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Isolation and Characterization of Oil-Soluble Calcium Naphthenates in North Sea Heavy Crude Oil

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Preface

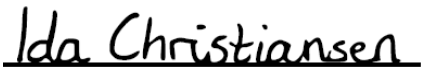
This master thesis was given by Statoil ASA in cooperation with Norwegian University of Science and Technology (NTNU), Faculty of Natural Sciences and Technology, Department of Chemical Engineering. The thesis was part of a specialization in Colloid and Polymer Chemistry, and was conducted in the period from 20th of January to 16th of June 2014. The work was carried out at Statoil's Research Centre at Rotvoll in Trondheim, Norway.

I would like to thank my supervisors at Statoil, Knut Vebjørn Grande, Heidi Mediaas and Hege Kummernes. Knut and Heidi helped me throughout the process when I had questions regarding the theory behind my work. Hege was very helpful to me during my laboratory work, and guided me through the different methods. I would also like to thank Jørn Jacob Grubbe Haugen for all the help in the laboratory, and Gunhild Neverdal for analyzing my samples with mass spectroscopy and processing them. I would never have been able to finish this master thesis without their help. Lastly I would like to thank my supervisor at NTNU, Johan Sjöblom for the guidance and help throughout the process.

Declaration of compliance

I, Ida Christiansen, declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

NTNU, Trondheim, Norway, 16.06.2014



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Abstract

Naphthenic acids are a diverse group of saturated mono- and polycyclic carboxylic acids that may account for as much as 10-12 weight % of crude oil. During production at several newer oil fields, there have been discoveries of oil that have very high acid and calcium content. This indicates that there are some naphthenic acids bound to calcium as calcium naphthenates present in the oil, and that these are oil-soluble.

Oil-soluble calcium naphthenates can cause problems during refinery, as the calcium present can lead to fouling and catalytic deactivation. The coke and fuel quality will also be affected. The removal of calcium in the refinery can be an expensive and comprehensive process, which results in the suppliers getting a lower price on their crude oil.

In this master thesis, naphthenic acids from non-soluble calcium naphthenates have been isolated by using an ion exchanger method and a Solid Phase Extraction-method. The work also consisted of neutral and acidic washing of the samples, measurements of water-content, Ca-content and total acid numbers. The different phases from the isolations have also been analyzed by using FT-IR Spectroscopy, APPI-MS and ESI-MS for characterization to see if the naphthenic acids bound to calcium differ from other acids.

The naphthenic acids that are bound to calcium in the crude oil have a higher average molecular weight than the other naphthenic acids, at 875 and 580 g/mole respectively. This result was confirmed by TAN-measurements and APPI-MS of samples after isolation with the Acid-IER method. The correlation between the TAN-measurements and the results from APPI-MS suggest that the acids can be characterized as monoacids. They do not have a particular molecular weight, but have a broad distribution between 150 and 2000 g/mole. It seems that the calcium naphthenate formation is controlled by the total amount of acids in the oil, their molecular weight and pH, and not as much on structure as first were presumed.

Sammendrag

Naftensyrer er en sammensatt gruppe av mettede mono-og polysykliske karboksylsyrer som kan utgjøre så mye som 10-12 vekt% av råolje. I løpet av produksjon ved flere nye oljefelt har det blitt gjort funn av olje som har svært høyt syre- og kalsiuminnhold. Dette gir en indikasjon på at naftensyrer bundet til kalsium er tilstede i oljen. Naftensyrer kan reagere med kalsium i formasjonsvannet, og danne kalsiumnaftenater som er oljeløselige.

Oljeløselige kalsiumnaftenater kan forårsake problemer som fouling og katalytisk deaktivering under raffinering. Kvaliteten på koks og drivstoff kan også bli påvirket. Fjerning av kalsium i raffineriet kan bli en kostbar og omfattende prosess, som kan resultere i at leverandøren får en lavere pris på råoljen.

I denne masteroppgaven, har naftensyrerer fra oiljeløselig kalsiumnaftenat blitt isolert ved hjelp av en ionebyttermetode og en fastfase-ekstraksjonsmetode. Arbeidet besto også av nøytralvask og syrevask av prøvene, måling av vann-innhold, Ca-innhold og totalt syretall. De forskjellige fasene fra isolering er også blitt karakterisert ved hjelp av FT-IR spektroskopi, APPI-MS og ESI-MS, for for å se om naftensyrene som danner oljeløselige kalsiumnaftenat er forskjellige fra andre syrer i råoljen.

Naftensyrene som er bundet til kalsium i råoljen har en høyere gjennomsnittlig molekylvekt enn de andre naftensyrene. Dette resultatet ble bekreftet av TAN-målinger og APPI-MS av prøvene etter isolasjon med ionebyttermetoden. Korrelasjonen mellom TAN-målingene og resultatene fra APPI-MS tyder på at syrene kan karakteriseres som monosyrer. De har ikke en bestemt molekylvekt, men har en bred fordeling fra 150 til 2000 g/mol. Det ser ut som om dannelsen av kalsiumnaftenat er avhangigav den totale mengden av syre i oljen, deres molekylvekt og pH, og ikke så mye av strukturen som først ble antatt.

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Abbreviations

Acid-IER	Acid Ion Exchange Resin – used for isolation of naphthenic acids
APPI	Atmospheric Pressure Photoionization
ASTM	American Society for Testing and Materials
FT-IR	Fourier Transform Infrared Spectroscopy
KF	Karl Fischer
KOH	Potassium Hydroxide
m/z	Mass to charge ratio
TAN	Total Acid Number – A measurement for the amount of acids in a sample
TBAOH	Tetrabutylammonium hydroxide used for TAN-analysis
WiO	Water in Oil content
SPE	Solid Phase Extraction

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1 Introduction

Naphthenic acids are a diverse group of saturated mono- and polycyclic carboxylic acids that may account for as much as 10-12 weight % of crude oil [1, 2]. In petroleum industry naphthenic acids are referred to as all organic acids in a crude oil, although the term traditionally classifies only the acids with cycloaliphatic derivatives. It is assumed that naphthenic acids have their origin from reservoir biodegradation of hydrocarbons, and they can provide information on the reservoir history. The naphthenic acids are a complex mixture of acids that have variations in molecular weight and structure [1]. Figure 1 presents some possible naphthenic acid structures.

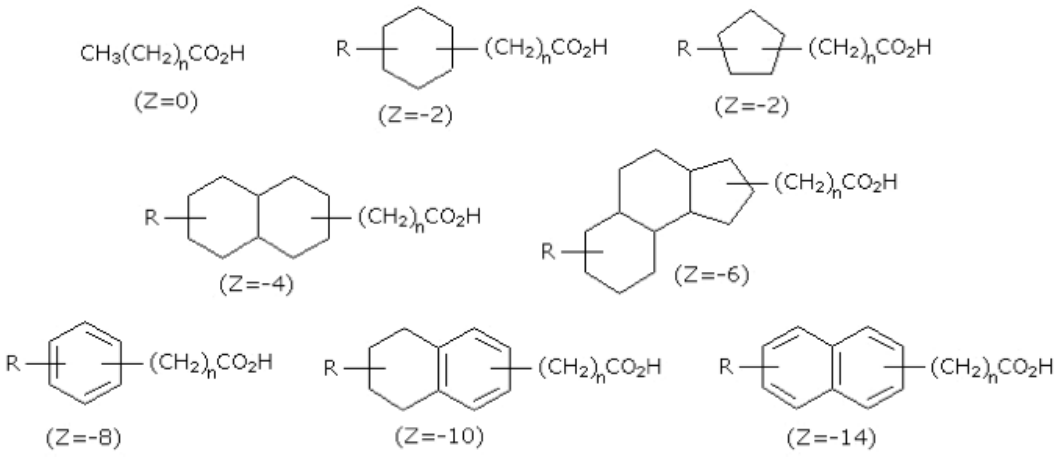

Figure 1 Examples of naphthenic acids structures [1]

The chemical composition of naphthenic acids, with a hydrophilic and a hydrophobic part, makes the acids able to be distributed between the oil and the water phase. Conditions like pH and salinity in the water phase strongly determine the distribution of acids between oil and water [3]. They may also contribute to the formation of stable emulsions due to the high surface tension they get when they merge to the interface between oil and water. At low pH-values, the acids are oil-soluble and will stay in the oil phase. An increase in the pH will dissociate the acids and increase their affinity towards the oil-water interface. The affinity towards the interface also depends on conditions like molecular structure, hydrophilic-lipophilic balance, concentrations and the salinity of the aqueous phase [1].

Naphthenic acids can cause problems during production and processing of oil due to their acidity, which may cause corrosion of the equipment. The corrosion rate increases with the presence of naphthenic acids and reactive sulphur, and it is especially the high temperature parts of the distillation unit that is influenced [4].

During oil production there will be a pressure drop during upstream processing. The pressure drop will lead to degassing of CO_2 following equation (1), which shows how water is naturally saturated with CO_2 in equilibrium with bicarbonate ions.

$$HCO_3^-(w) + H^+(w) \leftrightarrow CO_2(g) + H_2O(w) \quad \textbf{(1)}$$

The degassing will lead to an increase in pH and the naphthenic acids will dissociate and merge to the oil-water interface. If the pH-value is further increased the naphthenic acids can react with metal ions in the formation water and form metal naphthenates. The most common metal in oil production that interacts with naphthenic acids is calcium [5]. The calcium naphthenates that are formed during production can either be oil-soluble or non-soluble. Non-soluble naphthenates will precipitate, and cause problems in piping and equipment. Examples of calcium naphthenates deposits are shown in Figure 2.

Figure 2 Calcium naphthenate deposits[1]

In 2005, work was published that presented the discovery of the so-called ARN-acids, which is a family of 4-protic naphthenic acids with high molecular weight. These acids have a high tendency to react with calcium ions in the formation water to create calcium naphthenates,

which will precipitate at pH-values typically above 6.0 to 6.5 [6, 7]. The discovery explained where the naphthenate deposits in oil production originated from, and gave the industry a new understanding to how the naphthenic acids behaved.

It was believed that the ARN-acids were the main contributor to the formation of calcium naphthenates. However, during production at several newer oil fields, there have been discoveries of oil that have very high acid and calcium content. When treating the oil with an acidic wash, which will convert any calcium naphthenates into free acids, the amount of acids in the oil increased. This gave an indication that there were some naphthenic acids that were bound to calcium present in the oil. These calcium naphthenates however are oil-soluble and will not precipitate.

Oil-soluble calcium naphthenates can cause problems during refinery, as the calcium present can lead to fouling and catalytic deactivation. The coke and fuel quality will also be affected. The removal of calcium in the refinery can be an expensive and comprehensive process, which results in the suppliers getting a lower price on their crude oil [8].

Statoil ASA has a hypothesis that the acids that form oil-soluble calcium naphthenates might have different structures than other acids and that they are di-acids with two acid groups.

The main objective for the current master thesis is to identify and characterize the acids that can form oil-soluble calcium naphthentate. Specifically to investigate if the acid structure and characteristics differ from other naphthenic acids, or if the formation is purely dependent on high pH in the reservoir.

2 Experimental Theory

This chapter presents the theory behind all methods used in this thesis. The chapter is divided into two sections. The first section describes isolation of naphthenic acids that form oil-soluble calcium naphthenates, which includes neutral wash, acidic wash, water-in-oil content, TAN-measurements, isolation by an Acid-IER method and extraction by a SPE-method. The second section presents theory behind methods used to characterize naphthenic acids that form oil-soluble calcium naphthenates, which include mass spectrometry and infrared spectroscopy.

A hazardous activity identification and risk assessment for some of the analysis are given in Appendix D and E.

Characteristics for the North Sea heavy crude used in this thesis are presented in Table 1.

Table 1 Characteristics for the North Sea heavy crude oil

Characteristics		
°API	10.9	
Ca-content	500	[mg/kg]
TAN	9.6	[mg KOH/g oil]
TAN (after acidic wash)	10.6	[mg KOH/g oil]
Viscosity (50 °C)	1291	[mm^2/s]
Density (15 °C)	0.9927	[kg/L]

2.1 Isolation of Calcium Naphthenates

In order for the oil soluble calcium naphthenates to be characterized, it is necessary to isolate them from other naphthenic acids in the oil. The analysis chosen in this thesis is described in this section.

2.1.1 Neutral Wash

Crude oil can often contain impurities and water with metal ions such as calcium and sodium, due to chemicals used during production. In order for naphthenic acids to be properly isolated, these substances need to be removed. This can be done by performing a neutral wash with pH-neutral deionized water, which means that the oil sample is mixed together with neutral water to transfer any impurities from the oil to the water. The water must be neutral to avoid dissociation of the acids present in the crude. The water is removed to make sure that no Ca or other impurities in the water may affect the further experimental work.

At a neutral pH-value however, the concentration of H^+-ions are 1.0 x 10^{-7}, while the concentration of Ca^{2+} may be zero. This means that the equilibrium shown in equation (2) can be shifted towards the right.

$$Ca(RCOO)_2(o) + 2H_2O(w) \leftrightarrow 2RCOOH(o) + Ca^{2+}(w) + 2OH^-(w) \quad \textbf{(2)}$$

If the equilibrium in equation (2) shifts the calcium naphthenates present in the oil can become detached and the naphthenic acids are transferred back into their free form. To avoid this, the neutral wash needs to be done quickly, so that the contact time between oil and water are as short as possible, but still effective enough to remove unwanted impurities and salts.

Ca-content is often measured after neutral wash. Before the analysis is performed it is important to have a low water-in-oil content so that the results only show the calcium present in the oil and not the water. It the Ca-content is still high, an acidic wash can be performed to see if some of the calcium is bound to naphthenic acids.

2.1.2 Acidic Wash

The naphthenic acids that are bound to calcium needs to be released before they can be analyzed. This can be done by an acidic wash, which will dissociate the naphthenates and transfer them into free naphthenic acids, following equation (3).

$$Ca(RCOO)_2(o) + 2H^+(w) \leftrightarrow 2RCOOH(o) + Ca^{2+}(w) \quad \textbf{(3)}$$

An acidic wash can be performed at different stages in the analytical route when isolating acids. If the initial sample contains both free naphthenic acids and calcium naphthenates, the acidic wash should be performed on the non-polar phase after the first isolation. This phase would now only contain of calcium naphthenates without any free acids. The acidic wash will then turn these oil-soluble calcium naphthenates to free acids, and they can be isolated away from the other compounds in the oil. For a reference sample the acidic wash can be performed on the crude oil at the very start. This will give an insight into how many acids that is present in the oil in total, both free and bound to calcium.

2.1.3 Water Content by Karl Fischer Titration

It is important to measure WiO before Ca-content is analyzed to avoid any Ca in the water to interfere with the results. WiO-content below 0.05 wt% is considered to be the limit where the Ca in the water has no influence on the measurement. This limit is also set for TAN-measurements.

The water content of a sample can be measured by using Karl Fischer Titration. This method allows for the content of both free and bound water to be determined, and it can detect both small and large amounts of water [9]. The method uses a so-called Karl Fischer (KF) reagent, which is a solution of iodine and sulfur dioxide in a mixture of a base and methanol. The titration follows equation (4) and (5) .

$$CH_3OH + SO_2 + B \rightarrow [BH]^+SO_3CH_3^- \quad \textbf{(4)}$$

$$H_2O + I_2 + [BH]^+SO_3CH_3^- + 2B \rightarrow [BH]^+SO_4CH_3^- + 2[BH]^+I^- \quad \textbf{(5)}$$

Two different methods of Karl Fischer titration can be used, volumetric titration and coulometric titration. In this master thesis coulometric titration has been used, because it can detect lower amounts of water than the volumetric method. In the coulometric titration an electric current used for regenerating the reagent releases the stoichiometrically corresponding amount of iodine from the iodide-containing KF reagent by electrolysis. The electrolysis follows Faraday's law, given by equation (6).

$$m = \frac{M_w \times Q}{z \times F} \quad \textbf{(6)}$$

where

m	=	mass of converted substance [g]
M_w	=	molar mass [g/mole]
Q	=	measured amount of charge [A·s]
z	=	number of exchanged electrons (equivalence number, charge number)
F	=	electrochemical equivalent, 1F = 96485 [A·s/mole]

The determination of water content by coulometric titration is an absolute method, meaning that because iodine is generated electrolytically there is no need to determine a titer [9].

2.1.4 Total Acid Number by Thermometric Titration

Total acid number (TAN) is defined as the amount of Potassium hydroxide (KOH) in milligram that is required to neutralize the acidity of 1 gram oil. The method gives the total number of acid groups, but does not discriminate between mono-, di- and triacids. The base will titrate all available acid groups in a sample and consider all acids as mono-acids [10].

The TAN analysis is performed with thermometric titration. This is not an ASTM-approved method, but the analysis gives results that can be directly compared to the potentiometric titration found in method ASTM D664 [11]. The reaction that occurs during a titration is either exothermic or endothermic, and the change in temperature can be used to determine the concentration of the sample. The method uses a constant titration speed, while the temperature is constantly being measured. When all of the analyte have reacted with the titrant, the change in temperature (dT/dt) in the solution will change and an equivalent point will be shown in the temperature curve given by the instrument [12].

Total Acid Number can be calculated by using the following equation:

$$TAN = \frac{(V_t - V_b) \times C \times f \times 56.106}{m_s} \quad (7)$$

where

V_t	=	Volume of titrant (TBAOH) used for titration of sample [mL]
V_b	=	Volume of titrant (TBAOH) used for titration of solvent [mL]
C	=	Given concentration of the TBAOH-solution [M]
f	=	Titration factor for the TBAOH-solution [-]
m_s	=	Mass of the test sample [g]
56,106	=	Molecular weight of KOH

*TBAOH = Tetrabutylammonium hydroxide

If there are weak acids in the oil sample, these will not be detected due to the small change in temperature. To prevent this, paraformaldehyde is added to the sample as a catalytic indicator. When all the acids in the sample have reacted with the base, there will become an excess of hydroxide ions in the solution, which will lead to an endothermic hydrolysis/depolymerization of the paraformaldehyde, and a significant temperature drop of the solution [12].

In thermometric titration it is necessary to determine a blank value which can be subtracted from the equivalent point. This value varies depending on the oil and solvent present, and can be determined by the instrument if samples have not previously been analyzed. It is necessary to run a minimum of three parallels per sample with varying amount so that the instrument can run a regression of the results and find this value [12]. An example of the determination of a blank value is shown in Figure 3.

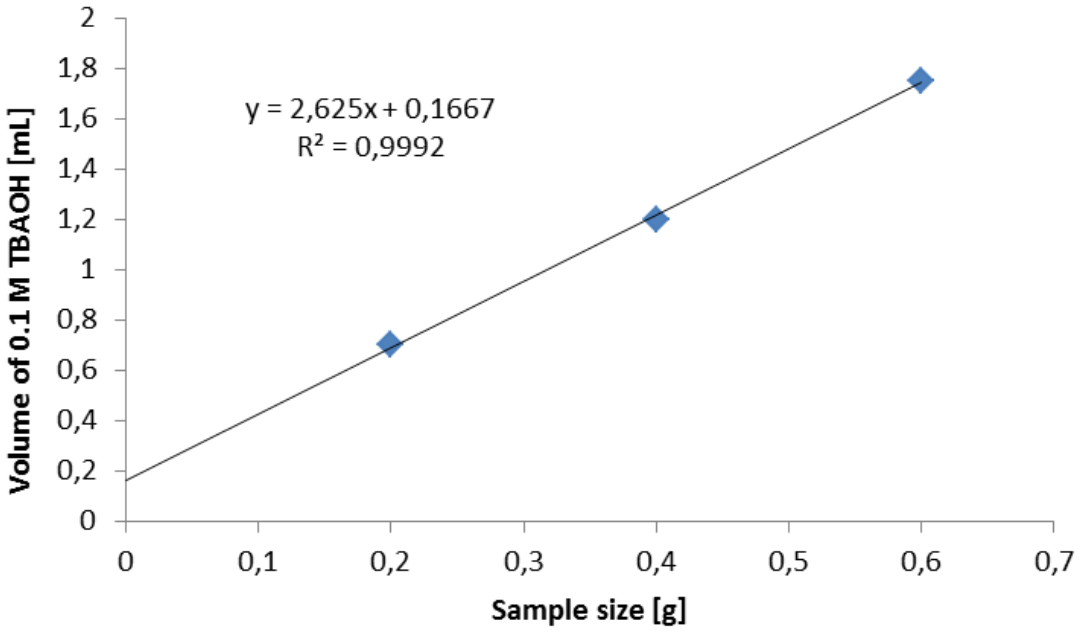

Figure 3 Example of blank determination

As seen from the figure, the blank value is determined by the intersection with the y-axis, which gives a blank-value of 0.1667 for this particular sample. If there is a shortage of sample, it would be possible to run only one parallel and use a previously measured blank-value.

After isolation, the polar phase contains only acids. The weight and TAN-value are then used to calculate the average molecular weight of the sample by using equation (8) . This can further be used to calculate the amount of acidic compounds present in moles [12].

$$M_w = \frac{m_n \cdot 1000}{(V_t - V_b) \cdot C} \quad \textbf{(8)}$$

where

M_w	=	Average molecular weight of the naphthenic acids [g/mole]
m_n	=	Mass of naphthenic acids [g]
V_t	=	Volume of titrant (TBAOH) used for titration of sample [mL]
V_b	=	Volume of titrant (TBAOH) used for titration of solvent [mL]
C	=	Given concentration of the TBAOH-solution [M]

2.1.5 Acid-IER Method

The Acid-IER method is an isolation method developed for selective isolation of carboxylic acids from crude oil or other organic solvents. It uses a sugar-based ion exchange resin called QAE Sephadex A-25 (Acid-IER). This resin is a strong negative ion exchanger, with a poly-1,6-glucose base and diethyl-(-2-hydroxy-propyl)aminoethyl as the ion exchange group [13].

The Acid-IER method is based on that carboxylic acids in the oil or organic solvent can be selectively extracted onto the ion exchanger. These acids can then be recovered by back-extraction to a suitable solvent by the addition of formic acids, which has a higher affinity towards the ion exchanger than the naphthenic acids. Before the isolation can begin, the ion exchanger needs to be saturated with bicarbonate ions, as can be seen in equation (9). This is due to the sites on the exchanger which are deactivated by chloride in its commercial form, to avoid reaction with other compounds when not in use.

$$Acid - IER - Cl + HCO_3^- \rightarrow Acid - IER - HCO_3 + Cl^- \quad \textbf{(9)}$$

The next step in the isolation process is to extract the carboxylic acids onto the ion exchanger as seen in equation (10):

$$Acid - IER - HCO_3 + HA \rightarrow Acid - IER - A + H_2CO_3 \quad \textbf{(10)}$$

After the extraction, the ion exchanger must be washed to remove residual solvents and co-solutes. When the exchanger is cleaned, the carboxylic acids can be recovered by adding formic acid [13]. The reaction is shown in equation (11):

$$Acid - IER - A + HCOOH \rightarrow Acid - IER - OOCH + HA \quad \textbf{(11)}$$

By using this method on an oil sample that contains both naphthenic acids and oil soluble calcium naphthenates, the idea is that the naphthenic acids will attach to the ion exchanger, while the calcium naphthenates will not. This means that they can be separated into one polar fraction which contains the naphthenic acids, and on non-polar fraction which contains the oil soluble calcium naphthenates in addition to the other components in the oil. If this is the case, the non-polar fraction can then go through an acidic wash, and transfer the naphthenates into naphthenic acids, and then be isolated once more. These acids can then be characterized by the same methods and techniques as regular acids.

2.1.6 SPE-Method

Solid Phase Extraction (SPE) is a broad term for methods that are being used to extract different compounds. One SPE-method developed and patented by Statoil ASA [14] is based on the Ca-selectivity of ARN-acids, and their ability to be isolated based on this. The method is optimized for samples containing maximum 100 ppm ARN-acids.

The following figure show how the SPE-method works when extracting ARN-acids from a sample from the Heidrun field. The initial sample contained 5 ppm ARN-acids.

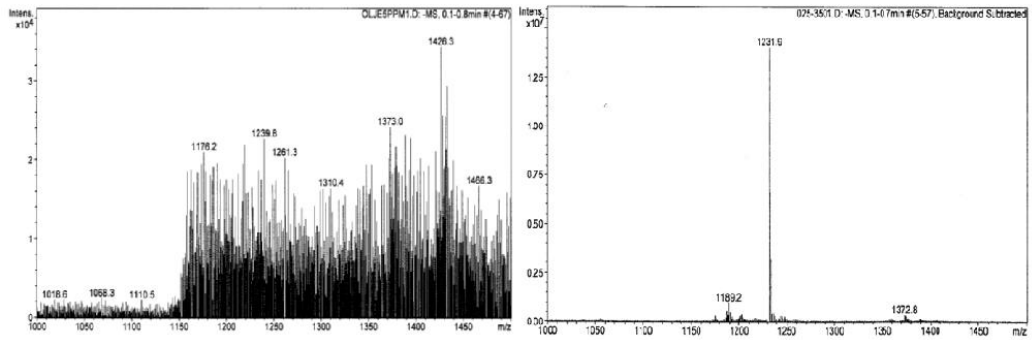

Figure 4 Example showing the effect of the SPE-method utilized to extract ARN-acids

As seen from the figure, before extraction the sample contained many different acids with various molecular weights, and the ARN-acids that are only present at 5 ppm are hidden between all other acids. After extraction however, almost all of these acids had been removed and the ARN-acids had attached to the calcium salt in the column. After back-extraction the analysts could characterize the ARN-acids without the interference of other acids or compounds [15].

In this thesis, this method was used to extract naphthenic acids with a high affinity towards calcium, and by that isolate them from other acids.

In order for this method to work, the acids need to be in their protonated form. They therefore have to undergo an acidic wash, as previously described. During extraction, the acids that have a strong affinity towards calcium will attach to the calcium salt in a column, while the others will travel through.

The acids that have attached to the calcium in the column can be back-extracted by adding a strong acid. The naphthenic acids will then detach from the column as described by the following equation:

$$R - COOCa + HCl \rightarrow R - COOH + CaCl \quad \textbf{(12)}$$

When all acids have been back-extracted, toluene can be added to transfer the naphthenic acids to the toluene phase. Both quantitative and qualitative analysis can then be performed to characterize the naphthenic acids[14] .

2.2 Characterization of Naphthenic Acids

2.2.1 Mass Spectrometry

Mass spectrometry is one of the most sensitive methods of molecular analysis. It can be used to determine the mass/charge ratio of components in a sample and as an aid during structure clarification of these components. In order for the mass spectrometer to detect the different components in the sample, they need to be transformed into ions, either positive or negatively charged. These ions are separated or filtered according to their m/z ratio and detected by the MS, and a mass spectrum showing the abundance of the generated ions as a function of the m/z ratio is retrieved [16].

A general mass spectrometer consists of an ion source, a mass analyzer and a detector. Figure 5 show a scheme of a general mass spectrometer. As the figure show, a data system is attached to the system as well, which is used to collect data as well as processing it. In the last 20 years, these data systems have also been utilized to control all functions of the instrument [17].

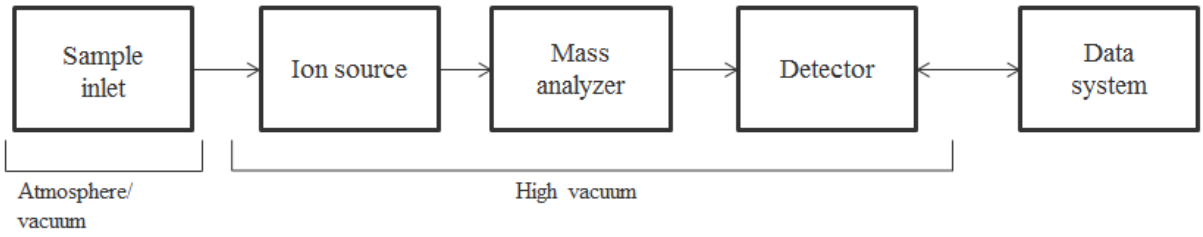

Figure 5 General scheme of a mass spectrometer.

There are often various sample inlets attached to the ion source housing, which allows for different ways of introducing the sample to the mass spectrometer [17].

Mass analyzers

There are a number of different mass analyzers available for use, like a magnetic sector, a quadrupole mass filter, a quadrupole ion trap, a so-called time-of-flight and Fourier-transform ion-cyclotron resonance instruments [16].

In this thesis the instrumentation was linear quadrupole mass spectrometer. The main advantages of using quadrupoles are that they have high transmission and they allow high

scan speeds. A linear quadrupole mass analyzer consists of four hyperbolically or cylindrically shaped rod electrodes [18]. The rods are extended in the z-direction and put together in a square figuration, where the two opposite rods are electrically connected. An equal but opposite DC voltage superimposed with a radio frequency (RF) AC voltage is applied to the diagonally placed pair of rods. The electrical field that occurs causes the ions to travel forward in the z-direction with an oscillating motion in the x-y plane. It is possible to control these oscillations so that only desired ions reach the detector [16]. The following figure shows a schematic of a single linear quadrupole mass analyzer.

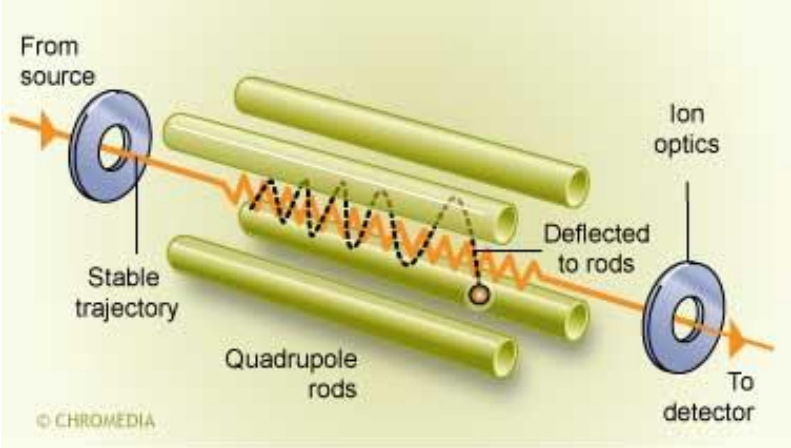

Figure 6 Schematic of a single quadropole mass analyzer [19]

As the ions enter into the quadrupole, a force is added to it by one of the rods with the charge opposite of the ionic charge.

A method often used with complex oil samples is known as fingerprinting. This method is based on full-scan mass spectrometry, where a single quadrupole LCMS is used. There is no chromatographic separation in this method, meaning that there is direct injection instead of utilizing the column [20].

Mass spectrum

The mass spectrum is a two-dimensional representation of signal intensity versus the mass-to-charge ratio. The intensity of the signals reflects the abundance of ionic species with that specific m/z ratio [17]. Commonly the highest signal is taken as 100 % abundance and all the other signals in the spectrum are presented as a fraction of this.

Ionization Methods

There are many different types of ionization methods that are available for mass spectrometry, where Electrospray Ionization (ESI), Atmospheric Pressure Chemical Ionization (APCI and Atmospheric Pressure Photoionization (APPI) are the most used [16]. In this thesis ESI and APPI are utilized.

APPI – Atmospheric Pressure Photoionization

When using APPI as a analyze technique the analyte is mixed with a solvent, which can increase the number of ions formed. The solution is then vaporized by an inert gas such as nitrogen, and enters an ionization chamber at atmospheric pressure. In the ionization chamber the mixture is exposed to UV light from a krypton lamp, as seen in Figure 7 [21]. Here it will vaporize and charged ions will be formed.

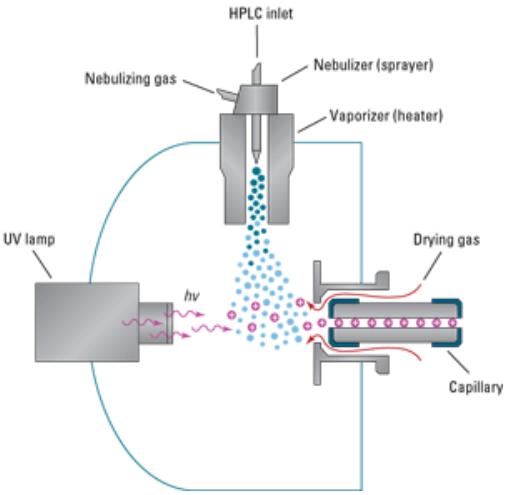

Figure 7 APPI Ionization chamber [22]

Two types of APPI-method can be used, i) direct APPI, where just the solvent and the analyte are exposed to the UV light, and ii) dopant-assisted APPI, where a dopant is introduced to the mixture. In direct APPI, only a small portion of the molecules will be ionized directly, while some can be indirectly ionized with the help of the solvent, and the photons can also excite the solvent, see equation (13).

$$M + hv \rightarrow M^{+\cdot} + e^{-} \quad \textbf{(13)}$$

Since the molecules are at atmospheric pressure, there are billions of molecular collisions per second. A small fraction of these collisions result in a chemical reaction where the solvent donates a proton to the analyte molecule, see equation (14). This means that the process ends up with two kinds of ions from one compound, where one is solvent dependent [21].

$$M + S + hv \rightarrow [M + H]^+ + [S - H]^- \quad \textbf{(14)}$$

In dopant-assisted APPI a third compound called a dopant is added, which can increase the number of analyte molecules that get ionized. It is possible to use different compounds as the dopant, where toluene may be the most commonly used. As for the direct APPI-method, the dopant-assisted APPI also give two different types of analyte ions. Dopant molecules are first ionized directly by the UV light, and then one of two things can occur. The dopant ion can donate a proton to the analyte molecule, see equation (15) or it receives an electron from the analyte molecule, see equation (16). In both cases, the result is an ionized sample molecule [21].

$$D^{+\cdot} + M \rightarrow [M + H]^+ + [D - H]^- \quad \textbf{(15)}$$

$$D^{+\cdot} + M \rightarrow M^{+\cdot} + D \quad \textbf{(16)}$$

where

M	=	Analyte molecule
$M^{+\cdot}$	=	Radical cation
S	=	Solvent molecule
$D^{+\cdot}$	=	Ionized dopant molecule
hv	=	Photon
e^-	=	Electron

ESI - Electrospray Ionization

When using ESI, the molecules are ionized by electrical energy prior to entering the MS part of the instrument [23]. Ion formation in ESI can be divided into three steps: 1) creation of an electrically charged spray, 2) dramatic reduction of droplets size, and 3) liberation of fully dissolved ions. A mist of micrometer-sized, electrically charged droplets is generated and the droplets shrink upon evaporation of the solvent. The shrinking causes the surface tension is overcome by electrostatic repulsion and the electric forces then tear the droplets apart. The shrinking and tearing of droplets occurs repeatedly and will lead to the formation of isolated ions in the gas phase [24].

ESI selectively generates quasimolecular ions at atmospheric pressure with minimal fragmentation of the analyte. It typically generates positively charged ions by protonation of basic species, and negatively charged ions by deprotonation of acidic species [25].

ESI has become a well-used method because of the small amount of sample needed and its ability to be coupled with various mass analyzers. It is also rarely necessary to add any chemical pre-treatment to a sample before injection [25]. Another advantage is the methods ability to detect molecules with a high variety of molecular weight. It is also one of the most "soft" ionization techniques that transfer ions from solutions into the gas phase. The transfer of ions from the condensed phase into the state of an isolated gas phase starts at atmospheric pressure and leads continuously into the high vacuum of the mass analyzer, which results in a very soft ionization [24].

During ionization of naphthenic acids, dimerization can occur between two acids that are either alike or different. This dimerization will cause the instrument to detect them with higher mass than they originally have. If the two acids bound together with this hydrogen bond are identical, the molecular weight seen in the scan will be twice as high. Dimerization can be avoided by using a high voltage when analyzing samples, but too high voltage could lead to fractionation of the molecules which is highly unwanted [26]. Acetonitrile is often used as the mobile phase when analyzing with ESI-MS. However, when analyzing ARN-acids, the compound cannot be used as the ARN-acids have very low solubility in acetonitrile, which may lead to precipitation inside the instrument and consequently no signal for these acids in the scan.

2.2.2 Infrared Spectroscopy

Infrared spectroscopy can be used to determine functional groups in organic and inorganic molecules, and can be used for both qualitative and quantitative analysis. The method is based upon that bonds in molecules will vibrate at different wavelengths depending on what it is attached to. The molecules will absorb infrared radiation when the radiant energy matches the energy of that specific molecules vibration, and the absorption excite the molecule from its lowest state to a higher one [1, 27].

There are two types of vibration that can occur in a molecule: stretching and binding. Stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angle between bonds with a common atom or the movements of a group of atoms with respect to one another. The IR spectrum only observes the vibrations that result in a rhythmical net change in the dipole moment of the molecule [1].

The IR spectrometer consists of the IR source, a beam splitter, a detector, and a processor. A scheme of the spectrometer is presented in Figure 8.

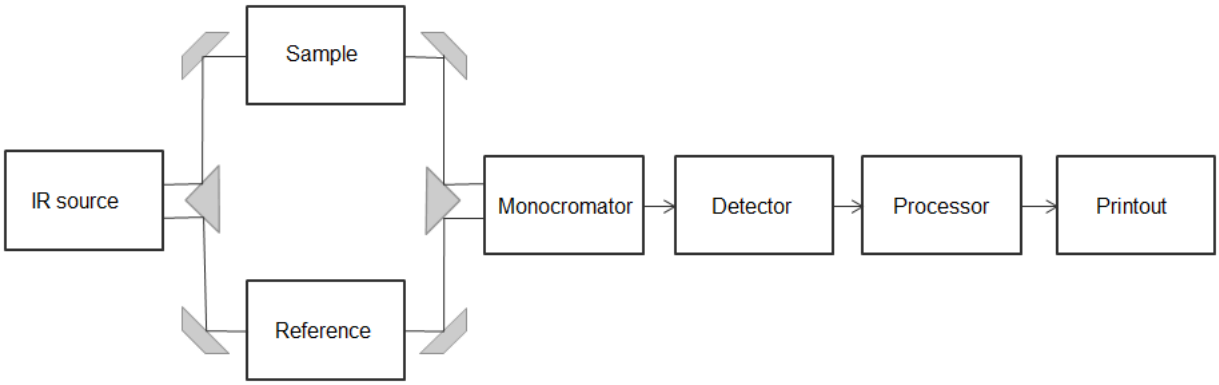

Figure 8 A schematic diagram of the different components in an IR spectrometer

IR light exits the source and become split into two beams by the beam splitter. One beam goes directly to the sample, while the other is used for reference. The intensity of the beam is measured by the intensity emitted divided by the intensity observed, also known as the transmittance.

A typical IR spectrum is shown in Figure 9. When the infrared light is sent through a sample, it will absorb different frequencies depending on the molecule. It is possible to present the results in either transmission or absorbance If the spectrum shows a frequency with 100 % transmission, it means that there are no structural groups in this molecule that can absorb that particular frequency [28].

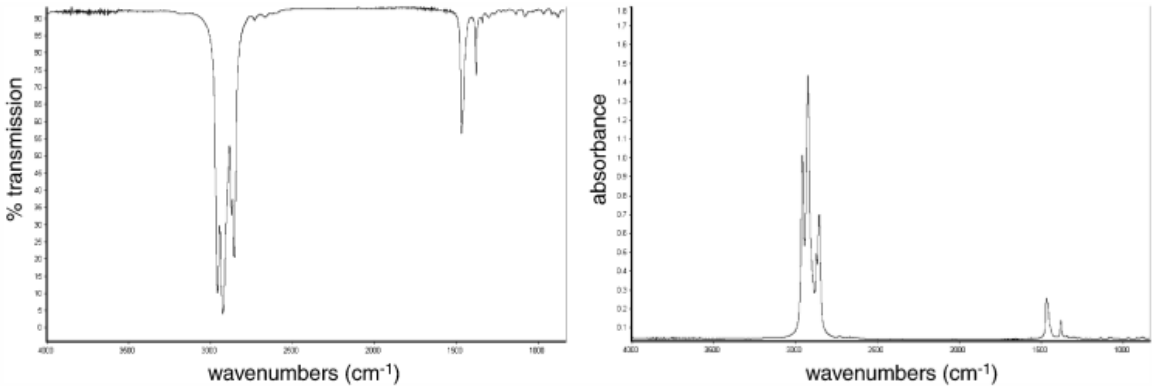

Figure 9 Typical IR spectrum

The calculation between transmittance and absorbance is given by Beer's law, see equation (17).

$$A = log_{10} \frac{P}{P_0} \qquad \textbf{(17)}$$

where

Transmittance, T = P/P_0

% Transmittance, %T = $100\ T$

Below 1500 cm^{-1} there are a very high sensitivity, which is the region where the C-C bond stretching and bending motions in an organic molecule overlap. This overlap makes it difficult to find functional groups in this area [29]. The position and intensity of the absorption bands of a substance are extremely specific, which means that the method is very accurate [27].

It is possible to separate between naphthenic acids and metal naphthenates using infrared spectroscopy due to the C=O bonds that will occur at different frequencies depending on

what the group is attached to. Naphthenic acids in a un-dissociated state have a wave number around 1705 cm^{-1}, while the vibration of the C=O bond in naphthenates have a wave number around 1540 cm^{-1} [1].

Fourier Transform Infrared (FT-IR) spectroscopy has been utilized in this thesis. One advantage that the FT-IR has over other IR spectrometers is that all wavelengths are measured simultaneously in an interferometer. They also detect less noise in the mid- and far-IR region, and it is better at retrieving higher signals. The wavenumber stability of the FT-IR instrument is very good, due to a He-NE laser which provides an internal reference for every interferogram [30].

3 Materials and Methods

3.1 Influence of pH on Oil-Soluble Calcium Naphthenates

Oil from two separate fields that normally have pH values of the formation water of around 5 to 5.5, were mixed with water with a pH of 7.5 and high calcium content to see if there were any formation of oil-soluble calcium naphthenates. The two oils were mixed with water 1:1 and placed on stir over night at 35 °C. WiO-content and Ca-content was measured before adding the water and after the water was removed.

3.2 Isolation of Naphthenic Acids

The oil used in this thesis had a high viscosity so it was first heated at approximately 70 °C in a heating cabinet and then shaken to achieve a homogeneous sample. A sample of the oil was then transferred into a bottle and the weight was noted. The same amount (weight) of xylene was added to the flask and shaken until the sample was homogeneous. The xylene was added to make the sample less viscous and the analysis process easier.

The oil sample was treated at two different analysis routes so that it would be possible to get information about the yield of the isolation process, and to see how large amount of the naphthenic acids that were bound to calcium. The following figures show the two different routes that were chosen.

Figure 10 presents the analytical route chosen for the oil sample. It was believed that this route could lead to the separation of naphthenic acids and calcium naphthenates by isolation.

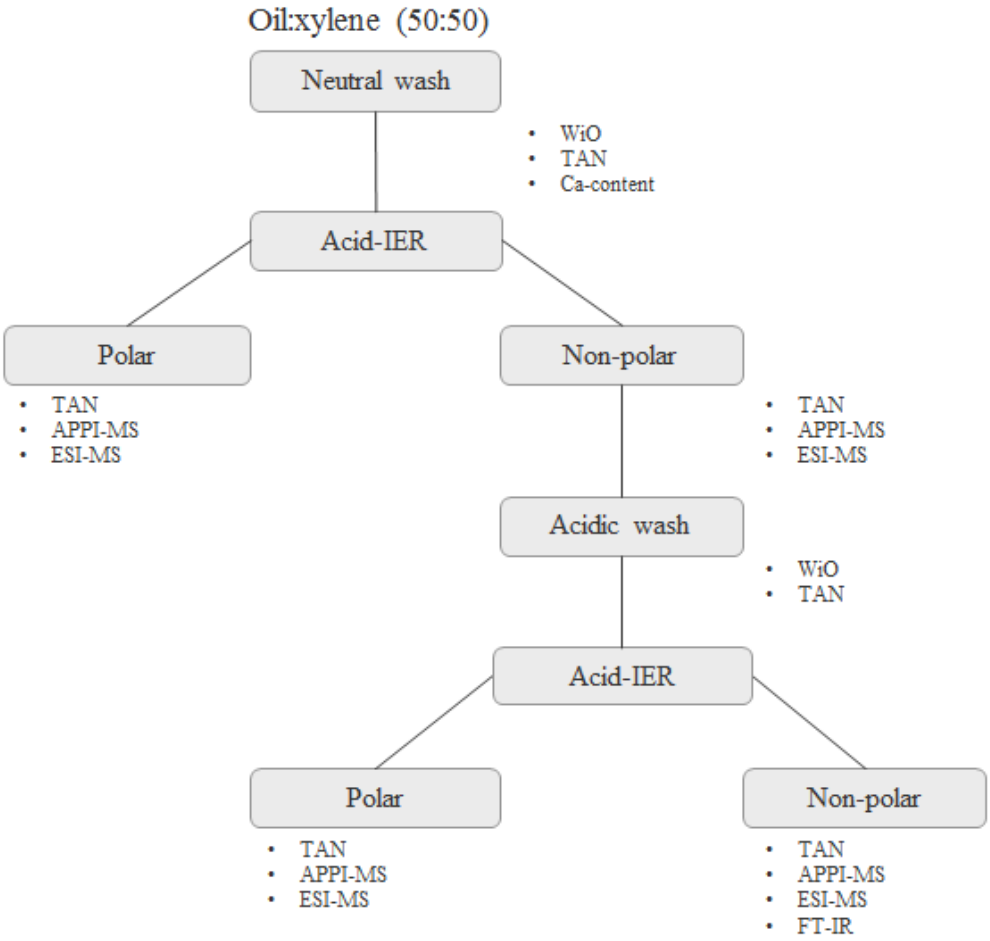

Figure 10 Analysis route to isolate naphthenic acids that form oil soluble calcium naphthenates

The neutral wash removed any excess cations in the oil or other impurities in the sample that could possibly attach to the ion exchanger. The Acid-IER method would isolate the acids that were not bound to calcium, and separate the sample into two fractions, one polar with the acids, and one non-polar with the calcium naphthenates and all other components in the oil. The non-polar fraction would then be treated with an acidic wash to release the naphthenic acids that were attached to calcium. Another isolation with the Acid-IER method would lead to a new polar and a non-polar fraction, where the acids would be in the polar fraction. In theory, the polar fraction would now only contain naphthenic acids that were able to form oil

soluble calcium naphthenates. This fraction could then be characterized by using different analysis. TAN was measured for every step to have control over the mass balance.

Another route, as seen in Figure 11, was performed as sort of a reference route in order for the analysis to be controlled.

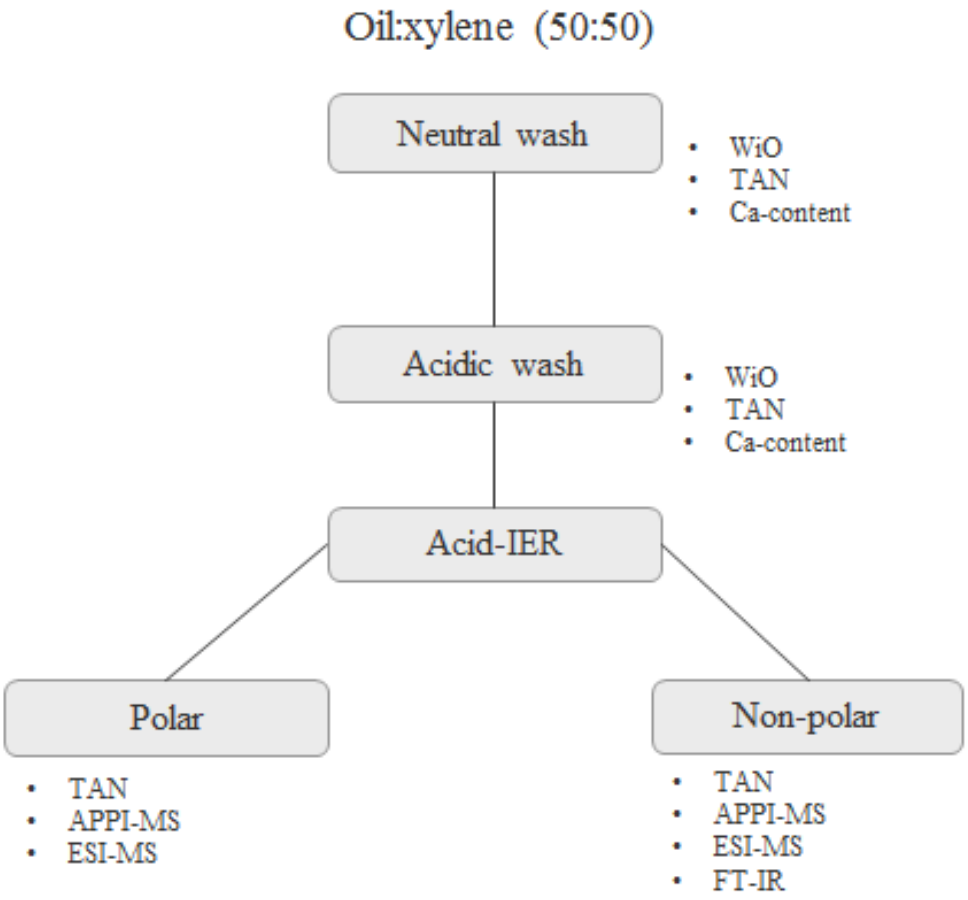

Figure 11 Analysis route to isolate all naphthenic acids in the crude oil (reference route)

Neutral wash was also the first step here, but the following was an acidic wash. This was done to transfer the oil soluble calcium naphthenates into naphthenic acids. Then the sample was isolated with an ion exchanger, and divided into a polar and non-polar section. This route was performed to see whether or not all the acids could attach to the ion exchanger. TAN was measured for every step to have control over the mass balance. All the analysis used in both these routes are explained more in detail in the following sections.

3.2.1 Neutral Wash

The first step in both routes described above, was a neutral wash of the sample to remove impurities and other components that could affect the isolation.

Equipment/chemicals

Centrifuge

pH-meter

NaOH – 0.1 M

Deionized water was made pH-neutral (not under pH 7) by adding a few drops of NaOH and added to the oil:xylene sample in relation 1 part water and 3 parts oil sample. The sample was shaken for 3.5 hours and then placed in a heating cabinet at 70 °C for about 2.5 hours to enhance separation. It was then placed in a vacuum fume at room temperature over night for further separation.

The next day, the oil phase was pipetted out and transferred to a new bottle where fresh pH-neutral water was added. This neutral wash was conducted three times. After the final wash, the oil was separated from the remaining water by a centrifuge. After centrifugation, the oil phase was pipetted out, and water content, TAN and Ca-content was measured.

The Ca-analysis showed that the Ca-content after neutral wash were much lower than previously work on this oil had suggested. This indicated that the neutral washed had removed some of the calcium from the oil, which could have been attached to naphthenic acids. To avoid this from occurring with the next batch, the sample was stirred for only one hour with neutral water before it was centrifuged for 30 minutes. The oil phase was then pipetted off, and the procedure was repeated three times. The oil would therefore only have contact with the neutral water for approximately 1.5 hours.

3.2.2 Ca-content measured at PTL Mongstad

The measurement of Ca-content was performed by another department at Mongstad. They used a Perkinelmer ICP-OES DV4300 to run the samples, where ICP-OES stands for Inductively Coupled Plasma Optical Emission Spectroscopy. The method that was used are quite similar to ASTM D5708 Method B [11], but other acids than the ones described in the method were used at Mongstad.

3.2.3 Water Content by Karl Fischer Titration

Equipment/chemicals

874 Oven Sample Processor

Water standard – 100 ppm

Karl Fischer titration was used to measure the water content of the samples. Two blanks and three water standards with 100 ppm water was used for quality check of the equipment. The blanks were also used to measure the humidity in the room and subtract it from the test samples. The oil sample was weighed to about 0.1 g per test tube, with three parallels per sample. Table 2 show an overview of the amounts and temperatures used for blanks, water standards and oil samples.

Table 2 Weight and temperature specifics for WiO-measurements

Sample	Weight [g]	Temperature [°C]
Blank	-	130
Water standard (100 ppm)	0.8 – 1.2	130
Oil sample	0.1	170

This analysis was run after every neutral wash and acidic wash performed in this thesis to make sure that the samples had less than 0.05 wt% water before they could be measured for TAN, Ca-content and go through isolation.

3.2.4 Total Acid Number by Thermometric Titration

Equipment/chemicals
814 Sample Processor
859 Titrotherm
TBAOH in methanol and 2-propanol
Benzoic acid
Paraformaldehyde
Solvent (toluene, propan-2-oil and distilled water)
0.1 M benzoic acid solution in 2-propanol (control sample)
Toluene (washing)
2-propanol

The amount of sample was calculated using equation (7), based on the expected TAN. If a lot of sample were available, three parallels with different amount of sample were analyzed to get a blank value for that particular sample and solvent. To save sample, in some cases only one parallel was run. Here the blank value was based on previously run samples. The TAN-values were used to see how much acids were present in each step of the isolation process. For the polar phases, which consisted only of acids, it was used to find the average molar mass and thus calculating the amount of acids in moles.

3.2.5 Acid-IER Method

Equipment/chemicals

Buffer solution (Na_2CO_3 + $NaHCO_3$)

Ion exchanger – QAE Sephadex A-25 (Acid-IER)

Toluene

Methanol

Formic acid

Büchner funnel

Before isolation of naphthenic acids could start, it was necessary to calculate how much ion exchanger that was needed for the experiment. The amount of acids (moles) per gram of oil was calculated from equation (18):

$$\frac{TAN}{M_{KOH} \times 1000} = \frac{acids\ [mole]}{oil\ [gram]} \quad \textbf{(18)}$$

Equation (19) could then be used to calculate the necessary amount of ion exchanger for each oil sample:

$$m_{ion\ exchanger} = \frac{n_{naphthenic\ acids} \times m_{oil}}{I_{ion\ exchanger}} \quad \textbf{(19)}$$

To make sure that all of the naphthenic acids would attach to the ion exchanger, 10-15 % more than the calculated weight was applied.

The ion exchanger needed to be saturated by a buffer solution before it could isolate the naphthenic acids. The buffer solution was made with 92.75 grams of Na_2CO_3 and 10.50 grams of $NaHCO_3$ per liter of distilled water. 75 mL buffer solution per gram ion exchanger was filtered through the ion exchanger by using a glass filter crucible. The buffer solution was added a little at the time, and the total amount of contact time between the ion exchanger and the buffer solution was at least 2 hours. The mixture was carefully stirred between each

addition of buffer solution to make sure that there were contact between the ion exchanger and the buffer solution. The same procedure was done with water and methanol, with 50 mL of water and 25 mL of methanol per gram of ion exchanger. It was very important to add a suction to remove remaining water before adding methanol. After the methanol was added, the ion exchanger was transferred into a Teflon cup together with the oil sample. The mixture was put on stir for at least 16 hours. It was very important that the magnet used for stirring was attached to a fishclip, which allows for the magnet to be floating in the air and not touch the Teflon cup. This was done to avoid breaking the ion exchanger by mechanical force.

The second day the mixture was filtered through a black ribbon filter using a Büchner funnel. The Teflon cup together with the magnet and fishclip used for stirring was cleaned with toluene and methanol to make sure that all of the ion exchanger was filtered. The ion exchanger was cleaned with 20 mL of toluene per wash. Each wash were left for 5 minutes before it was removed by suction. This was performed until the filtrate going through the filter was clear. The same procedure was performed once more, but this time with 14 mL toluene and 7 mL methanol per wash. The filter containing the ion exchanger was transferred into the Teflon cup with a tweezer, and any remains in the Büchner funnel was rinsed into the cup as well.

The non-polar phase, now remaining in the flask, was then filtered into a new flask through a blue ribbon filter, which had smaller pores than the first filter, in a Büchner funnel. It was very important to rinse the flask from the first filtration thoroughly with equal parts of toluene and methanol, to be sure that all of the ion exchanger would get transferred. The blue ribbon filter was also transferred to the Teflon cup and the Büchner funnel was rinsed into it. The ion exchanger was rinsed off the two filters with equal amounts of toluene and methanol.

If necessary, 25 mL toluene and 25 mL methanol per gram of ion exchanger was added to the Teflon cup. If there were a sufficiently amount for good stirring, this part was unnecessary. In addition 3.25 mL of 1.0 M formic acid per gram ion exchanger were added. The mixture was put on stir until the next morning.

After the sample had been stirred over-night, a new washing procedure was performed. Black ribbon filter was used in a Büchner funnel, and 14 mL of toluene and 7 mL of methanol was

used in each wash. The filter was transferred back to the Teflon cup as described above, and the polar phase was filtrated through a blue ribbon filter, which also were transferred. The two filters were rinsed and removed from the Teflon cup, and 0.5 mL of formic acid was added for each gram of ion exchanger. Again the sample was put on stir until the next morning. The same washing and filter procedure were conducted the next morning.

Both the polar and non-polar phases were transferred into a weighed round-bottomed flask each and a rotovapor was used to evaporate and dry the sample. The flasks were then placed in a heating cabinet at 70 °C and weighed over a number of days until stable weight was observed.

TAN-measurements were performed on both the polar and non-polar phase. The polar phase was diluted to a 1.0 wt% solution with 1:1 toluene:isopropanol as the solvent. Approximately 0.10, 0.13 and 0.16 grams of oil sample were then measured with thermometric titration to retrieve a TAN-value of the concentrated acids. This value was then used to calculate the average molecular weight of the acids in the polar phase and then determine the amount of moles present. The amount necessary for TAN-measurements of the non-polar phase was diluted 1:1 with xylene. The first measurement on a non-polar phase was run with three samples to retrieve a correct blank value, while the other included only one parallel to save sample.

3.2.6 Acidic Wash

Equipment/chemicals

Formic acid (30 %)

A 30 % formic acid solution was made from 333.3 mL of formic acid for one liters of solution. 1:4 30 % formic acid were then added to the oil sample, and the mixture was shaken overnight. The acid was pipetted off, and the sample was washed with distilled water three times to make sure that all of the formic acid was removed. The WiO-content waa measured to make sure that all of the water was removed before further analysis.

This was performed on the main sample after neutral wash in the analyze process as seen in Figure 11, and on the non-polar phases after the first isolation step seen in Figure 10.

3.2.7 SPE-method

Equipment/Chemicals
Ca-salt
Toluene
Toluene:isopropanol (1:1)
Column (10 ml)

For each sample, a Teflon filter house, which consisted of a quarts sinter, a filter, a stop-ring and the filter house itself was assembled and made sure that there was no leakage. A MN-sinter was added to the bottom of every column and 2.5 cm (about 2.5 grams) of calcium salt was added to the columns. It was very important to make sure that the salt in the columns were packed so that the sample would get good contact with the calcium in the salt. The sample was transferred into the column and it was released from the column at a speed of about one drop per second, so that the sample would have enough time in the column to react with the calcium present in the column. When the entire sample had gone through the column, the flask underneath was removed and replaced with a new one. This was so that it would be possible to separate the filtrate from the wash, which was the next step in the process. The wash consisted of 2x10 ml warm toluene, 3x10 ml toluene:isopropanol (1:1) and 2x10 ml warm toluene. Wash 2, 4 and 7 were left in the column for 2, 5 and 2 minutes respectively, before they were let through in the same speed as the sample.

Table 3 Overview of the washing procedure during the SPE-method

Solvent	Volume [mL]	Temperature [°C]	Time [min]
Toluene	10	60-70	-
	10		2
Toluene:isopropanol (1:1)	10		-
	10	20	5
	10		-
Toluene	10	60-70	-
	10		2

When the wash was completed the flask underneath were removed and the column and filter house with all its content were transferred to a new flask. About 100 mL of 6 M HCl was then added to the flask and it was set on stir over night. It was important to make sure that the salt was in contact with the acid and that pressure was released before it was set on stir, due to the exothermic reaction occurring. The next day, approximately 100 mL toluene was added to the flask and again it was set on stir over night. The following day the toluene phase, without the addition of HCl, was transferred to a round bottle. About 25 mL of new toluene was added to the flask to dilute the remaining concentration of carboxylic acids and after a gentle stir, this toluene was also transferred to the bottle. This was repeated at least seven times to make sure that the amount of carboxylic acids left in the flask was minimal. The solution in the round bottle was then reduced in volume with a rotavapor. TAN was measured on the filtrate, the wash and the extracted acids.

The SPE-method was performed three times during this master thesis work. As seen in Figure 12 the first round consisted of two parallels of 15 grams each. The oil samples were added to the column and the filtrate, wash and extracted acids were collected separately.

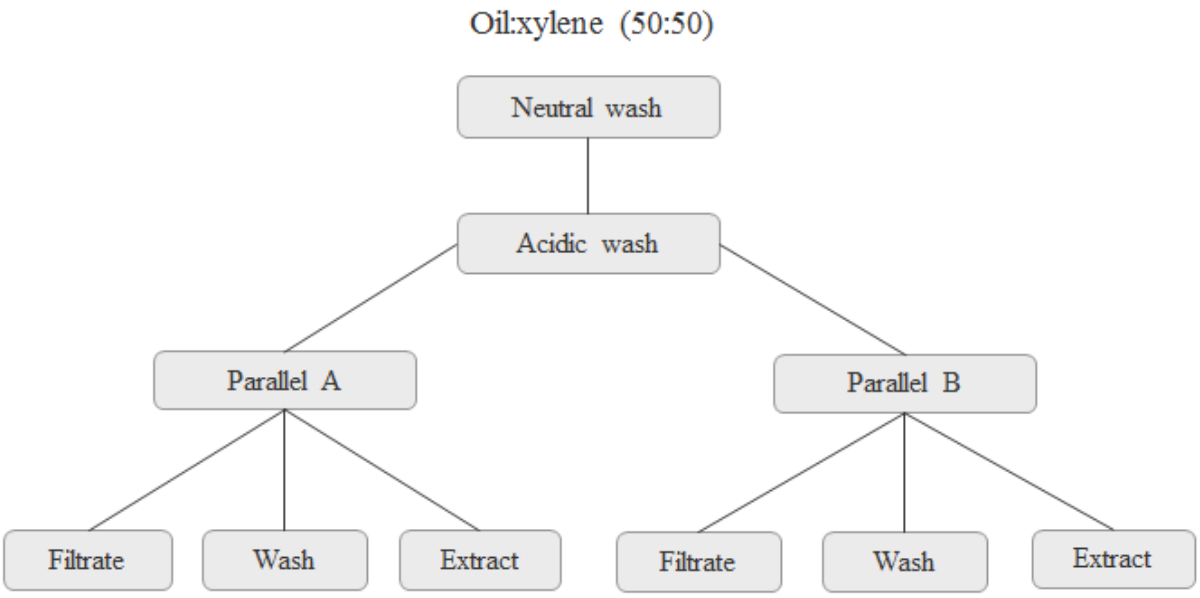

Figure 12 Scheme of the first extraction by the SPE-method with 15 gram per column (1 column per parallel)

The second extraction was performed on three oil samples of 5 grams each. As seen in Figure 13, these samples were not considered as parallels, but were combined after the samples had gone through the column. This was done to see if the calcium salt in the column had a higher capacity than what was indicated with the first run with SPE. In this way, the sample would be in more contact with the salt.

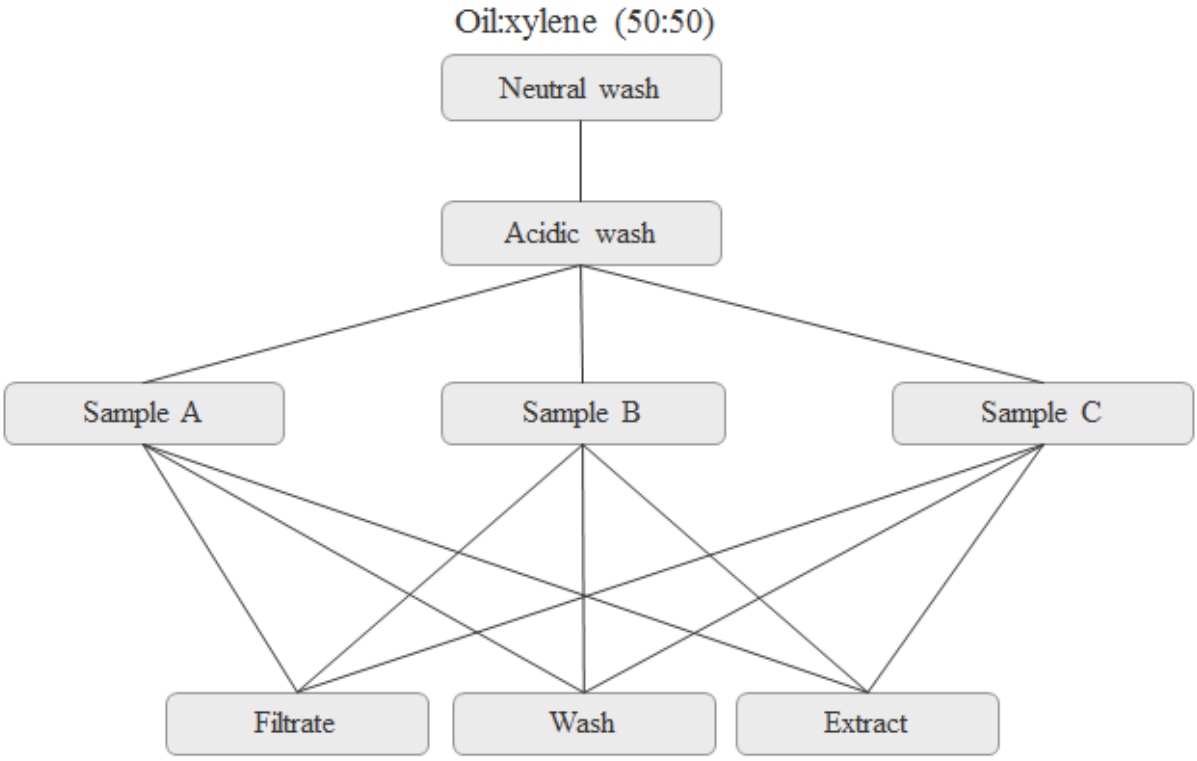

Figure 13 Scheme of the second extraction by the SPE-method with 5 gram per column (total of 3 columns)

The third and final run with the SPE-method performed in this thesis, consisted of 15 columns where 1 gram of oil were added to each, as seen in Figure 14. Like for the second setup, the filtrate, wash and extracted acids were combined to be able to compare them to the other experiments.

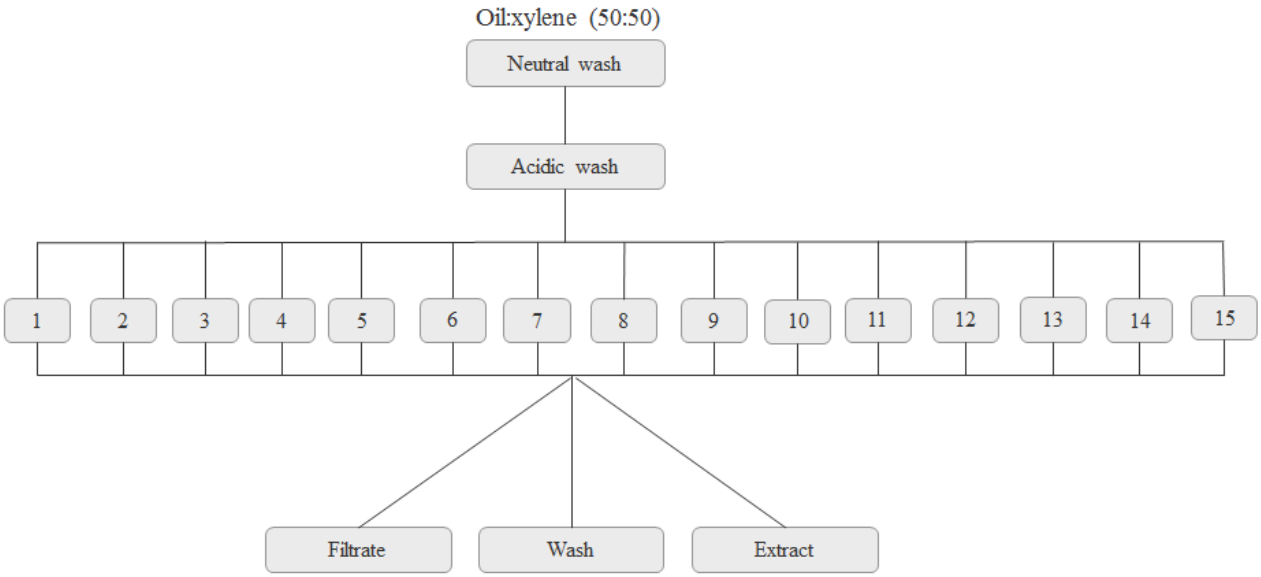

Figure 14 Scheme of the third extraction by the SPE-method with 1 gram per column (total of 15 columns)

3.3 Characterization of Naphthenic Acids

The samples that were to be analyzed with the LCMS were diluted to a suitable solution in order for the signal of the acids to be at the right strength. The samples were diluted with a 1:1 solution of toluene and isopropanol. The column in the LCMS instrument was not used in these experiments.

3.3.1 Atmospheric Pressure Photoionization-Mass Spectrometry

Equipment/chemicals
Agilent LC-MS (G1956)
Toluene:isopropanol (1:1)
Ammonium acetate (50 mM)

Both polar and non-polar samples were run with a 1 wt% solution at APPI negative mode. The mobile phase consisted of 90 % toluene:isopropanol in 1:1 relationship and 10 % ammonium acetate (50 mM). The mobile phase flow was 0.150 mL/min and 2 µL of sample was injected directly into the ionization chamber by an autosampler. Run time for each sample was 1.5 minutes, and each sample was injected five times where the mean values were further analyzed. All samples were scanned from 150 to 2000 m/z.

Additional settings	
Pressure	0 - 400 bar
Gas temperature	350 °C
Vaporizer temperature	400 °C
Electrical potential	4000 V
Drying gas	4.0 L/min

3.3.2 Electrospray Ionization-Mass Spectrometry

Equipment/chemicals
Agilent LC-MS (G1956)
Acetonitrile
Toluene
Ammonium acetate

As for the APPI-MS, the polar and non-polar phases were run with a 1 wt% solution at ESI negative mode. The mobile phase consisted of acetonitrile with 10 % toluene and ammonium acetate (50 Mm) (9:1). The acetonitrile was used due to no measureable signal during scans without the compound. The flow was set to 0.150 mL/min and 2 µL of sample were injected directly into the ionization chamber. Each run lasted for 1.5 minutes and each sample was injected five times where the mean values were further analyzed. All samples were scanned from 150 to 2000. Between the samples, washing with toluene:isopropanol (1:1) was performed three times.

Additional settings	
Pressure	0 - 400 bar
Gas temperature	350 °C
Electrical potential	3000 V
Drying gas	8.0 L/min

3.3.3 Infrared Spectroscopy

Equipment/chemicals

Perkin Elmer Specter One FT-IR Spectrometer

Universal HATR Sampling Accessory

The IR spectrometer was used to determine if there were any acids in the non-polar phase. The non-polar phase which had been dried to a stable weight was diluted 1:1 with toluene/isopropanol (1:1). This was done so that it would be easier to apply the sample on to the instrument. After applying the sample, the toluene and isopropanol was vaporized due to too large signals and interference in the instrument.

IR spectroscopy was also run on some polar phases trying to achieve semi-quantitative results, which could be compared to the non-polar phase. The polar samples were diluted to 25 wt%, 10 wt%, 1.0 wt% and 0.1 wt%.

All samples were scanned from 650 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}. 100 µL of diluted sample were placed upon the crystal, and as mentioned, the solvent was allowed to vaporize before the scan was started.

4 Results and Discussion

4.1 Influence of pH on Oil-Soluble Calcium Naphthenates

Water with pH of 7.5 and a high Ca-content were added to the two oils without any significant amounts of oil-soluble calcium naphthenates, to see if the amount would increase. The results are presented in Table 4.

Table 4 Ca-analysis before and after addition of water with high Ca-content and high pH

Sample	**1**	**2**
Ca in non-treated oil [mg/kg]	**56**	**64**
WiO in non-treated oil [wt%]	0.02	0.02
pH in water before wash	7.52	7.52
pH in water after wash	7.39	7.29
Wio after wash [wt%]	0.05	0.02
Ca after wash [mg/kg]	**192**	**240**

As can be seen from the table, the total amount of oil-soluble calcium naphthenates increase with increasing pH. This indicates that there is not necessarily a specific acid structure needed to form oil-soluble calcium naphthenates, but that it is more dependent on pH-values in the formation water. This is supported by the equation, which were presented previously in this work:

$$Ca(RCOO)_2(o) + 2H_2O(w) \leftrightarrow 2RCOOH(o) + Ca^{2+}(w) + 2OH^-(w)$$

If there is an addition of water with a high content of Ca^{2+}-ions and a high pH, the reaction will be shifted towards the left and oil-soluble calcium naphthenates will be formed. The results from this test indicate that this reaction equation is universal for all oils that have a high content of naphthenic acids.

4.2 Isolation of Naphthenic Acids

4.2.1 Neutral Wash

Samples before and after neutral wash, were sent to Ca-analysis at Mongstad. The results revealed that a significant amount of Ca was lost during the neutral wash. The following table shows the results from the Ca-analysis.

Table 5 Results from Ca-analysis performed at Mongstad

Sample	Ca-content [mg/kg]
Non-treated oil (WiO: 0.03 wt%)	**500**
Neutral washed (batch 1) (WiO:0.02 wt%)	**400**
Acidic washed	<0.2
pH-neutral water (blank)	<0.2
Water removed after neutral wash 1	2.9
Water removed after neutral wash 2	40
Water removed after neutral wash 3	48
Neutral washed (batch 2) (WiO: 0.04 wt%)	**360**

The results show a decrease in Ca-content of 100 mg/kg before and after neutral wash for the first batch. When the water used for neutral wash was tested, it was clear that the Ca present in the oil had been transferred to the water during the process. This indicated that the neutral wash removed more calcium than during previous experiments performed by Statoil ASA. It was assumed that the reason for this was that the contact between oil and water was too long and that the reaction previously presented went to equilibrium. This effect would be reduced by reducing the contact time.

As mentioned in the *Experimental Theory* chapter, equation (2) will be drawn towards equilibrium. Since fresh neutral water is added three times, the system will seek towards equilibrium three times, resulting in more transfer of calcium. Another reason for the reduction could be that the calcium is unevenly distributed through the initial sample, which will give faulty results.

For the second batch, the neutral wash was performed with less contact time between the sample and the neutral water to see if this would decrease the loss. The results show that the reduction in Ca-content was similar to the first batch.

Based on the results of the calcium analysis for the two batches used in this master thesis, it is clear that there is no difference in reduction of calcium whether the water-oil contact lasts 1.5 hours or 24 hours, and that 1.5 hours is enough for the reaction to reach equilibrium. In order for this to be avoided, the contact time could be shortened and less water could be used to avoid reaching equilibrium and transferring the calcium to the washing water.

4.2.2 Water Content

The water content was measured below 0.05 wt% for all samples analyzed. This means that the contribution of Ca-ions dissolved in the associated water is negligible compared to the overall Ca-content in the samples. The results from the Karl Fischer titrations are presented in Appendix A.

4.2.3 Acid-IER and Total Acid Number

Two isolation processes were executed on the neutral washed sample. This was done to get several parallels with trustworthy results.

Figure 15 presents an overview of the mass balance for the first run with neutral washed oil. The first process included two parallels (A and B) of the neutral washed initial sample, and the two non-polar phases after the first isolation step were combined before an acidic wash and a second isolation. Combining the two non-polar phases was done due to the small amount of sample present in the two parallels. All results are shown in millimole acids per sample.

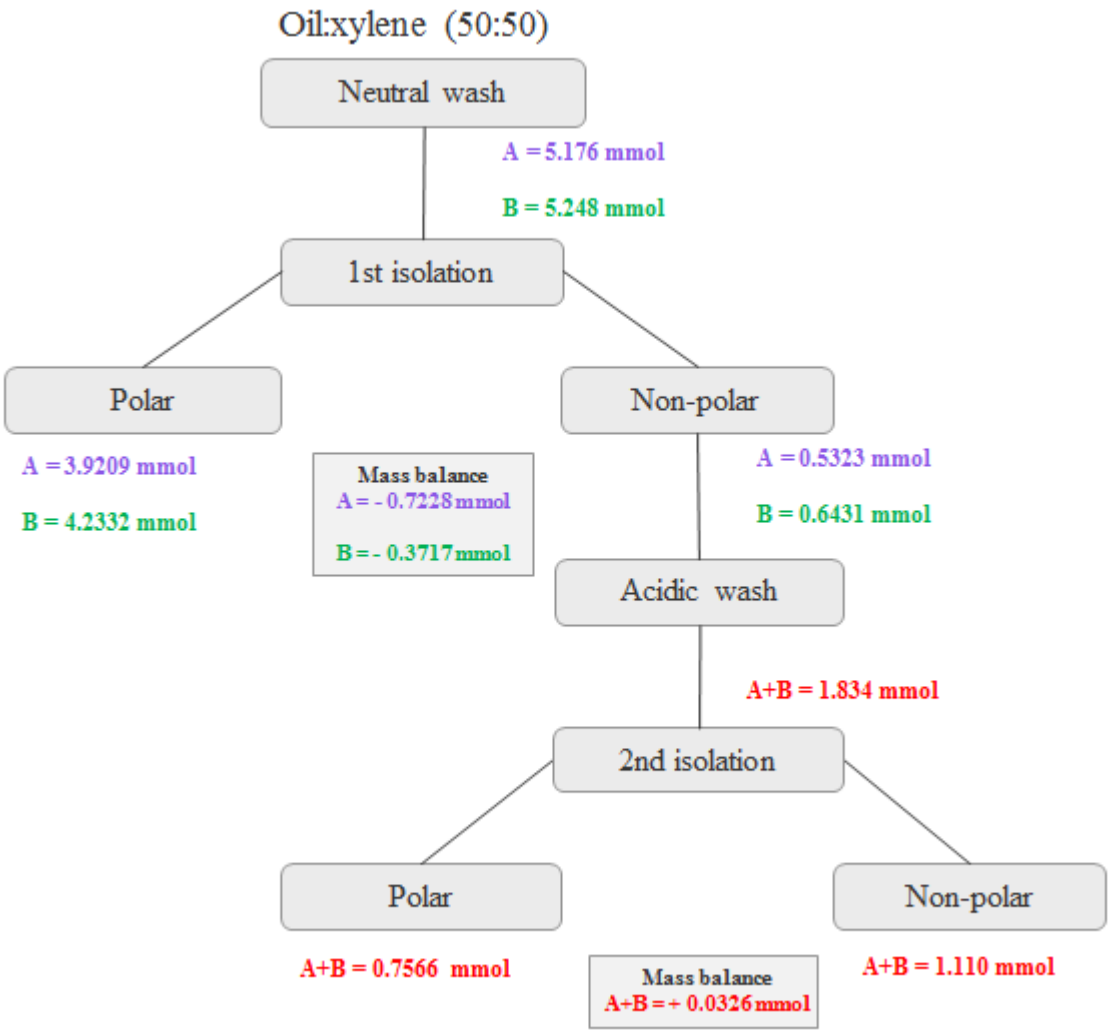

Figure 15 Mass balance from the first isolation process of neutral washed sample

The initial samples contained about 5.2 mmoles acids, based on calculations of the two parallels from the TAN-values. After the first isolation step the polar phases contained 3.9 and 4.2 mmoles, while the non-polar phases contained 0.53 and 0.64 mmoles. This gives a selectivity of the ion exchanger of 75 to 80 %, as presented in Table 6.

Table 6 Amount of acids in each phase compared to the initial sample (batch 1 of neutral washed sample) in %

Isolation step	Parallel	Polar	Non-polar	Mass balance
1	A	75.8	10.3	- 14.0
	B	80.7	12.3	- 7.1
2	A+B	41.3	60.5	+ 1.8

The amount of acidic compounds found with TAN-measurements in the non-polar phase after the first isolation step was unexpected, as the theory behind this method states that all free acids would be transferred to the polar phase. The TAN-value of the non-polar phase was around 1.2 for both of the two parallels, which indicated that some of the acids present in the sample did not get isolated by the ion exchanger. One theory was that some naphthenic acids had been transferred to the non-polar phase due to the ion exchanger's capacity.

The two non-polar phases was combined and went through an acidic wash, which increased the TAN-value from 1.2 to 1.9. This clearly shows that there were some acids in the sample that were bound to calcium, and after acidic wash became free acids that could be isolated.

The ion exchanger was added in a relatively large excess before the second isolation step was performed to make sure that the capacity of the ion exchanger would not be the limiting factor. After the second isolation step, the TAN-measurements still gave an indication that there were a significant amount of acidic compounds in the non-polar phase. As seen from Figure 15 the total amount of acids in the two non-polar phases are very similar, with 1.18 mmoles before the second isolation step and 1.10 mmoles after. These results strongly indicate that the compounds found in the non-polar phases have characteristics that can be titrated by a base, but will not attach to the ion exchanger. This could indicate that there are some acids present that have a structure that leads to steric hindrance when trying to attach to the ion exchanger, or it could be other compounds than acids that can be titrated.

The amount of acids that were found in the polar phase after the second isolation step also match the increase after acidic wash of the non-polar phase from the first isolation step. As seen in Figure 15 the total increase of acids were 0.66 mmoles after acidic wash and the polar phase consists of 0.76 mmoles. This indicates that all of the naphthenic acids that initially were connected to calcium have been transferred to the polar phase after second isolation. As seen from Table 7 these acids have a much higher average molecular weight than the acids in the polar phase after the first isolation. After the first isolation the average molecular weight were about 580-590 g/moles, while after the second it increased to 874 g/moles.

Table 7 TAN-values and calculated average molecular weight (batch 1 of neutral washed sample)

Sample		TAN	M_w [g/mole]
Neutral washed (batch 1)		9.7	
	Polar phase		589
			582
	Non-polar phase	1.1	
		1.3	
Acidic washed non-polar (batch 1)		1.9	
	Polar phase		874
	Non-polar phase	1.2	

After the second isolation step the mass balance showed an increase of acidic compounds of 1.8 %.This increase is probably because the weight of the samples were not stable when the TAN-measurements were performed.

In the second isolation process of the neutral washed initial sample, four parallels were obtained in the first isolation step (A, B, C and D). As for the previous process, two non-polar phases after the first isolation step were combined due to the needed amount of sample for the second isolation step after acidic wash. Figure 16 presents the results from the second batch.

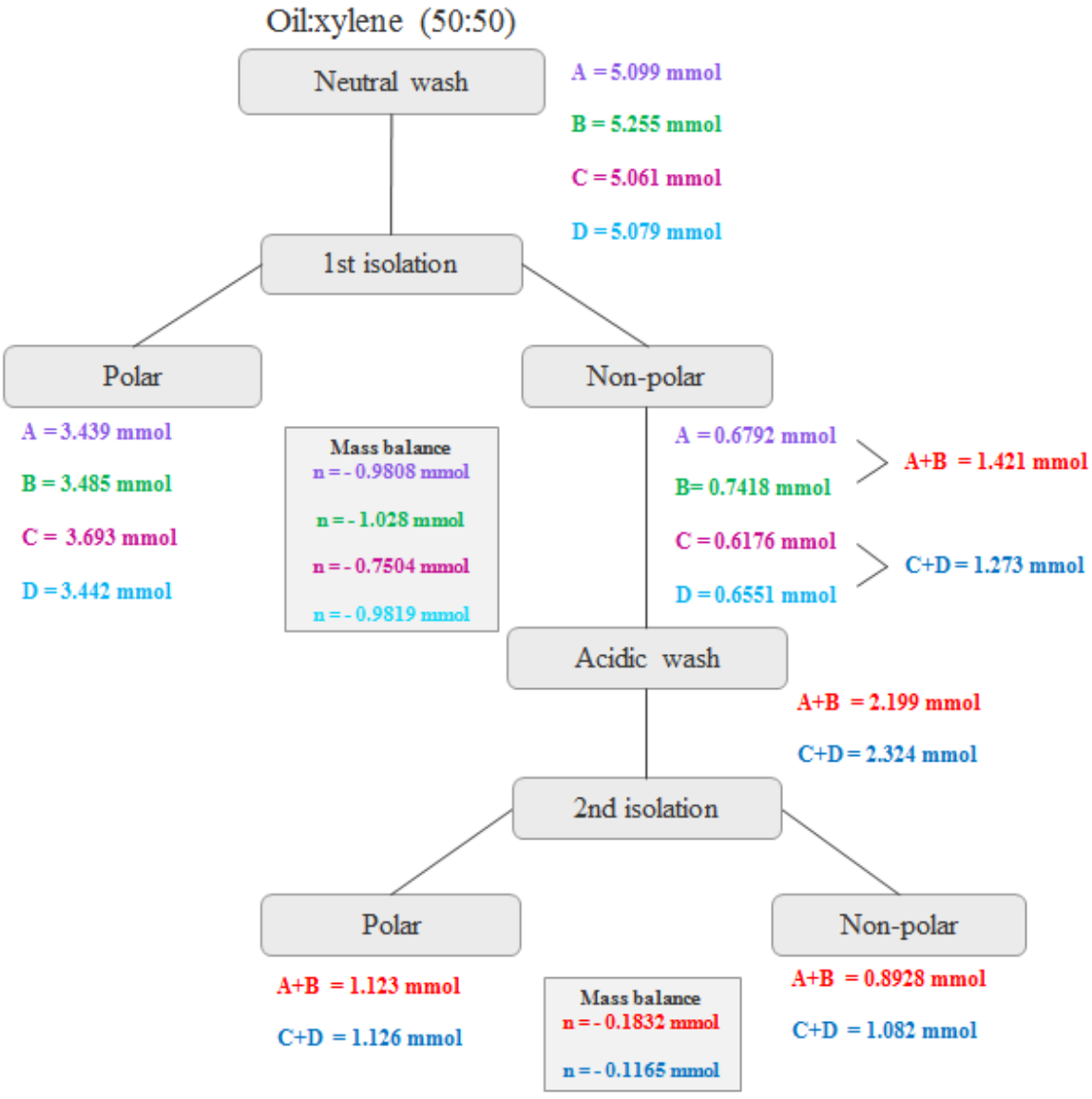

Figure 16 Mass balance from the second isolation process of neutral washed sample

As seen from Figure 16 and Table 8, the amount of acids in the polar phase after the first isolation is smaller than in the first batch. Also, the non-polar phase has a little higher amount and the loss of sample has increased. The parallels of the polar phase in this second batch however, are very similar, except for parallel C. After acidic wash and the second isolation of this batch, a higher percentage has been transferred to the polar phase and less to the non-polar phase compared to the first batch.

Table 8 Amount of acids in each phase compared to the initial sample (batch 2 of neutral washed sample) in %

Isolation step	Parallel	Polar	Non-polar	Mass balance
1	A	67.4	13.3	- 19.2
	B	66.3	14.1	- 19.6
	C	73.0	12.2	- 14.8
	D	67.8	12.9	- 19.3
2	A+B	51.1	40.6	- 8.3
	C+D	48.5	46.6	- 5.0

The amount of acids present in the non-polar phases after the second isolation step, gave a lower TAN-value than the non-polar phase before acidic wash. This indicates that some of the acids than were transferred to the polar phase during the first isolation in the first batch performed, have in this batch been transferred to the non-polar phase. However, when comparing the amount in the non-polar phase after the second isolation step with the corresponding phase in the first batch, they are very similar. This means that there are some acids that should have been isolated in the first isolation step that instead have been isolated in the second step. This may influence the average molecular weight of the samples. This does however not seem to be the case here, since the two polar phases gives an average molecular weight (847 and 904 g/mole) on opposite sides of the weight retrieved from the first batch (874 g/mole). It seems therefore safe to say that the polar and non-polar phases retrieved from the two batches can be considered as parallels.

It is believed that the loss of sample is caused by a too mild back-extraction, meaning that the acids did not get detached from the ion exchanger during the two final steps with formic acid.

Some part of these acids may have been lost when the samples were transferred between equipment, but it is unlikely that about 20 % of the sample would be lost this way. The amount that were lost for the four parallels are also very similar, which suggest that this is because of some special characteristics with this particular oil.

Table 9 presents the TAN-values retrieved and calculated average molecular weight for batch 2. As seen from the table, the values for all phases in batch 2 are quite similar to the first batch. The non-polar phases are a bit higher, and the increase in TAN in the non-polar phase after acidic wash is about 0.8 to 1.1, instead of 0.7 as it was for the first batch.

Table 9 TAN-values and calculated average molecular weight (batch 2 of neutral washed sample)

Sample	TAN	M_w [g/mole]
Neutral washed (batch 2)	9.5	
Polar phase		583
		561
		585
		586
Non-polar phase	1.5	
	1.5	
	1.3	
	1.4	
Acidic washed non-polar (batch 2)	2.3	
	2.5	
Polar phase		847
		904
Non-polar phase	1.1	
	1.1	

The results from the acidic washed oil sample, which works as a reference sample, are given in Figure 17 and Table 10. Three parallels (A, B and C) were isolated for this sample.

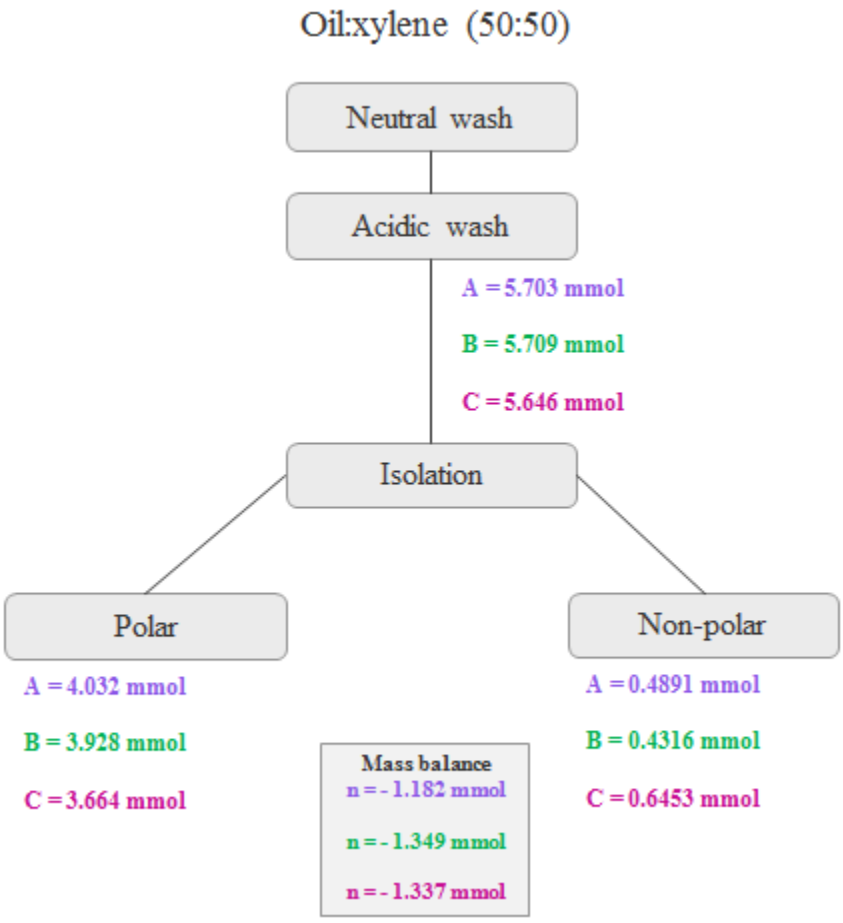

Figure 17 Mass balance from the isolation process of acidic washed sample

As seen from the figure and table, between 65 and 71 % of the initial sample were transferred to the polar phase. This phase would now consist of free acids, which included the acids that initially were bound to calcium. It would be expected that the total amount in the polar phase would be larger, but as can be seen from the figure and table, the total amount of acids in the mass balance is about - 20 %. This can, as said before, be due to acids not being back-extracted during the isolation process. Based on the previous experience maintained in this thesis, it was expected that some of the sample would transferred to the non-polar phase, as turned out to be the case in this isolation as well. This again gives an indication that these compounds differ from the naphthenic acids that are transferred to the polar phase.

Table 10 Amount of acids in each phase compared to the initial sample (acidic washed) in %

Isolation step	Parallel	Polar	Non-polar	Mass balance
1	A	70.7	8.6	- 20.7
	B	68.8	7.6	- 23.6
	C	64.9	11.4	- 23.7

Table 11 presents the TAN-values and average molecular weight calculated for the phases retrieved during isolation of acidic washed oil sample. Compared to the initial sample in the other two batches with the neutral washed sample, the TAN for the acidic washed oil was higher. This is because the naphthenic acids bound to calcium are released and transferred into free acids. The increase of around 1 in TAN-value indicated that there were around 10 % naphthenic acids that originally had been attached to calcium during production, in the acidic washed sample.

Table 11 TAN-values and calculated average molecular weight (acidic washed)

Sample	TAN	M_w [g/mole]
Acidic washed	10.7	
	10.6	
Polar phase		614
		633
		626
Non-polar phase	1.1	
	1.0	
	1.4	

The TAN-value, and thereby the average molecular weight of the polar phase, varies from the neutral washed samples. The molecular weight was calculated to be around 620 g/moles. Calcium bound naphthenic acids were presented with an average molecular weight of around 875 g/mole, and the free acids in the oil with a weight of 580 g/mole. This polar phase of acidic washed sample would contain all acids, both free and initially bound to calcium. Since the total amount of initially calcium bound acids are just below 10 wt%, the result correlates well with the previous retrieved molecular weights.

4.2.3.1 SPE-method

The first SPE-analysis was performed with two separate parallels, as seen in Figure 18. They both contained about 15 grams of oil, which were equivalent to 2.885 and 2.868 millimoles of acidic compounds.

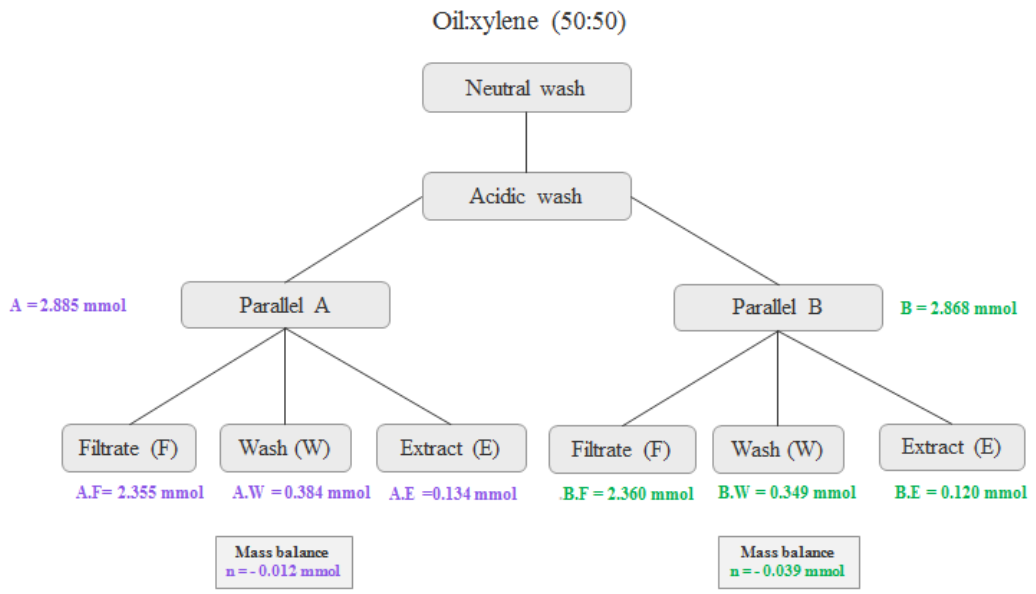

Figure 18 Mass balance from the first extraction with 15 gram samples

As seen from the figure and table, the two parallels are very similar. The amount of acidic compounds that went through the column and entering the filtrate was about 82 %, between 12 and 13 % was transferred to the wash and only about 4 % was detected in the extracted acid phase.

Table 12 Percentage of the amount of initial sample in the first extraction by SPE in %

Parallel	Filtrate	Wash	Extract	Mass balance
A	81.6	13.3	4.6	- 0.42
B	82.3	12.2	4.2	- 1.36

The amount of extracted acid was originally expected to be just below 10 %, and the small amount obtained is most likely due to the capacity of the salt. Previously, the salt has been used for extraction of ARN-acids, where samples of maximum 100 ppm acids were extracted. It is unknown if the salt have a higher capacity than 100 ppm, but in 15 grams of this oil, the amount of acids is much higher.

The second extraction with SPE was performed with approximately 5 grams of oil sample entering three different columns, which were equivalent to 0.951, 0.985 and 0.977 millimoles. The filtrate, wash and extracted acids from the three columns were combined, as shown in Figure 19.

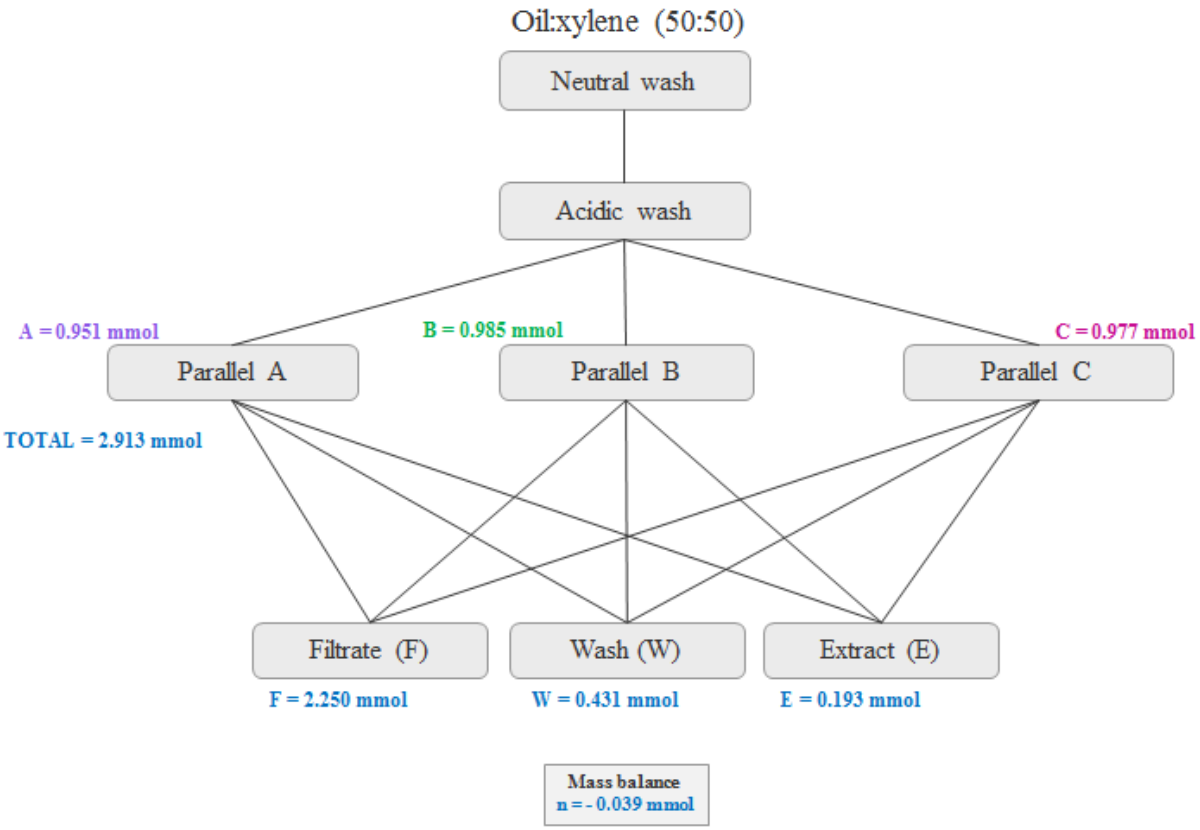

Figure 19 Mass balance from the second extraction with 3x5 gram samples

The second run showed a slight increase in the amount of acids that were extracted. Totally 6.6 % were extracted, which is still lower than what could be expected. The result does however show that more acids did get attached to the calcium in the column when given the opportunity.

Table 13 Percentage of the amount of initial sample in the second extraction by SPE in %

Parallel	Filtrate	Wash	Extract	Mass balance
A+B+C	77.2	14.8	6.6	- 1.3

The third extraction was performed with 15 columns with 1 gram of oil sample in each, as seen in Figure 20. The filtrate, wash and extracted acids from these 15 columns were combined like for the second extraction.

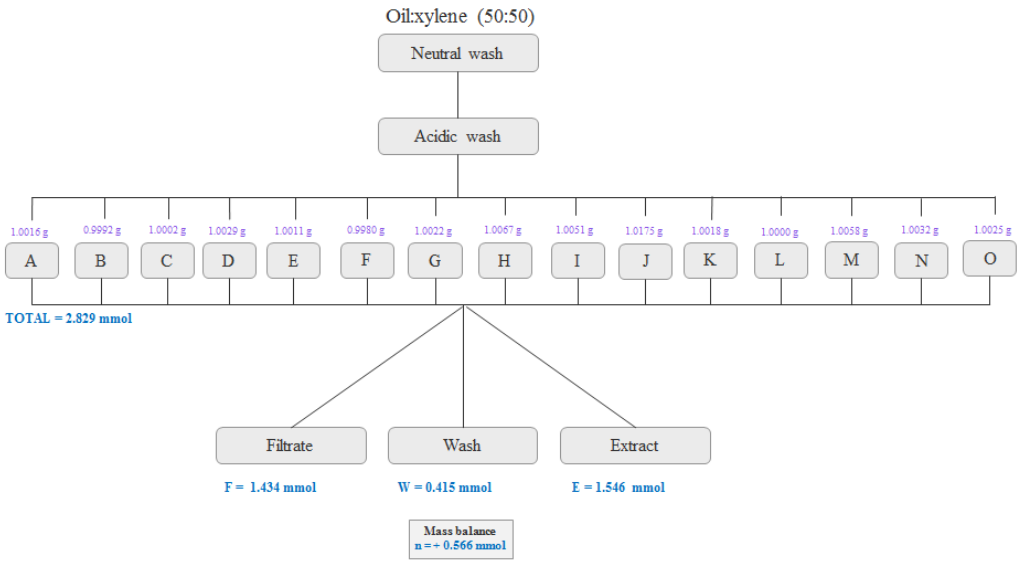

Figure 20 Mass balance from the third extraction with 15x1 gram samples

The third run using the SPE-method shows some indecisive results. More of the acids have attached to the salt in the column, which was expected when the amount of salt was increased. However, when adding up the amount in the filtrate, wash and extract, a gain of 20 % acids are observed.

Table 14 Percentage of the amount of initial sample in the third extraction by SPE in %

Parallel	Filtrate	Wash	Extract	Mass balance
A-O	50.7	14.7	54.7	+ 20.0

The reason for this gain is unknown, but one theory is that some of the HCl used during back-extraction have been transferred to the extract together with the naphthenic acids. This could influence the TAN-measurements in a large way, since the HCl used had a concentration of 6M. Regardless of this, there are still a significant amount of acids in the extracted phase. The reason for this is unknown, but it indicates that more acids have affinity towards calcium than the ones initially attached to calcium in the oil, and that if given the opportunity they will attach as well.

4.3 Characterization of Naphthenic Acids

4.3.1 Atmospheric Pressure Photoionization-Mass Spectrometry

A total of 35 samples were analyzed with APPI-MS, which included a number of parallels for most samples.

The following MS spectrums in Figure 21 are presented to get an overview of the different polar phases compared to each other and the raw oil sample. Spectrum a) represents the raw crude oil which have been neutral washed, while b), c) and d) are polar phases at different stages in the isolation process. The spectrum shown in b) are after the first isolation step of neutral washed oil, while spectrum c) is the polar phase after the second isolation step of acidic washed non-polar. The last spectrum presents the results from the polar phase after isolation of acidic washed oil. All spectrums have been scanned from 150 to 2000, which is given on the x-axis, and the y-axis show the signal.

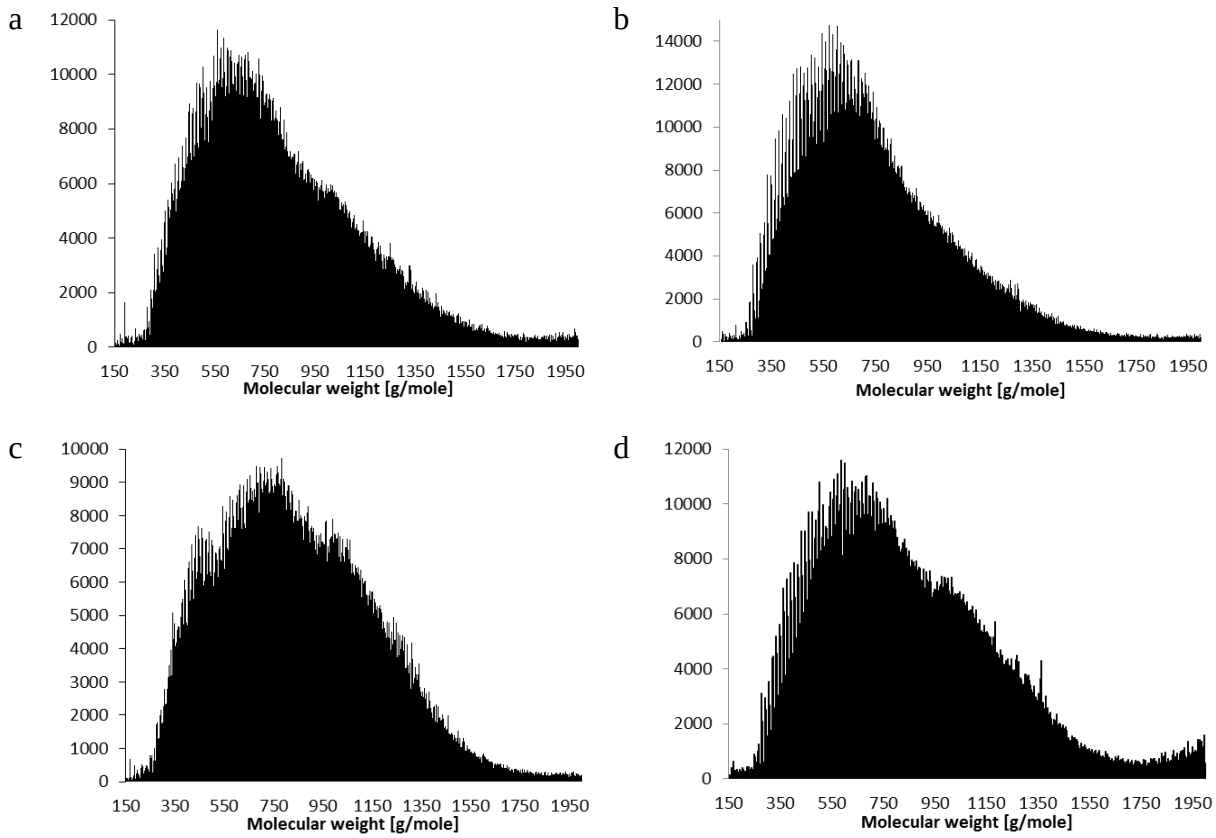

Figure 21 APPI-MS spectrums of a) raw oil, b) polar phase after first isolation step of neutral washed oil, c) polar phase after second isolation step of acidic washed non-polar, and d) polar phase after isolation of acidic washed oil

Figure 21 show that there is a slight difference between the three polar phases. In spectrum b) the average molecular weight seems to be the lowest, while c) has the highest. The spectrum of the polar phase from the acidic washed oil looks like it is somewhere in between the other two. This observation correlates well with the average molecular weights calculated from the TAN-measurements. Spectrum a) show the raw oil after neutral wash, and it is clear that the sample have less compounds in the region above 950 g/mole than the polar phase after second isolation and the polar phase after isolation of acidic washed sample. This also supports the current theory that the naphthenic acids that can form oil-soluble calcium naphthenates have a higher average molecular weight than the other acids in the oil. The raw oil does however consist of other components than acids, which also may have been ionized during the MS-analysis and can influence these results.

To look more closely into differences in the MS soectra, they have been overlayed in different figures. These figures are presented on the next few pages, where only the profile of each spectrum is shown so that it will be easier to see any difference between spectrums.

Figure 22 presents the polar phase after first isolation of neutral washed oil sample, from batch 2, and the polar phase after second isolation of acidic washed non-polar of the same batch. The spectrum given is not normalized.

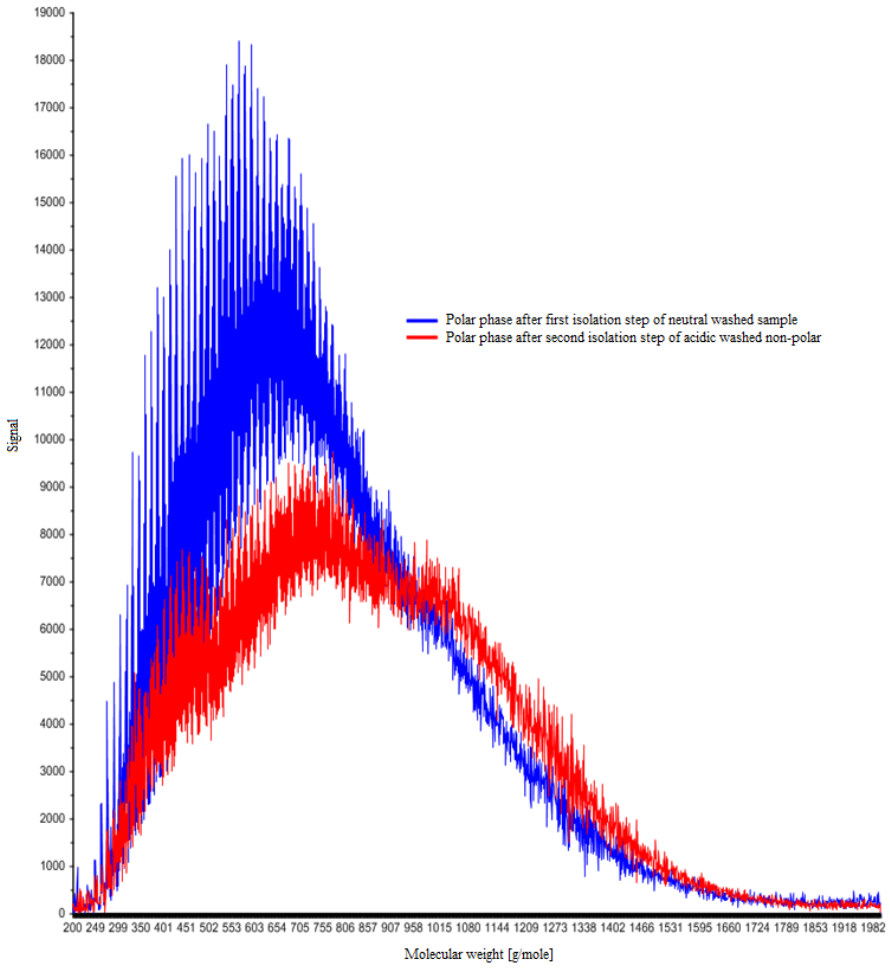

Figure 22 APPI-MS spectrum comparing polar phases

As can been seen from the figure, the polar phase after only neutral wash (blue) has as low average molecular weight. This sample would in theory only contain all naphthenic acids from oil-soluble calcium naphthenate. The red spectrum should in theory only contain naphthenic acids that were bound to calcium, which should have been released after acidic wash and transferred to the polar phase after the second isolation step. The figure shows that naphthenic acids that initially were bound to calcium have a higher average molecular weight than the ones in the others. There seems to be more of acids with a molecular weight in the area of 950 to 1500 g/mole than in the other sample.

The next spectrum presents the same two samples, but in addition the third polar phase (reference sample) retrieved in this work is presented. This third polar phase is showed as the green spectrum and is from the isolation of acidic washed oil. This polar phase would be expected to contain all naphthenic acids in the sample, both free and the ones bound to calcium.

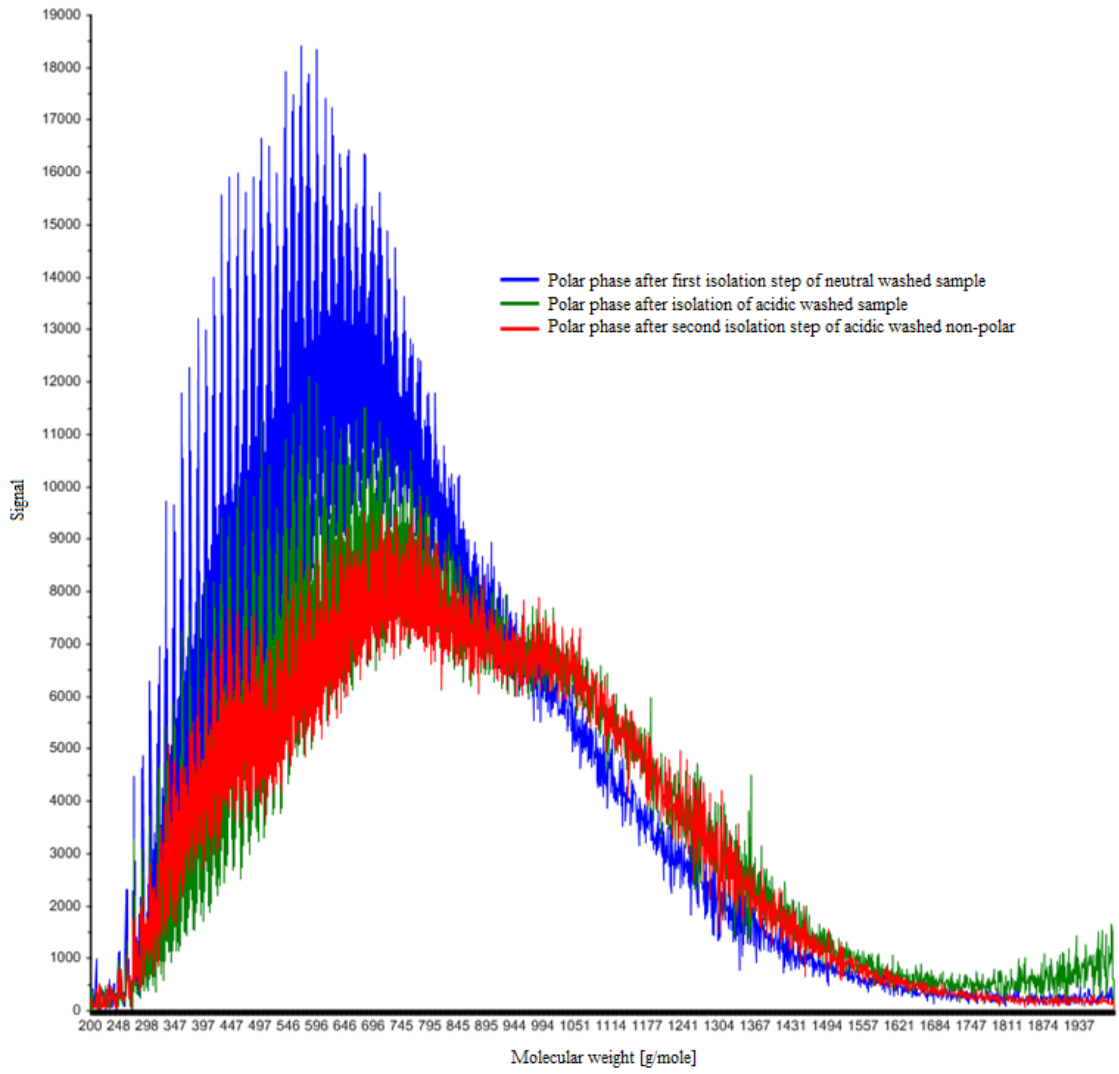

Figure 23 APPI-MS spectrum comparing polar phases

As can be seen from the figure, the third polar phase contains acids in both the lower and higher region.

The results from the APPI-MS analysis of these polar phases indicates that the results retrieved from the TAN-measurements are coherent. By looking manually at the spectrums obtained from the APPI-MS measurements, the average molecular weight for the polar phase after the first isolation is somewhere between 500 and 750, which correlates to the TAN-measurement of 580 g/mole. The same can be seen for the polar phase after second isolation, which in theory only contains naphthenic acids that were originally bound to calcium. The spectrum indicates that the average molecular weight is between 650 and 1000, and the TAN-measurement resulted in 875 g/mole. As for the acidic washed sample, it lies somewhere in between the other two, which also correlates well with previous results.

Since there were detected acidic compound in the non-polar phases when measuring TAN, two non-polar phases were compared to see if the MS-spectrums would be similar. Figure 24 presents a non-polar phase after the first isolation step of neutral washed sample and a non-polar phase after the second isolation of acidic washed non-polar.

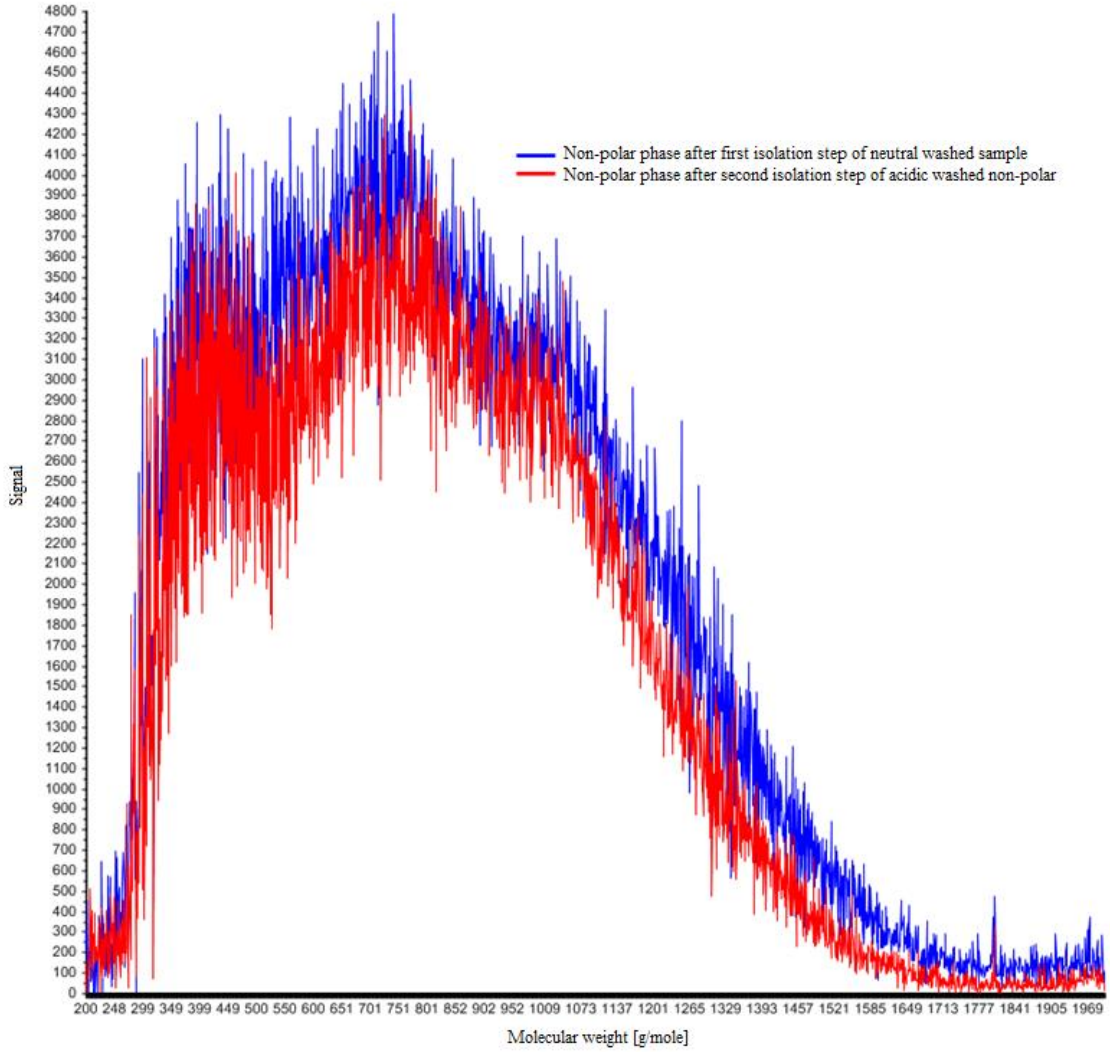

Figure 24 APPI-MS spectrums of two non-polar phases

The spectrum of the two non-polar phases that are presented show that these samples have a very similar distribution. It is clear that these compounds do not attach to the ion exchanger even though they go through isolation multiple times. This supports the conclusion that the capacity of the ion exchanger is not the reason for the acidic compounds found in the non-polar phase.

Since the results from the SPE-method were somewhat indecisive, the three phases with extracted acids from the three rounds were analyzed with APPI-MS. The spectrum initially had many high peaks that were considered as interference from the instrument. A modified spectrum is shown in Figure 25, while the initial spectrum is presented in Appendix C.

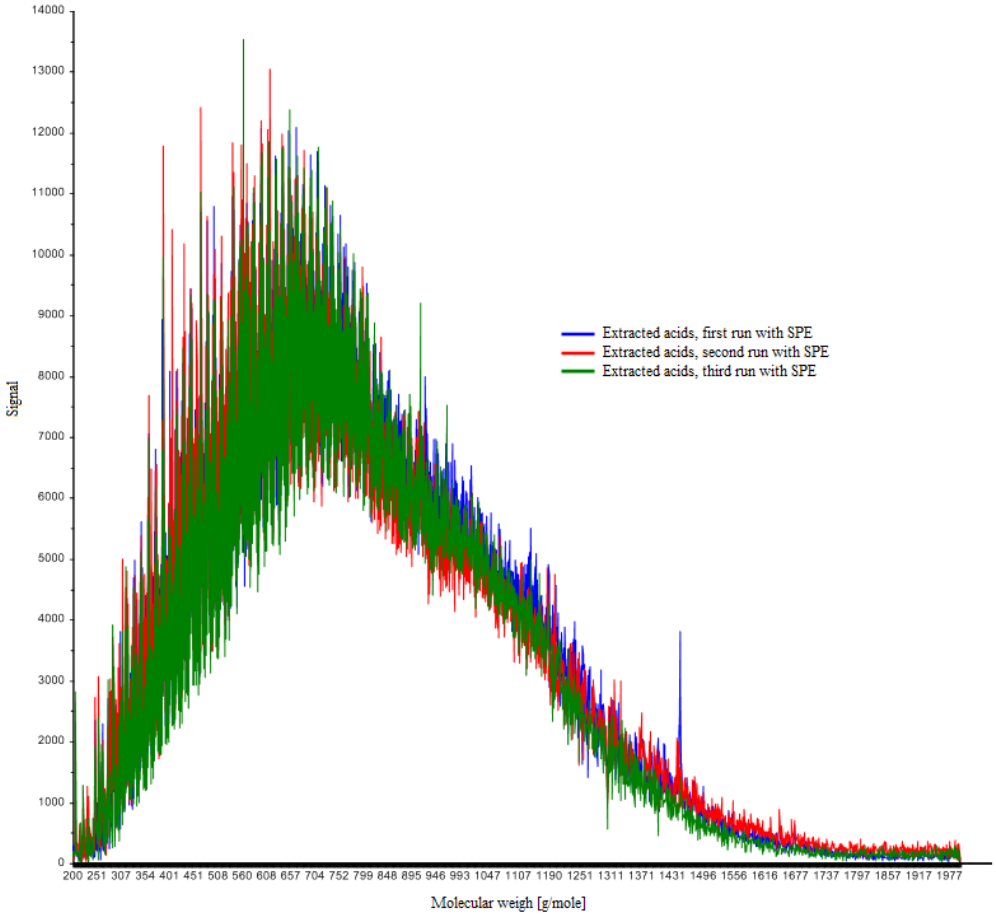

Figure 25 Modified APPI-MS spectrum of the extracted acids from the three SPEs

APPI-MS analysis of the SPE results of the three extracted acid phases shows that no noticeable difference can be seen between them. This indicates that the same type of acids are attaching to the calcium salt in the column independent of the amount of salt or acids. The distribution of these acids does however have a large molecular weight span. This indicates that not only a few special acids, but a wide range with different molecular weight are able to attach.

To see if there were a difference between the acids in the extracted phase and the filtrate and wash, these samples were all analyzed with APPI-MS. Figure 26 presents the extracted acids (blue), wash (green) and filtrate (red) from the last run with SPE, where 15 columns with 1 gram in each was used. This figure is also modified and the initial spectrum is given in Appendix C.

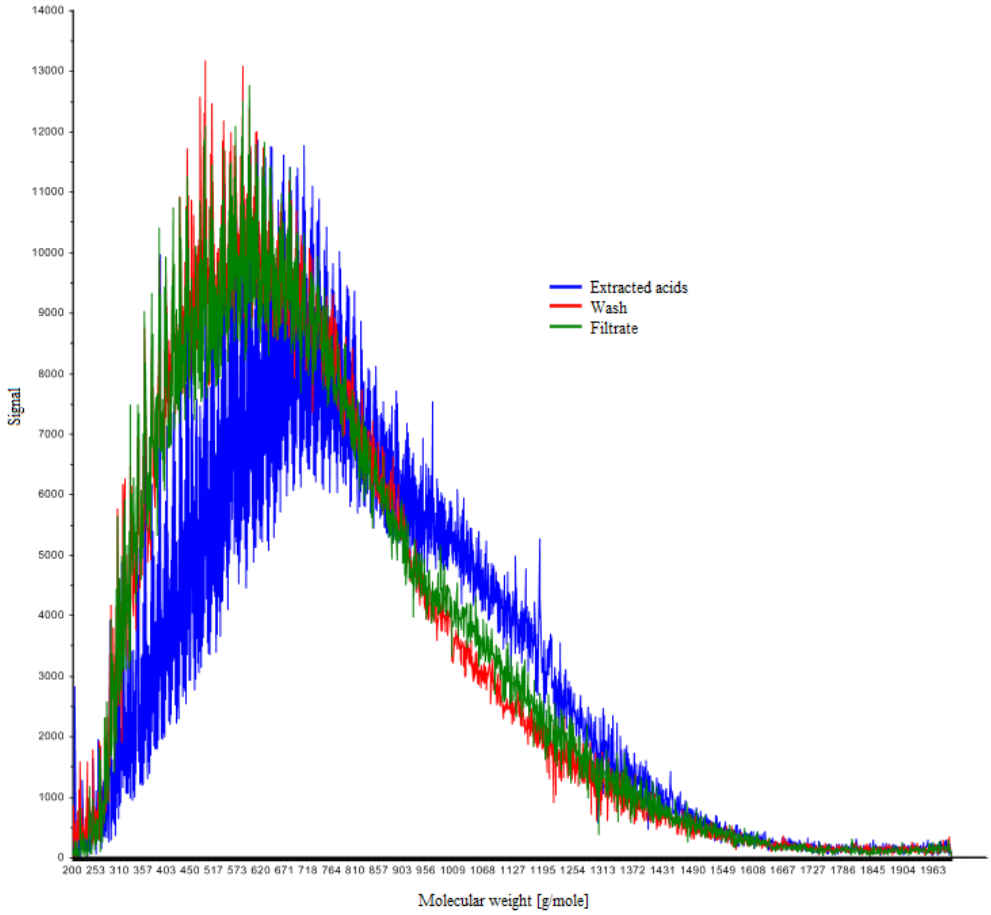

Figure 26 Modified APPI-MS spectrum of the extracted acids, wash and filtrate from the third SPE

It is clear from the figure that the wash and filtrate contains more of the compounds with low molecular weight than the extract. The extract however seems to have a higher average molecular weight. It is important to remember that the filtrate and wash consists of other compounds and not just acids as the extract does.

4.3.2 Electrospray Ionization-Mass Spectrometry

The results from the ESI-MS analysis gave a very different distribution in terms of molecular weight than the results from the APPI-MS. Figure 27 presents the comparison between the polar phase after the first isolation step of neutral washed oil sample and the polar phase after the second isolation step of acidic washed non-polar phase.

It was believed that the given distribution could have something to do with the acetonitrile used as mobile phase during the analysis. It is known that acids such as the ARN-acids have very low solubility in the compound, and this will cause precipitation during analysis and faulty results. This was not tested for these particular acids, but if this would be the case it could explain the inconsistent results. The decision to use acetonitrile during analysis was done due to poor spectrums being retrieved without. Figures presenting some polar phases are shown in this chapter to give an idea of what results that were retrieved.

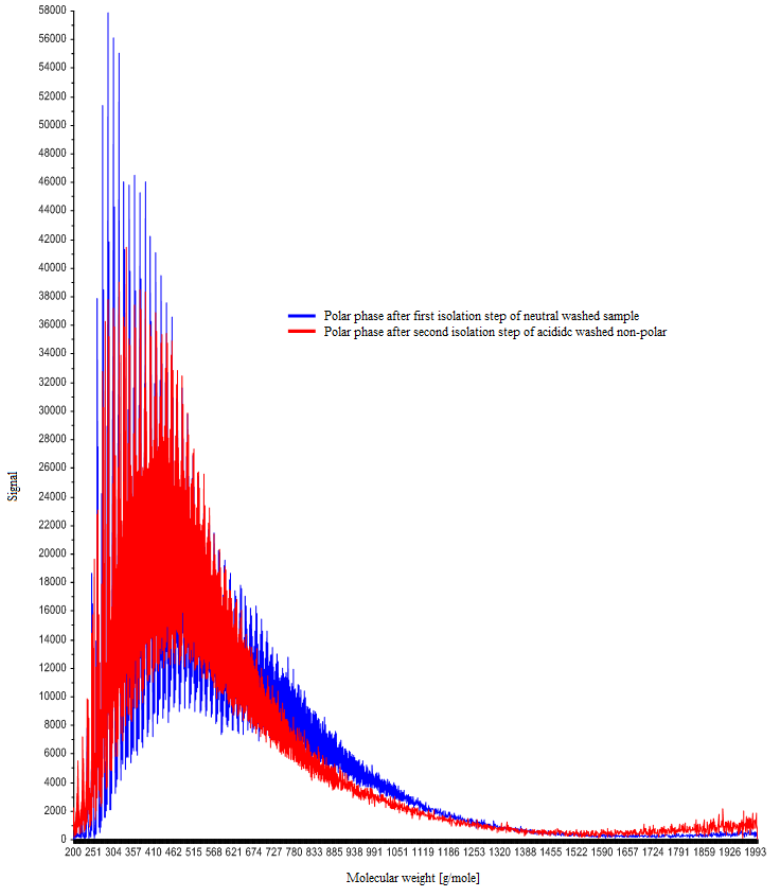

Figure 27 ESI-MS spectrum comparing polar phases

As can be seen from Figure 27, the polar phase after the second isolation step (red) seems to have a lower average molecular weight than the polar phase after the first isolation step (blue). This does not correspond well with the results retrieved from the APPI-MS analysis.

ESI is capable of ionizing molecules that have a very high polarity, but not as well with molecules that have low polarity. This indicates that some of the acids in the samples that have high molecular weight also have a low polarity, and are therefore detected only when using APPI.

4.3.3 Infrared Spectroscopy

The results presented from the isolation process with the Acid-IER method, show that some cmpounds are detected with TAN-measurements in the non-polar phases. These phases were analyzed with FT-IR to see if the compounds were acids or other titratable compounds.

Figure 28 presents the FT-IR results for three samples. The black line represents a non-polar phase (50 wt%) after the first isolation of acidic washed oil sample. Here it would be expected that there would be no naphthenic acids. The blue line is also a non-polar phase (50 wt%), but this one is after the second isolation of the acidic washed non-polar. Based on the theory of the Acid-IER method, it would also be expected that this phase would contain no acids. The red and green line represents the same sample, a polar phase after the first isolation of an acidic washed oil sample. The difference is the concentration, which is 0.1 wt% for the red line and 1 wt% for the green. The brown line is a blank-sample.

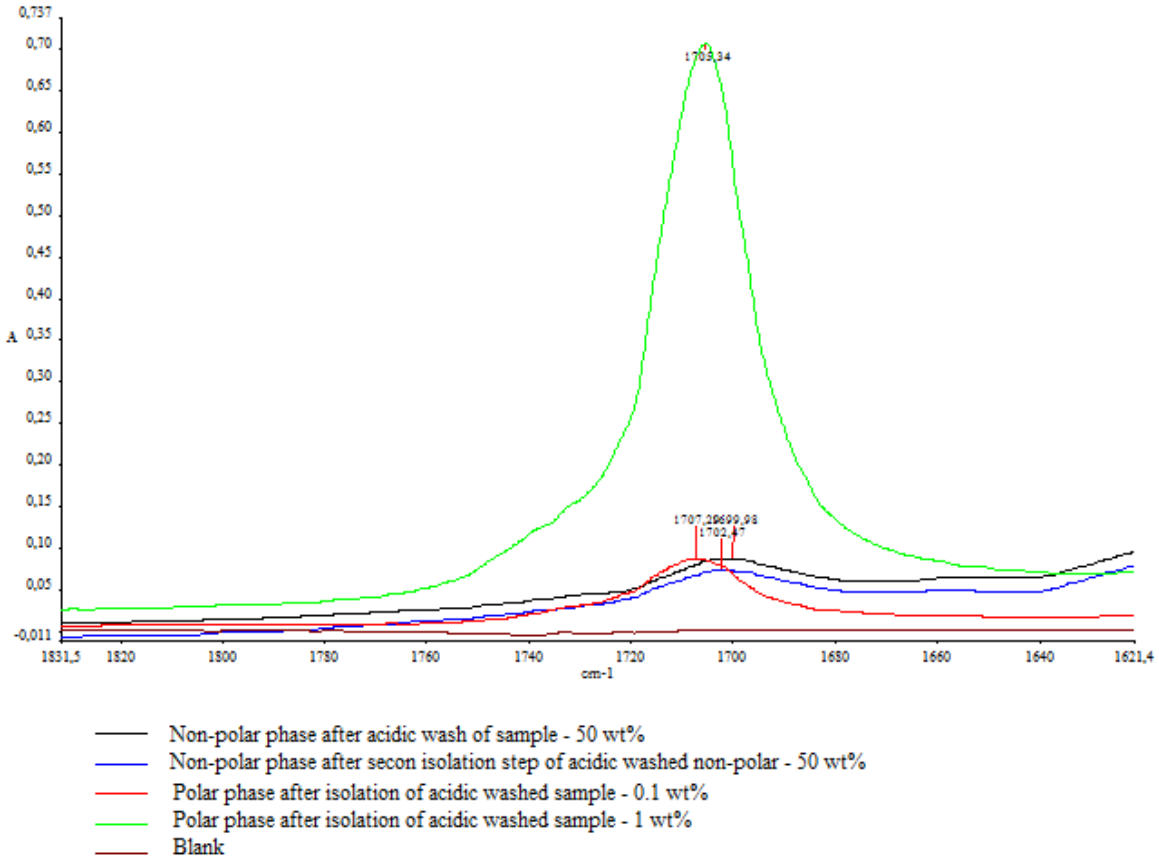

Figure 28 Results from FT-IR on polar and non-polar phases

As can be seen from Figure 28, both polar and non-polar phases have peaks that are near the expected peak for naphthenic acids. The peaks for the polar phase are at 1707.29 and 1705.34, while the non-polar phases have peaks at 1702.47 and 1699.98. There is obviously a difference between the peaks, but is not possible based on these results alone, to determine if these are in fact naphthenic acids or not.

To compare the heights of the peaks, the TAN-values for the 0.1 wt% and 1 wt% polar phase are estimated. The TAN-value retrieved from the measurement was 91.41 for the dried acid sample. This gives a TAN of around 0.09 for the 0.1 wt% sample and around 0.90 for the 1 wt% sample. The non-polar phases were both diluted with toluene:isopropanol to 50 wt% samples. One non-polar (black line) had a TAN-value of 1.41, which gives 0.71 for the diluted sample. The other non-polar (blue line) had a TAN-value of 1.11, which gives 0.56 for the diluted sample. When looking at these TAN-values, the amount of acids in the non-polar phases should have been in the middle of the two polar phases. As can be seen from the figure, this is not the case. This gives an indication that the compounds that are titrated in the non-polar phase may be other compound than acids, which can be titrated by a base but not attach to the ion exchanger.

5 Conclusion

The naphthenic acids that are bound to calcium in the crude oil have a much higher average molecular weight than the other naphthenic acids, 850-900 g/moles and 500-535 g/moles respectively. This result was confirmed by TAN-measurements and APPI-MS of samples after isolation with the Acid-IER method. The correlation between the TAN-measurements and the results from APPI-MS, indicates that the acids can be characterized as monoacids. They do not have a particular molecular weight, but have a broad distribution. It seems that the calcium naphthenate formation is controlled by the total amount of acids in the oil, their molecular weight and pH, and not as much on structure as first were presumed.

The two oils that initially had very low Ca-content, show a large increase of calcium naphthenate content after treatment with water that had high pH and a high content of Ca. This indicates that the formation of calcium naphthenate is dependent on pH, and will follow equation: $Ca(RCOO)_2(o) + 2H^+(w) \leftrightarrow 2RCOOH(o) + Ca^{2+}(w)$

Neutral wash proved to be quite effective on removing calcium from the oil, which means that a contact time of 1.5 hours is enough to reach equilibrium of the equation:

$$Ca(RCOO)_2(o) + 2H_2O(w) \leftrightarrow 2RCOOH(o) + Ca^{2+}(w) + 2OH^-(w)$$

when using a 1:3 relation between water and oil.Acidic wash proved to be a good method for dissolving naphthenic acids that are bound to calcium back into their free form.

It is clear that the ion exchanger used in the Acid-IER method is capable of isolating naphthenic acids that are connected to calcium from the other acids in an oil sample. The ion exchanger does not isolate all compounds that can be measured by TAN. Based on the IR-results, the non-polar phases contained compounds that could be titrated by a base but do not attach to the ion exchanger during isolation. This strongly indicates that most of these compounds are not naphthenic acids, but other compounds found in the oil like sulphur.

The SPE-method gave some indecisive results, but they seem to extract more acids than those who are initially bound to calcium. This method does not seem to work well for isolation of calcium naphthenates.

6 Further Work

The main purpose of neutral wash is to remove impurities from the oil without any loss of calcium attached to naphthenic acids. This could be done by avoiding the reaction to reach equilibrium. The contact time between oil and water and the amount of water used are factors that should be further investigated.

Both polar and non-polar phases should be further analyzed to characterize the different components in the different phases. Most important would be the polar phase after second isolation of the acidic washed non-polar, since this is the phase that contains the naphthenic acids initially bound to calcium. Possible routes for characterization would be to have a closer look at the MS spectrums retrieved in this thesis, to examine more closely the distribution of acids. Characterization could also be done with for instance NMR

It would also be very interesting to characterize the compounds in the non-polar phases as these gave a TAN-value, but which the IR spectroscopy showed as something other than acids. This could prove to be a complex task, as the non-polar phase contains many different oil compounds. An initial analysis would be to characterize the sulphur-components present in the sample, as it is known that this oil have some content of such compounds. Mercaptan and sulfides can be characterized by using GC-GC, but if the results show that there are less of those compounds than what the TAN suggests, other analysis should be performed.

The acids that were considered a loss may still be attached to the ion exchanger. All of the ion exchanger used in this master thesis is stored, and further tests can be conducted to see if there are still some acids attached to it. If the acids did not get back-extracted during the process, a strong acid could be added to release them from the ion exchanger.

The Ca-increase after water treatment of the two low Ca-content oils indicated that the formation of oil-soluble calcium naphthenates are strongly dependent on pH. This procedure should be performed ones more, but with the addition of TAN-measurements before and after the water treatment. If the TAN-value decreased with the increase of calcium, this indicates that the calcium have been attached to naphthenic acids in the oil and formed oil-soluble calcium naphthenates.

The results from the SPE-method clearly show that the method does not work well for this, since a large portion of the acids attach to the salt. It would be unnecessary to develop this method further, but instead focus on the Acid-IER method for isolating oil-soluble calcium naphthenates.

Further ESI-MS measurements should be performed were the acetonitrile is left out to see if that was the reason for the incomprehensible spectrums retrieved, or if low polarity of the acids may be the reason.

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Appendices

Appendix A Water Content by Karl Fischer Titration

Appendix B APPI-MS spectrums of Acid-IER samples

Appendix C APPI-MS spectrums of SPE samples

Appendix D Hazardous Activity Identification

Appendix E Risk assessment

Appendix A: Water content by Karl Fischer Titration

In this appendix, the WiO-content of the different samples is presented.

Table A-1 Water-in-oil content of samples

Sample	Parallel 1	Parallel 2	Parallel 3	Av. (wt%)
Neutral washed Batch 1 (first centr.)	0.17	0.20	0.19	0.187
Neutral washed Batch 1	0.02	0.02	0.02	0.02
Neutral washed Batch 2 (first centr.)	0.39	0.16	0.09	0.213
Neutral washed Batch 2 (second centr.=	0.04	0.04	0.03	0.037
Acidic washed	0.03	0.02	0.03	0.027
Acidic washed non-polar Batch 1 Parallel 1+2 (first centr.)	0.08	0.09	0.08	0.083
Acidic washed non-polar Batch 1 Parallel 1+2 (second centr.)	0.03	0.02	0.02	0.023
Acidic washed non-polar Batch 2 Parallel 1+2	0.02	0.02	0.02	0.02
Acidic washed non-polar Batch 2 Parallel 3+4	0.04	0.04	0.04	0.04

Table A-1 presents the WiO-measurements performed during this master thesis. As seen in the table, some of the values were too high according to the 0.05 wt% that was set. This lead to a second centrifuging of these particular samples.

Appendix B: APPI-MS spectrums of Acid-IER samples

This appendix presents a few more spectrums of samples analyzed with APPI-MS. The following four figures show parallels of polar and non-polar phases that have gone through neutral wash and acidic wash, to show that the parallels have similar distribution.

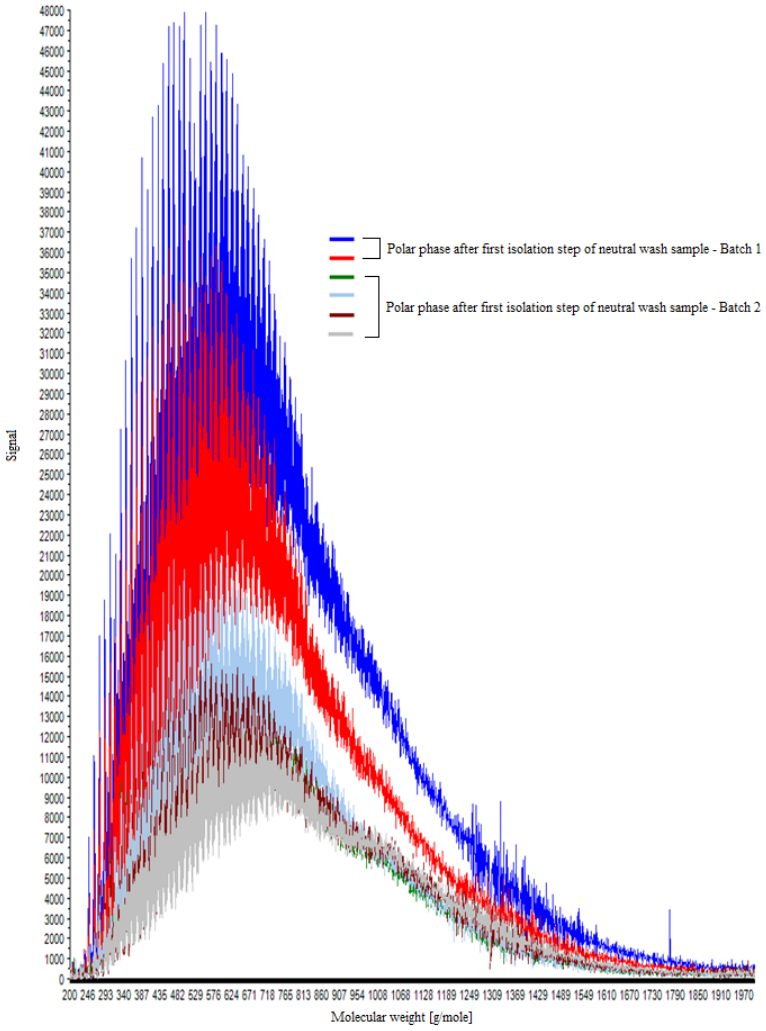

Figure B-1 APPI-MS spectrum of neutral washed polar phases

Figure B-1 show the spectrum of six parallels of the polar phase retrieved after the first isolation step of the neutral washed oil sample. It is unclear why the six parallels seem to have a loss in signal during analysis, but the distribution seems to be very similar. It was therefore responsible to use only one of these parallels when comparing this particular phase with other phases in the isolation process.

The following figure presents the three parallels for the polar phase retrieved after isolation of the acidic washed oil sample.

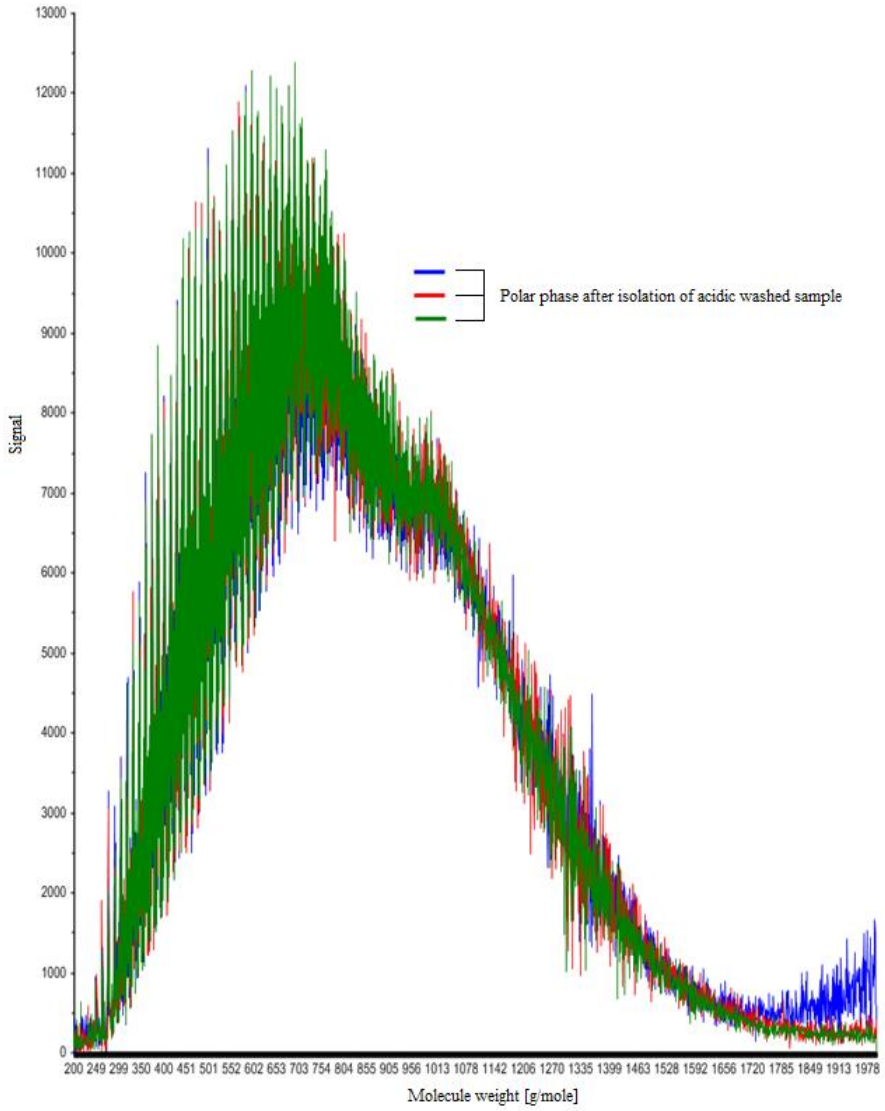

Figure B-2 APPI-MS spectrum of acidic washed polar phases

As can be seen from the figure, all these three parallels have very similar distribution. One exception is the deviation from 1720 to 2000 in molecular weight for parallel A. The reason for this could be some disturbance in the instrument during analysis. The area that has been looked at during this thesis does not involve such high molecular weight, and this deviation is therefore not significant.

Figure B-3 presents an APPI-MS spectrum of the non-polar phases retrieved after the 1st isolation of neutral washed oil sample.

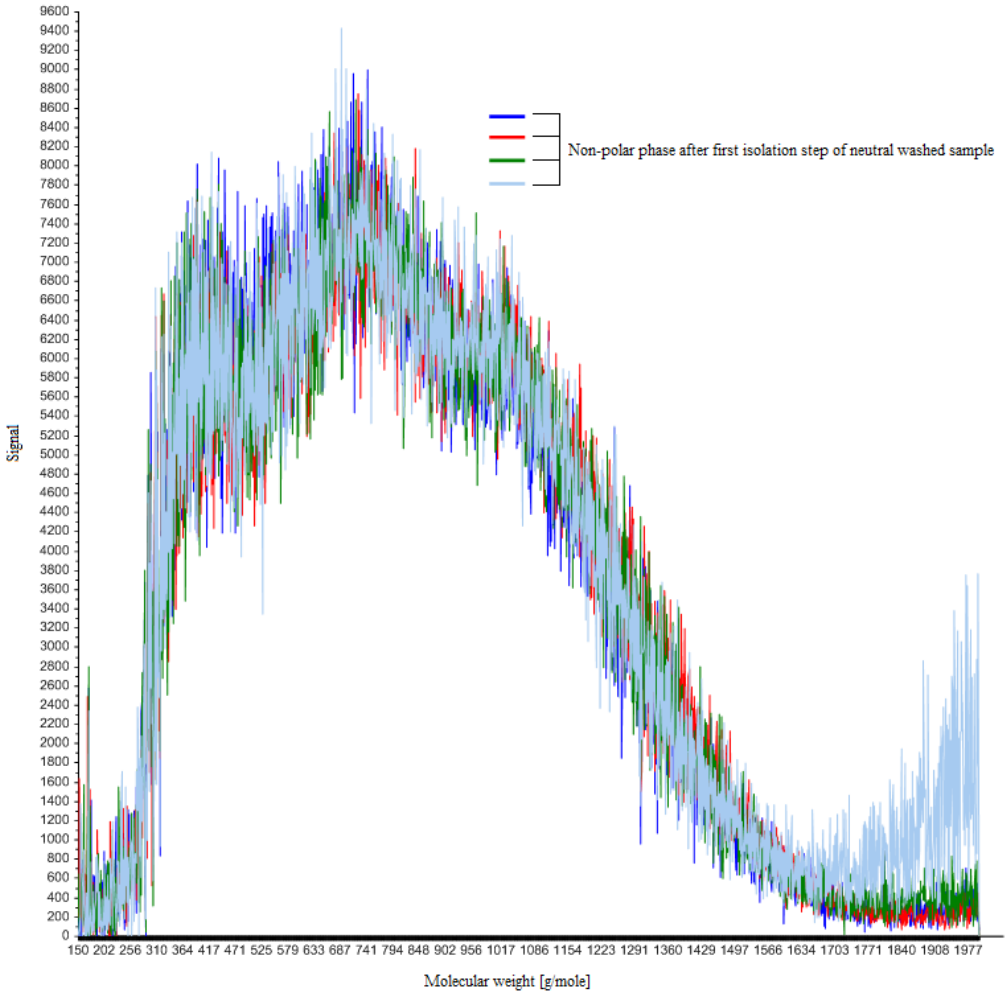

Figure B-3 APPI-MS spectrum of neutral washed non-polar phases

As for the previous spectrums, this also shows that the deviation between the parallels is very small. There is a deviation in the high molecular region here as well, this time for parallel D. Again, this seems to be an error occurring during analysis.

The following figure presents the APPI-MS spectrum for two parallels of non-polar phases that are retrieved after isolation of acidic washed oil sample. The two parallels in Figure B-4 show a very similar distribution.

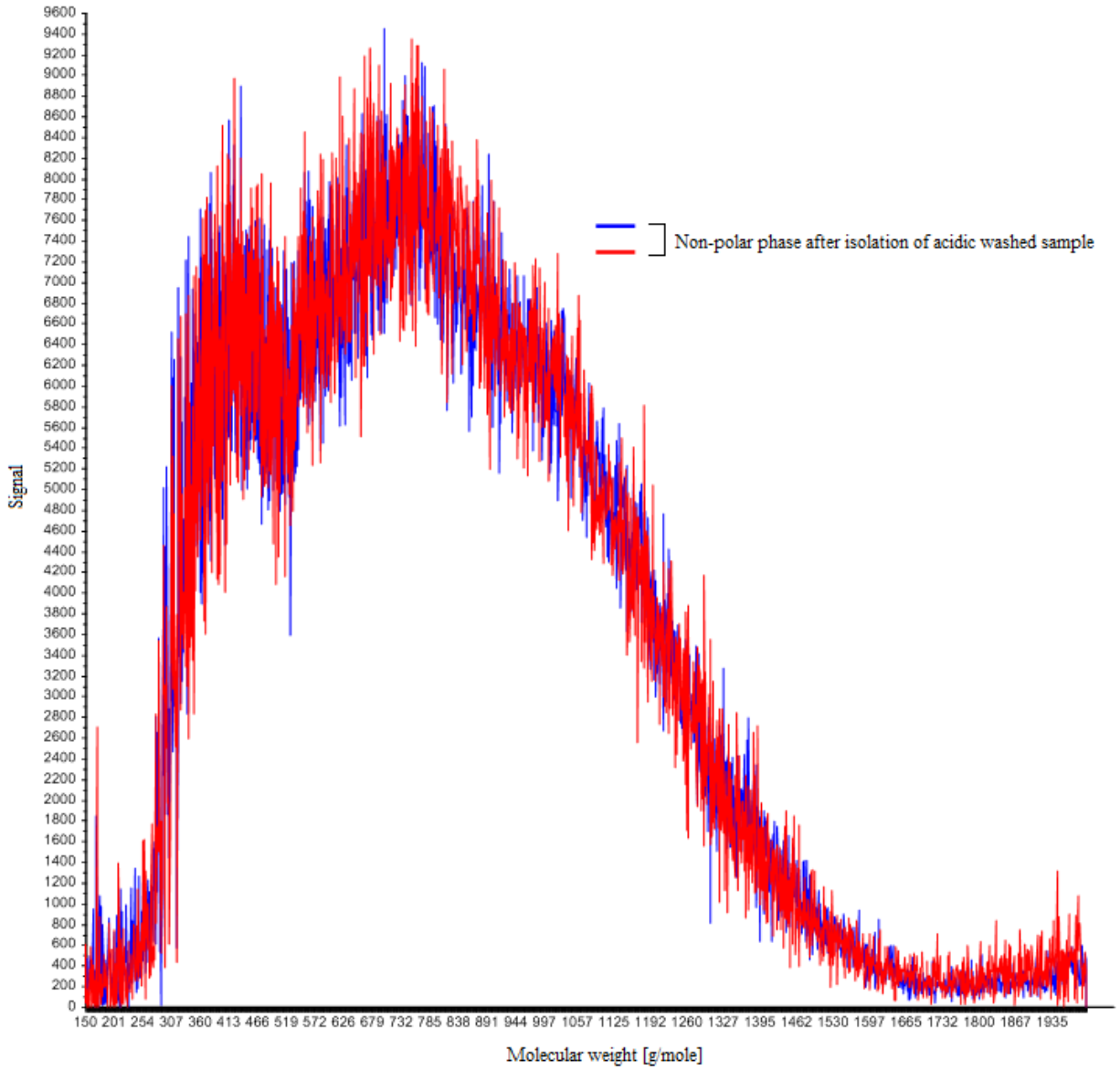

Figure B-4 APPI-MS spectrum of acidic washed non-polar phases

Appendix C: APPI-MS spectrums of SPE samples

Figure C-1 presents a spectrum for the extracted acids from the three different runs with the SPE method. A modified spectrum without the highest peaks is presented in the results.

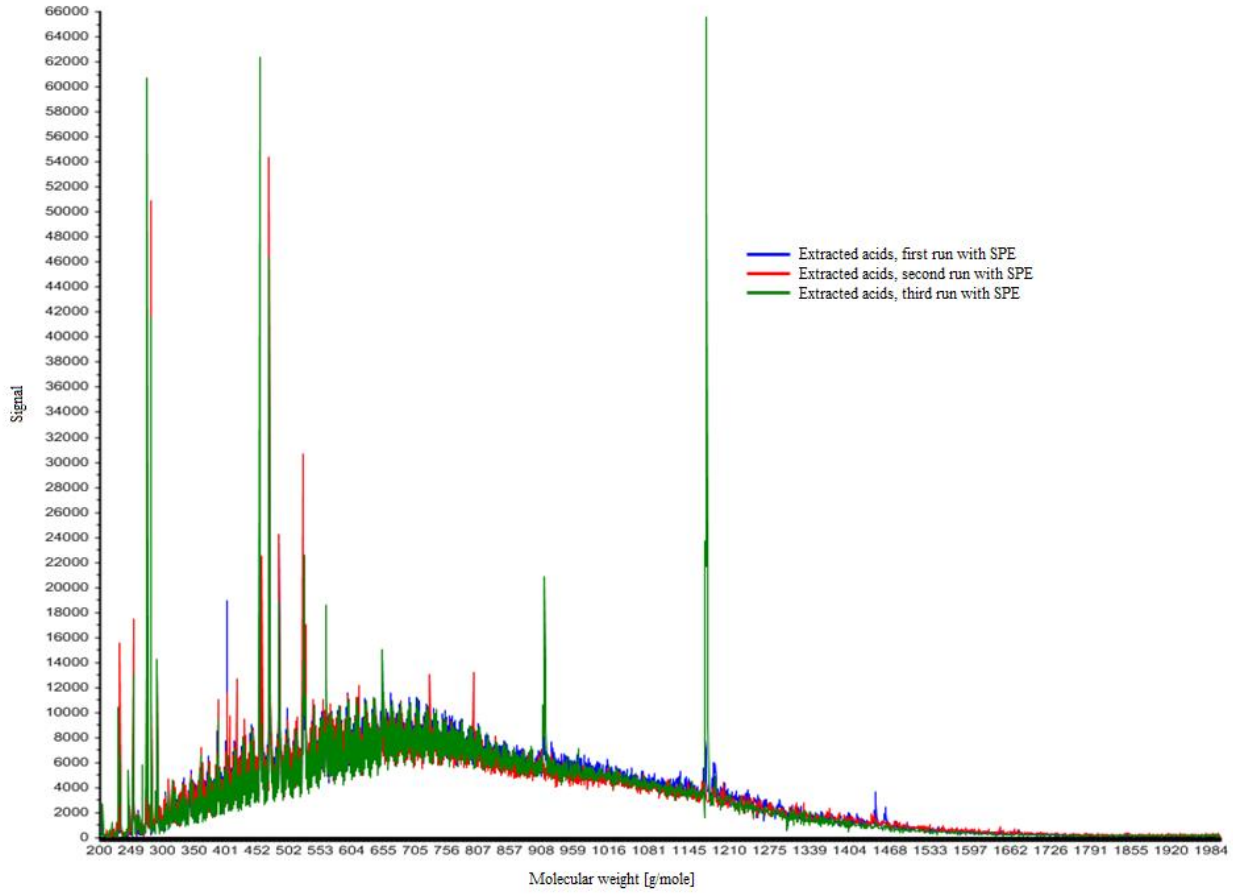

Figure C-1 APPI-MS spectrum of extracted acids from SPE

Figure C- 2 presents a spectrum of the three phases retrieved from the third run with the SPE-method, the extracted acids, the wash and the filtrate. A modified spectrum without the highest peaks is presented in the results.

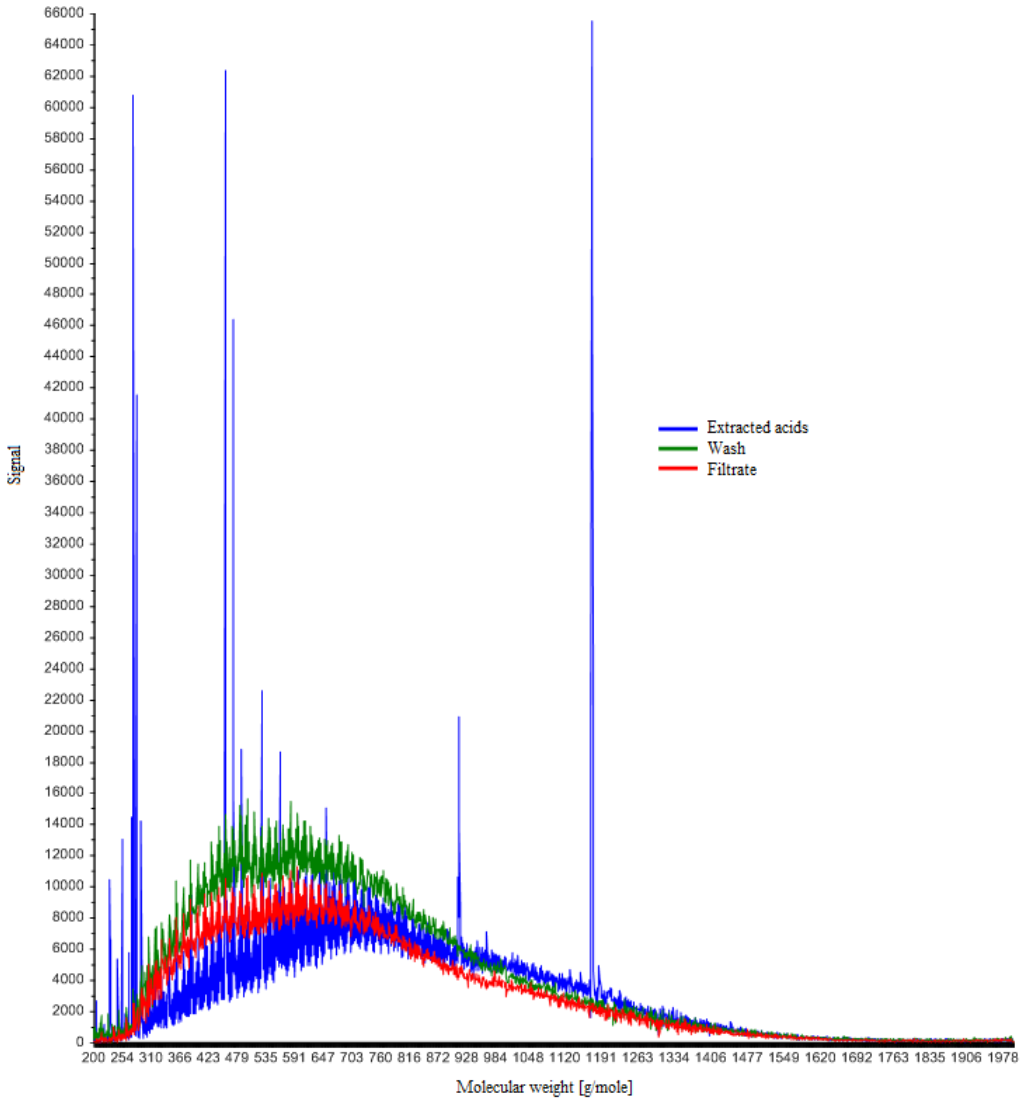

Figure C- 2 APPI-MS spectrum of extracted acids, wash and filtrate from SPE

NTNU HSE	Hazardous activity identification process	Prepared by	Number	Date
		HSE section	HMSRV-26/01	09.01.2013
		Approved by		Replaces
		The Rector		01.12.2006

Unit: Department of Chemical Engineering, Colloid and Polymer Chemistry **Date:** 20.01.2014

Line manager: Johan Sjöblom

Participants in the identification process (including their function)**:** Ida Christiansen (student) and Hege Kummernes (supervisor lab)

Short description of the main activity/main process: Master project for student Ida Christiansen. "Oil Soluble Calcium Naphthenates in Crude Oil".

Is the project work purely theoretical? (YES/NO): NO

Signatures: *Responsible supervisor:* *Student:*

ID nr.	Activity/process	Responsible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
1	Potentiometric titration using tetra-butyl-ammonium hydroxide (TBAOH) (titrator) + toluene and isopropanol (solvent)	Marion Rydningen	Porter et al. "Determination of the total acid number (TAN) using thermometric titration" (based on ASTM D 664).	Use of safety equipment such as gloves, eye protection, lab coat and exhaust ventilation.	MSDS for the three chemicals.	A well-used method at Statoil ASA.
2	Isolation of naphthenic acids by using the QAE Sephadex A-25 Acid-IER. Includes the use of methanol, toluene, isopropanol, formic acid and HCl	Hege Kummernes	Mediaas et al. (2002) SPE 80404 "The Acid-IER Method – a Method for Selective Isolation of Carboxylic Acids from Crude Oils and Other Organic Solvents"	Use of safety equipment such as gloves, eye protection, lab coat and exhaust ventilation.	MSDS for the chemicals.	A well-used method at Statoil ASA.
3	Extraction of naphthenic acids by using a SPE-method. Includes the use of toluene, isopropanol and HCl.	Hege Kummernes	Developed method at Statoil ASA	Use of safety equipment such as gloves, eye protection, lab coat and exhaust ventilation.	MSDS for the chemicals.	A well-used method at Statoil ASA.
4	Acidic wash of oil samples	Hege Kummernes	Developed method at Statoil ASA	Use of safety equipment such as gloves, eye protection, lab coat and exhaust ventilation.	MSDS for formic acid.	A well-used method at Statoil ASA.

NTNU HSE/KS	Risk assessment	Prepared by	Number	Date
		HSE section	HMSRV2603E	04.02.2011
		Approved by		Replaces
		The Rector		01.12.2006

Unit: Department of Chemical Engineering, Colloid and Polymer Chemistry **Date:** 20.01.2014

Line manager: Johan Sjöblom

Participants in the identification process (including their function)**:** Ida Christiansen (student) and Hege Kummernes (supervisor lab)

Short description of the main activity/main process: Master project for student Ida Christiansen. "Oil Soluble Calcium Naphthenates in Crude Oil".

Signatures: *Responsible supervisor:* *Student:*

Activity from the identification process form	Potential undesirable incident/strain	Likelihood:	Consequence:			Risk Value (human)	Comments/status Suggested measures
		Likelihood (1-5)	Human (A-E)	Environment (A-E)	Economy/ material (A-E)		
1.1 Potentiometric titration	Spill of titrator (TBAOH)	3	A	A	A	A3	Only small spills are likely. Use protective gloves and work with exhaust ventilation.
1.2 Potentiometric titration	Spill of solvent (toluene and isopropanol)	3	A	C	A	A3	Only small spills are likely. Use protective gloves and work with exhaust ventilation.
2.1 Isolation of naphthenic acids	Spill of QAE Sepadex A-25 Acid-IER	3	A	A	A	A3	Only small spills are likely. Use protective gloves and work with exhaust ventilation.
2.2/3.1 Isolation and extraction of naphthenic acids	Spill of toluene	3	A	C	A	A3	Only small spills are likely. Use protective gloves and work with exhaust ventilation.
2.3/3.2 Isolation and extraction of naphthenic acids	Spill of methanol	3	B	B	A	B3	Only small spills are likely. Use protective gloves and work with exhaust ventilation.
2.4/3.3 Isolation and extraction of naphthenic acids	Spill of HCl	3	A	A	A	A3	Only small spills are likely. Use protective gloves and work with exhaust ventilation.
2.5/3.4/4.1 Isolation and extraction of naphthenic acids	Spill of formic acid	3	A	A	A	A3	Only small spills are likely. Use protective gloves and work with exhaust ventilation.