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Evaluation of Extraction Method and Characterization of Water Soluble Organics from Produced Water by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Adam Lewis

THE FLORIDA STATE UNIVERSITY
COLLEGE OF ARTS AND SCIENCES

EVALUATION OF EXTRACTION METHOD AND CHARACTERIZATION OF WATER
SOLUBLE ORGANICS FROM PRODUCED WATER BY FOURIER TRANSFORM ION
CYCLOTRON RESONANCE MASS SPECTROMETRY

By

ADAM LEWIS

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Adam Lewis defended this thesis on March 22nd, 2013.

The members of the supervisory committee were:

Alan Marshall
Professor Directing Thesis

John Dorsey
Committee Member

Naresh Dalal
Committee Member

Ryan Rodgers
Committee Member

The Graduate School has verified and approved the above-named committee members, and certifies that the thesis has been approved in accordance with university requirements.

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TABLE OF CONTENTS

List of Tables	v
List of Figures	vi
Abstract	ix
CHAPTER ONE. INTRODUCTION: LIGHT OIL, HEAVY OIL, AND BITUMEN.....	1
Light Crude Oil.....	1
Heavy Crude Oil.....	2
Sweet versus Sour Crude Oil.....	3
Bitumen and Oil Sand	4
Steam Assisted Gravity Drainage.....	5
Petroleum Fouling	8
Extraction of Dissolved Bitumen	9
CHAPTER TWO. CHARACTERIZATION OF HYDROCARBON SPECIES BY HIGH RESOLUTION FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY	12
Ion Cyclotron Motion Theory	12
Excitation and Detection of Ion Cyclotron Frequency.....	13
Ion Trapping and Perturbation of Ion Motion	14
9.4 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer	15
Electrospray Ionization (ESI).....	16
Data Analysis.....	18
CHAPTER THREE. EXPERIMENTAL METHODS	21
Samples.....	21
Mass Spectrometry	22
Mass Analysis.....	23
CHAPTER FOUR. RESULTS AND DISCUSSION	24
Visual Evaluation of Solubility	24
Fluorometric Analysis	27
Determination of WSO.....	28
Turbidity Study.....	31
Mass Spectrometry	33
CHAPTER FIVE. CONCLUSION.....	48
REFERENCES	50
BIOGRAPHICAL SKETCH	54

LIST OF TABLES

4.1	Visual assessment of characteristics of produced water extract obtained by use of different extraction solvents.....	26
4.2	Bitumen (ppm; v/v) in produced water measured with fluorometric analysis.....	27
4.3	Comparison of WSO determination methods.....	30

LIST OF FIGURES

1.1	Photographs of four different variants of petroleum. Light crude oil (left) is transparent and nonviscous. Heavy crude oil (right) is dark and viscous. Bitumen (bottom two) is very viscous and flows very slowly, if at all. Tar sand (top) is a mixture of bitumen and soil.	5
1.2	Cross-sectional diagram of the SAGD process. Steam from the injector well flows up and outward to the edges of the steam chamber, as shown by the black arrows. Heated bitumen flows along the interface to the bottom of the steam chamber and into the producer well, as shown by the white arrows.	6
1.3	Simplified schematic of bitumen production by SAGD. At the steam generation stage, water is heated with natural gas to form steam. The steam is injected into the ground through a horizontal well. Bitumen and water are co-produced and separated at the separator stage, which may consist of several stages of knockout devices and chemical treatments. Separated bitumen may be diluted prior to transport to the upgrader. Separated water is treated to remove impurities from the bitumen and then recycled to form more steam. Fractional distillation is used to separate crude bitumen into asphaltenes and distilled bitumen. Asphaltenes are optionally sent to gasification where they are thermally degraded to form synthetic natural gas and hydrogen. Alternatively, these gases can be obtained from nearby sources, and are often coproduced with crude bitumen. The synthetic natural gas is used as a heat source for upgrading and steam generation. ¹ Hydrogen is sent along with upgraded bitumen to the hydrocracking stage, where the upgraded bitumen undergoes hydroprocesses to form synthetic crude oil.	7
2.1	Schematic of ion optics and vacuum chambers of the 9.4 T FT-ICR mass spectrometer located at the National High Magnetic Field Laboratory at Florida State University in Tallahassee, Florida. Pressures within each stage of pumping are shown. Multiple stages are necessary to achieve the low pressures required within the cell. Octopole 2 is operated at a higher pressure due to helium introduced for collisional cooling.	16
2.2	Diagram of the ESI process. Ions are ejected from the charged needle then enter the heated capillary where solvent is evaporated. As solvent is removed, the charge becomes more concentrated until the repulsive force of the charge exceeds the surface tension of the solvent droplets. The droplet splits apart, and the process repeats until only ions remain. The charged droplets and ions are guided into the instrument by their attraction toward the counter electrode.	17
2.3	Double bond equivalents vs. carbon number plots for the NO ₂ classes of two petroleum samples. All NO ₂ compounds are plotted on the same scale. Though both of these plots depict the same heteroatom class, the collections of molecules occupy different compositional spaces due to differences in the crude oils.	19
4.1	Visual comparison of solubility of bitumen in various solvents at same (high; 100ppt) bitumen concentration (left to right- cyclohexane/butyl acetate (7:3, v/v), cyclohexane, methylene chloride, <i>n</i> -hexane).	24

4.2 Visual comparison of solubility of bitumen in various solvents at same (low: 100 ppm) bitumen concentration (Left to right- <i>n</i> -hexane cyclohexane, methylene chloride, cyclohexane/butyl acetate (7:3, v/v)).	25
4.3 Visual comparison of produced water extracts obtained by use of various solvents. (Left to right- <i>n</i> -hexane, cyclohexane, methylene chloride, cyclohexane/butyl acetate (7:3, v/v)).	26
4.4 Reversible acid-base reaction to form oil solubles (neutral) or oil insolubles (charged).	29
4.5 Relationship between TOG (cyclohexane/butyl acetate) and turbidity for SAGD produced waters measured over 36 hour period.	31
4.6 Relationship between WSO (basified extraction) and TOG (cyclohexane/butyl acetate) for SAGD produced waters monitored over 36 hour period.	32
4.7 Qualitative heteroatom class distributions for acidic oxygenated species derived from negative-ion ESI FT-ICR mass spectra for produced water solvent extracts (<i>n</i> -hexane, cyclohexane, cyclohexane/butyl acetate) and sodium hydroxide back-extract. Note that the y-axis is unweighted with respect to the sample weight extracted (which is significantly higher for cyclohexane/butyl acetate (7:3, v/v) extract) and reflects only relative abundance within a sample. Therefore the abundance of a chemical species should be compared against the abundances of other species within the same sample, not against the same species in different samples.	34
4.8 Qualitative heteroatom class distributions for acidic SO _x classes derived from negative-ion ESI FT-ICR mass spectra of produced water solvent extracts (<i>n</i> -hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract. As in Figure 4.7, the y-axis is unweighted with respect to the sample weight extracted.	36
4.9 Color-coded iso-abundance contoured plots of DBE (double bond equivalents = number of rings plus double bonds to carbon) vs. carbon number for acidic oxygen classes derived from negative-ion ESI FT-ICR mass spectra of produced water solvent extracts (<i>n</i> -hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract.	38
4.10 Color-coded iso-abundance contoured plots of DBE (double bond equivalents = number of rings plus double bonds to carbon) vs. carbon number for acidic SO _x classes derived from negative-ion ESI FT-ICR mass spectra of produced water solvent extracts (<i>n</i> -hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract. Classes with below 0.5% relative abundance are not shown.	40
4.11 Qualitative heteroatom class distributions for basic NO _x classes from positive-ion ESI FT-ICR mass spectra <i>n</i> -hexane extract, cyclohexane extract, and cyclohexane/butyl acetate (7:3, v/v) extract. Classes with below 0.5% relative abundance are not shown. As in previous graphs, the y-axis is unweighted with respect to the sample weight extracted.	41

4.12 Qualitative heteroatom class distribution for basic SO _x classes derived from positive-ion ESI FT-ICR mass spectra of produced water solvent extracts (<i>n</i> -hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract. Classes below 0.1% relative abundance are not shown. As in previous class distribution graphs, the y-axis is unweighted with respect to the sample weight extracted.....	43
4.13 Color-coded iso-abundance contoured plots of DBE [(DBE = C# – 0.5(H# + N#) + 1)] vs. carbon number for basic NO _x classes derived from positive-ion ESI FT-ICR mass spectra of produced water solvent extracts (<i>n</i> -hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)). Sodium hydroxide back-extract showed too low spectral coverage to display a plot for any shown classes. Classes with below 0.5% relative abundance are not shown.	44
4.14 Color-coded iso-abundance contoured plots of DBE (double bond equivalents = number of rings plus double bonds to carbon) vs. carbon number for basic SO _x classes derived from positive-ion ESI FT-ICR mass spectra of produced water solvent extracts (<i>n</i> -hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)). Sodium hydroxide back-extract showed too low spectral coverage to display a plot for any shown classes. Classes with below 0.5% relative abundance are not shown.	46

ABSTRACT

With world consumption of crude oil at over 30 billion barrels per year,² petroleum provides the backbone for a multi-trillion dollar industry. However, this entire industry is built around the ability to convert crude oil into useful products, such as gasoline. Oil companies are, in essence, selling a collection of molecules. The composition of those molecules will determine every aspect of that oil's production and refining: how difficult it will be to extract the oil, what will need to be done to turn the oil into a valuable commodity such as gasoline, and ultimately what the oil is worth. Though petroleum fuels are expected to be the dominant form of energy for the next few decades, reserves of light, sweet crudes have diminished to the point that heavy and unconventional feedstocks are now being utilized. With these unconventional crudes come new problems in production and refining. Heavy crude and bitumen are extremely viscous and therefore require enhanced extraction techniques to produce them from a well. In addition, they are often very heteroatom-rich and require additional upgrading to remove oxygen, nitrogen, and sulfur. Information about a crude oil's molecular composition is therefore extremely valuable to oil companies, but petroleum samples are among the most complex mixtures known to science. Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry provides unequalled resolving power and mass accuracy, which has given us the ability to determine the molecular makeup of incredibly complex crude oils, often with no prior separation of the oil into less complex fractions. This technology can provide oil companies access to a vast amount of knowledge about a crude oil before production or refining, allowing associated techniques to be designed around specific crude oils.

Production of bitumen by steam assisted gravity drainage (SAGD) generates immense water streams that are often difficult to manage, and it is generally advantageous for oil

production companies to treat and reuse the water to make more steam. The produced water contains bitumen contaminants, which may drop out of solution and foul exposed surfaces. Characterization of the water produced with bitumen during SAGD is necessary to determine if contaminants are present that might cause fouling, and if so, which contaminants are responsible.

Chapter 1 is an introduction to light oil, heavy oil, and bitumen and their relevant extraction and production processes. Chapter 2 provides background on Fourier transform ion cyclotron resonance mass spectrometry, electrospray ionization, and mass spectral data analysis.

In Chapter 3, an alternative method to extract, quantify, and characterize water soluble organic (WSO) species in produced water from Steam assisted gravity drainage (SAGD) is evaluated by various techniques. By this method, cyclohexane/butyl acetate (7:3, v/v) is used as the solvent for extraction of WSO species from produced water. The ability of cyclohexane/butyl acetate (7:3, v/v) to efficiently isolate higher O_x species that are readily identified in production deposits is evaluated by use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometric analysis and fluorescence spectroscopy.

In Chapter 4, these results are compared to industry standard methods that employ extraction with *n*-hexane and cyclohexane. Results reveal that cyclohexane/butyl acetate (7:3, v/v) not only extracts more material from produced water than *n*-hexane or cyclohexane, but is also more efficient at extraction of polar species implicated in deposits of interest. Results suggest that cyclohexane/butyl acetate (7:3, v/v) is a better solvent for the quantitative extraction and analysis of WSO in produced water, which may help in the diagnosis and prevention of fouling problems associated with SAGD operations, as is concluded in Chapter 5.

CHAPTER ONE

INTRODUCTION: LIGHT OIL, HEAVY OIL, AND BITUMEN

For years, the global oil market has been centered around the production of conventional (less dense, low-sulfur) crude oil. Conventional crude oil is usually easy to produce, generally not requiring enhanced recovery techniques until late in a well's lifetime. It is also relatively easy to refine and produces a high yield of gasoline. Because of these factors, it is cheaper to produce and has more value than other types of petroleum. The higher production cost and lower value of high-density or high-sulfur crude oils ensure that it is not economically viable to produce them when the cost of conventional crude is low. However, as the price of conventional oil increases, it becomes economically feasible to produce other types of oil. With the cost of oil nearing \$100 per barrel and many easily-accessible sources of conventional crude near depletion, oil companies are looking to heavy oil and bitumen (extra heavy oil) to make up future feedstocks. However, these unconventional types of oil provide additional challenges to oil companies, during both production and refining.

Light Crude Oil

Light (conventional) crude oil is identified by its low boiling point and relatively low density. It is generally brown to black in color and is defined as a crude oil having an API gravity of greater than 20°. ³

$$API\ Gravity = \frac{141.5}{Specific\ Gravity} - 131.5 \quad 1.1$$

Though the terms *light* and *heavy* are not directly derived from composition, they can give clues as to the types of chemical species that make up a particular crude oil. Light crude oil tends to be composed mostly of paraffinic hydrocarbons, resulting in relatively low boiling point,

density, and viscosity.³ In addition to this, light crude oil tends to have fewer heteroatom-containing species than heavy crude. Light crude oil's lower boiling point means that more of it can easily be converted to valuable transportation fuels, and its low viscosity means it can flow through a pipeline without heat or dilution. Because of these factors, light crude oil is more desirable, and therefore more expensive. Due to the gradual depletion of easily accessible sources of light crude oil, the global market is shifting toward the use of unconventional crude oils, such as heavy crude and bitumen.

Heavy Crude Oil

In contrast to light crude oil, heavy crude is identified by its higher viscosity and higher boiling point. These factors are symptomatic of the presence of higher molecular weight, aromatic, or heteroatom containing compounds. Heavy crude oil is generally opaque and black in color and is defined by its API gravity of between 10° and 20°.³ Heavy crude contains only about 50% pure hydrocarbon molecules by weight, in contrast to light crude, which may be more than 90%.³

The high viscosity of heavy crude provides an enormous challenge during recovery, as it has very low mobility in the reservoir and cannot be recovered from the well by conventional methods. Extraction of heavy oils from the soil often requires the addition of heat or pressure to the well to achieve high yields, adding expense to the operation. In addition to this, heavy oils often require dilution with solvents or lighter crudes to lower their viscosity enough to be transported through pipelines.

The high heteroatom content and aromaticity provide another challenge during refining. Crude oils with high abundances of heteroatoms often react negatively with catalysts used during

refining or contribute to premature wear of metal parts they come in contact with. High aromaticity is associated with high boiling point and high viscosity, so it is often desirable to break apart large molecules and saturate aromatic rings in a process called cracking. Cracking can be efficiently performed through thermal processes involving catalysts and high partial pressures of hydrogen, known as hydrocracking.⁴ Hydrocracking can be performed simultaneously alongside hydrodesulfuration, hydrodenitrogenation, hydrodeoxygenation, and hydrodemetallization; each of which removes their respective heteroatoms by hydrogenolysis.⁵ During these processes, large molecules are split apart and heteroatoms removed to generate gaseous byproducts.³ Hydrocracking and hydrogenolysis, when performed on petroleum, are collectively known as hydroprocesses. Heavy crude oils containing more heteroatomic molecules or unsaturated species will require more hydrogen for hydroprocesses, which generally makes them more expensive to process.

Sweet versus Sour Crude Oil

Crude oil is often defined as either sweet or sour. Sweet crude is relatively low (less than 0.5%) in sulfur, whereas sour crude has a higher sulfur content (greater than 0.5%).⁶ The presence of sulfur and sulfur compounds in gasoline and diesel fuel promotes corrosion of engine parts and formation of engine deposits.³ Much of the developed world has strict standards on the amount of sulfur that can be present in such fuels. Therefore, crude oils higher in sulfur content must be further refined to remove these impurities if they are to be made into transportation fuels. Higher sulfur content means more hydrogen will be consumed during hydrodesulfuration, and therefore more expense associated with processing a sour crude. Due to this, sweet crude oil is considered higher quality and is more valuable than sour crude. Due to a lower overall heteroatom content, light crude oil tends to be sweet more often than heavy crude oil.

Bitumen and Oil Sand

Bitumen is a solid or near-solid crude oil with little or no mobility under reservoir conditions. It generally appears as a black solid or semisolid, contains less than 30% by weight hydrocarbons, and is defined as having an API gravity of less than 10°. ³ Bitumen is often found mixed with sand, clay, and water. ⁷ The resultant mixture of bitumen and rock (consolidated or unconsolidated) is known as oil sand, tar sand, or bituminous sand. Bitumen cannot be extracted by conventional recovery processes, nor will many enhanced recovery processes work. Common means of extracting bitumen include strip mining of the oil sands and steam assisted gravity drainage (SAGD).

Synthetic crude oil is a product with similar density and viscosity to light oil, and may be produced from bitumen by processes similar to those used to upgrade heavy crude oil. “Upgrading” is the term used to describe the collective processes by which bitumen is converted to synthetic crude. The first stage of upgrading is generally fractional distillation to separate the lighter fractions, followed by de-asphalting of the vacuum residue. The de-asphalted oil is treated by hydroprocesses then recombined with the lighter fractions to form synthetic crude.

Canada’s proven reserves of crude oil as of 2011 were 175 billion barrels, 11.4% of the world’s total proven reserves, putting them third in the world after Saudi Arabia and Venezuela. ⁸ Of those reserves, 169 billion barrels are contributed by bitumen from Alberta’s oil sands alone. ⁹⁻¹² Many companies are now looking into bitumen production, as high oil prices have made it economically viable, and the invention of SAGD has made accessible many reserves that were previously inaccessible.

Figure 1.1. Photographs of four different variants of petroleum. Light crude oil (left) is transparent and nonviscous. Heavy crude oil (right) is dark and viscous. Bitumen (bottom two) is very viscous and flows very slowly, if at all. Tar sand (top) is a mixture of bitumen and soil.

Steam Assisted Gravity Drainage

Steam assisted gravity drainage is a technique for extraction of bitumen reserves that are inaccessible by open-pit mining. It is gaining popularity as conventional oil reserves and surface-accessible bitumen reserves are depleting. It is a fast, inexpensive, and environmentally conscious thermal recovery process that allows for extraction of 60-80% of raw bitumen. SAGD calls for a pair of horizontal wells to be drilled, one above the other, separated by about five meters. Steam is injected into the upper well, which heats the surrounding soil. This heat increase lowers the viscosity of the bitumen to as low as 1 to 10 cp¹³, allowing it to flow into the lower well. From the lower well, the produced bitumen and condensed water are pumped to the surface.^{10,14}

The condensed steam from SAGD that returns to the surface is known as produced water. Because as many as three barrels of oil-contaminated water may be produced from an average well for each barrel of bitumen, management of the water is an important issue.^{9,16} Because the amount of water consumed by a SAGD operation is important to assessing its economic impact, and produced water cannot be easily returned to the environment due to contamination from bitumen components,^{9,10} often the water is recycled and used to generate more steam.

Figure 1.2. Cross-sectional diagram of the SAGD process. Steam from the injector well flows up and outward to the edges of the steam chamber, as shown by the black arrows. Heated bitumen flows along the interface to the bottom of the steam chamber and into the producer well, as shown by the white arrows.

Figure 1.3. Simplified schematic of bitumen production by SAGD. At the steam generation stage, water is heated with natural gas to form steam. The steam is injected into the ground through a horizontal well. Bitumen and water are co-produced and separated at the separator stage, which may consist of several stages of knockout devices and chemical treatments. Separated bitumen may be diluted prior to transport to the upgrader. Separated water is treated to remove impurities from the bitumen and then recycled to form more steam. Fractional distillation is used to separate crude bitumen into asphaltenes and distilled bitumen. Asphaltenes are optionally sent to gasification where they are thermally degraded to form synthetic natural gas and hydrogen. Alternatively, these gases can be obtained from nearby sources, and are often coproduced with crude bitumen. The synthetic natural gas is used as a heat source for upgrading and steam generation.¹ Hydrogen is sent along with upgraded bitumen to the hydrocracking stage, where the upgraded bitumen undergoes hydroprocesses to form synthetic crude oil.

There are several techniques available for separating oil from water. Most of them require the reverse-emulsion to be heated to a high temperature to assist in separation. Therefore, it is not uncommon for produced water exiting separation to retain a large amount of energy as heat. As a

cost saving measure, between separation and water treatment, countercurrent heat exchangers are often employed to transfer heat from the produced water to the water/bitumen reverse-emulsion entering separation. These heat exchangers will have immense volumes of bitumen-contaminated produced water pass through them. This contamination, combined with the high temperatures applied during production can lead to petroleum fouling.^{10,17}

Petroleum Fouling

Petroleum fouling is the process by which petroleum constituents adhere to and build up on a surface, which is often the result of reduced solubility of some components either from changes in temperature and concentration or decomposition of a compound to something less soluble. It is typical for countercurrent heat exchangers to be employed between the stages of production where water is separated from bitumen and those where it is treated to prepare it for steam production. The heat exchangers are often set up in such a way as to cool the produced water headed to water treatment and heat the incoming bitumen-water emulsion prior to separation.

This produced water contains contaminants from the bitumen, which may drop out of solution as the water is cooled. Thus, it is common for these contaminants to precipitate and adhere to the surfaces inside the heat exchangers, causing them to become fouled. Over time, this creates a build-up that provides an insulating barrier between the walls of the exchanger and the fluid which it is heating, and in some cases may obstruct flow. Therefore, these heat exchangers require regular cleaning, which generally slows bitumen production. Shutdown of individual heat exchangers delays bitumen recovery, costing oil companies time and money.

Large scale separation is performed on the water prior to heating, but these methods cannot remove all of the contamination. Therefore, a wider knowledge of what types of chemicals are present in the water is required so that the degree of fouling can be reduced. Current practice relies on a medley of chemical additives that both increase the efficiency of large scale separations and reduce the fouling tendencies of dissolved bitumen. If the compounds responsible for fouling the heat exchangers are identified, these chemical additives can be tailored to suit them. The ability to extract, quantify and identify organic species in produced water is necessary for proper diagnosis, monitoring, and mitigation of downstream process issues such as heat exchanger fouling, warm lime softening, anaerobic and aerobic waste water treatment, etc., as well as compliance issues around environmental requirements.⁹ The development of better techniques for extracting oil contamination from produced water may lead to a better understanding of the nature of the contaminants plaguing SAGD operations, and in turn, fewer shutdowns and more efficient oil production.

Extraction of Dissolved Bitumen

Extraction techniques are available to remove petroleum constituents from produced water so that the contaminants can be identified and the amount of contamination can be quantified prior to reuse. Typical residual oil and grease analysis protocols call for acidification of the water then extraction with an organic solvent followed by determination of hydrocarbon content by gravimetric or spectrophotometric methods.^{18,19} Bitumen derived from oil sands is known to possess considerable polarity and high asphaltene content. The polar constituents are more soluble in polar solvents, including water, compared to non-polar compounds of similar molecular structure. The polar asphaltenic components have limited solubility in crude oil or bitumen and are presumably solvated by other components such as resins and other amphiphiles

via polar-polar interactions, and many polar asphaltenic components are insoluble in toluene.^{20–22} Various heteroatomic (nitrogen, oxygen, sulfur) functionalities have been identified in asphaltenes. The surface active fractions of crude oil and bitumen, primarily resins and asphaltenes, accumulate at the interface and have a key role in stabilizing emulsions and sludges.^{20–22} It is highly plausible that polar, interfacially active compounds in the crude oil adsorbed at the oil/water interface are acidic in nature, and some potentially ionize or dissociate into the aqueous phase upon emulsification.²³

In the USA, oil and grease in produced water is defined as the material that can be extracted with a solvent and not removed during the solvent removal process at 70°C and is capable of being weighed.^{24,25} *N*-hexane is the most commonly used solvent for this extraction,^{18,19,24,25} but previous detailed characterization of emulsion interfacial materials and WSO species has catalogued thousands of highly oxygenated (polar) species whose solubility in *n*-hexane is poor.^{17,26–28} These oxygen functionalities are predominantly characterized as hydroxylic, carboxylic, and ether type groups. The acidic components are the first sub-fraction to precipitate and are also implicated in forming asphaltene films that stabilize emulsions.^{20,23}

Due to the immense complexity of crude oils and bitumen, separation techniques such as distillation are not applicable and solubility-based precipitation of asphaltenes followed by chromatographic fractionation (SARA – saturate, aromatic, resin, and asphaltene) of the remaining fluid is used as a convenient tool to separate and characterize heavy oils.²⁹ SARA thus utilizes the solubility and adsorption characteristics of the crude oil and fractionates saturates, aromatics, resins, and asphaltenes based on their polarities. Extrography (i.e., extraction and chromatography) is another means of separation of crude oil components into reproducible fractions according to their specific chemical characteristics (heterocyclic composition,

aromaticity, polarity, molecular weight).³⁰ Extrographic separation entails orderly adsorption of the crude oil components on the adsorbent followed by selective extraction by solvents of increasing polarity or strength. The most polar components are adsorbed by the most active sites on the surface of the adsorbent whereas the least polar components are retained in the pores.³⁰ Therefore, extrography provides a given number of fractions of well-defined chemical composition according to aromaticity, polarity, and molecular weight.³⁰⁻³² Given the established extraction methodologies for the extraction and separation of polar crude oil components, it seems counter-intuitive to employ *n*-hexane to extract water soluble organic species. It is therefore expected that current practices provide an inadequate measure of water soluble organics in the produced water streams, given the polarity of this material, and it is necessary to find an alternative extraction solvent which can efficiently extract bitumen from water.

CHAPTER TWO

CHARACTERIZATION OF HYDROCARBON SPECIES BY HIGH RESOLUTION FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

Ion Cyclotron Motion Theory

A charged particle moving in a spatially homogeneous magnetic field is subject to a force defined by

$$F = m \frac{dv}{dt} = qv \times B \quad 2.1$$

in which m , q , v , and B are ionic mass, ionic charge, velocity, and magnetic field strength. The vector cross product indicates that the direction of the force experienced by the ion in the magnetic field is perpendicular to the plane defined by v and B , which results in a circular ion path within the magnetic field. Angular acceleration is defined by

$$\frac{dv}{dt} = \frac{v^2}{r} \quad 2.2$$

in which r is the radius of the circle travelled by the ion. Substitution of equation 2.2 into equation 2.1 results in

$$\frac{mv}{r} = qB \quad 2.3$$

Angular velocity about the z -axis (opposite to the direction of B) is defined by

$$\omega = \frac{v}{r} \quad 2.4$$

so that substitution of equation 2.3 yields

$$m\omega = qB \quad \text{or} \quad \omega = \frac{qB}{m} \quad 2.5$$

Angular velocity can be converted to frequency with

$$\nu = \frac{\omega}{2\pi} \quad 2.6$$

Substitution of equation 2.6 into equation 2.5 and conversion of charge to elementary charges and mass to Daltons gives

$$\nu = \frac{1.535611 \times 10^7 B}{m/z} \quad 2.7$$

in which ν is frequency in Hz, m is ionic mass in Da, and z is ionic charge in units of elementary charge. By this equation, m/z can be directly calculated from ion cyclotron frequency knowing only magnetic field strength. It is important to note that frequency is independent of ion velocity, meaning it will not require focusing of translational energy.³³

Excitation and Detection of Ion Cyclotron Frequency

Ion cyclotron motion due to thermal energy alone is not useful for determination of mass to charge ratio. Ions may be accelerated to a larger orbital radius by application of a sinusoidally oscillating spatially uniform electric field perpendicular to B . Acceleration to a larger radius serves two purposes. The first is to group the ions together into a coherent ion packet so that they induce a charge on the conductive detection plates in the cell; the second is to increase their radius so that this charge is large enough to be detected.³³ The cyclotron motion of a single ion packet is detected as a sinusoidally oscillating electric field, the frequency of which corresponds to the cyclotron frequency of the ions. If the applied excitation frequency is constant, the ions

with a corresponding cyclotron frequency will be excited by it. However, the process of turning on and off the excitation voltage results in the excitation of other frequencies. Therefore, brief application of a single excitation frequency will accelerate ions with a broad range of cyclotron frequencies. However, the ions of different cyclotron frequencies are not excited in equal amounts, that is, excited with an uneven excitation curve. A superior means of exciting ions over a broad range of cyclotron frequencies is by application of a frequency sweep (chirp) excitation.³⁴ This form of excitation applies a radio frequency voltage that varies in frequency from low to high over the period of excitation, allowing ions of multiple frequencies to be excited over a relatively flat excitation curve with a lower excitation voltage than what would be required at a single frequency.³³

Ion Trapping and Perturbation of Ion Motion

Ions in the cell are trapped in the x and y directions by the magnetic field applied in the z direction, but the magnetic field alone cannot confine them along the z axis. A small electrostatic potential allied at each end of the cell prevents ions from escaping parallel to the magnetic field by creation of an electric field which traps the ions axially. However, finite electrodes cannot produce a truly spatially homogeneous electric field. Imposition of a direct current (DC) trapping potential that is not spatially homogeneous produces a radial force described by

$$F = qE(r) = \frac{qV\alpha}{a^2}r \quad 2.8$$

in which r is the radial position of the ion in the x-y plane, V is the potential difference between the charged end caps, a is the separation distance of the end caps, and α is a constant depending on trap shape. This phenomenon occurs because the electric field applied by the end electrodes is stronger in the radial center of the trap than it is at the edges of the trap.

Due to this force, the DC trapping potential effectively reduces the ion cyclotron frequency. This alteration of the ions' motions can be corrected for through a mass calibration equation³⁵

$$m/z = \frac{A}{\nu} + \frac{B}{\nu^2} \quad 2.9$$

in which A and B are constants derived from the known m/z of at least two calibrant ions and ν is the ion cyclotron frequency. Analyte and calibrant ions experience the same level of perturbation during the same experiment. Therefore, calibration by use of this equation with an internal calibrant is very effective.

9.4 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer

A home-built 9.4 T FT-ICR MS which was used to acquire the FT-ICR mass spectral data shown in Chapter 3. The Instrument is equipped with a passively shielded Oxford 9.4 T superconducting magnet^{36,37} and is controlled by a modular ICR data acquisition system (Predator.)^{38,39} Charged solvent droplets generated at atmospheric pressure through electrospray ionization (ESI) enter the instrument through a heated metal capillary, which desolvates the droplets, generating ions.

The ion optics and stages of differential pumping are shown in Figure 2.1. Past the capillary is the first stage of vacuum pumping, which is operated at around 2 Torr. After passing through the skimmer, the ions enter a radio frequency (rf)-only octopole, the second stage of differential pressure, operated around 3×10^{-3} Torr. Ions are accumulated here (0.1-10s)⁴⁰ then transferred through a quadrupole (mass-transfer mode) to a second rf-only octopole. In this region, ions are accumulated for around 1 ms and collisionally cooled by helium gas at 3×10^{-3} Torr. Three further octopole ion guides, operated between 1.5-2.0 MHz and 170-240 V_{p-p} rf

amplitude, facilitate transfer of ions to an open cylindrical Penning ion trap. Multiple time-domain acquisitions are co-added, Hanning-apodized, and zero-filled. They are then fast Fourier transformed prior to magnitude calculation and frequency conversion to mass-to-charge ratio to obtain the final mass spectrum.⁴¹

Figure 2.1. Schematic of ion optics and vacuum chambers of the 9.4 T FT-ICR mass spectrometer located at the National High Magnetic Field Laboratory at Florida State University in Tallahassee, Florida. Pressures within each stage of pumping are shown. Multiple stages are necessary to achieve the low pressures required within the cell. Octopole 2 is operated at a higher pressure due to helium introduced for collisional cooling.

Electrospray Ionization (ESI)

Figure 2.2 depicts an ESI source similar to what was used to collect the mass spectral data shown in Chapter 3.⁴² An electrospray apparatus consists of a small needle, to which an electric potential is applied. A syringe pump is used to flow analyte solution through the needle, where it absorbs charge. Polarization along the surface of the solution causes the liquid to be drawn into a cone shape (Taylor cone)⁴² at the tip of the needle. At the tip of the cone, a jet of

liquid is ejected. The liquid breaks into small multiply-charged droplets, which are dispersed radially by their like charges. Droplets are attracted to the front of the instrument, where a counter-electrode is applied (usually operated at ground.) Some of the charged droplets pass into the heated capillary at the front of the mass spectrometer, where their solvent is evaporated and their charge concentrated.

Figure 2.2. Diagram of the ESI process. Ions are ejected from the charged needle then enter the heated capillary where solvent is evaporated. As solvent is removed, the charge becomes more concentrated until the repulsive force of the charge exceeds the surface tension of the solvent droplets. The droplet splits apart, and the process repeats until only ions remain. The charged droplets and ions are guided into the instrument by their attraction toward the counter electrode.

When the charges within the droplets become too concentrated, the coulomb repulsion of the contained charges becomes greater than the surface tension of the droplet. The droplets then break apart into smaller droplets, and the process repeats itself.⁴³ Gas phase ions are formed by one of two proposed methods: either the solvent continues to evaporate from the droplet until only individual charged molecules remain, some of which will be analyte molecules; or the daughter droplets eventually become small enough with high enough charge that ions at their surfaces can be desorbed into the surrounding gas.⁴⁴ The primary advantage of ESI is that it

allows for liquid-phase samples to be easily and non-destructively converted to the gas phase. ESI also allows for analysis of high-mass molecules because it is capable of generating multiply-charged species with an m/z well within the range of most MS techniques. The primary disadvantage of ESI is its inability to ionize nonpolar species efficiently. However, polar species are often the most problematic in terms of petroleum production and refining, so this may be advantageous in some situations, as is the case in the experiments shown in Chapter 3.

Data Analysis

With petroleum samples, individual elemental formulas (peaks) are generally classified by their heteroatom class and double bond equivalents (DBE). Peaks within an individual heteroatom class will all have the same non-carbon, non-hydrogen elements in their chemical formula. Double bond equivalents is the number of rings plus double bonds to carbon within a molecule and is given by

$$\text{Double Bond Equivalents} = C - \frac{H}{2} + \frac{N}{2} + 1 \quad 2.10$$

where C, H, and N are the number of carbon, hydrogen, and nitrogen atoms in a molecule. DBE is a measure of hydrogen deficiency within the molecule. Elemental formulas of the same heteroatom class with the same DBE are said to belong to the same homologous series, i.e. $C_{10}H_{12}O$ would belong to the O_1 class and would have a DBE of 5. All other molecules in the O_1 class with a DBE of 5 would belong to the same homologous series as $C_{10}H_{12}O$.

It is often convenient to convert mass spectra from IUPAC mass scale to Kendrick mass scale, which is based on $CH_2 = 14.0000$ Da.⁴⁵

$$\text{Kendrick Mass} = \text{IUPAC Mass} \times \left(\frac{14.00000}{14.01565} \right) \quad 2.11$$

The advantage offered by this mass scale is that all ions within a given homologous series will differ by multiples of exactly 14 Da. They will also have the same Kendrick mass defect (KMD).

2.12

Use of a Kendrick mass scale allows mass spectral peaks to be organized into homologous series based on their KMD without identification of their molecular formulas. For petroleum samples, where a homologous series often spans the entire mass distribution, internal calibration can be performed based on homologous series identified by their KMD. That is, if the identity of a single peak is known, calibration can often be performed across the entire molecular weight distribution.

Figure 2.3. Double bond equivalents vs. carbon number plots for the NO₂ classes of two petroleum samples. All NO₂ compounds are plotted on the same scale. Though both of these plots depict the same heteroatom class, the collections of molecules occupy different compositional spaces due to differences in the crude oils.

The Kendrick mass scale allows molecular formulas to be assigned for almost all of the peaks in a petroleum mass spectrum. However, the issue remains of how to organize and present the data in such a way as to highlight similarities and differences between samples. A commonly used tool for this is double bond equivalent vs. carbon number plots. These plots are useful for displaying petroleum mass spectral data because they provide a rough measure of the distribution of molecular sizes and aromaticities. Figure 2.3 is an example of two DBE vs. carbon number plots.

CHAPTER THREE

EXPERIMENTAL METHODS

Samples

A sample of produced water was obtained from the water dump of a Canadian SAGD pilot plant. All solvents were procured from known commercial sources and were used as received. For visual evaluation of extraction efficiency, fluorometric analysis, and mass spectrometric analysis, five produced water extracts were prepared. Approximately 80 mL of produced water sample was measured in a graduated cylinder, acidified with 2 mL of concentrated hydrochloric acid, and gently shaken. The cyclohexane/butyl acetate (7:3, v/v) was added to the graduated cylinder at 10% of the recorded volume of the water sample (8 mL). The graduated cylinder was capped and shaken for 1 minute, and the layers were allowed to separate. A portion of the top layer was analyzed for bitumen content by use of the TD-500D fluorometer. This value was recorded as the total oil and grease (TOG.) The TOG extraction and measurement was repeated with dichloromethane, *n*-hexane, and cyclohexane. A 1.5 mL aliquot of the organic layer from the cyclohexane/butyl acetate (7:3, v/v) extraction was transferred to a 10 mL graduated cylinder, and 1.5 mL of 50% aqueous sodium hydroxide (NaOH) solution was added. The cylinder was capped and shaken, and the layers were allowed to separate. A portion of the top layer was analyzed for bitumen content with a TD-500D fluorometer. This value was subtracted from the TOG value, and the difference was recorded as the WSO value. All extracts except dichloromethane were dried under N₂ gas to remove extraction solvents, and then re-dissolved in toluene to a concentration of 1 mg/mL. For negative-ion electrospray, a 200 µL aliquot of each sample was spiked with 200 µL of 2% ammonium hydroxide (NH₄OH) in methanol to facilitate deprotonation of the acidic species to yield [M-H]⁻ ions. Final

concentration of solution for negative-ion electrospray was 500 ppm sample and 1% ammonium hydroxide. For positive-ion electrospray, another 200 μ L aliquot of each sample was spiked with 200 μ L of 2% formic acid (HCOOH) in methanol to facilitate protonation of the basic species to yield $[M+H]^+$ ions. Final concentration of solution for positive-ion electrospray was 500 ppm sample and 1% formic acid.

Mass Spectrometry

The four samples were analyzed with a custom built FT-ICR mass spectrometer.⁴⁶ A modular ICR data acquisition system (Predator) was used to acquire high resolution mass spectra.³⁸ Each sample was delivered to the mass spectrometer electrospray ionization (ESI) source⁴⁷ via a syringe pump at a rate of 500 nL/min through a 50 μ m inner diameter fused silica micro-ESI needle under typical ESI conditions (2.0 kV; tube lens, 350 V; heated capillary current, 4.20 A). Ions generated at atmospheric pressure from ESI enter the skimmer region at approximately 2 Torr through a heated metal capillary into the first radio frequency (rf)-only octopole. Ions pass through a quadrupole to a second octopole, in which they accumulate for 200-1000 ms.⁴⁰ Helium gas introduced during accumulation collisionally cools the ions for efficient transfer through a 91 cm rf-only octopole into a capacitively coupled open cylindrical Penning ion trap (10 cm inner diameter, 30 cm long). Octopole ion guides were operated at 2.0 MHz and 240 V_{p-p} rf amplitude. Broadband frequency chirp excitation (700-70 kHz at a sweep rate of 50 Hz/ μ s and amplitude, $V_{p-p} = 700$ V) accelerates the ions to a cyclotron orbital radius detected by the differential current induced between two opposed electrodes of the ICR cell. Multiple (100) time-domain acquisitions were co-added for each sample, Hanning-apodized, and zero-filled once prior to fast Fourier transform and magnitude calculation.⁴⁸

Mass Analysis

All mass spectra were externally calibrated with Agilent G2421A electrospray HP mix followed by internal calibration with respect to the most abundant homologous alkylated series for each sample.⁴⁹ Singly charged ions with a relative abundance greater than 6 times the standard deviation of the baseline root-mean-square (rms) noise were Kendrick sorted ($\text{CH}_2=14.0000$ Da) and imported into Microsoft Excel for identification with a formula calculator as per a previously reported procedure.¹¹

CHAPTER FOUR

RESULTS AND DISCUSSION

Visual Evaluation of Solubility

For visual examination of the solubility of bitumen in *n*-hexane, cyclohexane, dichloromethane and cyclohexane/butyl acetate (7:3, v/v), 100 ppt and 100 ppm solutions of bitumen in each solvent were prepared by dissolution of 1 g and 1 mg in 10 mL of solvent. At 100 ppt, the bitumen completely dissolved in dichloromethane, cyclohexane, and cyclohexane/butyl acetate (7:3, v/v) but left a thick precipitate in *n*-hexane (Figure 4.1).

Figure 4.1. Visual comparison of solubility of bitumen in various solvents at same (high; 100ppt) bitumen concentration (left to right- cyclohexane/butyl acetate (7:3, v/v), cyclohexane, methylene chloride, *n*-hexane).

At 100 ppm, a concentration more likely to be encountered in produced water, the bitumen completely dissolved in dichloromethane, cyclohexane, and cyclohexane/butyl acetate (7:3, v/v), but left behind a colloidal precipitate in *n*-hexane (Figure 4.2).

Figure 4.2. Visual comparison of solubility of bitumen in various solvents at same (low: 100 ppm) bitumen concentration (Left to right- *n*-hexane cyclohexane, methylene chloride, cyclohexane/butyl acetate (7:3, v/v)).

The extracts and water from the extractions with *n*-hexane, cyclohexane, and cyclohexane/butyl acetate (7:3, v/v) were also visually examined. Darkness of the extract and water clarity were chosen as criteria because molecules that fluoresce also absorb UV light and appear colored. It was therefore reasoned that the darker the extract and cleaner the water, the more efficient the extraction. Emulsion tendency was chosen as a criterion because solutes are not distributed homogeneously throughout an emulsified sample, which may result in inaccuracies in the fluorometric measurement. Based on visual inspection of the physical

properties of the extracts, the cyclohexane/butyl acetate (7:3, v/v) mixture was clearly the best extraction solvent (Figure 4.3 and Table 4.1).

Figure 4.3. Visual comparison of produced water extracts obtained by use of various solvents. (Left to right- *n*-hexane, cyclohexane, methylene chloride, cyclohexane/butyl acetate (7:3, v/v))

Table 4.1. Visual assessment of characteristics of produced water extract obtained by use of different extraction solvents.

Solvent	Darkness of Extract	Water Clarity	Emulsion
<i>n</i> -hexane	Very pale	colored	Yes, tight
Cyclohexane	pale	colored	Yes, tight
Methylene chloride	dark	colorless	Yes, very tight
Cyclohexane/ butyl acetate (7:3, v/v)	dark	colorless	Yes, slight, easily broken

The extract from the cyclohexane/butyl acetate (7:3, v/v) mixture was the darkest and yielded the cleanest water after extraction. Cyclohexane and *n*-hexane both produced very pale,

highly emulsified extracts and yielded highly colored water. Although the methylene chloride extract was very dark and the water was clean, the extract was the most emulsified of all the samples (Figure 4.3).

Fluorometric Analysis

For calibration of the TD-500D fluorometer, a 1 ppt solution of standard bitumen in cyclohexane/butyl acetate (7:3, v/v) was prepared by addition of 10 μ L bitumen to 10 mL of the solvent mixture. This fluorometer was used to measure the fluorescence levels to determine the content of bitumen in the produced water sample extracts.

Of the solvents used, the cyclohexane/butyl acetate (7:3, v/v) mixture produced the highest bitumen in water reading of 160.5 ppm, whereas methylene chloride, cyclohexane, and *n*-hexane produced significantly lower values (Table 4.2). The relative order of these measured values was in agreement with the visual assessment completed above.

Table 4.2. Bitumen (ppm; v/v) in produced water measured with fluorometric analysis.

Extraction solvent	Bitumen in water
cyclohexane/butyl acetate (7:3, v/v)	160.5 ppm
Methylene chloride	98.2 ppm
Cyclohexane	49.6 ppm
<i>N</i> -hexane	38.0 ppm

Determination of WSO

Despite the overall nonpolar nature of bitumen, several constituent polar classes exhibit significant water solubility. With respect to the operational and environmental implications of this WSO component it is often desirable to determine WSO content in the TOG. WSO determination is typically achieved by acidification of the water followed by extraction of the TOG with *n*-hexane following, measurement of the TOG, removal of WSO from TOG with silica gel and re-measurement of the modified TOG (TOG_m). The difference in these measurements is accepted as WSO content (i.e. $WSO = TOG - TOG_m$). The theoretical reasoning for this process is that the more polar WSO will adsorb onto the silica gel and will be removed from the solution when it is re-measured. One potential issue with this measurement is that all molecules with polar constituents (alcohols, thiols, carboxylic acids, etc) will adsorb onto the silica gel regardless of their water solubility. Attempts at isolating WSO from the TOG extracted from SAGD fluid with cyclohexane/butyl acetate (7:3, v/v) failed to produce any meaningful results. This effect is most likely because the more polar cyclohexane/butyl acetate mixture prevented the adsorption of the WSO onto the silica gel. Due to the inability to measure WSO content accurately in the cyclohexane/butyl acetate (7:3, v/v) extract of the SAGD fluid, an alternative method for the determination of WSO needed to be developed if this technique is to be used.

In the determination of TOG, the first step upon sample collection is the acidification of the water. Acidification protonates and neutralizes the charge on the WSO compounds which allows them to be extracted by the organic solvent. Presumably most of what is extracted by this method is acidic species. Once the WSO compounds are extracted from the water and the TOG measured, it is reasoned that the WSO components can be put back into the aqueous phase upon

treatment with a base. Reaction of the acidic species with a base removes a proton to regenerate a charged, water soluble species (Figure 4.4).

Figure 4.4. Reversible acid-base reaction to form oil solubles (neutral) or oil insolubles (charged).

After the initial extraction and measurement is completed with the organic solvent to determine TOG, a concentrated solution of sodium hydroxide (50 wt% in H₂O) is added to the extract and the mixture shaken. Upon separation, the top organic layer is re-analyzed for oil content (TOG_{base}). This value was then subtracted from the initial TOG measurement and the difference (TOG- TOG_{base}) recorded as the WSO content.

The validity of the base extraction method to determine WSO content was examined on a produced water sample obtained from the field which was divided in three parts. The first third of the water was first filtered (0.45 μ m filter), acidified (HCl acid; pH2), solvent extracted (*n*-hexane), and the organic content determined by fluorometry. In this case, the organic content of the water can be assumed to be all WSO as the dispersed organics would be removed with the filter. The second third of the sample was directly acidified, extracted, and the TOG was determined. The WSO (TOG- TOG_{base}) was determined by alkalization of the organic layer with 50% NaOH(aq) and re-measurement of the fluorescence of the organic layer (TOG_{base}). For comparison, the WSO content for the final third of water was determined by use of the standard silica gel method. In this analysis, the sample was acidified (hydrochloric acid; pH2), extracted

with *n*-hexane (the butyl acetate/cyclohexane mixture was found to be too polar in several instances) and the TOG of the extract was measured. Silica gel was then added to the extract, the extract re-analyzed (TOG_m) and WSO calculated in the standard way (TOG- TOG_m).

The base extraction method produced a WSO value of 3.5 ppm, and filtration method also produced a WSO value of 3.2 ppm (Table 4.3). These values are very similar, which supports the accuracy of the base extraction method for the determination of WSO content. The WSO value for the filtration measurement is assumed to be the true value, as all water soluble organics should remain in the water and therefore pass directly through the filter. The silica gel method produced a WSO value of 78.5 ppm, much higher than the base extraction and filtration methods. If this measurement were accurate, the filtration method would have yielded a WSO value much closer to that of the filtration method because this material should have passed through the filter. Instead, the more likely reason for the high WSO value obtained with the silica gel method was adsorption of dispersed organics with polar constituents onto the silica, followed by subsequent measurement as WSOs.

Table 4.3. Comparison of WSO determination methods.

Method	TOG	WSO
Silica gel	88.8 ppm	78.5 ppm
Base extraction	83 ppm	3.5 ppm
Filtration	-	3.2 ppm

Turbidity Study

Turbidity is an expression of the optical property of a sample and involves passing visible light through an oily sample. Turbidity measurement is a well-established industry practice to monitor water quality and involves measuring the average volume of light scattered in an oily sample over a defined angular range. The presence of particles causes light to be scattered and absorbed, and a reduced amount would be than transmitted. Turbidity is therefore a measure of relative sample clarity.

Figure 4.5. Relationship between TOG (cyclohexane/butyl acetate) and turbidity for SAGD produced waters measured over 36 hour period.

Turbidity is measured in Nephelometric Turbidity Units or NTU, which represents the average volume scattering over a defined angular range, and is a function of particle size and concentration of suspended solids as well as total dissolved solids. The instruments measure concentration of suspended solids, often in parts per million. Turbidity measurements were performed with a Hach hand-held EPA compliant turbidity meter.

Figure 4.6. Relationship between WSO (basified extraction) and TOG (cyclohexane/butyl acetate) for SAGD produced waters monitored over 36 hour period.

The TOG and WSO content of a SAGD system was monitored over the span of 36 hours with the new test method (cyclohexane/butyl acetate extraction of TOG and basification for extraction of TOG_{base}). The measured TOG values were found to correlate significantly though

not strongly ($R^2=0.6372$) with the measured turbidity of the produced water (Figure 4.5). As turbidity is often used to monitor hydrocarbons in water, this correlation indicates that the new protocol is a valid method to monitor bitumen in water.

There was a strong positive correlation ($R^2 = 0.9711$) between TOG values and the WSO values (Figure 4.6). As the ratio of WSOs to TOG in produced water is expected to remain relatively constant during stable production, this strong correlation further validates the new extraction protocol for this produced water sample.

Mass Spectrometry

The three produced water extracts and the sodium hydroxide back-extract were analyzed by positive and negative ion ESI FT-ICR MS to identify and characterize the dissolved organic species. Figure 4.7 shows the relative abundance graph of the acidic oxygen species from *n*-hexane extract, cyclohexane extract, cyclohexane/butyl acetate (7:3, v/v) extract, and sodium hydroxide back-extract. The relative abundance of O_2 is greater than those of other oxygen species in the *n*-hexane and cyclohexane extracts, which is not the case in cyclohexane/butyl acetate (7:3, v/v) extract. However, it is important to note that the y-axis represents the amount of each class detected relative to the other detected species. In addition to this, ion suppression effects are common in electrospray applications and cause the signal magnitude of more easily ionized analytes to be greater than that of less easily ionized analytes. Although the magnitude of the class relative abundance is not considered to be directly proportional to the concentration of each class in the sample, species with similar chemistries are likely to ionize with similar efficiency. All of the species studied contain oxygen and their ionization in negative ESI is most likely due to deprotonation of carboxylic and other oxygenated acidic functional groups. Because the principle focus of this study is oxygenated species, the results are therefore semi-quantitative

within a single sample analysis. Comparison of class relative abundances between samples requires the addition of an internal standard, and was not pursued in this study in light of the gravimetric results.

Figure 4.7. Qualitative heteroatom class distributions for acidic oxygenated species derived from negative-ion ESI FT-ICR mass spectra for produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate) and sodium hydroxide back-extract. Note that the y-axis is unweighted with respect to the sample weight extracted (which is significantly higher for cyclohexane/butyl acetate (7:3, v/v) extract) and reflects only relative abundance within a sample. Therefore the abundance of a chemical species should be compared against the abundances of other species within the same sample, not against the same species in different samples.

The relative abundances of acidic O₅ through O₈ classes are much greater in cyclohexane/butyl acetate extract, and O₇ and O₈ do not appear in the mass spectrum for

n-hexane and cyclohexane extracts, which indicates that higher oxygen acidic species have much greater solubility relative to other acidic species in cyclohexane/butyl acetate (7:3, v/v) than in *n*-hexane or cyclohexane. The cyclohexane/butyl acetate (7:3, v/v) extraction is able to extract all O_x species up to O_8 with more consistent efficiency, whereas *n*-hexane and cyclohexane preferentially isolate low oxygen O_x species. The sodium hydroxide back-extraction preferentially extracted O_3 and higher species from the organic phase, which suggests that the WSO consists mostly of higher-oxygen species, and crude oil carryover may contribute to O_2 concentrations.

Figure 4.8 shows the relative abundances of the acidic SO_x species from *n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v), and sodium hydroxide back-extract. The relative abundances of SO_1 - SO_3 are greater in the *n*-hexane and cyclohexane extracts. Again, it is important to note that this does not mean that more material is extracted. The relative abundances of SO_5 and higher are much greater in cyclohexane/butyl acetate extract. Some of the higher SO_x species did not produce signal in the *n*-hexane and cyclohexane extracts. As with Figure 4.7, this implies that higher oxygen SO_x species are more soluble relative to other acidic species in cyclohexane/butyl acetate than in *n*-hexane or cyclohexane. Cyclohexane/butyl acetate (7:3, v/v) provides more consistent extraction efficiency with SO_x species up to SO_8 , whereas *n*-hexane and cyclohexane preferentially isolate lower SO_x species. The sodium hydroxide back-extraction preferentially extracted SO_5 and higher species from the organic phase, which suggests that most of higher-oxygen sulfur-containing species are water-soluble, and crude oil carryover probably supplies most of the lower-oxygen SO_x compounds.

Figure 4.8. Qualitative heteroatom class distributions for acidic SO_x classes derived from negative-ion ESI FT-ICR mass spectra of produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract. As in Figure 4.7, the y-axis is unweighted with respect to the sample weight extracted.

Figure 4.7 shows the relative abundance for O₁ and O₂ classes of oxygenated species to be higher for *n*-hexane and cyclohexane extract relative to the other two extracts. The same is true of SO₁-SO₃ in Figure 4.8. However, it is important to note that this only represents their abundance in relation to the other species present within that sample. The DBE vs. carbon number plots (Figures 4.9 and 4.10) show the distributions for O₁, O₂, and SO₁-SO₃ to be equally broad if not broader for cyclohexane/butyl acetate (7:3, v/v) or its back-extract compared with

n-hexane or cyclohexane, which indicates that these classes are extracted at least as efficiently by the cyclohexane/butyl acetate solvent mixture as by *n*-hexane or cyclohexane.

Figure 4.9 shows the negative-ion isoabundance-contoured plots of double bond equivalents ($\text{DBE} = [\#C - 0.5(\text{H}\#) + 0.5(\text{N}\#) + 1]$) versus carbon number for acidic oxygen species from *n*-hexane extract, cyclohexane extract, cyclohexane/butyl acetate (7:3, v/v) extract, and sodium hydroxide back-extract. As can be observed from the contour plots, all three solvents extract acidic O₂ and O₃ species with approximately equal efficiency. For O₄ and higher, the distribution spans across a broader carbon number and DBE distribution for the cyclohexane/butyl acetate extract, which indicates that a broader range of compounds are extracted by this solvent. For O₆ and higher, very little material (none detected) was extracted by *n*-hexane and cyclohexane, whereas cyclohexane/butyl acetate (7:3, v/v) continued to show broad DBE versus carbon number distributions. For O₂, O₃, and O₄ species detected in sodium hydroxide back-extract, similar compositional coverage is seen in terms of DBE to *n*-hexane and cyclohexane. However, at higher carbon number, sodium hydroxide back-extract had a greater number of detectable species than any of the other extracts. In addition, the O₁ species detected from sodium hydroxide back-extract occupy a completely different compositional space than the other extracts. This result is expected for *n*-hexane and cyclohexane as cyclohexane/butyl acetate (7:3, v/v) should provide a better extraction for water-insoluble oil and grease. However, an improvement in compositional coverage over the original cyclohexane/butyl acetate (7:3, v/v) extract is not expected, as material has only been removed between the two extractions.

Figure 4.9. Color-coded iso-abundance contoured plots of DBE (double bond equivalents = number of rings plus double bonds to carbon) vs. carbon number for acidic oxygen classes derived from negative-ion ESI FT-ICR mass spectra of produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract.

This effect is likely due to ion suppression. In negative-ion ESI, at high concentration, the more acidic species will often absorb a disproportionately high amount of charge compared to the weakly acidic species. It stands to reason that the most acidic species would also be very water soluble, so a basic aqueous back-extraction would likely extract many of the species that contribute most to ion suppression. Therefore, the species seen in the sodium hydroxide back-extract are also present in the cyclohexane/butyl acetate (7:3, v/v) extract, but cannot be observed by this method until the more easily ionized species are removed. Back-extraction with sodium hydroxide increases this technique's qualitative applicability, as it allows for analysis by negative-ion ESI MS of both the more easily ionized species and the less easily ionized species, which are not usually visible due to the dynamic range limits of ESI mass spectrometers.

Negative-ion isoabundance-contoured plots of DBE versus carbon number for acidic SO_x species (Figure 4.10) from *n*-hexane extract, cyclohexane extract, and cyclohexane/butyl acetate (7:3, v/v) extract show these solvents to be equally effective at extraction of acidic SO_2 species as can be observed from the contour plots. For SO_3 and higher, the compounds detected in cyclohexane/butyl acetate (7:3, v/v) extract span across a broader carbon number and DBE distribution for the cyclohexane/butyl acetate extract, which indicates that a broader range of compounds are extracted by this solvent. For SO_6 and higher, a very small or undetectable amount of material was extracted by *n*-hexane and cyclohexane, whereas cyclohexane/butyl acetate (7:3, v/v) continued to show a broad DBE versus carbon number distribution.

Figure 4.10. Color-coded iso-abundance contoured plots of DBE (double bond equivalents = number of rings plus double bonds to carbon) vs. carbon number for acidic SO_x classes derived from negative-ion ESI FT-ICR mass spectra of produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract. Classes with below 0.5% relative abundance are not shown.

For SO_2 and SO_3 , the sodium hydroxide back-extract shows similar DBE coverage to *n*-hexane and cyclohexane. However, sodium hydroxide back-extract had better carbon number coverage than any of the other extracts. In addition, the SO_1 and SO_4 species for sodium hydroxide back-extract occupy a completely different compositional space than the other extracts. This result is expected for *n*-hexane and cyclohexane, but an improvement in compositional coverage over the cyclohexane/butyl acetate (7:3, v/v) extract is not expected. This effect is again likely do to ion suppression mechanisms as described above.

Figure 4.11. Qualitative heteroatom class distributions for basic NO_x classes from positive-ion ESI FT-ICR mass spectra *n*-hexane extract, cyclohexane extract, and cyclohexane/butyl acetate (7:3, v/v) extract. Classes with below 0.5% relative abundance are not shown. As in previous graphs, the y-axis is unweighted with respect to the sample weight extracted.

The relative abundance graph of the basic NO_x species from produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) (Figure 4.11) shows that the relative abundance of NO₁ is greater in the *n*-hexane and cyclohexane extracts. Relative abundances of basic NO₂ and NO₃ compounds are greater in the cyclohexane/butyl acetate (7:3, v/v) extract, whereas NO₄ through NO₇ do not appear in the mass spectrum for *n*-hexane and cyclohexane extracts. This difference indicates that higher oxygen basic NO_x species have much greater solubility in relation to other basic species in cyclohexane/butyl acetate (7:3, v/v) than in *n*-hexane or cyclohexane. As with O_x and SO_x in the acidic species, the cyclohexane/butyl acetate (7:3, v/v) extraction is able to extract basic NO_x (NO₁–NO₈) with more consistency. This solvent shows less preference for one heteroatom class over another, whereas *n*-hexane and cyclohexane preferentially isolate low oxygen NO_x species.

Figure 4.12 shows the relative abundance graph of the basic SO_x classes from *n*-hexane extract, cyclohexane extract, and cyclohexane/butyl acetate (7:3, v/v) extract. The abundances of all SO_x species are higher with respect to other heteroatom classes for the cyclohexane/butyl acetate (7:3, v/v) than for the *n*-hexane or cyclohexane extracts. SO₆ and SO₇ do not show significant signal in the *n*-hexane and cyclohexane extracts, which implies that higher-oxygen SO_x species (SO₄–SO₇) are more soluble relative to other basic species in cyclohexane/butyl acetate than in *n*-hexane or cyclohexane. Again, cyclohexane/butyl acetate (7:3, v/v) appears to provide more consistent extraction efficiency at higher oxygen number. This solvent shows less preference for one heteroatom class over another, whereas *n*-hexane and cyclohexane preferentially isolate lower SO_x species.

Figure 4.12. Qualitative heteroatom class distribution for basic SO_x classes derived from positive-ion ESI FT-ICR mass spectra of produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)) and sodium hydroxide back-extract. Classes below 0.1% relative abundance are not shown. As in previous class distribution graphs, the y-axis is unweighted with respect to the sample weight extracted.

Figure 4.13 shows the positive-ion isoabundance-contoured plots of DBE versus carbon number for basic NO_x species from *n*-hexane, cyclohexane and cyclohexane/butyl acetate (7:3, v/v) produced water extracts.

Figure 4.13. Color-coded iso-abundance contoured plots of DBE [(DBE = C# – 0.5(H# + N#) + 1)] vs. carbon number for basic NO_x classes derived from positive-ion ESI FT-ICR mass spectra of produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)). Sodium hydroxide back-extract showed too low spectral coverage to display a plot for any shown classes. Classes with below 0.5% relative abundance are not shown.

For NO_1 species, the distribution spans across a broader carbon number and DBE distribution for *n*-hexane and cyclohexane, which indicates that a broader range of compounds are extracted by these solvents. *N*-hexane and cyclohexane appear to be better extractants for NO_1 species, which makes sense as these species would likely be less polar than species that contain a greater number of oxygens. All three solvents are equally effective at extraction of basic NO_2 species, as can be observed from the contour plots. For NO_3 cyclohexane/butyl acetate (7:3, v/v) extract showed slightly better coverage in terms of DBE. For NO_4 and higher, very little material was extracted by *n*-hexane and cyclohexane, whereas the cyclohexane/butyl acetate (7:3, v/v) extract continued to show broad DBE versus carbon number distributions all the way up to NO_8 .

Figure 4.14 shows the positive-ion isoabundance-contoured plots of DBE versus carbon number for basic SO_x species from *n*-hexane, cyclohexane and cyclohexane/butyl acetate (7:3, v/v) produced water extracts. All three solvents are equally effective at extraction of acidic SO_2 - SO_3 species as can be observed from the contour plots. For SO_1 , cyclohexane/butyl acetate (7:3, v/v) extract shows slightly better compositional coverage at high DBE and carbon number. For SO_4 and higher, class distributions above 0.5% were only observed for the cyclohexane/butyl acetate (7:3, v/v) extract and could not be seen for any other extract, which indicates that higher-oxygen containing sulfur compounds are more efficiently extracted by this solvent.

Figure 4.14. Color-coded iso-abundance contoured plots of DBE (double bond equivalents = number of rings plus double bonds to carbon) vs. carbon number for basic SO_x classes derived from positive-ion ESI FT-ICR mass spectra of produced water solvent extracts (*n*-hexane, cyclohexane, cyclohexane/butyl acetate (7:3, v/v)). Sodium hydroxide back-extract showed too low spectral coverage to display a plot for any shown classes. Classes with below 0.5% relative abundance are not shown.

FT-ICR mass analysis of sodium hydroxide back-extract by positive-ion ESI failed to produce meaningful results, and is therefore not shown. Given that only acidic species should be removed during the back-extraction, it is assumed that the mass spectrum for sodium hydroxide back-extract should look very similar to that of cyclohexane/butyl acetate (7:3, v/v) extract. Therefore, a positive-ion electrospray mass spectrum would not provide data useful to this experiment, and further data collection on this sample was not pursued.

CHAPTER FIVE

CONCLUSION

The negative-ion ESI FT-ICR MS data show that cyclohexane/butyl acetate (7:3, v/v) is more effective at extraction of acidic O_x and SO_x species than *n*-hexane or cyclohexane. The positive-ion ESI FT-ICR MS data point to a similar conclusion. Thus, the gravimetric results suggest that cyclohexane/butyl acetate (7:3, v/v) is a better extraction solvent for more polar species of interest in the produced water samples, and the FT-ICR MS results confirm that the number of polar classes and the compositional diversity of these classes are greater for the cyclohexane/butyl acetate (7:3, v/v) extraction solvent. The positive-ion ESI FT-ICR MS data show that cyclohexane/butyl acetate (7:3, v/v) is more effective at extraction of basic NO_x and SO_x species than *n*-hexane or cyclohexane. Along with gravimetric data and fluorescence data, these data indicate that cyclohexane/butyl acetate (7:3, v/v) solvent extraction of produced water is a more viable method for determination of WSO species and holds potential for WSO determination in petroleum applications which involve produced water streams.

A detailed comparison has been given of various methods of extraction of polar species from produced water. A mixture of cyclohexane/butyl acetate (7:3, v/v) is recommended as an efficient alternative to common current practices of extraction with solvents such as *n*-hexane and cyclohexane. Visual observation and fluorometry measurements on the cyclohexane/butyl acetate (7:3, v/v) deem this extraction method as superior to the dichloromethane, *n*-hexane, and cyclohexane extractions. Ultra-high resolution FT-ICR MS analysis of produced water extracts provides a detailed landscape of the water soluble organic species, and confirms that the cyclohexane/butyl acetate (7:3, v/v) mixture is more efficient than *n*-hexane or cyclohexane at

isolation of polar, oxygen-containing hydrocarbons of the type that are readily identified in production deposits. The cyclohexane/butyl acetate mixture is much more efficient at extraction of hydrocarbon species with five or more oxygen atoms. It provides a broad DBE versus carbon number distribution up to O₉, whereas *n*-hexane and cyclohexane are only effective up to O₅. Similar observations are made for the polar acidic and basic SO_x basic NO_x classes as well. Back-extraction of cyclohexane/butyl acetate (7:3, v/v) with aqueous sodium hydroxide efficiently removes water soluble organics from this solvent. Mass spectral results from the back-extracted solvent show that cyclohexane/butyl acetate (7:3, v/v) is also more efficient at extraction of lower oxygen containing species, as can be seen when the more acidic species are removed. The cumulative results suggest that a cyclohexane/butyl acetate (7:3, v/v) mixture is a better solvent for the quantitative extraction and analysis of WSO in produced water.

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BIOGRAPHICAL SKETCH

Adam Lewis was born in Conroe, TX in 1988. From 2006 to 2010, he attended the University of South Alabama, in Mobile, AL, where he obtained a B.S degree in chemistry. In Fall, 2010, he began graduate school at Florida State University, and in Spring, 2011, he joined Dr. Alan Marshall's research group. Adam obtained his M.S. degree from FSU in Spring, 2013.