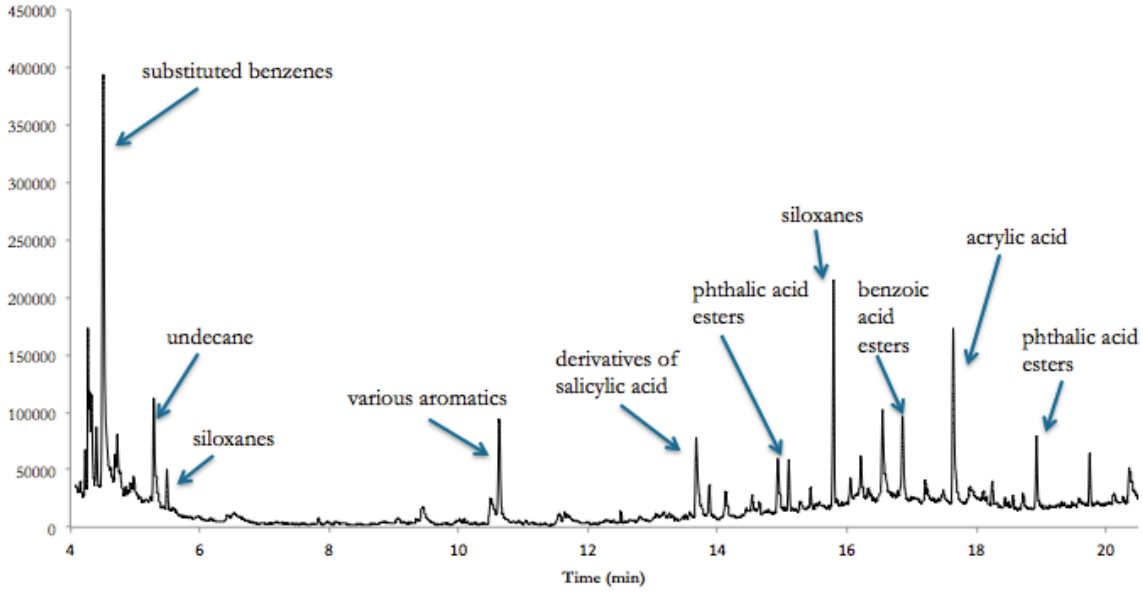

Figure B.1 Total ion chromatogram - 100 mL seawater from St. John's Harbour extracted by EPA Method 525

A 50 mL aliquot of produced water was extracted using EPA Method 525 and analyzed by GC-MS using method PAHMULTIRAMP in scan mode. Characterization results are shown in Figure B.2.

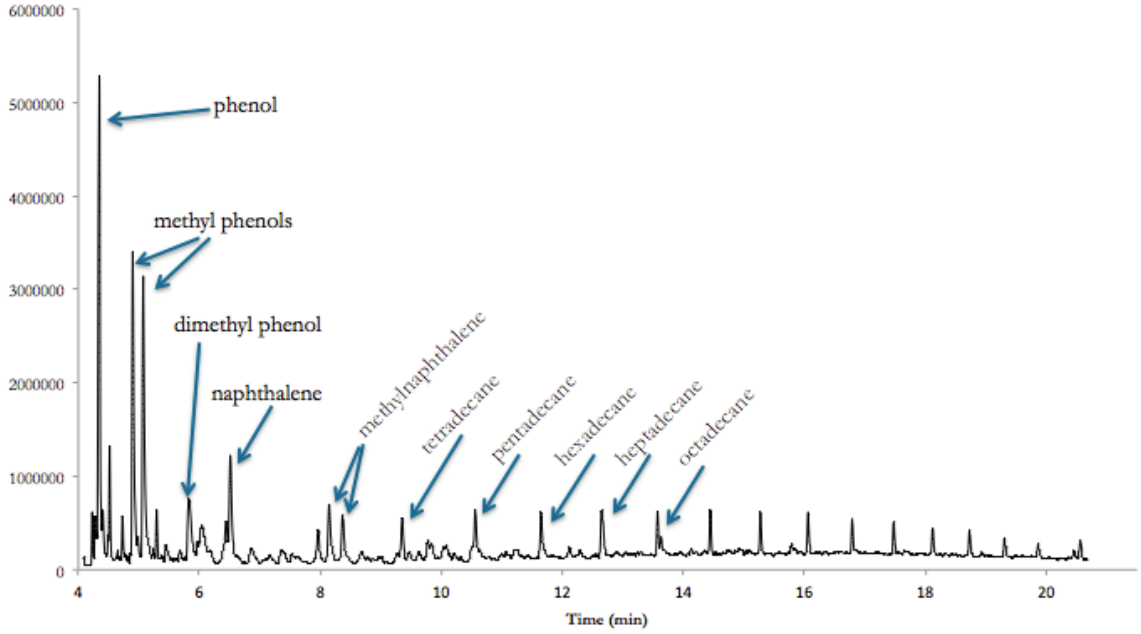

Figure B.2 Total ion chromatogram - 50 mL produced water extracted by EPA Method 525