NORSK OLJE OG GASS

Quantification of Naphthenic Acids in Produced Water

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Intertek West Lab AS
Postboks 139, 4098 Tananger
Norway
E: norway.westlab@intertek.com
T: (+47) 51 94 01 00
Org. no: 979 911 947 MVA

Worley Origo Process AS
Postboks 54, 4086 Hundvåg
Stavanger, Norway
E: origo@origop.no
T: (+47) 51 93 24 80
Org. no. 984 517 858 MVA

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Are Bertheussen Øyvind Kvalvåg Trond Erik Havre	Trond Erik Havre	

Summary

The Norwegian Environment Agency requires that the content of naphthenic acids in produced water released to sea are to be analysed and reported.

On initiative from the Norwegian petroleum companies, represented by The Norwegian Oil and Gas Association (Norsk olje og gass), Intertek West Lab have worked together with Worley Origo Process to develop a method for such quantification. The Norwegian Environment Agency (Miljødirektoratet) have funded part of the work.

A literature review has been performed to identify the current status for naphthenic acid quantification methods.

Quantification methods for the determination of naphthenic acid content in an oil solvent by GS-MS and GC-FID has been developed. The GC-MS method allows the determination for both the total content of naphthenic acids and the content of different naphthenic acid species. The GC-FID method allows only the determination for the total content of naphthenic acids, however the accuracy of the quantification is superior to the GC-MS quantification. It was demonstrated that the oil in water calibration method is suitable to use for calibration when measuring naphthenic acid concentration by GC-FID.

The naphthenic acids from produced water samples were successfully extracted and isolated. The GC-MS analysis of the samples demonstrate that the measured compounds are naphthenic acids and that any pollution from production chemicals or phenols are negligible.

The content of naphthenic acids in 10 produced water samples obtained from the Norwegian Continental Shelf ranged from 1 mg/L to 45 mg/L. The standard addition method was applied to validate the concentrations measured by direct measurement. The naphthenic acids extracted from the produced water samples had widely different structural compositions, indicating that the method's robustness for different produced water samples. The method accuracy has been determined to be within 76%-112% of the concentration in produced water. Comparing this to the oil in water OSPAR 2005-15 method for spiked samples, which assumes 80-110%, the measurement method established for naphthenic acids in this project has an equivalent accuracy.

The method quantifies: Toluene extractable components from pH 2 produced water, which can be extracted to a water phase at pH 12 and backextracted to a fresh toluene phase at pH 2. The components must be able to undergo derivatization and elute after n-hexanoic acid on GC-FID set-up as per OSPAR 2005:15 (including BAM calibration). The method captures acids down to C_7 acids and there is an existing method which captures C_1-C_6 acids.

An accreditation of the method at Intertek West Lab AS has been performed by a certified by the national accreditation body of Norway, Norwegian Accreditation. A proposed method is ready to be applied in the industry with defined limit of detection and lower limit of quantification.

Table of Contents

Acronyms

A	**a**
APPI	Atmospheric Pressure Photoionization
B	**b**
BSTFA	N,O-Bis(trimethylsilyl)trifluoroacetamide
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
D	**d**
DCM	Dichloromethane
F	**f**
FID	Flame Ionisation Detector
FT-IR	Fourier Transformed Infrared Spectroscopy
ESI	Electrospray Ionization
E	**e**
EIC	Extracted Ion Chromatogram
EIF	Environmental Impact Factor
EI-MS	Electron Ionisation Mass Spectrometry
ENV	Hydroxylated polystyrene divinylbenzene copolymer used as highly retentive non-polar SPE phase, for the extraction of polar analytes.
EPA	Environmental Protection Agency (USA)
G	**g**
GC	Gas Chromatography
H	**h**
HLB	Hydrophilic Lipophilic Balanced
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
I	**i**
IOR	Ione Exchange Resin
L	**l**
LC	Liquid Chromatography
LLE	Liquid Liquid Extraction
M	**m**
MS	Mass Spectrometry

MTBSTFA	*N-tert*-Butyldimethylsilyl-*N*-methyltrifluoroacetamide
MSTFA	*N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide
m/z	Mass to charge number ratio
O	**o**
OSPAR	Oslo/Paris convention for the protection of the marine environment of the North-East Atlantic
OSPW	Oil Sands Process-affected Water
P	**p**
PYB	1-Pyrenebutyric Acid
S	**s**
SIM	Selected Ion Monitoring
SPE	Solid Phase Extraction
T	**T**
TBDMSCl	*tert*-Butyldimethylchlorosilane
TEX	Toluene, Ethylbenzene and Xylene
TIC	Total Ion Chromatogram
TMCS	Trimethylchlorosilane
TOF	Time of Flight
U	**u**
UPLC	Ultra-performance liquid chromatography
UV-Vis	Ultraviolet - Visible
W	**w**
WSO	Water Soluble Organics

1. Phase 1 Current scientific status for naphthenic acid quantification methods and the development of GC-MS Method for Quantification

1.1 Introduction

According to Guideline M-107 [1] from the Norwegian Environment Agency, the content of naphthenic acids in produced water released to sea are to be analysed and reported.

On initiative from the Norwegian petroleum companies, represented by The Norwegian Oil and Gas Association (Norsk olje og gass), Intertek West Lab have worked together with Worley Origo Process to develop a method for such quantification. The Norwegian Environment Agency (Miljødirektoratet) have funded part of the work.

In Chapter 1.2, and introduction to naphthenic acids and their chemistry in water/oil systems is presented. A literature review has been performed to identify the current status for naphthenic acid quantification methods. The results from this are presented in Chapter 1.3.

A method for determination of naphthenic acids in an oil solvent by GS-MS has been determined. The method development and results of this are presented in Chapter 1.4.

This is the first revision of this report. It is planned to develop a method for extracting naphthenic acids from produced water to an organic solvent and a quantification method by GC-FID. This will be included in the next revision of the report that will be issued within 2021.

1.2 Naphthenic Acid Chemistry

In recent years, the production of crude oils with high amounts of naphthenic acids has increased. Acidic crudes represent more than 15% of the global production [2]. Crude oils can contain up to 4% w/w acids [3] although in the great majority of cases, the total acidity range from 0.1% to 1% w/w [4].

Naphthenic acids are classified as carboxylic monoacids of the general formula RCOOH, where R represents any cycloaliphatic structure. Generally, the term “naphthenic acid” is used to account for all carboxylic acids present in crude oil, including acyclic and aromatic acids. Their molecular structure is further described in Chapter 1.2.3.

Crude oil composition can be described by the SARA fractions where naphthenic acids are a part of the resin fraction. This is described in Chapter 1.2.1. Naphthenic acids are amphiphilic, meaning that they have an affinity for both the oil phase and the water phase, like a soap molecule. Naphthenic acids will partition between the crude oil and the produced water. Chapter 1.2.2 gives a short introduction to produced water chemistry and Chapter 1.2.4 describes the partitioning behaviour.

1.2.1 Crude Oil Composition

Crude oil is organic matter which has decomposed for millions of years under high temperatures and pressures. From a compositional perspective, crude oil is a notoriously complex mixture and due to this reason it is often practical to subdivide it by a hydrocarbon group type determination called SARA fractionation, which divides the crude oil into the following four fractions: saturates, aromatics, resins and

asphaltenes [5]. Asphaltenes represent the heaviest, polar fraction of crude oil. These large molecules, soluble in aromatics, form aggregates that can deposit in flow lines [6] or stabilize emulsions [7]. Resins represent the remaining polar fraction of the crude oil after asphaltene extraction, which translates to molecules with functional groups containing oxygen, nitrogen, and sulphur. In SARA fractionation, they are isolated by adsorption onto polar surfaces or by precipitation in liquid propane [8]. The resin content ranges from 1-25 wt. % [5, 9]. Naphthenic acids are a subclass of the resin fraction [10] and in general resins account for approximately 90% of the acidic functional groups in crude oil [11-13]. The remaining crude oil acid fraction is found in the asphaltenes. The other two SARA fraction, saturates and aromatics, are non-polar hydrocarbons of various size and proportion.

1.2.2 Produced Water

As the reservoir formation is usually saturated with water prior to crude oil formation and migration, and water can be injected to increase the production of oil, some water will inevitably be co-produced with the oil even at the start of production. This water phase is referred to as the produced water. Due to the prolonged exposure to hydrocarbons and solid minerals in the reservoir, and the mixing forces during production, produced water consists of a complex mixture of particulate, and dissolved organic and inorganic material [14]. Figure 1.1 gives an overview of produced water constituents [15]. Production chemicals are also added during production and although the majority of the added chemicals are oil soluble, some water-soluble additives like biocide, oxygen scavengers and scale inhibitors also end up in the water phase [16].

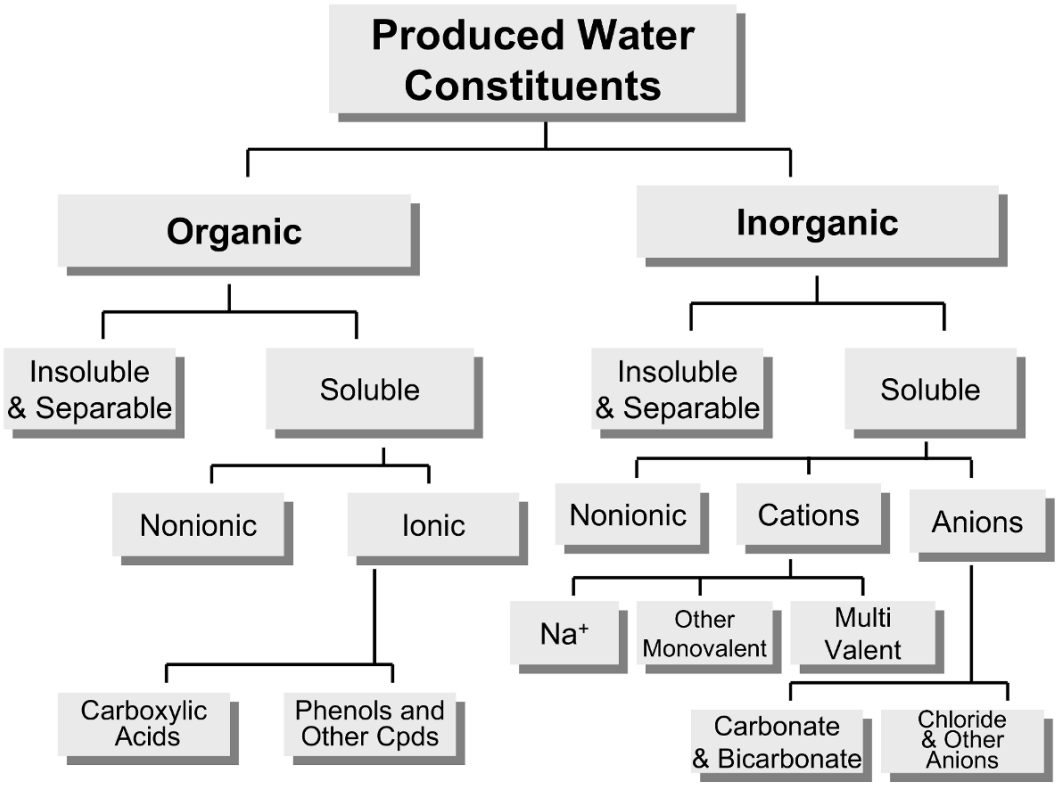


Figure 1.1: Representation of produced water constituents. Image reproduced from Hayes and Arthur [15].

1.2.2.1 Oil in Produced Water

At the upstream facility, produced water is subjected to treatment in order to meet local regulations for discharge [17] or injection criteria for injection into a reservoir. In offshore operations, produced water has traditionally been discharged to the sea. For environmental reasons, there are discharge and disposal legislation for produced water. In the Mediterranean Sea and the Red Sea, monthly average of oil in discharge water is 40 ppm. In the North Sea and the Gulf of Mexico, the limit is ~30 ppm while in the Baltic Sea the limit is 15 ppm.

The oil content in produced water is continuously measured with a variety of measurement methods to show regulatory compliance and collect data for control and optimization purposes. The oil can be both in the dispersed and dissolved state. Dispersed oil is small oil droplets which have formed as a result of high shear history combined with low interfacial tension [18]. Dissolved oil is mainly lower molecular weight aromatics and polar hydrocarbons like organic acids and phenols.

Yang [17] presents different measurement methods applied for oil in water measurement like ISO 9377-2 GC-FID and the EPA Method 1664. Similar for the two methods is that the water is acidified to pH 2 before the organic compounds are extracted from the water. This change in pH makes the larger organic acids oil soluble again while it has a negligible effect on small fatty acids like acetic acid [18, 19]. In the OSPAR methods, which is used in the North Sea, the polar components like organic acids and phenols are removed by florisil adsorbent before the measurement is taken, thus these species are not included in the result [17]. However, in the US this fraction is included in the oil and grease measurement [20] [17] which can make it difficult to reach compliance with regulatory discharge limits.

A recent regulatory change in Brazil has caused a spike in interest for the content of polar water soluble organic compounds in produced water [21]. In 2018, Brazil's National Environment Council (CONAMA) changed the measurement method to include the content of these compounds in the produced water, which will now be measured and recorded as part of the total oil and grease measurement. More specifically, a silica gel clean-up step in the pre-treatment method was removed. This will cause a water treatment challenge for fields where the discharged produced water contains large amounts of polar water-soluble organic compounds. Petrobras and other producers are now forced to understand this new class of molecules and how to eliminate it from the discharged produced water. Operators, service companies, and technology companies like TÜV SÜD NEL (Dr. Ming Yang) are currently researching how to solve this issue.

Bostick, Luo [22] was tasked with mapping the water-soluble organics (WSO) in produced water from the Gulf of Mexico. The conditions investigated were pH (6.5±2, salinity (35k-150k ppm), pressure (1-100 bar) and temperature (25-100 °C). In a typical example, they extracted 20 mg/L of WSO, of which aromatics accounted for 0.2 mg/L and saturated hydrocarbons accounted for 0.02 mg/L. The remaining WSO was primarily polar in nature and distributed between the C_6-C_{10} and C_{10}-C_{20} ranges. These are most likely predominantly naphthenic acids.

1.2.3 Naphthenic Acids Definition and Structure

Crude oil acids are composed of various oxygen, nitrogen and sulphur containing hydrocarbon molecules, of which the naphthenic acids are the most abundant [23].

The term “naphthenic acids” has been used to describe all organic acids found in crude oil although the traditional definition describes a carboxylic acid with a saturated ring (i.e. cyclo-alkanoic acids) [24, 25]. Like other crude oil components, they span over a large spectrum of sizes and structures. Size wise, they have been reported to have a molecular weight ranging between 200-700 g/mol [26] or C_{15}-C_{55} [27], although their weight can exceed this number by far [12] like the tetrameric acid, ARN, with a molecular weight of 1230 g/mol[28]

As naphthenic acids are crude oil components, they are not a single structure like the pure organic acids available from vendors. Instead, naphthenic acids have a large variety of different structural isomers. To illustrate this, the number of structural isomers per chemical formula for alkanes is shown in Table 1.1. Here an increasing number of carbon atoms allow for more possible branch structures in the molecule. Adding another variable like the carboxyl group increases the number of possible structural isomers.

Table 1.1 Number of structural isomers per chemical formula for alkanes

Molecular Formula	Number of Structural Isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{14}H_{30}$	1858
$C_{18}H_{38}$	60,523
$C_{30}H_{62}$	4,111,846,763

Structure-wise, naphthenic acids are often described by the isomer formulas $C_nH_{2n+Z}O_2$ [29] for monoacids or $C_nH_{2n+Z}O_x$ [30] allowing for additional oxygen functional groups like acids with hydroxyl groups or diacids. In either case, the *n* refers to the number of carbon atoms, the *Z* is a negative integer referring to the hydrogen deficiency of the naphthenic acid molecule and the *x* refers to the number of oxygen atoms. This isomer formula is however limited, as it does not account for other heteroatoms like sulphur and nitrogen. Headley, Peru [31] defined the term naphthenic acid fraction components (NAFC) aimed at giving scientists

a more descriptive term for crude oil acids, accommodating for more functional group combinations with oxygen, sulphur, nitrogen, and aromatic rings. Examples of these acids are shown in Figure 1.2.

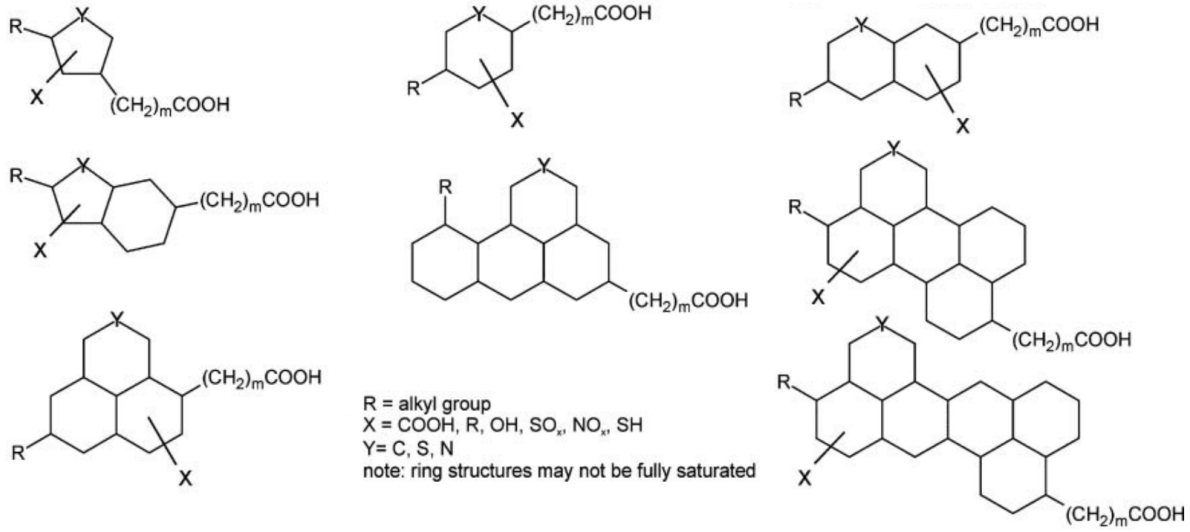


Figure 1.2: Examples of possible naphthenic acid fraction components (NAFC) as described by Headley, Barrow Mp Fau - Peru [32]. Image reproduced from Headley et al. [32]

For the purposes of this report, a more simplistic representation of the naphthenic acid molecule can be represented as such:

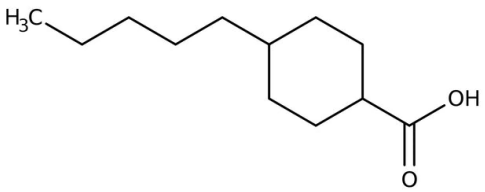


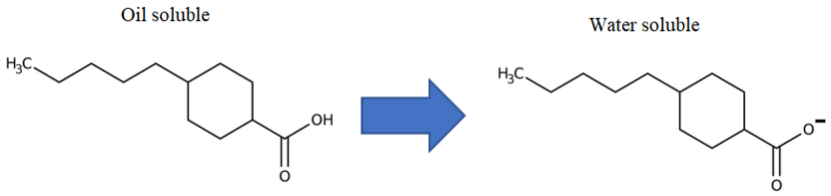
Figure 1.3 Simplified representation of naphthenic acid molecules for the purposes of this report.

1.2.4 Oil-Water Partitioning

Although the traditional understanding of oil and water mixtures is that they are mutually insoluble, most crude oil components will inevitably have some solubility in water. The polarity of the crude oil acids makes them more water soluble than their non-polar counterparts. Alkyl chains increase hydrophobic surface area which decreases the aqueous solubility, whilst branching, polar or aromatic groups decrease this area in turn increasing the aqueous solubility [33]. As one would expect, Stanford, Kim [33] reports that the water soluble acids in crude oil are the smaller acids. External parameters like pH, temperature, salinity, and pressure can also affect the partitioning of naphthenic acids.

Bostick, Luo [22] remarked that, in analysing the effect of pH on water-soluble crude oil organics, significant quantities of C_{10}-C_{20} range compounds become markedly soluble above pH 7. Typical North Sea produced water pH values are reported to range between 5.8-8.5 [26, 34, 35], while the pH in the North Sea formation water range from 5-6.5 [36]. These numbers serve to illustrate the increase in pH caused by the release of CO_2 to the gas phase as the pressure drops from the reservoir to the surface facilities [37].

This increase in pH leads to increased partitioning of naphthenic acids, from the oil phase to the water phase by ionization of the naphthenic acids as such.



The pH increase also favours the precipitation of calcium carbonate, which can lead to inorganic scale formation [38, 39]. Rousseau, Zhou [39] also noted that due to the buffer capacity of bicarbonate in the produced water the pH remains fairly constant while naphthenic acids are dissociated, allowing more naphthenic acids to partition into the water phase. Hurtevent, Bourrel [37] showed through experiments on 10 different crude oils that naphthenic acids can start to partition to the water phase at pH values as low as pH 6.

Like all weak organic acids, crude oil acids have a dissociation constant in the aqueous phase,

$$K_{a,HA} = \frac{[A^-]_w[H^+]}{[HA]_w} \qquad (1)$$

where $K_{a,HA}$ represent the acid dissociation constant, and $[A^-]_w$ is the conjugate base in the water phase.

The crude oil acids all have a pK_a of around 5 Brient, Wessner [40] Havre, Sjöblom [41]. This means that in an aqueous solution at pH 5, half the acids are dissociated. As pH is a logarithmic parameter 10% of the acids are dissociated at pH 4 and 90% dissociated at pH 6. However, when there is an oil phase present another factor also plays a role, the partition ratio, $K_{wo,HA}$. For acids in oil-water systems the partitioning of the non-ionized forms of the acid in each phase can be described by,

$$K_{wo,HA} = \frac{[HA]_w}{[HA]_o} \qquad (2)$$

where $K_{wo,HA}$ represent the partition ratio for an acid. $[HA]_w$ represent the acid concentration in the water phase, and $[HA]_o$ represent the acid concentration in the oil phase.

$K_{wo,HA}$ is in practice not dependent on pH. An example can be used to illustrate how naphthenic acids are distributed between oil and water as a function of pH. For an acid with pK_a = 5 and $K_{wo,HA}$= 0.01, at pH=5 there will be 1% acid on dissociated form in the aqueous phase, 1% on the undissociated form in the aqueous phase and 98% in the oil phase. Partitioning at other pH values are shown in Table 1.2

Table 1.2 Distribution between oil and water for an example naphthenic acid with pK_a = 5 and $K_{wo,HA}$= 0.01, Values are in percent of total amount of acid

pH	Concentration of dissociated acid in water	Concentration of undissociated acid in water	Total concentration of acid in water	Concentration in oil
2	0.001	0.990	0.991	99.009
5	0.98	0.98	1.96	98.04
6	9.01	0.90	9.91	90.09
9	99.00	0.01	99.01	0.99

For the partition ratio the size of the acids plays in. Larger acids will have a lower partition ratio which translates to a higher pK_{wo}. By adding the pK_a and pK_{wo} you can predict how much of an acid is in the oil and the water phase at a given pH. For example, if the pK_{wo} of the crude oil acid molecule is 3 then 50% of this type of crude oil acid would be in each phase at pH 8.

As mentioned, the crude oil acids are very different in structure and size and all of these have different partition ratios. Through partition experiments with crude oil and water, Havre determined the partition ratio of several naphthenic acid structural isomers. This and other studies show that there is a linear relationship between the pK_{wo} of crude oil acids and the molecular weight of the acids. This means that the molecular weight distribution of naphthenic acids in the produced water differs from the distribution of naphthenic acids in the crude oil. The produced water will contain more of the smaller naphthenic acids and less of the larger naphthenic acids. Although larger naphthenic acids are less soluble, with high precision analytical technique it has been reported acids up to C_{41}, 600 g/mol in neutral water after contact with crude oil [33].

By extracting and analysing the crude oil acids from a North Sea crude oil, Havre also set up a method to predict the content of each naphthenic acid isomer in the water phase based on pH, using the equations of the partition ratio and dissociation constants along with the mass balance. This pH-based prediction method was then tested on the produced water from the same platform as shown in Figure 1.4. The results show that a prediction method based on pH measurement of the produced water gives fairly accurate concentrations for naphthenic acids.

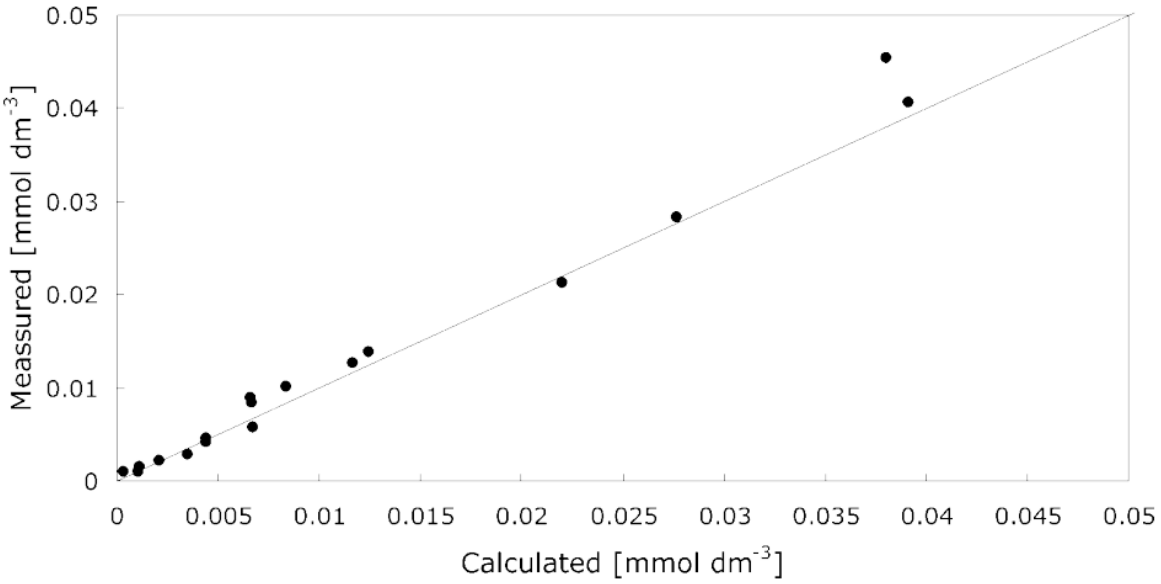


Figure 1.4 Calculated vs. measured naphthenic acid content in produced water from a Norwegian continental shelf oil field. The calculated values were based on pH, Equations 1 and 2 above and identified pK_a and oil water partitioning constants.

Bertheussen, Simon [42] performed partitioning experiments on commercial naphthenic acid mixtures (C_{10}-C_{20}) and crude oil extracted naphthenic acids (C_{10}-C_{40}). As shown in Figure 1.5a and b, at low pH the acids stay in the oil phase, while they gradually go over to the water phase as the pH increases. For the commercial naphthenic acid mixture, it was shown that although most of the naphthenic acids transferred to the water phase at pH 8, a small amount of the naphthenic acids was still in the oil phase at pH 12. For the crude oil extracted naphthenic acids, most of the naphthenic acids were insoluble in the water phase at pH 12 and only a small fraction partitioned over to the water phase.

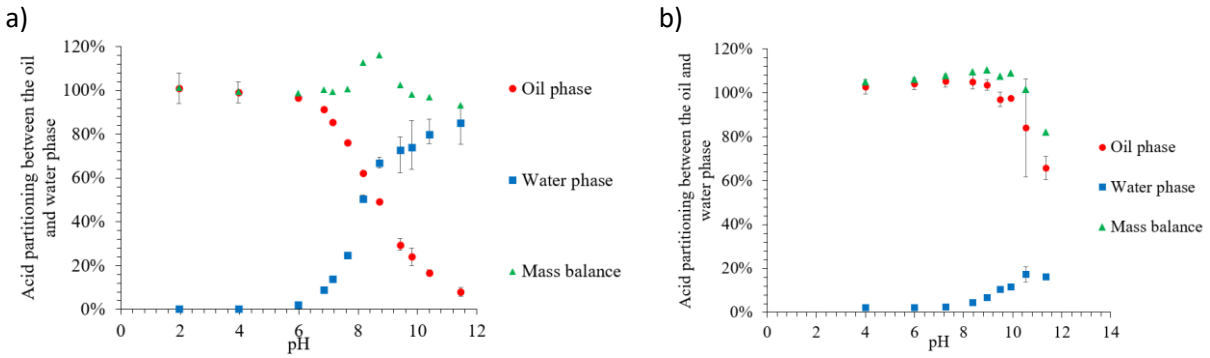


Figure 1.5 Partitioning of a) Fluka commercial naphthenic acid mixture and b) crude oil extracted naphthenic acid mixture from pH 2 to 12. The content of acid mixture in each phase is shown on the y-axis while the pH is shown on the x-axis.

The choice of solvent also affects the partitioning. Indeed, more polar solvents like alcohols give a better solubility for polar organic compounds like acids and bases, compared to less polar solvents, e.g. aromatics or alkanes. The benzene ring in aromatics also make them more polar compared to alkanes. Figure 1.6 below shows how a C_{14} naphthenic acid partitions in an aromatic solvent, toluene, compared to an alkane, heptane. In the less polar solvent, heptane, the naphthenic acid goes over to the water phase at a lower pH, around pH 8, compared to when the solvent is more polar, i.e. toluene. To translate this into crude oil

characteristics, it means that the naphthenic acids in a less polar crude oil, typically a light crude oil may transfer to the water phase at a lower pH compared to if the crude oil had had more polar characteristics, i.e. more aromatics, resins and asphaltenes.

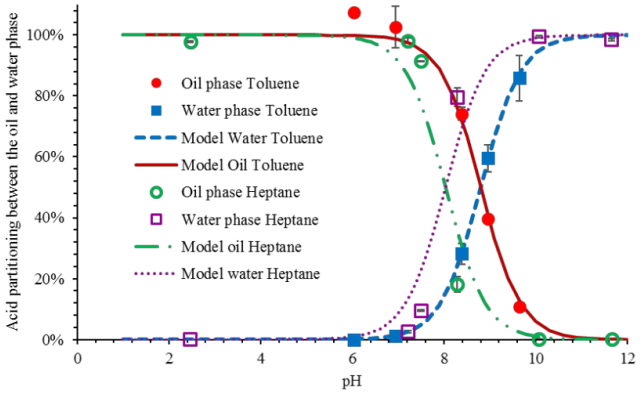


Figure 1.6 Experimental results showing how a C_{14} naphthenic acid partitions in an aromatic solvent, toluene, compared to an alkane, heptane. In the less polar solvent, heptane, the naphthenic acid goes over to the water phase at a lower pH, around pH 8, compared to when the solvent is more polar, i.e. toluene [42].

Other parameters like pressure, temperature and salinity can also influence the partitioning of polar species in crude oil. Computer simulations on how temperature affects the partitioning of naphthenic acids show that the partitioning coefficient goes towards unity at increased temperature [43]. This qualitatively correlates with the experimental findings of Bostick, Luo [22] who did an experimental matrix on a Gulf of Mexico crude oil with synthetic brine. With a pH of 7 and temperature from 25-75°C, the total amount of polar organics (most of which were found to be organic acids) in the water remained unchanged although the concentration of C_{10}-C_{20} components (more oil soluble) increased, while the concentration of C_6-C_{10} (more water-soluble) components decreased. Jacobs, Grant [34] report a temperature range from 3 to 80°C for produced water in the North Sea sector.

The same study by Bostick, Luo [22] found that pressure has a minor effect on the water-soluble organic content. The salinity was also found to not have a significant effect on the WSO. This sounds reasonable since the saturates and aromatics fraction of the WSO was low and salinity has a higher influence on the solubility of non-polar components than naphthenic acids in their dissociated form.

Another phenomenon which can affect naphthenic acids in oil water systems is when there are divalent cations present in the water phase. These can react with dissociated naphthenic acids either in the water phase or in the oil/water interface to form divalent metal naphthenates. An example of this can be the reaction of calcium with two dissociated naphthenic acids as shown.

$$2R\text{-}COO^- + Ca^{2+} \rightarrow (R\text{-}COO)_2Ca$$

As divalent cations react with two naphthenic acids the resulting metal naphthenate is larger compared to the metal naphthenate formed with monovalent cations like sodium. These larger divalent metal naphthenates can become oil soluble if the naphthenic acids are large enough. This is shown in Figure 1.7 below which demonstrate how large and small naphthenic acids partition between the oil and water phase at increasing pH with or without divalent cations in the water phase.

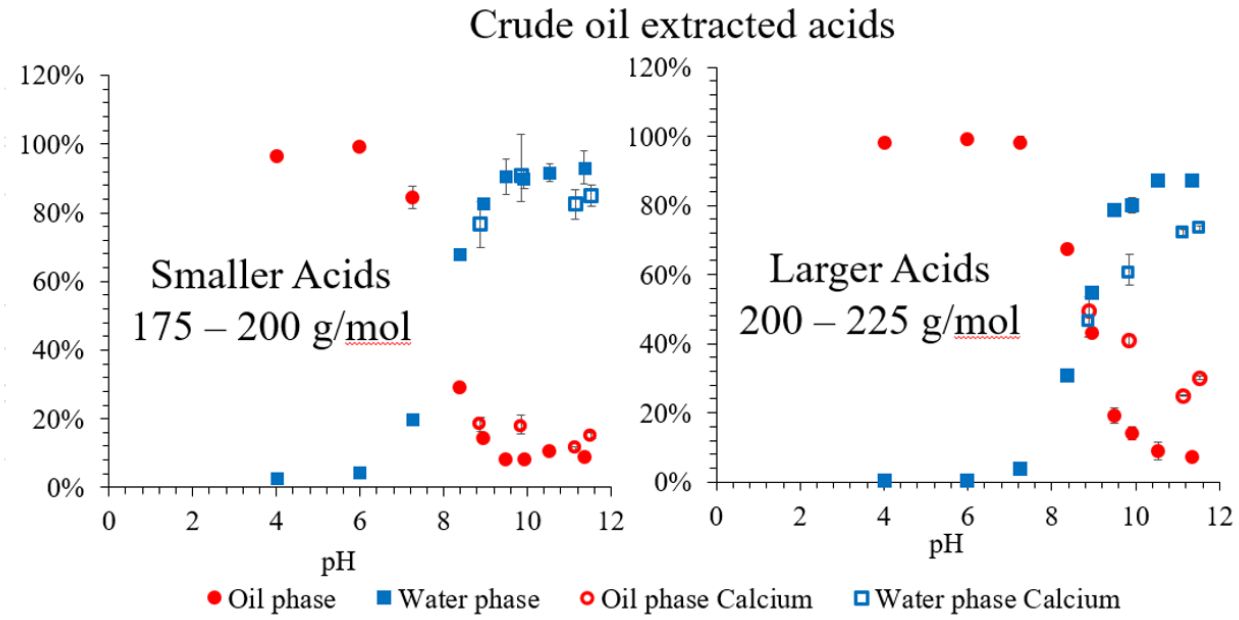


Figure 1.7 Demonstration of how large and small naphthenic acids partition between the oil and water phase at increasing pH with or without divalent cations in the water phase [42]. For the non-hollow data points, the water phase contained monovalent cations (sodium). At high pH larger acids (+200 g/mol) which react with divalent cations like calcium after dissociation can transfer into the oil phase again as it is preferably oil-soluble.

There are also other phenomena in oil water mixtures with naphthenic acids like dimerization and micellization. These will not be elaborated on in this report and are expected to have a minor impact on the experiments and analysis method. Emulsion formation, however, is another problem which can occur due to the soap-like nature of naphthenic acids, and emulsions can impede the experiments due to loss of sample.

1.2.5 Environmental Impact

In recent years, naphthenic acids have become immensely more popular as a research topic [30], likely caused by the advent of concerns linked to open air tailing ponds of oil sands process-affected water (OSPW) [44] in Alberta, Canada, where some of the cyclic and aromatic naphthenic acids have been shown to be toxic and carcinogenic [45].

In Norway, an environmental impact factor (EIF) study of naphthenic acids in produced water from offshore installations was performed in the early 2000's. Here it was demonstrated that even though naphthenic acids had previously been left out of the EIF analysis it was now found to be the dominant contributor to the total EIF as shown in [46]. As the knowledge of the environmental impact of naphthenic acids has increased, the factor is likely to be lower today. The study was conducted on produced water with a measured naphthenic acid concentration of 50 mg/L, average molecular weight of 210 g/mol and the molar ratio of acids with one, two and three condensed rings in acid structure was determined to be roughly 2:4:1.

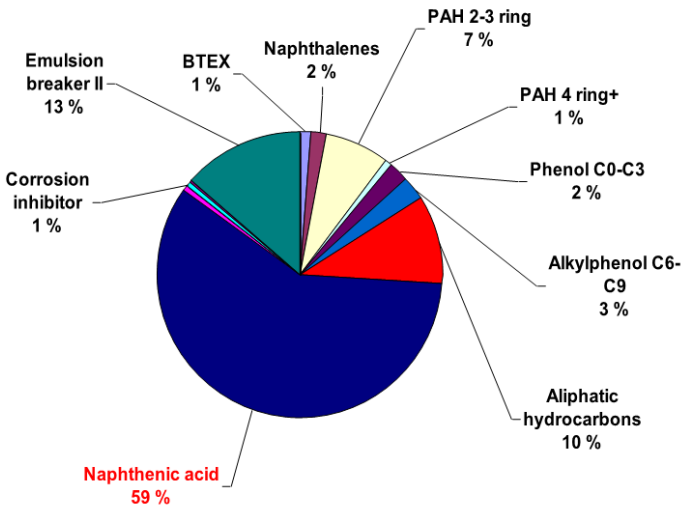


Figure 1.8 Environmental impact factor (EIF) of naphthenic acids compared to other components found in produced water. Numbers are from the early 2000's and are likely to be different today [46].

1.3 Status of Naphthenic Acid Quantification

With the interest in naphthenic acids over the recent decades, numerous extraction methodologies and qualitative and quantitative analysis methods have been applied. For a successful quantification of naphthenic acid in a water sample, the issues listed below need to be addressed.

- The naphthenic acid needs to be extracted from the water phase into a suitable organic phase without loss of acid.
- A suitable method for identification of the naphthenic acids in the organic solvent is needed.
- For the method to be quantitative, calibration and a suitable internal reference standard are required.

Regarding naphthenic acid quantification specifically, the main problem which have been highlighted over the years has been the lack of suitable calibration standard to the sample one wants to measure. With a water sample of unknown concentration and molecular weight distribution of naphthenic acids; how can one create a method that quantifies the total naphthenic acid amount and the amount of each naphthenic acid structure.

A literature review has been performed, and in the following, a short description of the different approaches and the results obtained in solving the issues listed above is given.

1.3.1 Analytical Methods

1.3.1.1 Sampling and transport

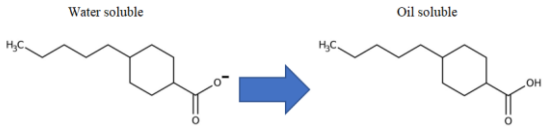
To ensure that the analysis is performed on a representative sample, steps should be taken to preserve the naphthenic acids. Naphthenic acids are biodegradable so in order to preserve the naphthenic acid content the pH should be lowered the pH or biocide should be added. To protect the naphthenic acids from photooxidation, the sample should also be stored in an amber glass container or in the dark.

1.3.1.2 Extraction methods

To isolate the naphthenic acids from the produced water and the other compounds which are present in the water phase, an extraction method is often used. When extracting naphthenic acids from a sample, the choice of extraction phase (liquid vs. solid phase), solvent, temperature and pH will play a role. Surrogate acids can be added to the sample prior to extraction to aid in both quantification and %recovery for result correction. The surrogates are usually deuterated organic acids when using mass spectrometry detection as these can be differentiated from the actual extracted from the sample. Other methods such as GC-FID, necessitates a surrogate which elutes prior or after the extracted naphthenic acids.

Solid-phase extraction is an extraction technique by which compounds that are dissolved in a liquid mixture are separated from other compounds according to their physical and chemical properties. The liquid mixture passes through a solid phase extraction device (solid phase extraction column, solid phase extraction membrane, etc.) equipped with a solid adsorbent under the action of positive pressure, negative pressure, or gravity. For naphthenic acids this often involves cartridges with weak and strong-anion-exchange resins [47]. The naphthenic acids attach to the solid surface of the resins. The resins can then be washed to remove impurities before another elution solvent is passed through which releases the naphthenic acids from the solid resin surface. ENV+ cartridge [48] Oasis HLB sorbent cartridges [49] and ion exchange resin (acid-IER) [50] have all been successfully used to isolate naphthenic acids from water samples.

For liquid-liquid extraction, an organic solvent is added to the produced water and the water phase is acidified to pH 2. At this low pH, all the naphthenic acids with pK_a around 5 will go from the deprotonated form and into the protonated form.



As the pH greatly affects the partitioning of naphthenic acids as described in Chapter 1.2.4, the protonated naphthenic acids will partition into the organic phase. The organic solvent can be a polar solvent like chloroform, dichloromethane (DCM) or a hydrocarbon solvent like heptane or toluene. Salt, 150 g/L NaCl, can also be dissolved in the water phase to aid in the removal of organics from the water phase through the salting out effect [51]. Different solvents have been researched to attain how effective they are in extracting naphthenic acids. Figure 1.9 below show how much naphthenic acids that is measured by LC-MS by using different organic solvent as the extraction medium. For the graph to the left, the measured naphthenic acid quantity extracted by solid phase extraction (ENV+) is also shown, and this appears to give the highest overall extraction efficiency.

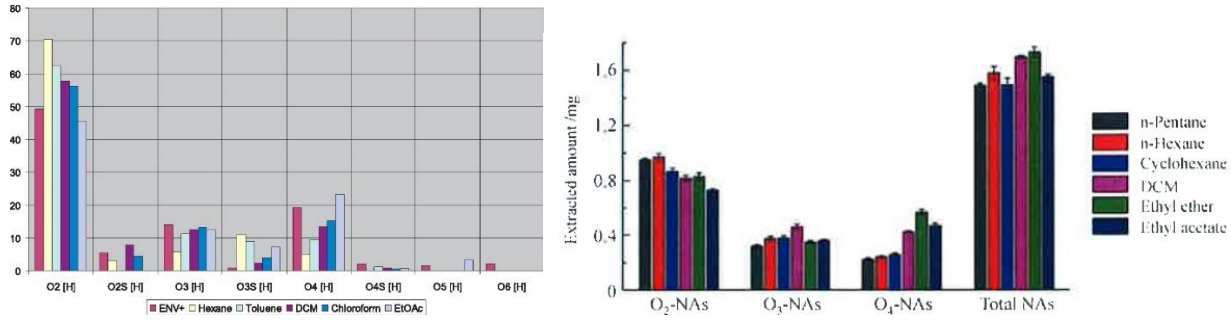


Figure 1.9 Demonstration of the extraction efficiency of various liquid extraction solvent and one solid phase extraction resin [52] [53]. The x-axis notes the chemical composition of the naphthenic acids with regards to oxygen content and sulphur content.

Here it can be noted that solvents like DCM, toluene and hexane gives a good overall extraction efficiency. The liquid extraction solvent most commonly used in naphthenic acid extraction is DCM [54]. the research behind the figure below was conducted on OSPW (oil sands process-affected water), which has a richer array of naphthenic acid structures, both because the heavier oil sand has more naphthenic acids than the average crude oil, and because the high pH in the production water allows more of the naphthenic acids to partition into the water phase.

After the extraction, the extraction solvent now contains all extractable organic compounds originally present in the produced water. To isolate the naphthenic acids from the other organic compounds extracted into the extraction solvent, the naphthenic acids can be extracted into a high pH water phase before a new solvent phase is added and the pH is lowered to get a solvent phase with naphthenic acids, free from other organic compounds.

Another approach to isolate the naphthenic acids is to increase the pH in the produced water to alkaline levels and extract the non-naphthenic organic compounds with organic solvent first, before lowering the pH to 2 and extracting the naphthenic acids with a polar solvent [41].

A different method which is often used to analyse the OSPW for naphthenic acids is extraction to DCM at low pH before evaporation and re-solvation into pH 13 water.

Performing repeated extractions is preferential to ensure the best extraction recovery of naphthenic acids. For liquid-liquid extraction (LLE), the low molecular weight acids will not be captured by the organic extraction solvent, as even the protonated form of these acids holds a high affinity for the water phase. Using theoretical equations, this issue can be demonstrated in Table 1.3 [41]. For hexanoic acid, even at low pH, only 76% will be captured with LLE into an organic phase. For aromatic acids which are more water soluble, this problem is more prominent. Mediaas, Grande [50] reported that after 3 extractions with DCM, only 50% of the benzoic acids in the sample water were recovered and even in the 12th extract, significant amounts of benzoic acids were found.

Table 1.3 Table demonstrating the partitioning of smaller organic acids between the organic phase and the water phase at low pH (pH=2).

Name	Number of C atoms	Molecular weight	Concentration in oil	Concentration in water
Formic acid	C_1	46	1%	99%
Acetic acid	C_2	60	4%	96%
Propanoic acid	C_3	74	11%	89%
Butanoic acid	C_4	88	27%	73%
Pentanoic acid	C_5	102	52%	48%
Hexanoic acid	C_6	116	76%	24%
Heptanoic acid	C_7	130	91%	9%
Octanoic acid	C_8	144	97%	3%
Nonanoic acid	C_9	158	99%	1%

Temperature will also play a role in LLE. At higher temperatures, the larger naphthenic acids will become more water soluble and the smaller naphthenic acids will become more oil soluble. For the purposes of this report, let say that at low pH, C_7 acids are 90% in oil and 10% in water and C_3 acids are 10% in oil and 90% in water. A higher temperature at the same would then give a higher percentage of the C7 acids in the water phase and a higher percentage of C_3 acids in the oil phase. As we are solely interested in capturing the larger acids here ($+C_7$), extraction from a water phase into an organic phase at ambient temperature would be preferrable.

1.3.1.3 Quantification Methods

At the outset, it is important to note that several challenges exist when attempting to quantify, or semi-quantify, naphthenic acid concentrations in any sample by any analytical method. The first problem is that, because naphthenic acids are always present as complex isomeric homologue mixtures, there is no perfect authentic standard with which to calibrate. However, several methods have been developed to do naphthenic acid quantification.

1.3.1.3.1 FT-IR

Fourier transformed infrared spectroscopy (FT-IR) can be used to quantify naphthenic acids due to the specific absorbance of the carboxylic group. Naphthenic acids forms dimers in solutions which affect the infrared absorption. For example the monomeric C=O bond absorbs photons at 1743 cm^{-1}, while the dimer absorbs at 1704 cm^{-1} [51]. The absorbances at these characteristic peaks are measured and compared to a calibration curve to quantify the content of naphthenic acids in the sample. The detection limit can be as low as a 1 mg/L [51]. For quantification, a commercial acid mixture is often used as a calibration standard to translate the FT-IR signal of the unknown sample into a concentration in mg/L. However, as the average molecular mass of the unknown sample is different than the average molecular weight of the commercial acid mixture, this method can be inaccurate in predicting the mass concentration of the unknown sample [37]. The oil sands industry standard method for measuring naphthenic acid concentration in water samples

uses an FT-IR spectroscopy method with Kodak acids as the calibration standard. Using the same calibration standard, Yen et al. [55] showed that a HPLC method with derivatization was in good agreement with the FT-IR method. FT-IR can also show the presence of metal naphthenates which have an asymmetric absorbance at 1600-1500 cm^{-1} similar to esters [56-58]. Metal naphthenates are the salt formed from dissociated naphthenic acids and a cation, e.g. sodium, calcium, strontium or magnesium attached.

1.3.1.3.2 Chromatographic methods

Chromatography is a useful analytical technique to separate the different components in mixtures. Chromatography refers to a separation process, where molecules of a sample are separated through a column based on their size, structure, or other properties. The separated compounds allow for individual detection and analysis as the different molecules consecutively exit the column. Both gas and liquid chromatography is used in quantification of naphthenic acids. Liquid chromatography has an advantage for analysing all the naphthenic acids in crude oil as it does not require the molecule to go into the vapor phase, something that can be hard to achieve with gas chromatography. With this LC, even the largest naphthenic acid molecules (>600 g/mol, >C41) can be analysed.

To detect the compounds as they exit the column, a detector is used. This can be a UV-Vis detector, flame ionization detector (FID) or a mass spectrometry detector (MS).

UV-Vis measures the absorbance of ultraviolet and visible light as the compounds elute through the column.

For FID, the sample gas is introduced into a hydrogen flame. Any hydrocarbons in the sample will produce ions when they are burnt. Ions are detected using a metal collector which is biased with a high direct current voltage. The current across this collector is proportional to the rate of ionisation which in turn depends upon the concentration of hydrocarbons in the sample gas. Hydrocarbons where all the carbons are bonded to hydrogen, generally have molar response factors that are equal to the number of carbon atoms in their molecule, while compounds containing heteroatoms like oxygen tend to have a lower response factor.

The UV-Vis and FID detectors can measure the response as the signal comes out from the column and the signal response can then be integrated to quantify the content of the sample. As naphthenic acid samples contain very many molecules with similar sizes and structures, they do not elute from the column as separate discrete peaks, but as an unresolved hump. Nevertheless, GC-FID can be used to quantify naphthenic acids using this unresolved hump. Both Herman, Fedorak Pm Fau - MacKinnon [59] and Jones, Watson [23] used GC-FID to quantify naphthenic acids by integrating the area of the unresolved peak and compare it to the area of an internal standard. Jones, Watson [23] also used a surrogate standard to correct for the recovery of naphthenic acids.

To explain why the molecules in naphthenic acids mixtures do not elute from the column in discrete peaks but in an unresolved hump, it can be informative to observe the number of structural isomers per mass isomer in Table 1.1. This table is made for branching possibilities for saturated alkanes. With the carboxyl group added as a variable the number of possible structures increases. As can be seen the number of possible structures increases greatly with the number of carbon atoms in the molecule.

Each of these structures will have different boiling points, e.g. branched molecules will have lower boiling points compared to linear molecules. This causes a mass isomer to elute from the column over a broader retention time window. This retention time window overlaps with the structural isomers for molecules with 1 ring structure, which overlaps with the retention time window of the structural isomers for molecules with 2 rings and so on.

Determining the total naphthenic acids concentration might not be sufficient to explain the toxicity. Here the molecular structures and compositions of naphthenic acids are needed to completely understand these effects. To gain more information about the compound which elute at a specific time, chromatography coupled with a mass spectrometry detector is a more powerful tool. A general description of the mass spectrometry detector is that molecules are ionized by an ionization source as they exit the column, their trajectory is altered with electrical fields and when they impact the detector, qualitative and quantitative data about registered mass to charge (m/z) ratios at that time can be acquired. With this technique the ion fragments of the compound can be analysed to either identify the compound, or to isolate the signal from different compounds which elute through the column simultaneously. This is useful for naphthenic acid quantification as naphthenic acids tend to elute from the column, not as separate discrete peaks, but as an unresolved hump. Naphthenic acid mass tables based on an isomer formula $C_nH_{2n+Z}O_2$, as shown in Table 1.4, can then be used to identify the naphthenic acid. Depending on the resolution of the mass spectrometer, different isomers (same elemental composition) and isobars (same nominal mass, but different elemental composition) can be detected to map the molecular composition of the sample. With sufficient high resolution the exact molecule, $C_cH_hN_nO_oS_s$, can be identified based on the mass tables using the elemental atomic masses. E.g. each carbon atom weighs 12 atomic units, each hydrogen weighs 1.007825 atomic units, each oxygen atom weighs 15.994915 atomic units, sulphur weighs 31.972 atomic units and nitrogen weighs 14.003 atomic units.

Table 1.4 Expected nominal masses as observed by MS, based on carbon number (17–25) and Z numbers (0 to -12), which fulfill the naphthenic acid definition, given the formula $C_nH_{2n+Z}O_2$ [60]

Carbon number	*Z* number						
	0	−2	−4	−6	−8	−10	−12
17	$C_{17}H_{34}O_2$[a] 270[b]	$C_{17}H_{32}O_2$ 268	$C_{17}H_{30}O_2$ 266	$C_{17}H_{28}O_2$ 264	$C_{17}H_{26}O_2$ 262	$C_{17}H_{24}O_2$ 260	$C_{17}H_{22}O_2$ 258
18	$C_{18}H_{36}O_2$ 284	$C_{18}H_{34}O_2$ 282	$C_{18}H_{32}O_2$ 280	$C_{18}H_{30}O_2$ 278	$C_{18}H_{28}O_2$ 276	$C_{18}H_{26}O_2$ 274	$C_{18}H_{24}O_2$ 272
19	$C_{19}H_{38}O_2$ 298	$C_{19}H_{36}O_2$ 296	$C_{19}H_{34}O_2$ 294	$C_{19}H_{32}O_2$ 292	$C_{19}H_{30}O_2$ 290	$C_{19}H_{28}O_2$ 288	$C_{19}H_{26}O_2$ 286
20	$C_{20}H_{40}O_2$ 312	$C_{20}H_{38}O_2$ 310	$C_{20}H_{36}O_2$ 308	$C_{20}H_{34}O_2$ 306	$C_{20}H_{32}O_2$ 304	$C_{20}H_{30}O_2$ 302	$C_{20}H_{28}O_2$ 300
21	$C_{21}H_{42}O_2$ 326	$C_{21}H_{40}O_2$ 324	$C_{21}H_{38}O_2$ 322	$C_{21}H_{36}O_2$ 320	$C_{21}H_{34}O_2$ 318	$C_{21}H_{32}O_2$ 316	$C_{21}H_{30}O_2$ 314
22	$C_{22}H_{44}O_2$ 340	$C_{22}H_{42}O_2$ 338	$C_{22}H_{40}O_2$ 336	$C_{22}H_{38}O_2$ 334	$C_{22}H_{36}O_2$ 332	$C_{22}H_{34}O_2$ 330	$C_{22}H_{32}O_2$ 328
23	$C_{23}H_{46}O_2$ 354	$C_{23}H_{44}O_2$ 352	$C_{23}H_{42}O_2$ 350	$C_{23}H_{40}O_2$ 348	$C_{23}H_{38}O_2$ 346	$C_{23}H_{36}O_2$ 344	$C_{23}H_{34}O_2$ 342
24	$C_{24}H_{48}O_2$ 368	$C_{24}H_{46}O_2$ 366	$C_{24}H_{44}O_2$ 364	$C_{24}H_{42}O_2$ 362	$C_{24}H_{40}O_2$ 360	$C_{24}H_{38}O_2$ 358	$C_{24}H_{36}O_2$ 356
25	$C_{25}H_{50}O_2$ 382	$C_{25}H_{48}O_2$ 380	$C_{25}H_{46}O_2$ 378	$C_{25}H_{44}O_2$ 376	$C_{25}H_{42}O_2$ 374	$C_{25}H_{40}O_2$ 372	$C_{25}H_{38}O_2$ 370

[a] Chemical formula corresponding to the expected mass.
[b] Expected formula mass for a compound with the corresponding carbon and *Z* numbers.

1.3.1.3.3 Derivatization

As naphthenic acids have a carboxylic acid group, the hydrogen bonding between the molecules will increase the boiling point of these compounds. This can lead to problems in chromatography where, especially in gas chromatography, where the naphthenic acid might not elute from the column due to the high boiling point. Another issue is that the elution peak of the naphthenic acids that exit is not sharp, but very elongated with a long tail.

By derivatizing the carboxylic group of the naphthenic acid molecule, this hydrogen bonding property can be eliminated and the derivatized naphthenic acid gets properties similar to an ester. Derivatization is achieved by replacing the hydrogen in the carboxyl group with an organic molecule. Shepherd, van Mispelaar [61] evaluated different derivatization chemicals for naphthenic acid analysis; BF_3/MeOH, TBDMSCl, MTBSTFA, MSTFA, BSTFA and concluded that MTBSTFA and BSTFA had the best overall performance.

An especially useful property of derivatization chemicals is that they tend to reduce the fragmentation of the molecule in GC-MS analysis. This property is especially prominent for BSTFA and MTBSTFA which both produce a characteristic ion fragment which can be correlated to the molecular weight of the naphthenic acid. In this manner, the advantages of more advanced mass spectrometry techniques like ESI, APPI and TOF can be obtained with a more simplistic analysis method. Although the derivatization chemicals, BSTFA and MTBSTFA, have been used by many authors over the years, few have taken advantage of the possibilities this characteristic ion fragment unleashes when it comes to quantification. It has mainly been used to analyse the naphthenic acids qualitatively and those who have used the derivatization chemical in sample preparation for quantitative experiments have used SIM scan for one or a few ions [51].

Although derivatization can be an aid in naphthenic acid quantification, it also has drawbacks. It can be a time-consuming additional step in the analysis, the derivatization can be incomplete, naphthenic acids with a hydroxyl group (-OH) or an additional carboxyl group (-COOH) will get multiple derivatization groups and will elute later and can be misidentified in the following analysis. Commercial naphthenic acid mixtures generally have low content of O3 (acids with additional hydroxyl group) and O4 (diacids) so the quantification of these naphthenic acids mixtures are not expected to suffer from derivatization [30]. However, as O3 and O4 acids are necessarily more water soluble compared to O2 acids at the same pH, due to the additional polarity and dissociation. Produced water might therefore contain a higher content of these types of acids. Kovalchik, MacLennan [62] reviewed the method design considerations for naphthenic acid quantification. Here it was recommended not to derivatize the sample, due to the additional laboratory time required.

Different methods have been used to quantify the naphthenic acid content in samples. Some authors have used a single ion 267 m/z to quantify the content of naphthenic acids in the unresolved hump [51] while Headley, Peru Km Fau - McMartin [63] used 5 major naphthenic acid ions present (namely m/z 205, 223, 237, 251, 265) to quantify. Selective ion monitoring for m/z=74 after BF_3-MeOH derivatization has also been used to quantify naphthenic acid mixtures [64, 65].

1.3.1.3.4 Calibration

To quantify a chemical in an unknown sample, a calibration curve can be created by using your analysis method on samples with known and increasing amounts of the chemical. From here the concentration of your unknown sample can be obtained. The best choice would be to use the same chemical as you are attempting to quantify, as the response in your quantification method is the same for identical chemicals.

For quantification of naphthenic acids this can pose a problem for samples that contain a mixture of different acid molecules. With this mixture, very precise chromatographic methods are required to isolate the response from single naphthenic acid isomers. And there is no calibration standard with a similar mixture of acid molecules from which you can create a calibration curve with known concentrations.

To demonstrate how the response factors differ for single model naphthenic acids, Hindle et al. [66] compared their responses through LC-HRMS. The results of the study showed that response factors varied considerably, with no discernible trends related to retention time, accurate mass, carbon number, oxygen content or z-value. Clemente and Fedorak [67] also warned about overinterpretation of chromatographic data obtained with MTBSTFA derivatized GC-MS analysis, showing that a mixture with six model acids, 0.4 mM of each acid, rather than having similar GC-MS responses, were captured with great variation in their response. In the absence of suitable model compounds, the most logical approach is to use an average response factor. This average response factor can be obtained by using commercial naphthenic acid mixtures.

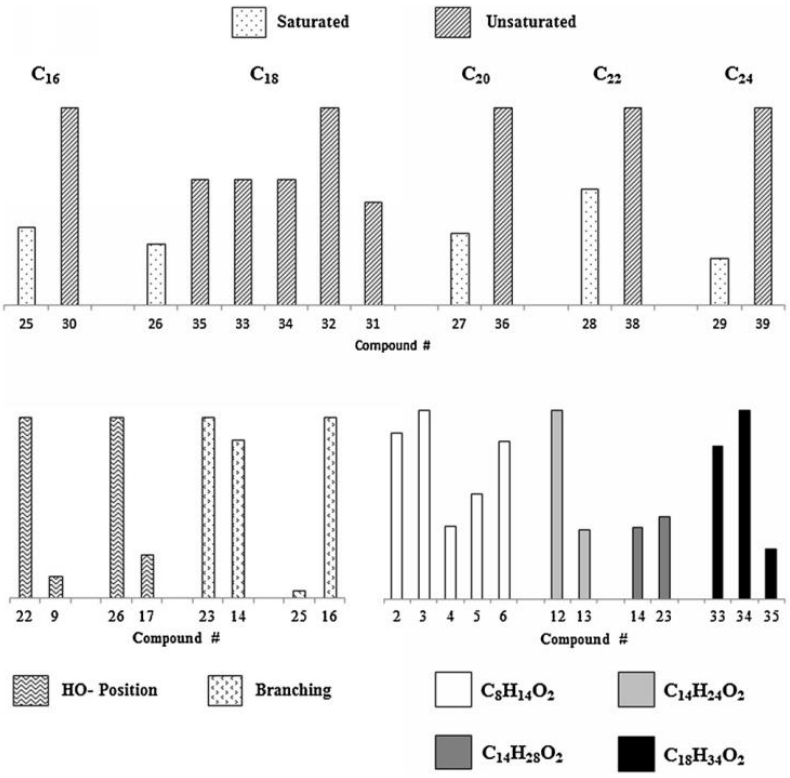


Figure 1.10 Trend evaluation of response factors for model naphthenic acid compounds. The top plot compares saturated and unsaturated compounds grouped by carbon number. The effect of hydroxylation and methylation (branching) are shown in the bottom left. Three sets of isobars are contrasted on the bottom right. Compound numbers are based on the data shown in Table 1. Absolute response has been normalized within each grouping.[66]

As a result of the above challenges, commercial mixtures of naphthenic acids are often used as a calibration standard used to quantify the content of naphthenic acids in an unknown sample. These are typically referred to by their vendor name, Merichem, Acros, Kodak, Fluka or Sigma Aldrich. The naphthenic acids in commercial acid mixtures are recovered from petroleum distillation cuts using caustic extraction. This extract is then acidified to return the naphthenic acids to their protonated form [68]. As commercial

naphthenic acid mixtures do not have the same mixture of naphthenic acids which is present in the unknown sample one wish to measure, it will have different response factors compared to the naphthenic acids in the unknown sample. This type of quantification is therefore described as semi-quantitative. Hindle, Noestheden [66] used the summed-up area response for all naphthenic acid isomers in the commercial acid mixture to create an average response factor. However, as the commercial naphthenic acids used for calibration were different, different quantitative results were also obtained depending on the commercial naphthenic acid mixture used. Researchers have also noted that commercial acid mixtures differ greatly not just from vendor to vendor, but also in between the same vendor [69]. As it is a petroleum distillation cut this is probably caused by shifts in crude oil stock or refinery strategies. Figure 1.11 below illustrates how different commercial acid mixtures from the same vendor can be.

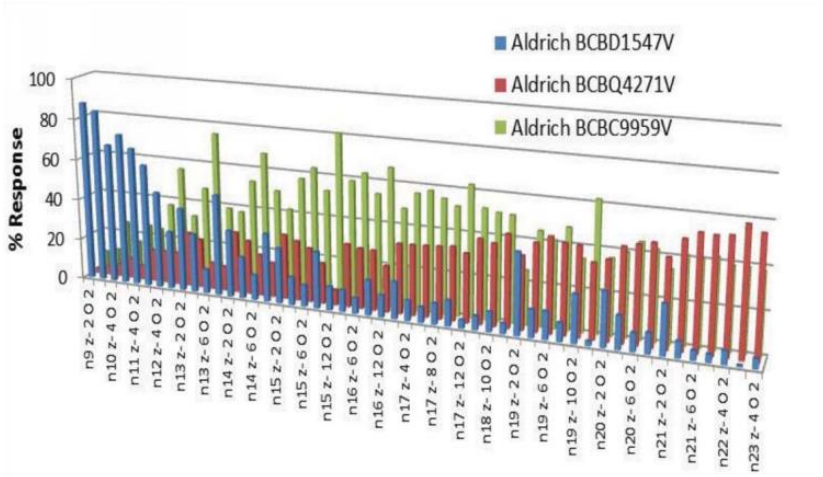


Figure 1.11 Example of how different commercial acid mixtures from the same vendor can be over time.[70]

For commercial mixtures of naphthenic acids, some contain solely saturated acids with no ring structures while others have a more diverse distribution of naphthenic acid structures. In the choice of which commercial naphthenic acid mixture to choose, the better choice is likely to be the one which has a naphthenic acid distribution most similar to the naphthenic acid mixture to be quantified.

1.3.1.3.5 Promising quantification methods

There are several papers which have published quantitative data on naphthenic acid quantification.

Samanipour, Reid [71] used LC-HRMS with ESI ionization to identify and quantify different naphthenic acid isomer groups across 6 produced water samples. The produced water samples were gathered in triplicates and adjacent to the discharge point for produced water. The water was acidified to pH 2, stored cold and dark and filtered with technical-grade glass fiber filters. After spiking with deuterated octanoic acid as an internal standard, the samples were analysed without extraction or concentration of the sample. The soft ionization achieved by ESI allow for low molecular fragmentation. The signal was screened at high resolution for 181 naphthenic acid isomer groups, where the molecule types were restricted to monoacids (O_2) with or without sulphur. The high resolution allows for filtering out the signal from other organic molecules which does not fit the molecular masses belonging to naphthenic acids. Around different 22 naphthenic acid isomer groups were detected in each of the produced water samples with a total concentration ranging from 6 mg/L to 52 mg/L. Figure 1.12 below allows for a better representation of the

results obtained. Interestingly, no sulphur containing naphthenic acid isomer groups were detected in any of the 6 produced water samples.

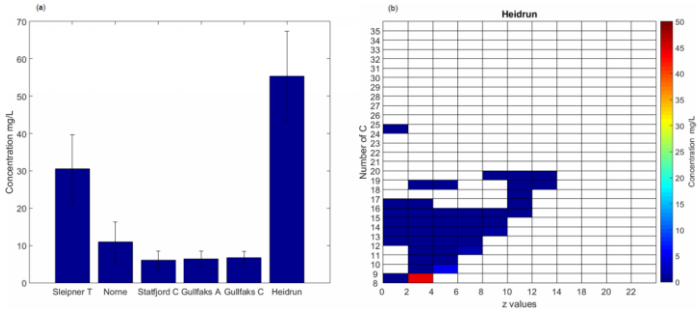


Figure 1.12 Total naphthenic acid concentration with the observed standard deviation for each platform and (b) detailed averaged concentration distribution of each NA isomer group for the samples taken from the Heidrun platform.

To quantify the naphthenic acid isomers, external calibration curves were made with commercial naphthenic acid mixture and the internal standard deuterated octanoic acid. The integrated octanoic acid-d_{15} scaled signal of each naphthenic acid isomer group in the commercial acid mixture was used to generate the external calibration curve and similar response factors were assumed for naphthenic acids isomer groups in the commercial acid mixture and the produced water. E.g. it was assumed that C_{14} acids with 1 ring structure in both the produced water and the commercial acid mixture would give the same response in the analysis. Calibration curves with regression coefficients (R^2) ≥ 0.85 were considered adequate for the quantification. The calibration curves were made with commercial naphthenic acid mixture dissolved in isopropanol. For the total concentration of naphthenic acids, the concentrations of all naphthenic acid isomer groups in the samples were summed up. To validate the method, the same commercial naphthenic acid mixture was dissolved in seawater to simulate produced water. The quantification method was considered validated with a standard error of quantification of <63% for the individual naphthenic acid isomer groups and of <34% for the total naphthenic acid concentration. The error here can seem high, however, without concentrating the sample beforehand, the resulting signal in the analysis is necessarily lower, which introduces more uncertainty for the quantification.

Both total naphthenic acid concentration and naphthenic acid isomer group concentration results are reported in mg/L. It is not known how naphthenic acid isomer group concentrations were determined. It is assumed that the integrated area response percentage for each naphthenic acid isomer group was multiplied with the concentration of the total naphthenic acid mixture. This is illustrated in Figure 1.13 below.

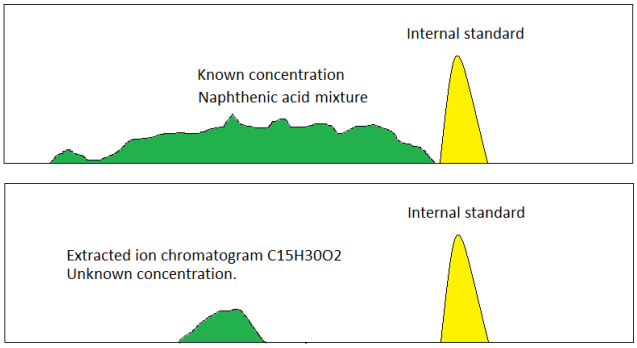


Figure 1.13 Illustration showing the chromatogram for a commercial naphthenic acid mixture with known concentration and the extracted ion chromatogram of a naphthenic acid isomer group with unknown concentration.

The paper advocates the use of commercial naphthenic acid mixtures with similar naphthenic acid distributions to the sample to be measured. The commercial naphthenic acid mixture they used in the research was impressively diverse in the distribution of naphthenic acids as shown in the figure below.

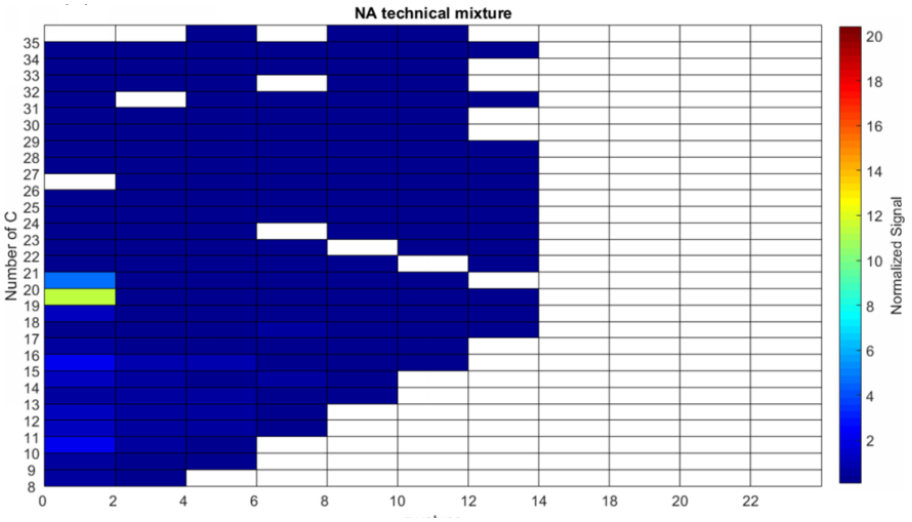


Figure 1.14 Distribution of the normalized signal of naphthenic acid isomer groups based on the number of carbons (i.e. n value) in the technical mixture, Sigma-Aldrich, Norway (purchase date February 2016).

This method has also been employed by Ross, Pereira [72] to quantify different naphthenic acid isomers in OSPW adjacent waters. Here liquid-liquid extracted field samples were run through LC-HRMS and naphthenic acid isomer group concentrations were obtained through calibration curves of the same naphthenic acid isomer groups in a commercial naphthenic acid mixture. Here, it is also assumed that the concentrations of naphthenic acid isomer groups were set equivalent to their relative area. Total naphthenic acid concentration was set to the sum of the naphthenic acid isomer groups.

Samanipour, Hooshyari [73] has also recently compared different extraction methodologies the recovery of naphthenic acids to analyse produced water samples. Three different extraction methods were compared, one liquid-liquid extraction method with DCM, and two solid phase extraction methods with ENV and HLB. It was argued that even though the total amount of naphthenic acids recovered were similar for the three extraction methods, there were large differences in the recoveries for naphthenic acid structures. The LLE method was good for separating out straight chain alkanes, while solids phase extraction methods capture a larger range of naphthenic acids structures. Larger naphthenic acid structures and naphthenic acid

structures with rings were left behind with the LLE method and these naphthenic acids could only be properly extracted with the solid phase extraction methods. Care should be taken in the choice of extraction methods as different naphthenic acid distributions will affect the resulting toxicity profiles. Leaving out large naphthenic acids with ring structures can give an inaccurate risk assessment. This is especially important for produced water samples as they tend to contain more ringed naphthenic acids than saturated acids.

The author argues that the naphthenic acids (C_{31+}) were too large to be soluble in DCM. This seems counterintuitive as larger naphthenic acids are less polar than smaller naphthenic acids and should much prefer to leave the polar water phase for the organic phase. DCM is used to dissolve asphaltenes, molecules which are much larger and more complex compared to the naphthenic acids discussed here. Bertheussen, Simon [42] partitioned crude oil acids back and forth several times between water phases and toluene. These crude oil acids were mostly two to three ringed naphthenic acids and the mass balance did not show a loss of sample.

However, UPLC Q-TOF-MS is non-standard equipment. They also used response from naphthenic acid isomer groups in technical mixtures to quantify naphthenic acid isomer groups in produced water. Quantification method based on technical acid mixtures were then validated by dissolving the same technical mixtures in water.

A similar quantification method was employed by Woudneh, Coreen Hamilton [74] who used LC MS/MS to quantify different naphthenic acid isomer groups. Water samples from oil sand producing regions in Canada were collected, filtered with glass fibre filter, and extracted with solid phase extraction HLB cartridges at pH 5-7. By derivatization of the acids, it was ensured that all naphthenic acids would produce a product ion with mass to charge ratio 129 m/z. This ion was used to quantify all naphthenic acids as they eluted from the column. Two deuterated internal standards were utilized in addition to 1-Pyrenebutyric acid which was used as a sort of external standard. All concentrations were reported as 1-Pyrenebutyric acid (PYB) equivalent concentrations. A PYB equivalent concentration of a naphthenic acid isomer peak is a concentration of naphthenic acids that will produce a signal which is equal in strength to that produced by a PYB solution of the same concentration. For a solution prepared with only commercial acid mixture, the sum of all naphthenic acid isomers in PYB equivalent concentration indicated that PYB equivalent concentration could be translated to commercial naphthenic acid mixture equivalent concentration by multiplying with 0.38. Here, the relative response factor was calculated for each naphthenic acid isomer group with regards to the internal standard and PYB. The research show that similar naphthenic acid isomer groups elute at the same time for both commercial acid mixtures and field samples.

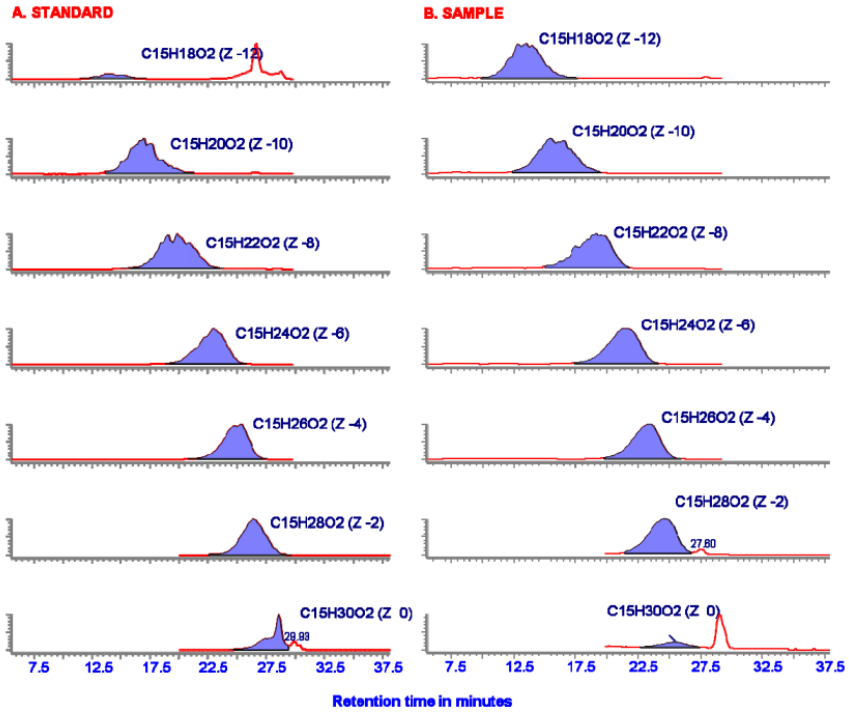


Figure 1.15 Chromatograms show that similar naphthenic acid isomer groups elute at the same time for both commercial acid mixtures and field samples [74]

The research also provided a good example of how branched structures in the same isomers elute faster than the linear fatty acid in that isomer as seen in Figure 1.16.

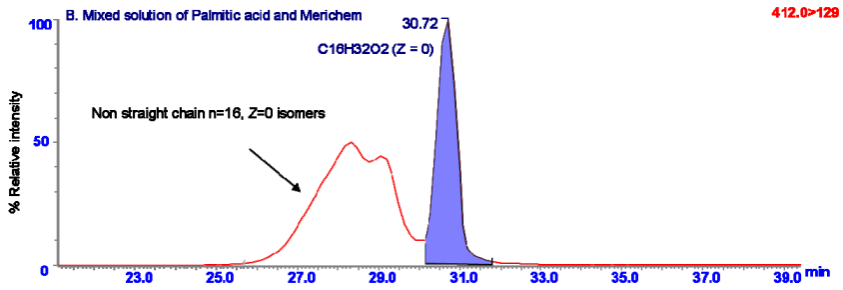


Figure 1.16 Example of how branched structures in the same isomers elute faster than the linear fatty acid in that isomer.

Brunswick, Hewitt [70] used LC-HRMS to perform a quantitative study on three commercial naphthenic acid mixtures and a OSPW extracted naphthenic acid mixture. Naphthenic acids mixtures were weighted and dissolved in ammonium hydroxide aqueous solutions without derivatization. Naphthenic acid mixtures and naphthenic acid isomer groups were run with internal standard decanoic d_3 acid. Concentrations were reported as equivalent to deuterated decanoic d_{19} acid concentrations. Some of the commercial naphthenic acids sourced from Merichem, Aldrich, Acros, and Kodak has similar “equivalent to decanoic-d19 acid” concentration ratios to nominal as shown in Figure 1.17, although two of the acid mixtures were distinctly different, emphasizing that analyses performed using different commercial mixtures for calibration are not equivalent. Slightly more disheartening is the low response of the acid extractable organics from oil sands process water AEO from OSPW. Again, it should be noted that OSPW has a richer array of naphthenic acid structures and sizes due to the high pH in the process. The current assessment of naphthenic acids mixtures

against one another by concentration equivalent ratios, allows for the correction of concentration values when comparing data collected using different naphthenic acid calibrant mixtures.

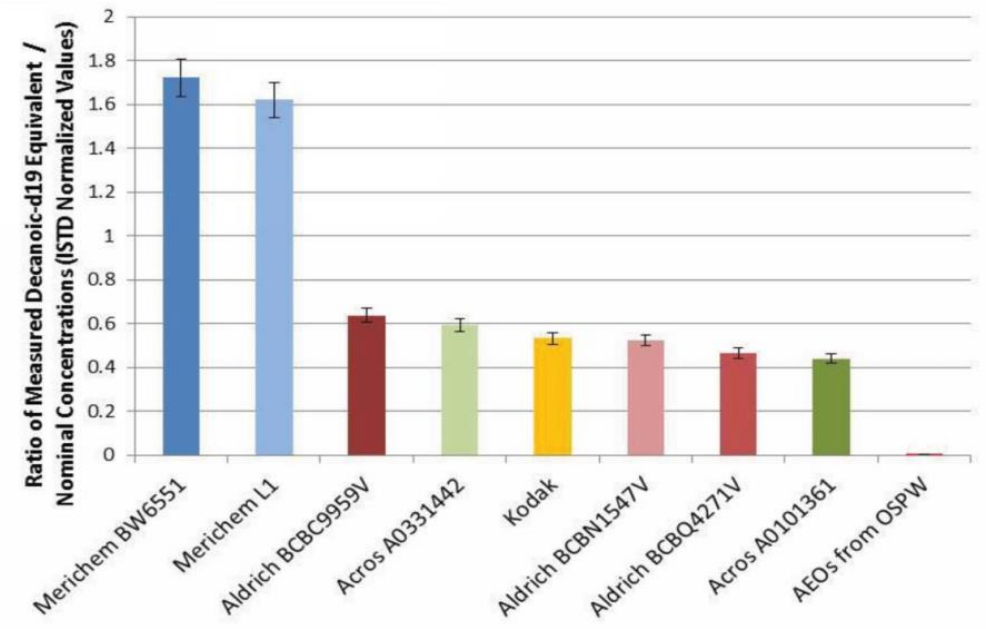


Figure 1.17 Comparison of naphthenic acid mixtures (O2 and O4 Species) with reference to decanoic-d19 acid (64 representative homolog ions). AEO refers to the field sample of acid extractable organics from oil sands process water (OSPW)

Havre, Sjöblom [41] investigated the partitioning of crude oil acids between the crude oil and the water phase by using GC-MS in scan mode. Here, the crude oil acids from a 2 wt% acid crude oil were isolated by using a solid phase extraction with ion exchange resins called the Acid IER method [50]. These isolated crude oil acids provided an excellent mixture to create a calibration curve. After all, the naphthenic acids in the produced water came from the same crude oil. This crude oil extracted naphthenic acid mixture was derivatized with BTSFA (N,O-bis (trimethylsilyl)trifluoroacetamide). This derivatization agent allows for stable GC-EI MS fragments to be created. From the GC-MS chromatogram, single fragment masses could be extracted in an extracted ion chromatogram. Here it is also assumed that the concentration of each naphthenic acid isomer group was set equivalent to the area ratio of said naphthenic acid isomer group.

With Havre, Sjöblom [41] method the naphthenic acid mixture was extracted from stabilized crude oil. Here the crude oil had already lost some of the naphthenic acids to the produced water prior to the extraction of the acids. In his research of water-soluble heavy crude oil organic-acids, Stanford, Kim [33] showed that Species of high abundance in the three parent oils are not necessarily high in abundance for their respective water-soluble fractions. In other words, the distribution of naphthenic acids in the produced water does not match the distribution of naphthenic acids in crude oil. An even more representative sample of the naphthenic acids in the produced water would be take an unseparated sample of well-stream from the inlet manifold and acidify it to pH 2 to partition all the acids into the crude oil phase. This crude oil could then undergo naphthenic acid SPE extraction to make a representable naphthenic acids mixture with which to calibrate and quantify produced water samples. If the inlet stream cannot be sampled, crude oil from the crude oil export sampling station can be reintroduced with produced water from the produced water sampling station in water cut equivalent volumes prior to pH adjustment. Havre showed that with an overview of the total naphthenic acid concentration in both the water phase and the oil phase the concentration in each phase of each acid isomer can be estimated based just on pH alone.

In Canada, they have long been interested in naphthenic acids due to their production of oil from oil sand. Here they dig up oil sand and rinse it with caustic high pH water. That way they separate the oil from the solid sand. The high pH water activates the surfactants in the oil, e.g. naphthenic acids, which rinses the oil from the sand and encapsules it into droplets. The wastewater from this process is stored in tailing ponds which due to the high pH, is rich in naphthenic acids transferred from the oil sand oil. Canadian researchers have therefore been interested in naphthenic acid measurement and have done a lot of work in this field. For water samples from the environment in Canada, the composition and concentration of the originating naphthenic acid source is unknown. Here they are gathering synthetic reference material for oil sand specific naphthenic acids to be used as an analytical standard for quantification. The sample will be made nationally available by NRC for the benefit of NPRI and international oil spill research efforts. However, the aim of the project is more to separate the naphthenic acids from oil sand production from the naphthenic acids in the natural oil sand-influenced groundwater. In contrast to offshore petroleum reservoirs, the oil sand is just below the surface. The naphthenic acids in oil sands are also somewhat different than the naphthenic acids from crude oil. Oil sand is rich in resins and asphaltenes compared to crude oils. The high pH treatment also shifts the distribution of relevant naphthenic acids to higher masses as larger naphthenic acid molecules becomes water soluble at high pH. Typical North Sea produced water pH values are reported to range between 5.8-8.5 [26, 34, 35]. In theory this can also be done for naphthenic acid quantification of produced water. Collecting and combining produced water from some of the 90+ producing fields on the Norwegian shelf, extracting the naphthenic acids and create a reference sample with known mass content and distribution. This can then be distributed to all platforms for them to use as an external standard against which naphthenic acid content can be measured.

1.3.2 Discussion and Concluding Remarks

In the literature, the recommended extraction medium for naphthenic acids is solid phase extraction with Env$^+$ resin or dichloromethane solvent. However, both toluene and hexane also give adequate results.

Although GC-MS analysis of naphthenic acids with MTBSTFA derivatization has been performed by many researchers, previous researchers have failed to take advantage of the full quantitative possibilities this derivatization chemical allows for. As examples the quantitative response from one or a few ions have been used to represent the quantity of the whole naphthenic acid mixture. By applying appropriate quantification analysis, a better approach can be developed, similar to the one quantitative method used by Havre, Sjöblom [41].

The most promising quantitative naphthenic acid results have been obtained with high resolution LC-MS. The soft ionization methods used in LC-MS allows for molecular ions to be produced, simplifying the data analysis. The high resolution also allows for better distinction into naphthenic acids with or without additional functional groups like carboxyl, hydroxyl, nitrogen, or sulphur.

The GC-MS method with MTBSTFA also allows for molecular ions to be analysed thus gaining the same advantage as the LC-MS, however the lower resolution does not allow for any distinction between naphthenic acids with or without added functional groups.

As commercial naphthenic acid mixtures change from vendor to vendor and from bottle to bottle, an argument can be made for using a different mixture for external quantification. The standard oil in water calibration mineral oil has a disadvantage in that it is dissimilar in chemical nature, however it is a constant and synthetic mixture. This can be a strength compared to using single organic acids, as the molecular isomer response averages in the standard oil in water calibration mineral oil can be more representative for

the molecular isomer response averages in produced water samples of naphthenic acids. However, the literature has also suggested fixed reference standards with which to correlate results obtained with different commercial naphthenic acid mixtures. This fixed reference standard might allow for commercial naphthenic acid mixtures to be used to create external calibration curves.

One of the most interesting questions regarding the literature is how the authors have obtained the concentration of the naphthenic acid isomers. It is assumed that this is set equal to the area percentage, however this is not elaborated in the texts. More information and or validation needs to be gathered/performed on this point.

1.4 Quantification of Naphthenic Acids by GC-MS

1.4.1 Introduction

The method for quantification of naphthenic acids by GS-MS is largely based on prior experience by Worley Origo Process. The quantification method was adjusted based on the theoretical background for produced water samples covered in Chapter 1.3.1.3.5.

The chemicals and methods specifications/evaluations are covered in Chapter 1.4.2 and the results obtained are covered in Chapter 1.4.3.

1.4.2 Experimental

1.4.2.1 Chemicals

The chemicals listed below have been utilised. The three first chemicals are mixtures of various naphthenic acids.

- Naphthenic and other organic acids
  - Naphthenic acid, Acros Organics, practical grade.
    Acid number 233 mg_{KOH}/g = 241 g/mol.
  - Naphthenic acid, Fluka, technical grade, Donated by Ugelstad Laboratory at NTNU (Fluka is now a part of Sigma Aldrich and it is likely to be the same product as the naphthenic acid from Sigma Aldrich. There are batch-wise variations in these naphthenic acid mixtures, so they do not have the same composition). Acid number 230 mg_{KOH}/g = 243 g/mol
  - Naphthenic acid, Sigma Aldrich, technical grade. Acid number 230 mg_{KOH}/g = 243 g/mol
  - Capric acid, Sigma Aldrich, Supelco®, M-Clarity™ quality level = MQ100
  - Palmitic acid, Sigma Aldrich, Supelco®, M-Clarity™ quality level = MQ100
  - 4-*n*-heptyl benzoic acid, Alfa Aesar, >99%
- Reference standards candidates
  - Benzoic acid, from solution also containing *p*-Tuloic acid and 2,4-dimethylbenzoic acid, Chiron, S-4281-100-T Batch 3626
  - 4-*n*-heptyl benzoic acid, Alfa Aesar, >99%
  - Capric acid, Sigma Aldrich, Supelco®, M-Clarity™ quality level = MQ100
  - Palmitic acid, Sigma Aldrich, Supelco®, M-Clarity™ quality level = MQ100
  - 4-(nonyloxy)benzoic acid, Acros Organics, 97%
- Derivatisation agents
  - MTBSTFA+TBDMSCl, N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide with 1% tert-Butyldimethylchlorosilane, Sigma Aldrich, >95%
  - BSTFA + TMCS, N,O-Bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane, Supelco, or GC derivatization, LiChropur™, contains 1% TMCS, 99% (excluding TMCS)
  - MTBSTFA, N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide, Sigma Aldrich, >97%
    Comments: The TBDMSCl and TMCS part of the derivatization agents are catalysts which increases the derivatization potential where e.g. more sterically hindered molecules will also be derivatized. As there have been some reports of chromatographic pollution with TBDMSCl,

a derivatization reagent without TBDMSCl was acquired in case this should cause an issue with the results obtained.

- Solvents
  - Toluene, Merck, SupraSolv® for GC-ECD/FID, Supelco®, M-Clarity™ quality level = MQ100
  - *n*-Heptane, Merck, M-Clarity™ quality level = MQ100

1.4.2.2 Methods

1.4.2.2.1 Solvents

The choice of solvent can affect various aspects of the method like extraction efficiency, solvent peak duration in the GC-MS, and the ability to perform derivatization. The last effect is linked to a temperature elevation to 60°C during the derivatization step. Higher temperature will increase the reaction kinetics and ensure a faster and more complete derivatization reaction. As such, solvents with low boiling points such as DCM (boiling point 40°C) were considered too volatile, and a less polar solvent, toluene was chosen to be the preliminary solvent for this part of the project. The high boiling point of toluene (>100°C) allows it to remain in liquid form during the derivatization step.

As described in the theoretical discussion, toluene could be a less efficient extraction solvent compared to DCM. However, the overall extraction performance makes it an adequate solvent. The higher boiling point increases the duration of the solvent peak in the chromatogram, which could make some of the smaller acids nondetectable if they elute from the GC column in this solvent peak. DCM would have a shorter solvent peak in this regard.

A toluene solvent could also raise some concerns regarding the later applicability for GC-FID analysis. The TEX (toluene, ethylbenzene, xylene) content of oil in water measurements are performed on GC-FID to subtract the TEX content from the measured oil in water content. As such there was a concern that excessive amounts of toluene might contaminate the GC-FID column and give a false peak in further oil in water measurements. However, after some tests with GC-FID and pure toluene, it was found that this effect could be eliminated by washing the column with pentane.

1.4.2.2.2 GC-MS Set-up

Agilent GC (7890A)/MS(5975C) equipped with an DB-5MS 60m,0.25mm,0.25µm, Supelco 28472-U, capillary column. The injection was run in splitless mode. The helium carrier gas flow rate was kept at 1 mL/min. The inlet temperature and the GC-MS interface temperature were both kept at 330 °C. An initial temperature of 100 °C was held for 5 minutes before a ramp of 5 °C/minute until a maximum temperature of 325 °C, which was held for 10 minutes. Solvent delay was set to 15 minutes. The GC/MS was operated in electron impact ionization mode with ion source temperature and quadrupole temperature at 230 and 150 °C, respectively. This instrument was set to scan from m/z 42 to m/z 600. injection volume was set to 1 µL.

The data obtained from GC-MS analysis allows different chromatograms to be used for further analysis.

Total ion chromatograms (TIC) are chromatograms which show the sum of all intensities for all masses registered by the detector over time.

The extracted ion chromatogram (EIC) shows the sum of intensities for a specific mass or mass range registered by the detector over time.

1.4.2.2.3 Derivatization

The commercial naphthenic acid mixtures and the organic acids evaluated for internal standards where derivatised with “MTBSTFA + TBDMSCI” and with “BSTFA + TMCS” (details about the derivatisation agents are given in Chapter 1.4.2.1).

The procedure is as follows: 10 µl derivatisation standard was added to 100 µl sample and the samples were heated to 60°C in a heating cabinet for 30 minutes. As it was discovered that the heating step might not be required according to the vendor, derivatization without heating during the 30 minutes was also performed to evaluate if this heating step could be excluded (Chapter 1.4.3.6.1).

1.4.3 Results and Discussion

1.4.3.1 Derivatization - Initial Tests

To test the derivatization efficiency and the difference in chromatographic response with derivatization, the commercial naphthenic acids were run through the GC-MS with and without derivatization.

The procured commercial naphthenic acids mixtures, Acros, Fluka and Sigma, were dissolved in toluene into 3 solutions of approximately 1000 mg/L. Two volumes from each solution were taken out where one was derivatized with MTBSTFA. The resulting chromatograms are shown below.

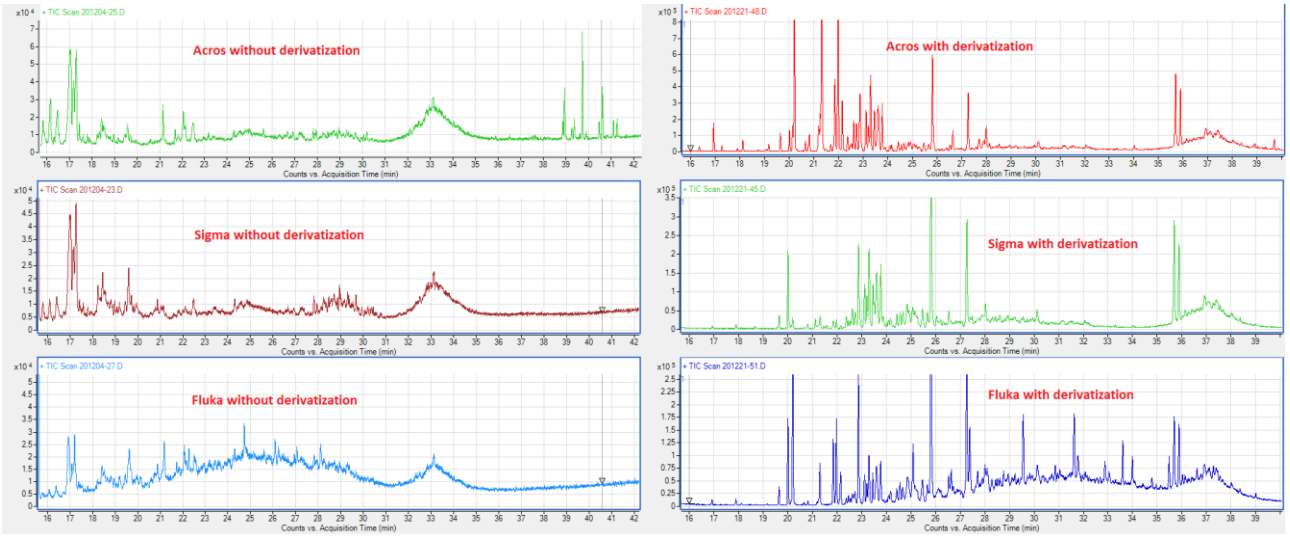


Figure 1.18 Chromatograms of the naphthenic acid mixtures with and without prior derivatization. The chromatograms on the right have a y-axis which is one order of magnitude higher than the chromatograms on the left.

In the chromatogram to the left, the naphthenic acids have not undergone derivatization, whereas in the chromatogram to the right, they are derivatized. First it can be noted that the molecules in the naphthenic acid mixture does not elute in discrete humps as is often the norm for GC analysis. Instead, as described in the theoretical chapter, they elute as a continuous hump due to the large number of molecules with overlapping boiling point properties. Secondly, it can be noted that the hump has shifted to the right for the naphthenic acids which are derivatized. This is caused by the increase in molecular weight caused by the attachment of the derivatization molecule to the naphthenic acid, each acid becomes approximately 100 g/mol heavier. In fact, the smallest naphthenic acids in the nonderivatized sample elute inside the solvent peak at which time the detector is not turned on due preserve the equipment. Thirdly, the absolute response recorded by the GC-MS after derivatization has increased 5-fold compared to the response recorded with no derivatization. This will reduce the impact of noise for produced water samples with presumably low concentrations and consequent low signal response.

Furthermore, it can be observed that as the hump has retained most of its shape and no longer show a response in the retention time region where there was no overlap. This points to the purity of the naphthenic acid mixtures, where most of the content appears to have undergone derivatization and therefore must be a molecule which reacts with the derivatization agent. Hydrocarbons are for example, not affected by derivatization. Another aspect which highlights this point is the mass spectra registered at specific points in the chromatograms as shown below.

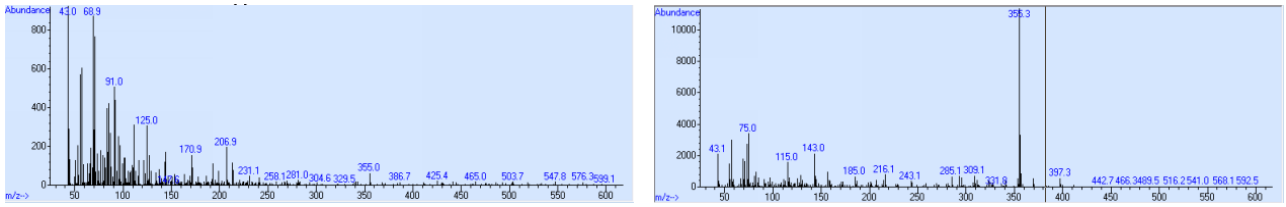


Figure 1.19 Mass spectra for the hump in the chromatogram for Fluka naphthenic acids, not derivatized on the left and derivatized with MTBSTFA on the right (spectra taken at minute 33 and 37 respectively). The hump is present in all three naphthenic acid mixtures.

Here, the mass spectra detected at minute 33 for the nonderivatized acids and minute 37 for the derivatized acids are shown. It can be shown that the peak which was previously thought to be pollutants is a large content of fatty C_{19} acids (which have a characteristic ion fragment of 355 m/z).

In the Acros naphthenic acid mixture however, some compounds around minute 39-41 were identified as pollutants. These did not derivatize and therefore cannot be naphthenic acids or any other compound which can be derivatized. As the pollutants did not get more mass during the derivatization step, these compounds elute at the same time in the chromatograms for Acros mixture with and without derivatization as can be seen in Figure 1.20.

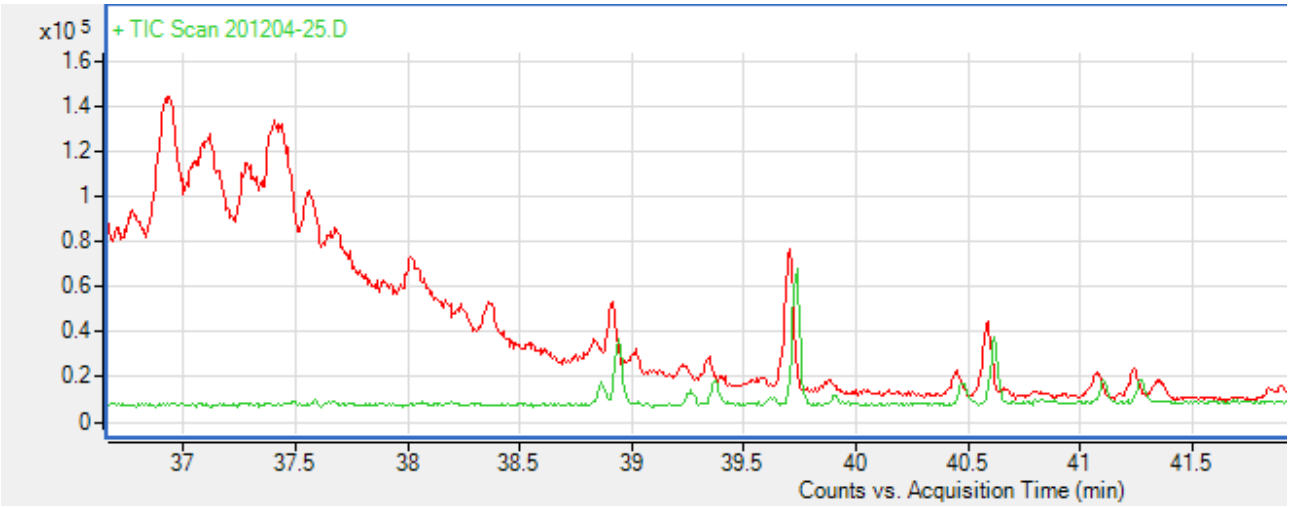


Figure 1.20 demonstrating the pollutants in the Acros naphthenic acid mixture. The figure shows a zoomed in view of the chromatograms for Acros mixture without derivatization (green) and with derivatization (red). The pollutants did not undergo derivatization and therefore elute at the same time in both chromatograms.

From the initial tests with and without derivatization it was concluded that all subsequent experiments should be run with a derivatization step in the method. Further evaluation of derivatization is given in Chapter 1.4.3.4 and 1.4.3.6.

1.4.3.2 Internal Standards

In GC/MS to enable a better quantification of naphthenic acids, it can be useful to add a suitable internal standard at a known concentration to the sample to be analysed. Differences in the volume of GC injected analyte leads to differences in the areas of the peaks in the chromatogram and any quantitative results are more suspect. To compensate for this error, a known amount of an internal standard (a second compound that does not interfere with the analysis of the primary analyte) is added to all solutions (standards and

unknowns). This way if the injection volumes (and hence the peak areas) differ slightly, the ratio of the areas of the analyte and the internal standard will remain constant from one run to the next.

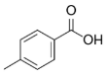
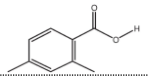
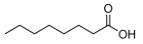
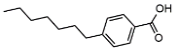
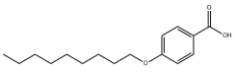
$$\frac{Area_{Sample}}{Area_{Internal\ Standard}} = F \cdot \frac{Concentration_{Sample}}{Concentration_{Internal\ Standard}}$$

$$\frac{Area_{Sample1}/Concentration_{Sample1}}{Area_{Internal\ Standard1}/Concentration_{Internal\ Standard1}} = F = \frac{Area_{Sample2}/Concentration_{Sample2}}{Area_{Internal\ Standard2}/Concentration_{Internal\ Standard2}}$$

A good internal standard should not have overlapping signal response with a compound in the sample, should be eluted close to the target component, should have similar chemical properties and should be chemically stable.

The seven organic acids listed below were considered for use as internal standard.

Table 1.5 showing the seven organic acids listed which were considered for use as internal standard. The acids are listed with name, isomer, molecular weight, and molecular structure.

Organic acid	Isomer	Molecular weight [g/mol]	Structure
Benzoic acid	$C_7H_6O_2$	122.12	
p-Tuloic acid	$C_8H_8O_2$	136.15	
2,4-dimethylbenzoic acid	$C_9H_{10}O_2$	150.17	
Capric acid	$C_{10}H_{20}O_2$	172.26	
Palmitic acid	$C_{16}H_{32}O_2$	256.4	
4-*n*-heptyl benzoic acid	$C_{14}H_{20}O_2$	220.31	
4-(nonyloxy)benzoic acid	$C_{16}H_{24}O_3$	264.36	

Through GC-MS analysis using the method described in Chapter 1.4.2.2.1, the retention times for the internal standard candidates were identified and listed below in Table 1.6. Due to the choice to evaluate two different derivatization chemicals which adds a different mass to each acid molecule, the retention times are different depending on which derivatization chemicals is used.

Table 1.6 Retention time of the organic acids considered as internal standard.

Organic acid	Retention time with BTSTFA [min]	Retention time with MTBTSTFA [min]
Benzoic acid	16.5	22.9
p-Tuloic acid	20.0	25.8
2,4-dimethylbenzoic acid	21.5	27.3
Capric acid	22.0	27.3
Palmitic acid	33.4	27.4
4-*n*-heptyl benzoic acid	34.8	37.9
4-(nonyloxy) benzoic acid	39.6	43.7

For the three commercial naphthenic acid mixtures, the two derivatization chemicals also add a different mass to each acid molecule. Consequently, the elution of the naphthenic acid hump is altered by the choice of retention times are different depending on which derivatization chemicals is used.

Table 1.7 Retention times for commercial acid mixtures with two different derivatization agents

Commercial acid mixtures	Retention time with BTSTFA [min]	Retention time with MTBTSTFA [min]
Acros	16 min – 36 min	20 min – 40 min
Sigma	16 min – 36 min	20 min – 40 min
Fluka	16 min – 36 min	20 min – 40 min

Depending on the derivatization chemical used, naphthenic acids mixtures used in this study have retention times between 16 and 36 minutes or 20 and 40 minutes with the current GC method. As internal standards should elute close to the sample, a good internal standard would be one that eluted in the middle of the naphthenic acid hump with a signal which can easily be isolated from the other acids, like a deuterated acid with an odd number of deuterium atoms. Deuterated components are often used in MS analysis to enable the isolation of the signal if the internal standard elute simultaneously as the molecules in the sample. As such these compounds often have similar retention times as the sample molecules. However, the GC-MS quantification method should also be used for comparative purposes to GC-FID in later stages of the project. The GC-FID method lacks the ability to isolate out deuterated molecules from the sample signal. As such it was found prudent to choose an internal standard which elutes outside the retention time interval of the sample. 4-(nonyloxy) benzoic acid is a good reference standard since has a retention time which is later than the elution hump of the naphthenic acid mixtures. Using 4-(nonyloxy) benzoic acid as the internal standard for both GC-MS and GC-FID allows for a more direct comparison between the two methods.

It was concluded that 4-(nonyloxy) benzoic acid is to be used as the internal standards for quantification method development of naphthenic acids, described in Chapter 1.4.3.6.

1.4.3.3 Concentration Range to Evaluate

In order to ensure that the method would be applicable to measure naphthenic acids in produced water in later stages of the project, a relevant concentration range for naphthenic acids was needed. To predict which concentrations to expect in the sample extract from the produced water, first one must obtain information regarding the naphthenic acid concentrations in produced water. Some typical produced water concentrations are shown in Figure 1.21 below.

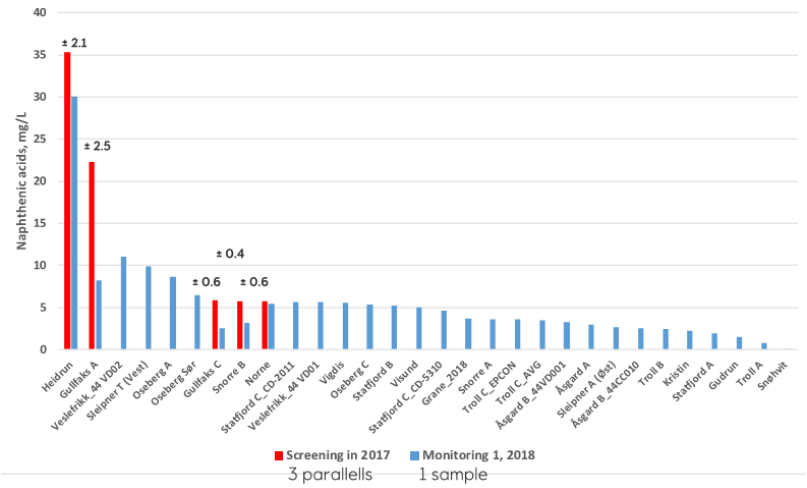


Figure 1.21 Graph showing the measured content of naphthenic acids in produced water from various Norwegian production fields. Source: Equinor ASA.

Based on the current extraction norm for produced water samples, the concentration ranges for the commercial naphthenic acid mixtures were calculated. 800 mL water extracted into 50 mL solvent concentrates the sample sixteen-fold. With an average concentration of 10 mg/L in produced water, this translates to an extract concentration of 160 mg/L. However, this concentration range was evaluated to be too small to serve as the initial concentration range as more signal tend to give a cleared result. The 50 mL of extraction solvent also allows the sample to be further concentrated by solvent evaporation. The concentration range for naphthenic acid concentration was therefore set between 150 and 1 600 mg/L. The extraction method is to be further developed in this project and the factor between concentration in produced water and in the solvent may change.

Various concentrations of the commercial naphthenic acid mixtures were prepared in toluene at the concentrations listed in Table 1.8.

Table 1.8 Chosen concentration ranges for commercial naphthenic acid mixtures used.

Fluka	Acros Organics	Sigma Aldrich
1 472 mg/L	1 592 mg/L	972 mg/L
736 mg/L	796 mg/L	486 mg/L
147 mg/L	159 mg/L	97 mg/L

1.4.3.4 Derivatisation

The commercial naphthenic acid mixtures and the organic acids evaluated for internal standards where derivatised with “MTBSTFA + TBDMSCI” and with “BSTFA + TMCS” (details about the derivatisation agents are given in Chapter 1.4.2.1). Derivatization allows for naphthenic acids molecules to behave more like non-polar molecules in the GC-MS analysis. The specific derivatization chemicals used here also allows the molecules to fragment into one stable ion, which is directly correlated to the molecular mass.

1.4.3.4.1 Derivatization of single organic acids

The samples were analysed on GC-MS as described in Chapter 1.4.2.2.2. With derivatization, the fragmentation is limited and both derivatization chemicals produce a dominant ion with 57 m/z added to the molecular weight of the acid found from Table 1.4. Two examples of the low degree of mass fragmentation are shown in Figure 1.24 below. The left spectrum in Figure 1.19 is a good representation of what a non-derivatized mass spectrum for a single acid would look like.

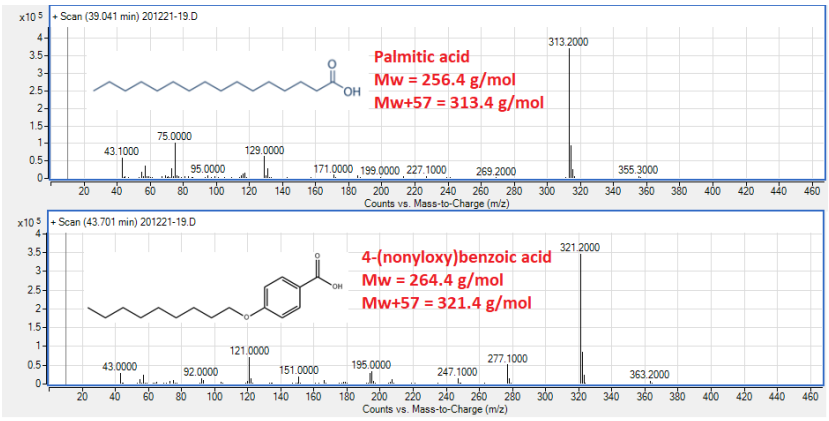


Figure 1.22 Mass spectra of the organic acids to demonstrate the low degree of fragmentation after derivatization.

For the single organic acids, both derivatization chemicals produced a dominant mass fragment, however the abundance of the mass fragment was not similar for the two derivatization chemicals. This can be demonstrated by dividing the signal response of the extracted ion chromatogram by the signal response of the total ion chromatographic response. Figure 1.25 below illustrate the signal response from TIC and EIC.

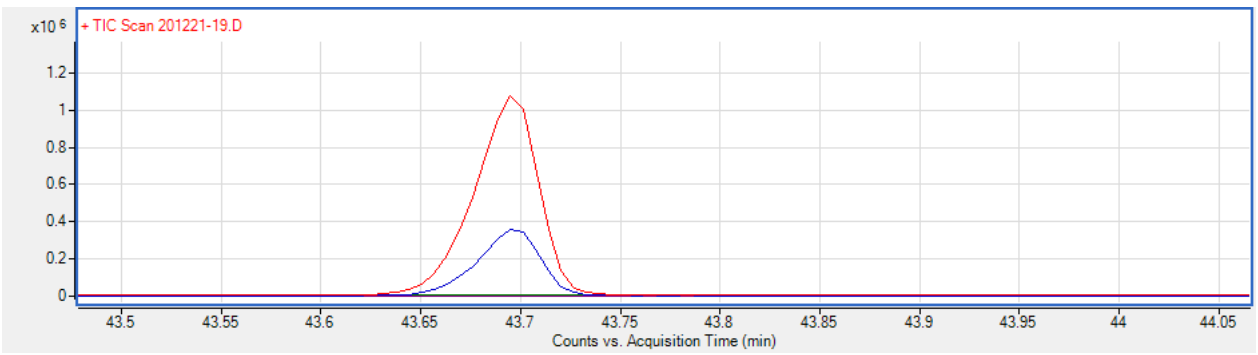


Figure 1.23 The extracted ion chromatogram (EIC) and total ion chromatogram (TIC) for 4-(nonyloxy)benzoic acid.

Table 1.9 show the different EIC/TIC ratio for the single acids derivatized with the two derivatization chemicals. On average MTBTSTFA produces a more stable ion fragment.

Table 1.9 The different EIC/TIC ratio for the single acids derivatized with the two derivatization chemicals.

Organic acid	EIC/TIC ratio with BTSTFA	EIC/TIC ratio with MTBTSTFA
Benzoic acid	20%	25%
Capric acid	15%	30%
Palmitic acid	30%	35%
4-*n*-heptyl benzoic acid	15%	35%
4-(nonyloxy) benzoic acid	15%	35%

1.4.3.4.2 Derivatization of naphthenic acid mixtures.

For the naphthenic acid mixtures, derivatization allows for more insight into the chromatogram. For instance, the last hump in all the commercial acid mixture samples looks similar. It could be the same compound, but without more information, it is not possible to say. With this derivatization technique, one can look at the mass spectra of this hump and discover that it is the same compound for all three acid mixtures. Figure 1.24 shows the mass spectra for Fluka naphthenic acid mixtures as an example. Figure 1.25 shows that the mass 355 is present in all the acid mixtures, likely with identical composition judging from the shape similarity.

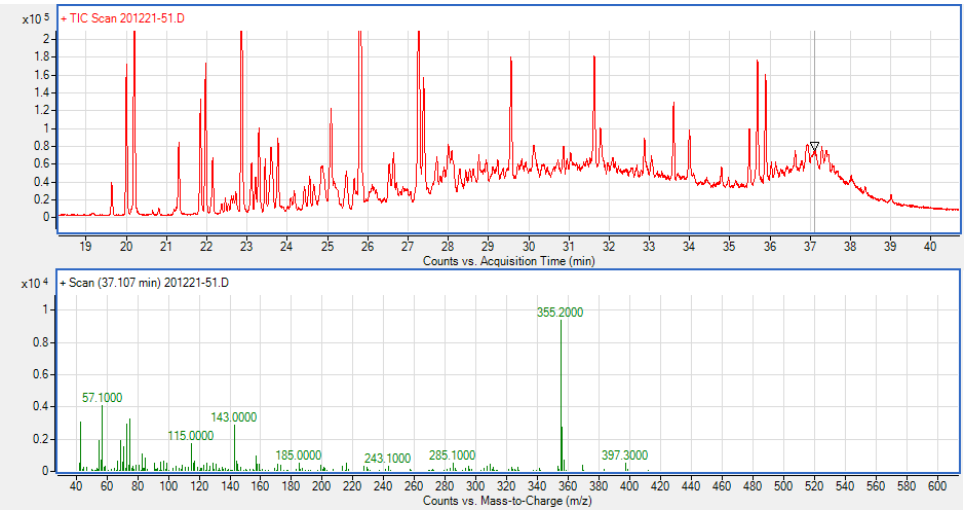


Figure 1.24 showing the mass spectra at minute 37 for Fluka naphthenic acid mixture.

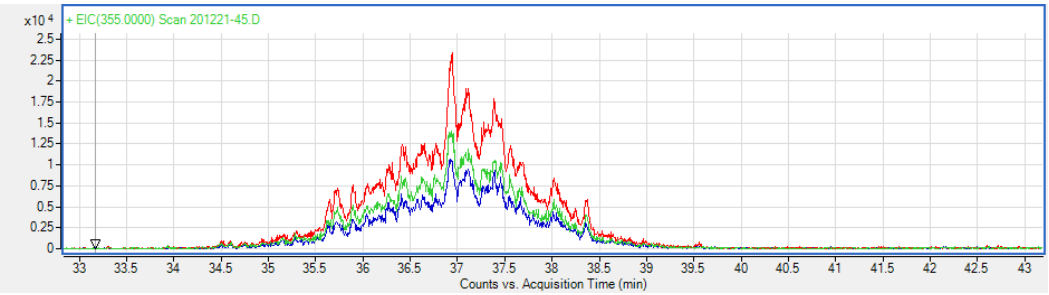


Figure 1.25 showing the extracted ion chromatogram for mass 355 for all three commercial naphthenic acid mixtures.

The mass 355 after subtracting 57 fits into the category of saturated C_{19} acids from Table 1.4. As the hump is present in the underivatized chromatogram, and the hump did not shift more than 5 minutes with derivatization, this is likely to be various structural isomers of C_{19} acids without any diacids or hydroxyl groups. Diacids or hydroxyl groups would after derivatization have increased the mass such that the compound eluted slower through the column. Why this acid is so prevalent in the naphthenic acid mixtures is not known. It may be that the production method used to produce these commercial naphthenic acids, where they are taken from a specific distillation cut, is selective for saturated C_{19} acids. However, as can be seen in the literature on commercial naphthenic acid analysis, saturated C_{19} acids are not prevalent in all mixtures.

With the stable fragment in the GC-MS after derivatization, the mass spectra recorded increases with the retention time.

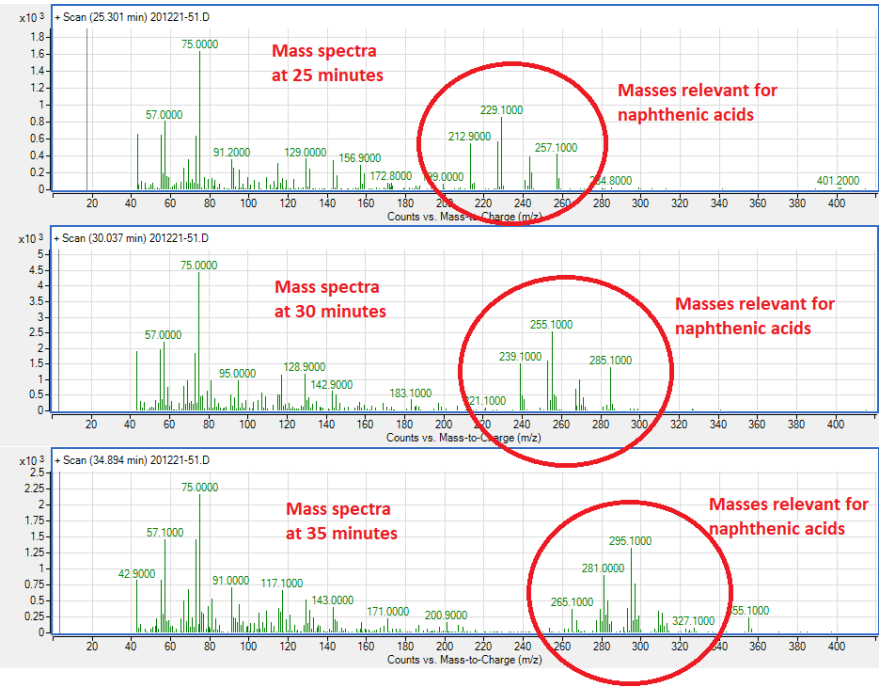


Figure 1.26 How the mass fragments increase over the elution time of the naphthenic acid mixture.

1.4.3.4.3 Derivatization Agent Conclusion

On average MTBTSTFA produces a more stable ion fragment and is a preferred derivatization chemical.

1.4.3.5 Chromatograms and identified composition of the commercial naphthenic acid mixtures

By allowing the identification of the naphthenic acids present in the mixture, three-dimensional naphthenic acid distribution plots can be created. By using the mass tables for naphthenic acid isomers displayed in Appendix C, the signal from one naphthenic acid isomer can be identified and the area% of the integrated chromatographic response of all the naphthenic acid isomers can be calculated.

In Figure 1.27 below, the TIC and the three-dimensional naphthenic acid distribution plot are shown for the three naphthenic acid mixtures. In the three-dimensional plots, the number of carbon atoms in the acid is displayed on one horizontal axis while the structure given as the number of rings is displayed on the other horizontal axis. From the three-dimensional plots, the Acros mixture appears to have solely saturated naphthenic acids. This is reflected in the shape of the chromatogram with little overlap between the peaks. The Sigma mixture also contains mainly saturated acids with a small amount of acids with one ring structure. The naphthenic acids with ring structures will, due to their boiling point, elute at different times compared to the saturated acids and the presence of both these structures makes the chromatogram more continuous. For the Fluka mixture, there is a greater diversity in naphthenic acid isomer distribution with even amounts of saturated acids, acids with 1 ring and acids with 2 rings. The chromatogram of the Fluka mixture reflects this composition with a continuous hump of the elution of the naphthenic acids. With the mass resolution of the GC-MS, it will not be possible to distinguish naphthenic acids with the traditional formula $C_nH_{2n+Z}O_2$ from naphthenic acids containing more oxygen or other elements like sulphur, or nitrogen. For the same Fluka naphthenic acid mixture used in this project, it has previously been shown that it contains no sulphur or nitrogen [75].

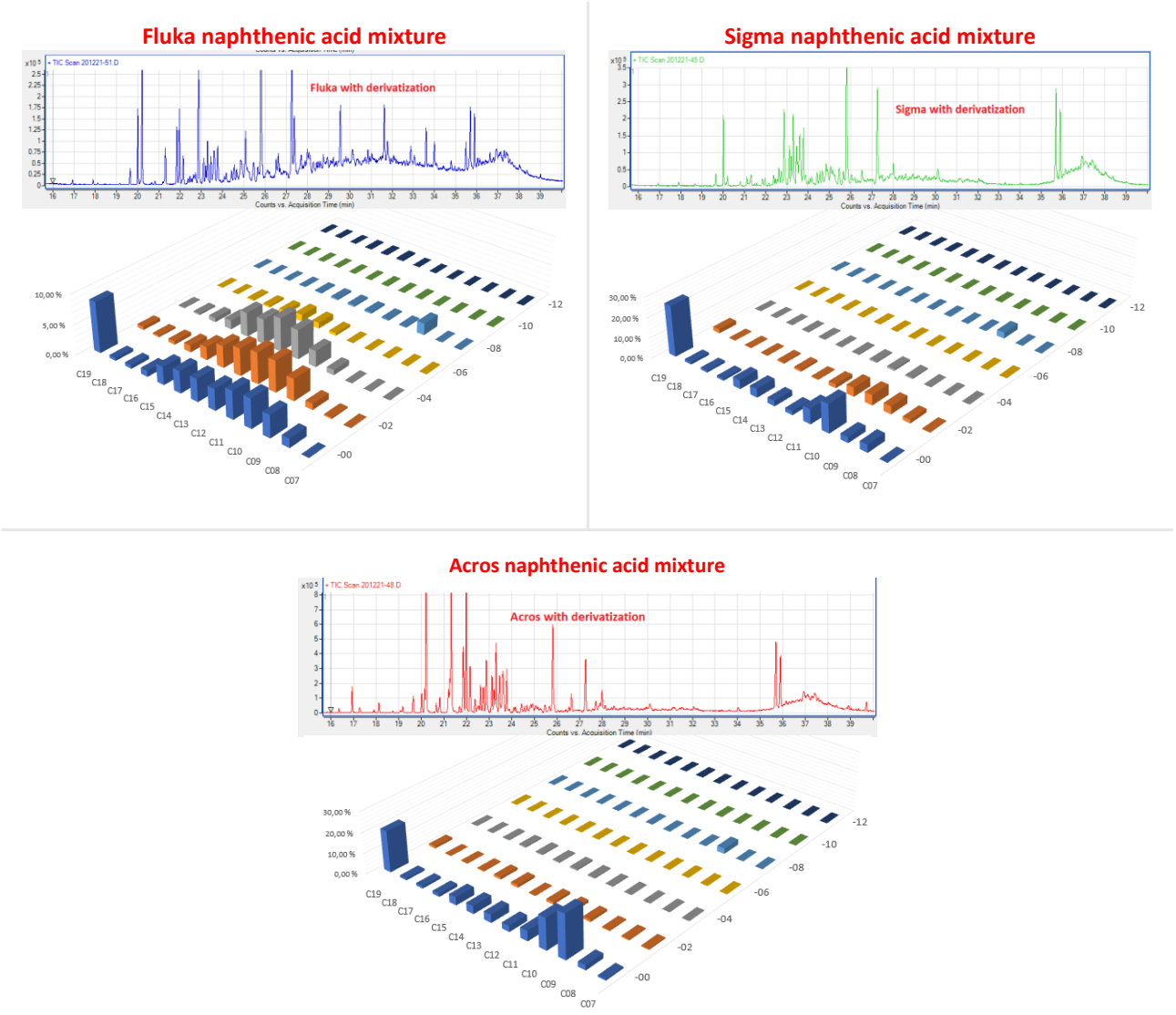


Figure 1.27 Chromatograms and three-dimensional distribution plots for each of the naphthenic acid mixtures.

1.4.3.6 Calibration and Reference Standards

The three commercial acid mixtures were analysed with the GC-MS method with the following parameter matrix. As such 36 GC vials were prepared (3 x 3 x 2 x 2 x 1).

Table 1.10 Experimental parameters investigated in this chapter.

Concentration	Commercial naphthenic acid mixture	Derivatization chemicals	Derivatization reaction temperature	Internal standards
High	Fluka	MTBSTFA	20°C	4-(nonyloxy) benzoic acid and Benzoic acid
Medium	Acros	BSTFA	60°C	
Low	Sigma			

The resulting chromatograms for Fluka naphthenic acid mixture at the three concentrations are shown in Figure 1.28.

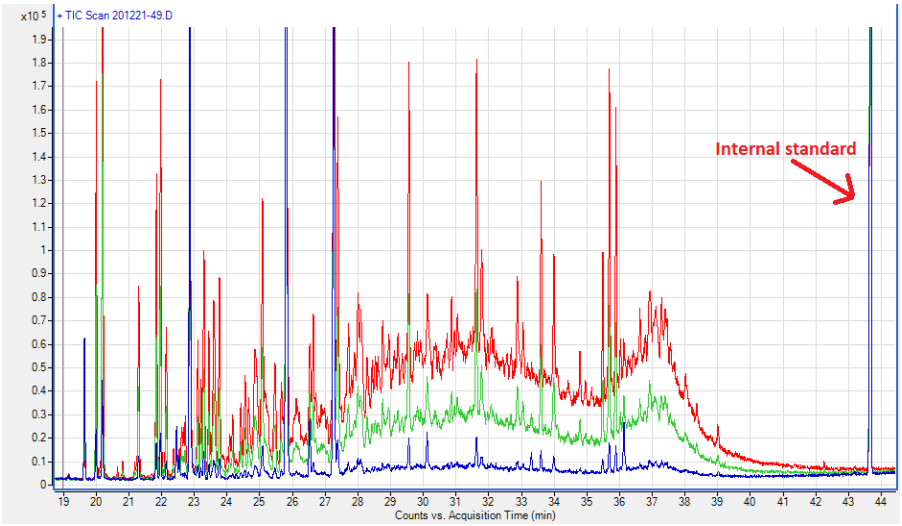


Figure 1.28 Chromatogram for Fluka naphthenic acid mixture at high, medium, and low concentration.

Unless specifically specified, all the results below are shown with 4-(nonyloxy) benzoic acid as the internal standard.

The calibration curves obtained for all the experiments yielded an overall similar trend as shown in Figure 1.29.

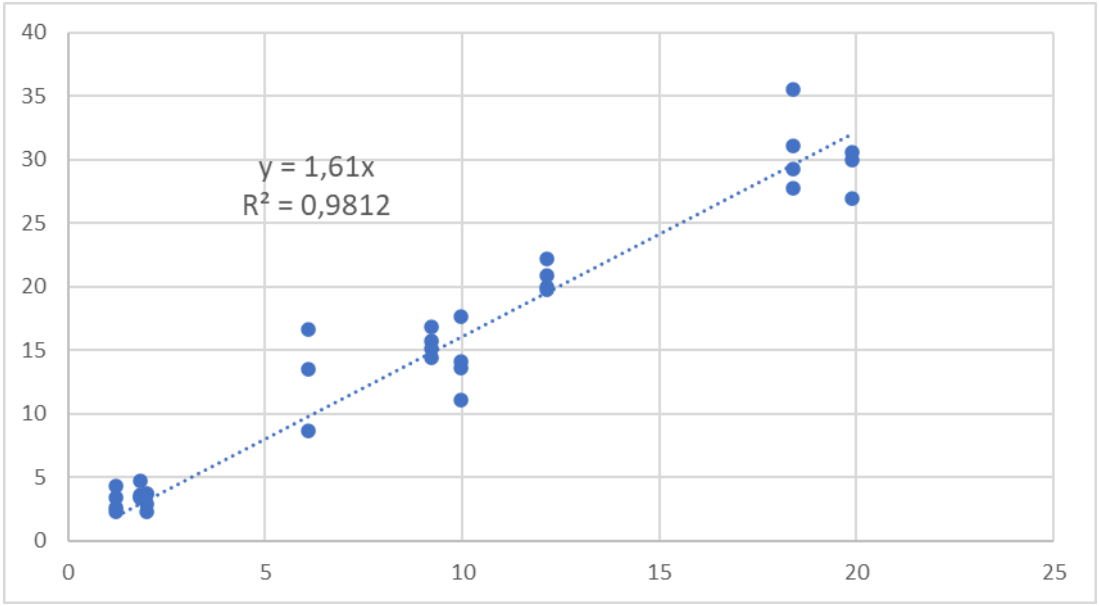
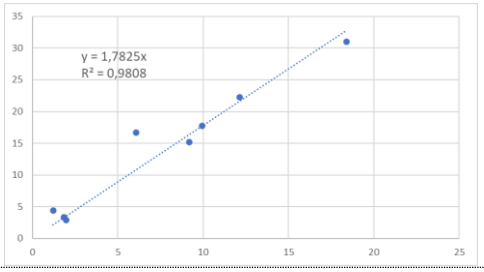
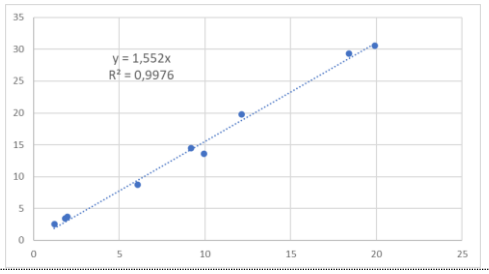
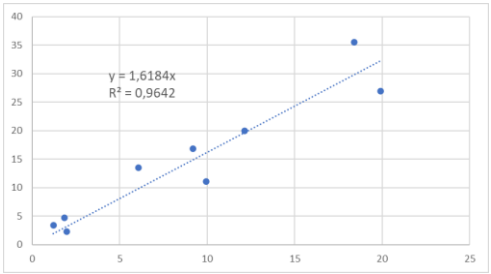
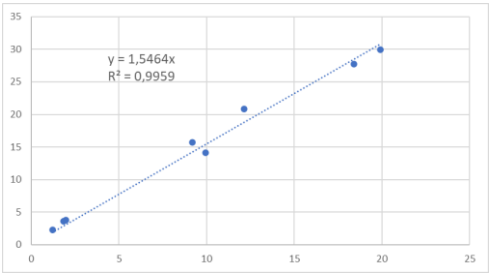


Figure 1.29 Overall calibration curve for all 36 experiments listed in Table 1.10. Here the area ratio is given on the y-axis and the concentration ratio is given on the x-axis.

1.4.3.6.1 Temperature dependence

As it was discovered that the heating step used during derivatization might not be required according to the vendor, derivatization without heating during the 30 minutes was performed to evaluate if this step could be excluded. To evaluate the temperature dependence of the derivatization chemicals the calibration curves for the naphthenic acid mixtures can be evaluated from experiments where the derivatization has been performed at high and low temperature. These calibration curves are shown in Table 1.11 below.

Table 1.11 Calibration curves obtained for the three naphthenic acid mixtures (3 points for each naphthenic acid mixture in each plot) combined with two different derivatization chemicals and two different temperatures used during derivatization. The area ratio is given on the y-axis and the concentration ratio is given on the x-axis.

Temperature	BSTFA as derivatisation agent	MTBSTFA as derivatization agent
	$\frac{Area_{Sample,TIC}}{Area_{Internal\ Standard,TIC}} = F \frac{Concentration_{Sample,TIC}}{Concentration_{Internal\ Standard,TIC}}$ (X, Y)	
20°C		
60°C		

For MTBSTFA, the calibration curve shows the same trend for both high and low temperatures (both with slopes 1.55). As can be observed in Appendix A, the shape of the chromatograms is also identical. For BSTFA, a clear shift in the calibration could be observed when the derivatization had been performed at 20°C. The results show that the temperature can have a tendency to skew the results. It is hard to evaluate if this is due to lower derivatization reaction equilibrium as both the internal standard and the naphthenic acid mixture would be affected by this phenomenon. It was determined that results obtained with MTBSTFA with derivatization at 20°C were to be assumed identical to results obtained at 60°C.

1.4.3.6.2 Quantification from total ion chromatogram.

As can be seen in the calibration curve in the top right corner of Table 1.11, the three naphthenic acid mixtures all have the same slope in the calibration curve. This was unexpected as the naphthenic acid mixtures are not similar in their composition. They are however similar in their average molecular weight which could explain the overlap in calibration curves.

In other words, if water was spiked with Acros or Sigma naphthenic acid mixtures, the naphthenic acid content of the water would be accurately quantified with a calibration curve based on Fluka naphthenic acid mixture.

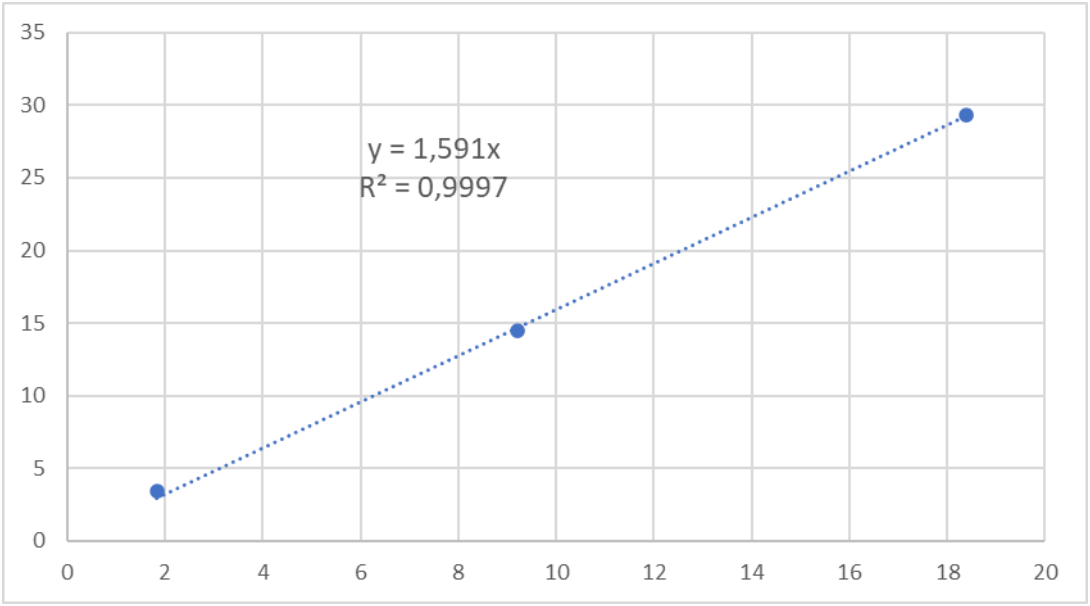


Figure 1.30 Calibration curve for Fluka naphthenic acid mixture, 147 mg/L - 1472 mg/L, derivatized with MTBSTFA at 20 °C. The area ratio is given on the y-axis and the concentration ratio is given on the x-axis.

In the later phases of the project, it might be possible to use the calibration curve directly to quantify the content of naphthenic acids in produced water. However, careful considerations need to be taken before such a simplification can be made. The literature is full of examples with pitfalls where commercial naphthenic acids have proved to be unable to properly quantify the naphthenic acid content of a tailing pond or produced water sample. At least for the tailing pond water, the composition of the naphthenic acids and the average molecular weight is different compared to the commercial acid mixtures. For produced water however, commercial acid mixtures should be more relevant in their average molecular weight. Another pitfall with using commercial naphthenic acids as the calibrant is that they change over time so any calibration curve from a commercial acid mixture will also change over time. This can of course be corrected for by correlating the chromatographic response of a commercial acid mixture to a single compound and correlating the results obtained as has been done in the literature [70, 74]. Although naphthenic acid quantification and derivatization with this chemical is not new, this specific application of the naphthenic acid analysis is brand new and by correcting for the average molecular weight of the acid mixture between the calibrant mixture and the unknown sample, we are expecting solid results. As an example of what is referred to, a 1000 mg/L solution of an acid mixture with average molecular weight of 100 g/mol would give a larger GC-MS response compared to a 1000 mg/L solution with an acid mixture with average molecular weight of 200 g/mol. The solution with the lighter acids contains twice the number of molecules.

1.4.3.6.3 Quantification from extracted ion chromatogram

In addition to the total ion chromatograms, the extracted ion chromatogram can also be used for quantification. Instead of showing the accumulated response per second for all the fragments which hits the detector, the extracted ion chromatograms show only the signal from one or a group of masses. By extracting the chromatogram signal for all the naphthenic acids masses in Table 2.29, the extracted ion chromatogram for Fluka naphthenic acids can be extracted as shown below in Figure 1.31.

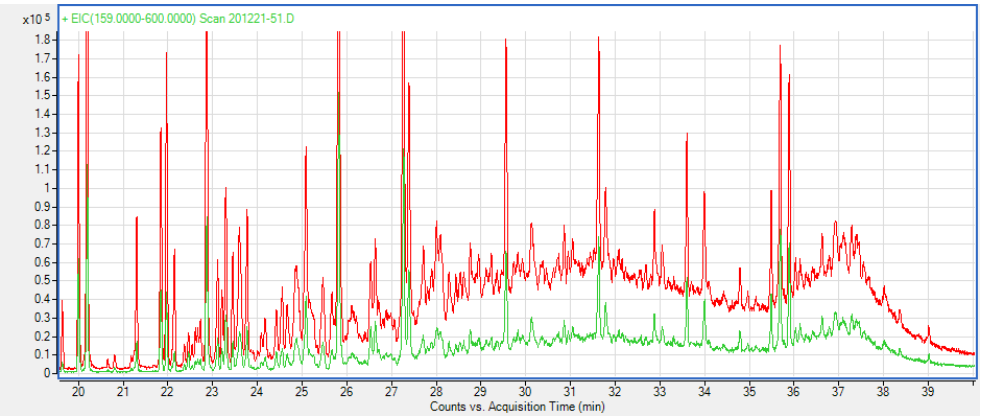


Figure 1.31 TIC and EIC for Fluka naphthenic acids.

The EIC will also give a linear calibration curve as it is simply a fraction of the TIC. However, an advantage with the EIC can manifest itself if the sample extracted from produced water is polluted with other organic compounds. With the EIC, one can isolate the signal from the compounds which are able to be derivatized. These compounds will create a large, stable, and dominant mass fragment, while other compounds will create many fragments of which most will be smaller mass fragments. An illustration of this effect can be observed in Figure 1.19 where the mass spectra for the last part of the chromatogram is shown both before and after derivatization. The large, stable, and dominant mass fragments from derivatized compounds could allow quantification based on EIC where the naphthenic acid sample still contain some other organic components/pollutants saving time in extractions and clean up steps. Here one assumption would be that the large mass fragments from compounds which are not derivatized, and happen to register as a naphthenic acid mass, have a negligible contribution compared to the large and dominant mass fragments from naphthenic acids which undergo derivatization. PAH's could for example interfere with the mass spectra due to low fragmentation. EIC also allows for a quick quality assurance to check if the TIC signal is reflecting the content of a pure sample.

To compare the two derivatization chemicals, for MTBSTFA the EIC is 18% of the TIC while for BTSFTA the EIC/TIC ratio is 6%. If the EIC is to be used, MTBSFTA gives a better signal response compared to BTSFTA.

1.4.3.6.4 Quantification from extracted ion chromatograms for single naphthenic acid isomers

As previously discussed in Figure 1.23, the signal of single naphthenic acid isomers can also be isolated from the chromatogram and calibration curves with these single naphthenic acid isomers can be made. As shown in Figure 1.13, the concentration for the naphthenic acid isomer is not known. However, by using the concentration of the total naphthenic acid mixture as a stand-in, a generic calibration curve can be created to demonstrate the linear response of the naphthenic acid isomers as the concentration increases. Figure 1.28 shows a generic calibration curve for naphthenic acid isomer $C_{15}H_{30}O_2$ in the three naphthenic acid mixtures. Other authors have used the calibration curves for each naphthenic acid isomer in a commercial acid mixture to calculate the content of single naphthenic acid isomers in a sample. The total amount of naphthenic acids in the sample is found by taking the sum of all the single naphthenic acid isomers.

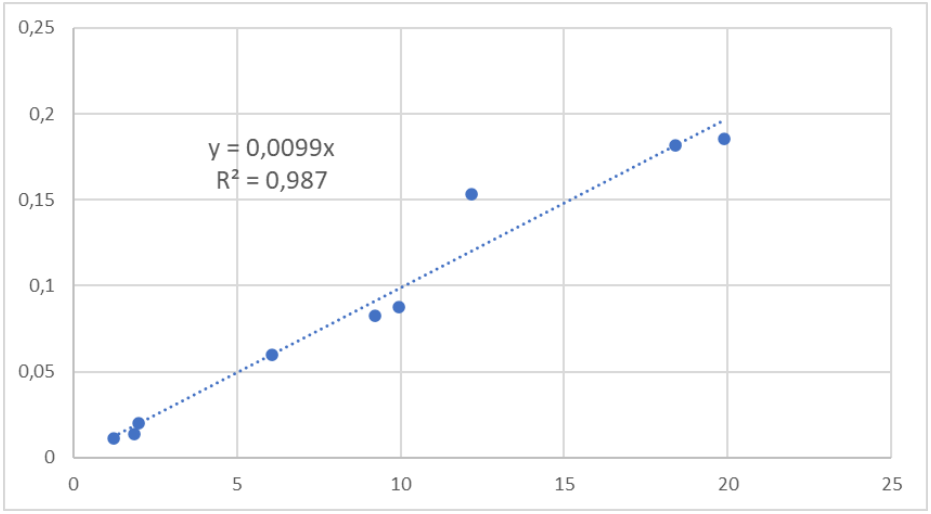


Figure 1.32 Graph showing a generic calibration curve for naphthenic acid isomer $C_{15}H_{30}O_2$ in the three naphthenic acid mixtures. Here the area ratio is given on the y-axis and the concentration ratio is given on the x-axis.

1.4.3.6.5 Internal standards

Two internal standards were used in the experiments. 4-(nonyloxy) benzoic acid and benzoic acid. Benzoic acid was added as a second internal standard to evaluate if this internal standard would yield better calibration curves for smaller naphthenic acids which elute first. An internal standard, which elutes close to the retention time of the sample, should give a better quantitative correlation. Having a peak both in front and behind the naphthenic acid elution hump was also regarded to give additional analytical insight for future GC-FID evaluations. Benzoic acid elutes slightly within the hump and this can be corrected for in the area integration. The calibration curve with benzoic acid as the internal standard also yields good results as shown in Figure 1.33.

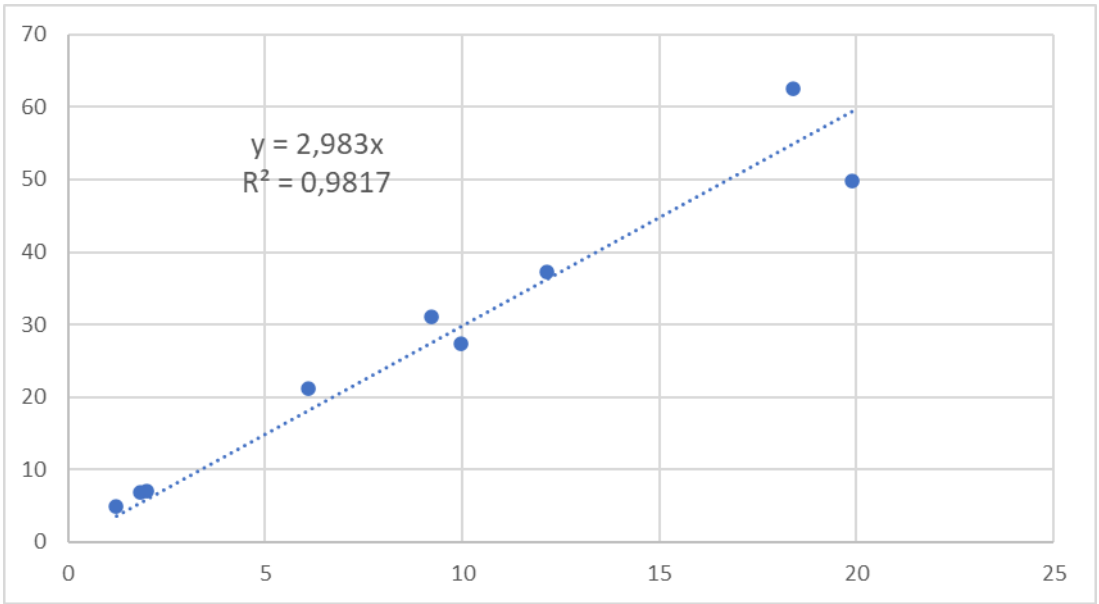


Figure 1.33 Calibration curve for the three commercial naphthenic acid mixtures with benzoic acid as the internal standard. Here the area ratio is given on the y-axis and the concentration ratio is given on the x-axis.

Summary of results obtained.

Based on the results obtained for the three naphthenic acid mixtures in Chapter 1.4.3.4 and 1.4.3.6, the following conclusions were drawn. As a derivatization agent, MTBSTFA is superior to BTSTFA for naphthenic acids. Of the three naphthenic acid mixtures, Fluka naphthenic acids is deemed to be better suited for quantification of naphthenic acids in produced water due to the broader distribution of naphthenic acid structures.

1.4.3.6.6 Validation of the quantitative method.

As a simple test, the quantitative capabilities of the calibration curve, three organic acids, capric acid, palmitic acid, and 4-heptylbenzoic acid were dissolved in toluene and run through the GC-MS method. Using the calibration curve for Fluka with 4-(nonyloxy) benzoic acid as the internal standard, the method overestimated the content of the single organic acids by a deviation of 24-56%.

Table 1.12 Quantification of a mixture with three organic acids quantified by a calibration curve based on Fluka naphthenic acid mixture.

Concentration of mixture with 3 organic acids	Concentration based on calibration for Fluka naphthenic acid mixture.	Deviation from weighted in amount
25 mg/L (8+8+9)	31 mg/L	24%
62 mg/L (20+20+22)	97 mg/L	56%
125 mg/L (40+40+45)	185 mg/L	48%

The inability for the Fluka naphthenic acids to give an accurate quantification for the mixture with three organic acids can be explained by the differing response factors shown in Figure 1.10. The ionization step in the GC-MS causes organic molecules to give a different signal response based on their structure. This is different from GC-FID for example, which is more dependent on the number of ionizable carbon atoms. Single organic molecular structures will give a distinct response with concentration in the GC-MS. Linear saturated acids as two of the acids used in this experiment were, will give a different response compared to branched saturated acids. The Fluka naphthenic acid mixture is made up from naphthenic acid isomers where the response factor for each naphthenic acid isomer is the average of the response factors for all the structures in the isomer. For example, the saturated $C_{14}H_{30}O_2$ naphthenic acid isomer can contain more than 1800 molecular structures. A linear molecular structure with the acid functional group on one end of the molecule is only one of these 1800 possible structures.

1.4.3.6.7 Development of bottom-up method:

An elegant method used by other authors in the quantification of naphthenic acids, is to create calibration curves for each naphthenic acid isomer from a commercial naphthenic acid mixture, which is then used to quantify all naphthenic acid isomers in a sample assuming the isomer in the sample has the same calibration curve as the isomer in the commercial naphthenic acid mixture. However, in order to make the calibration curve for the single naphthenic acid isomers, one would first need to know the concentration of each of the naphthenic acid isomers in the mixture and this number is not known. Setting the concentration% equal to the area% could give a high degree of error if the different components in the mixture have different response factors (signal increase with concentration).

As an example, in Table 1.13 below is a mixture with 4 different organic acids with different response factors. Here it can be seen that the if the calibration curves for single naphthenic acid isomer is set based on concentrations = area%*total concentration of naphthenic acid mixture, this would give a faulty content of each naphthenic acid isomer.

Table 1.13 Example showing that a mixture with acids which have different response factors, will not give an area% equal to the %concentration. In this example the total concentration is 40.

Acids Total concentration = 40	Content in mixture	Response factor for single acid	Measured response factor acid in mixture*	Area	Area %
$C_{component\ 1}$	15%	0.7	0.105	4200	15%
$C_{component\ 2}$	20%	0.87	0.174	6960	25%
$C_{component\ 3}$	55%	0.5	0.275	11000	39%
$C_{component\ 4}$	10%	1.5	0.15	6000	21%
C mixture	100%		0.7	28160	

**For the measured response factor for the acid in the mixture, the total concentration of acids in the mixture is used as the concentration of each acid is unknown.*

One could argue that equivocating area response to molar response is a faulty strategy as researchers have shown that different naphthenic acids have widely different response factors in GC-MS or LC-MS analysis as demonstrated in Figure 1.10. Indeed, researchers have also used this as a reason to specifically warn against equivocating the area response with molar response for MTBSTFA derivatized organic acids in GC-MS analysis. As demonstrated by Clemente and Fedorak [67] and in our test of 3 organic acids, the total naphthenic acid concentration was widely overestimated compared to the concentration prepared for the analysis. However, here is an opportunity where the complexity of the crude oil can actually be an advantage. As there are thousands of different molecular structures in each naphthenic acid isomer group measured, it can be assumed that the response from one naphthenic acid isomer group is not notably different compared to the response from another naphthenic acid isomer group. Why indeed should the processes which over millions of years produced crude oil naphthenic acids with thirteen carbon atoms give rise to a combination of molecular structures different to that of naphthenic acids with 16 carbon atoms? This can be illustrated by Figure 1.34 which show the response for molecular mass ranges of extracted crude oil acids. Here the evenly distributed peaks demonstrate the response factors for each acid structure is averaged out by the sheer number of different structures in the mixture.

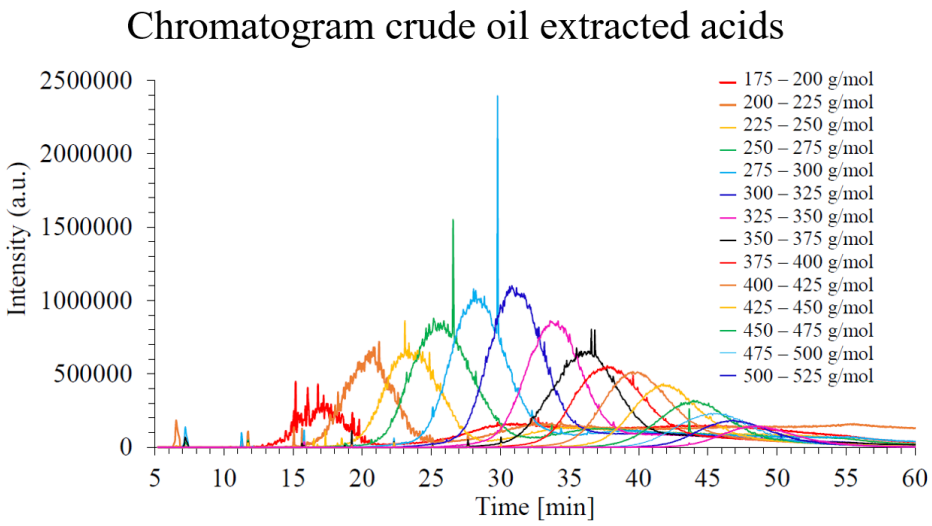


Figure 1.34 Illustration of how the acids in crude oil acid mixtures are evenly distributed as there are different response factors for each acid structure is averaged out by the sheer number of different structures.

By assuming equal response factors for the four acids in the mixture, the example above can be repeated as shown in Table 1.14. Now the area percentage does reflect the concentration percentage.

Table 1.14 Example showing that a mixture with acids which have equal response factors, will give an area% equal to the %concentration. In this example the total concentration is 40.

Acids Total concentration = 40	Content in mixture	Response factor for single acid	Measured response factor acid in mixture*	Area	Area %
$C_{component\ 1}$	15%	0.7	0,105	4200	15%
$C_{component\ 2}$	20%	0.7	0,14	6960	20%
$C_{component\ 3}$	55%	0.7	0,385	11000	55%
$C_{component\ 4}$	10%	0.7	0,07	6000	10%
C mixture	100%		0,7	28160	

**For the measured response factor in for the acid in the mixture, the total concentration of acids in the mixture is used as the concentration of each acid is unknown.*

By assuming similar response factors for each naphthenic acid isomer, an approximation can be made for each naphthenic acid isomer by equivocating the area response to the molar concentration. Thus, an approximate mass concentration can be calculated for each naphthenic acid isomer and summed up to the total concentration of naphthenic acids in an unknown sample. This can be done by applying the response factors from a calibration with commercial naphthenic acid mixture to the naphthenic acid isomer group response in the unknown sample. The assumption of similar response factor for all naphthenic acid isomers has not been done in the literature. However, Havre, Sjöblom [41] assumed similar response factors for all homologues, i.e. structures like 1 ringed, 2 ringed 3 ringed, etc. e.g. all columns in Table 1.4 have the same response factor. It would be prudent to examine if this method can also be applied in our analysis.

By using the molar calibration curve for each naphthenic acid isomer in the Fluka naphthenic acid mixture, with concentrations for each isomer based on area percentage, the summed-up mass concentration for the mixture can be obtained as shown below in Table 1.15.

The quantification procedure is as described below.

- Assume molar concentration of naphthenic acid isomer = area% multiplied with total molar concentration of acid mixture.
- Make molar calibration curve for each naphthenic acid isomer.
- Calculate molar concentration for each naphthenic acid isomer in sample based on the calibration curve.
- Calculate the mg/L per naphthenic acid isomer with molecular weight for isomer.
- Sum up to find the total naphthenic acid concentration of the sample.

Table 1.15 Concentration of Fluka naphthenic acid mixture calculated from molar calibration curves for each naphthenic acid isomer.

Fluka naphthenic acids	Sum of naphthenic acid isomer concentrations	Weighted concentration	Deviation
High	1374	1 472	7%
Medium	660	736	10%
Low	153	147	4%

By using the bottom-up approach, the calibration curves for isomers in Fluka naphthenic acid mixture was able to describe the total naphthenic acid concentration with an appropriate accuracy.

However, using the same Fluka based calibration curves to describe the other two naphthenic acid mixtures does not yield the same accuracy as shown in Table 1.16. The reason for this might be that these mixtures contain either more or less structural isomers per chemical formula, which yields a different average response factor for that isomer compared to Fluka. Looking at the chromatogram for the three naphthenic acid mixtures it looks like the Sigma and Acros mixtures have more discrete peaks pointing to fewer structures per isomer. This is also reflected in the fact that the naphthenic acid isomers in the Sigma and Acros mixtures have different calibration curves after concentration is correlated to area percentage compared to the same calibration curves for Fluka.

Table 1.16 Concentration of Sigma and Acros naphthenic acid mixtures calculated from molar calibration curves for each naphthenic acid isomer in the Fluka naphthenic acid mixture.

Sigma	Sum of naphthenic acid isomer concentrations	Weighted concentration	Deviation
High	793	972	18%
Medium	307	486	36%
Low	90	97	7%

Acros	Sum of naphthenic acid isomer concentrations	Weighted concentration	Deviation
High	1034	1592	35%
Medium	490	796	40%
Low	135	159	15%

Another useful property of setting the area percentage equal to the concentration percentage is that one can estimate the average molecular weight for the naphthenic acid mixture in this manner.

To perform the bottom-up approach, the commercial naphthenic acid mixture with the most structures per isomer would give the best calibration curves for naphthenic acids in produced water. Although it is not known if Fluka has more structures per isomer than the other two acid mixtures, it does have more broader distribution of different naphthenic acid isomers, with an even distribution of acids with no rings, 1 ring and 2 rings.

Fluka naphthenic acids is therefore assumed to give the best naphthenic acid isomer calibration curves to be used for produced water samples. As described in 1.3.1.3.5, the best calibration mixture for this approach would be to take an unseparated sample of e.g. the Heidrun wellstream from the inlet manifold (or recombine stabilized crude with treated produced water) and acidify it to pH 2 to partition all the acids into the crude oil phase. This crude oil could then undergo naphthenic acid solid phase extraction to make a naphthenic acids mixture which can be weighed, titrated to find the average molecular weight and the total weight of acids. This solution would have a large number of structural isomers per chemical formula and would be an excellent calibration standard with which to calibrate and quantify naphthenic acid isomers in produced water samples with the bottom-up approach.

An interesting observation regarding the experiment with the three organic acids in the mixture is that the area percentage for each acid is very much correlated to the concentration. This is not similar to the reports by Clemente 2004 who said that equimolar concentrations of single acids produce very different area percentages. However, one difference between our approach and Clemente is that he took the fragments over the whole chromatogram and not just the peak at the specific retention time. This will lead to random fragments from the other acids eluting later in the chromatogram being counted as smaller naphthenic acids. We have specified the retention time for each naphthenic acid isomer so that smaller fragments from larger acids eluting at a later retention time are not counted as smaller naphthenic acids. It could be that specifying the retention time window for the acid fragment, will cause the area percentage to equal the concentration percentage. However, it could also be a coincidence. Hindle, Noestheden [66] who reported

widely different response factors for single naphthenic acids, did not use a derivatization agent. And Woudneh, Coreen Hamilton [74] who reported that while most different naphthenic acid isomers often had similar response factors, some of them have widely different response factors. Here it was not specified how these response factors were calculated. If the area percentage was set equal to the concentration percentage, the response factor for all isomers should be equal. However, for acid isomers with low concentration this could cause a deviation due to the low signal.

1.4.4 Conclusion

A GC-MS method was developed to allow for quantification of naphthenic acid samples at later stages in the project.

It was decided that derivatization yields the best result and that of the two derivatization chemicals considered, MTBSFTA should be used.

Seven organic acids were considered for use as internal standard and 4-(nonyloxo)-benzoic acid was chosen as it had a retention time outside the retention time window of the naphthenic acid mixtures.

Three naphthenic acid mixtures were analysed and found to have different compositions of naphthenic acids. Fluka naphthenic acid was found to be the preferred of the three naphthenic acid mixtures in that it contains a broader distribution of naphthenic acid structures e.g. acids with 1 ring and 2 rings. The naphthenic acid composition in produced water is assumed to be broad and the literature recommends the greatest possible distribution overlap if commercial mixtures are to be used for produced water analysis. In this respect, the Fluka naphthenic acid mixture is superior to the other two mixtures tested. However, better alternatives might be to extract acids from an acidic crude oil/produced water sample or get hold of the commercial naphthenic acid mixture used by Samanipour, Reid [71] which had a very broad size-wise and structure-wise distribution.

Calibration curves for the three naphthenic acid mixture were similar even though their compositions were different. As the calibration curves for all three acid mixtures were similar, this could potentially mean that they can be used as an external quantification standard. If the quantification responses from commercial naphthenic acid mixtures can be correlated with each other through the comparison with the response of a single acid as has been suggested in the literature [70, 74], commercial naphthenic acids might be suited for external calibration curves. The quantification of an unknown sample should be corrected for with the average molecular weight difference between the sample and the calibrant mixture.

- **TIC calibration:** This would be an external calibration standard with total ion chromatogram of commercial naphthenic acids, in our case Fluka.
- **EIC calibration:** Extracted ion chromatograms can also be used to obtain results for samples which are still polluted and consequently have a TIC which does not accurately represent the naphthenic acid content.
- **Bottom-up approach:** Calibration curves for each naphthenic acid isomer can be obtained from Fluka naphthenic acid mixture with the assumption that area percentage equals concentration percentage. Using the methodology used in the literature where naphthenic acid isomers in the sample are set to have the same calibration curve as the naphthenic acid isomers in the commercial naphthenic acid mixture. From here the amount of each naphthenic acid isomer in the sample mixture can be quantified and summed up to the total naphthenic acid content. This quantification

method should be independent of average molecular weight difference between the sample and the calibrant mixture.

Moving forward in the project towards extraction methodologies and naphthenic acids in real produced water samples, these three quantification methods can be validated and adjusted if necessary. As the TIC signal calibration curves from the three commercial acid mixtures were comparable, this looks like a promising method from a method-based approach. However as seen in the theory chapter, commercial acid mixtures can change over time and give very different responses.

With this GC-MS method, great qualitative and quantitative insights can be obtained and used in the later stages of the project. By being able to zoom into the chromatogram and see which acid is eluting from the column at a specific time, the GC-MS has granted us the same advantages as is given by soft ionization methods employed by LC analysis, but with much less sophisticated equipment. This allows us more data to troubleshoot with, perform more in-depth analysis, and draw more rigid conclusions. Quantitative knowledge of the different naphthenic acid structures can also be used for environmental impact factor evaluations.

It should be mentioned that the during the development of the current GC-MS method, Intertek has implemented a high degree of automation into the data processing. Intertek has a good methodology where time saving tools and templates have been identified and implemented throughout the data analysis. This will be beneficial moving forward in the project as the time saved on data processing can be spent gaining better analytical insights. The automation of the data processing will also be beneficial for the final product which is envisaged to give the total naphthenic acid concentration and concentration and distribution of naphthenic acid isomers in the sample with the click of a button. Examples of how the results could look are included in Appendix A.

It will be interesting to see if the additional information gained by the GC-MS can be used for additional analytical insight of the results obtained with GC-FID. Preliminary results from GC-FID shows that it is not suitable for the speciation (e.g. quantity of different isomers and structures) of naphthenic acids, however for quantifying total naphthenic acid content, GC-FID look promising. The GC-MS allows us to see the molecular weights of the compounds exiting the column, and give an estimate for the average molecular weight of the sample which can be informative for both GC-FID responses and FTIR responses. It would be interesting to see if a FTIR calibration method could be adjusted with the average molecular weights of the naphthenic acid mixture. Naphthenic acid mixtures of different average molecular weights could be obtained through partitioning back and forth in oil water systems at different pH levels and measuring average molecular weight with GC/MS.

An additional advantage of the GC-MS is that in a polluted sample with other organic compounds, the derivatization allows for the signal from naphthenic acids to be isolated through the extracted ion chromatogram. This allows for quality assurance that the total ion chromatogram is actually representing the signal from naphthenic acids. The extracted ion chromatogram may also be used to analyse a less isolated sample, saving time in extractions and clean up steps. Compounds which do not undergo derivatization will be fragmented into small pieces while acids which undergo fragmentation will mainly fragment into one piece. However, here it should be noted that alkylphenols and amines are also available for derivatization. Alkylphenols and amines are expected to be present in low concentrations compared to the naphthenic acids, especially after the extraction steps.

1.4.5 Suggestions for further work in additional project.

To test if the quantification of naphthenic acids can be measured with the whole chromatogram, TIC or EIC, 1500 mg/L acid mixture in toluene can be mixed with buffered pH 8 water at which pH, half the acids should be in the water phase according to Figure 1.5. The partitioned extract can then be back-extracted to DCM (at low pH). DCM extract can be analysed by GC-MS to obtain the average molecular weight and the total weight of the sample can be measured after solvent evaporation with rotavapor. In this manner it can be observed measured concentrations Note that the rotavapor uses low pressure instead of elevated temperature. Rotavapor evaporation of a solvent with the small benzoic acid was tested in 2015 and there was no mass lost during the evaporation [76]. Another validation method could be to buy in multiple naphthenic acid mixtures from multiple vendors and multiple batches to validate the quantification method's independency from the commercial acid mixture.

To test if the area percentage of naphthenic acid isomers can be equivocated to concentration percentage, naphthenic acid mixtures can be split into smaller distributions by performing successive partitioning at various pH levels. The partitioned extracts can then be back-extracted to DCM (at low pH). DCM extract can be analysed by GC-MS to obtain the average molecular weight and the total weight of the sample can be measured after solvent evaporation with rotavapor. In this manner it can be observed if the summed concentrations of naphthenic acid isomers can predict the weight of the dried acid sample.

2. Phase 2 - Development of GC-FID Quantification Method and Extraction and Quantification of Naphthenic Acids from Produced Water

2.1 Introduction

In order to quantify the amount of naphthenic acids discharged from offshore installations, a robust and reliable quantification method is required. The aim of this project was to develop and demonstrate such a method to be applied in the industry.

In the previous project phase, a literature review was performed to identify the status for naphthenic acid quantification methods. In addition, a quantification method for determination of naphthenic acid content in an oil solvent by GC-MS was developed. This method allows the determination for both the total content of naphthenic acids and the content of different naphthenic acid species.

This part of the report will cover the results, discussions, and conclusions from the second phase of the project. In this phase, a quantification method for determination of naphthenic acid content in an oil solvent by GC-FID was developed. A method to extract and isolate naphthenic acids from produced water samples to an oil phase was also developed and demonstrated. The extracted and isolated samples were confirmed to contain naphthenic acids by GC-MS analysis. These samples were then quantified with the quantification methods developed for GC-FID and GC-MS to measure the content of naphthenic acids in the produced water samples.

The development of the GC-FID quantification method is described in Chapter 2.3.

The extraction and quantification of naphthenic acids from produced water is described in two parts where the first part details the initial test on 4 of the 10 different produced water samples and described in Chapter 2.4.1.

The results from the extraction of naphthenic acids from produced water is given in Chapter 2.4.1.1.

The GC-MS analysis of the naphthenic acids isolated from produced water is detailed in Chapter 2.4.1.2 and 2.4.1.3. The GC-FID quantification results are presented in Chapter 2.4.1.4.2.

For the second part, where the extraction method was further optimized, the results for the remaining produced water samples are given in Chapter 2.4.2.

The method accuracy and lower limit of detection and quantification for the method is described in Chapter 2.4.3. A discussion of the impact of production chemicals and phenols is given in Chapter 2.4.6.

2.2 Experimental

2.2.1 Chemicals

The chemicals listed below have been utilised.

- Naphthenic acid, Fluka, technical grade, Donated by Ugelstad Laboratory at NTNU (Fluka is now a part of Sigma Aldrich and it is likely to be the same product as the naphthenic acid from

Sigma Aldrich. There are batch-wise variations in these naphthenic acid mixtures, so they do not have the same composition). Acid number 230 mg_{KOH}/g = 243 g/mol

- Reference standard
  - 4-(nonyloxy)benzoic acid, Acros Organics, 97%
- Other chemicals for analysis
  - Benzoic acid, from solution also containing *p*-Tuloic acid and 2,4-dimethylbenzoic acid, Chiron, S-4281-100-T Batch 3626
  - 4-*n*-heptyl benzoic acid, Alfa Aesar, >99%
  - Capric acid, Sigma Aldrich, Supelco®, M-Clarity™ quality level = MQ100
  - Palmitic acid, Sigma Aldrich, Supelco®, M-Clarity™ quality level = MQ100
  - Abietic acid technical 75%, Sigma Aldrich 00010-25G LotBCCD4341
- Derivatisation agents
  - MTBSTFA+TBDMSCl, N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide with 1% tert-Butyldimethylchlorosilane, Sigma Aldrich, >95%
- Solvents
  - Toluene, Merck, SupraSolv® for GC-ECD/FID, Supelco®, M-Clarity™ quality level = MQ100
  - *Pentane* , VWR Pestinorm 83964.320

Produced water samples from 10 different production platforms in the North and Norwegian Sea were obtained from the project's industry partners.

For labelling, the table below will be used for this report.

Table 2.1 Produced water letter identification and Sample ID for produced water from 10 different offshore production platforms

Produced water sample	Sample ID
A	2021-02390
B	2021-02522
C	2021-02710
D	2021-02751
E	2021-02792
F	2021-02794
G	2021-02847
H	2021-03180
i	2021-03248
J	2021-03503

2.2.2 Method

2.2.2.1 Liquid-liquid extraction

The method developed to extract naphthenic acid from produced water samples are given below. The produced water samples are acidified to pH 2 upon sampling offshore.

Step 1. 45 ml of toluene was added to the bottle before it was shaken to rinse the insides of the bottle. The bottle was stirred for 30 minutes at minimum 1000 rpm with the vortex reaching the bottom of the bottle. As the pH of the water is low, the naphthenic acids will transfer to the organic solvent phase. The bottle was then placed on the bench for 16 hours to allow the oil phase and water phase to separate. Over the course of the project, salt with divalent cations (40 g/L $MgCl_2$) was dissolved in the produced water prior to stirring with toluene. Salt with divalent cations facilitates oil water separation in oil in water emulsions by suppressing the electrostatic repulsion of the charged droplet surfaces.

Step 2. The oil phase was recovered by microseparator shown in Figure 2.1. The oil phase was recovered into a 50 mL flask. 3 mL of toluene was used to rinse the microseparator and the flask was filled up to the 50 mL mark with fresh toluene. This oil phase contains the crude oil droplets and the oil in water.

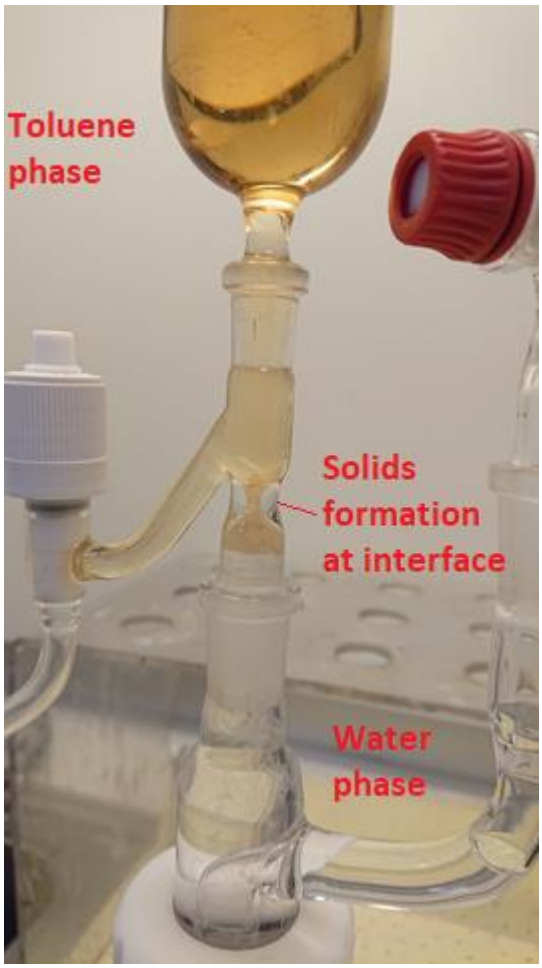


Figure 2.1 Picture of the toluene solvent extraction after the first extraction step using a microseparator.

The weight of the produced water bottles was measured when they contained only produced water and when they were empty after the liquid-liquid extraction. This weight was combined with a generic density (1000 g/L) to get the volume of produced water.

Step 3. Equal volumes (~10 mL) of the oil phase from the flask and pH 12 saltwater (3.5 wt% NaCl) were shaken at 200 rpm for 30 minutes on an orbital shaker. As the pH of the water is high, the naphthenic acids will transfer to the aqueous phase. The vial was then placed on the bench for 15 minutes to allow the oil phase and water phase to separate. The water phase was extracted. Fresh pH 12 saltwater (3.5 wt% NaCl) was added to the oil phase and the procedure was repeated and the water phases were combined. This water phase (~20 mL) now contained the naphthenic acids from the produced water.

Step 4. Fresh toluene (~20 mL) was added to the water phase from the previous step. The pH was adjusted to <2 with HCl and the vial was shaken at 200 rpm for 30 minutes on an orbital shaker. As the pH of the water is low, the naphthenic acids are transferred to the organic solvent phase. The vial was then placed on the bench for 15 minutes to allow the oil phase and water phase to separate. This oil phase now contains the naphthenic acids from the produced water.

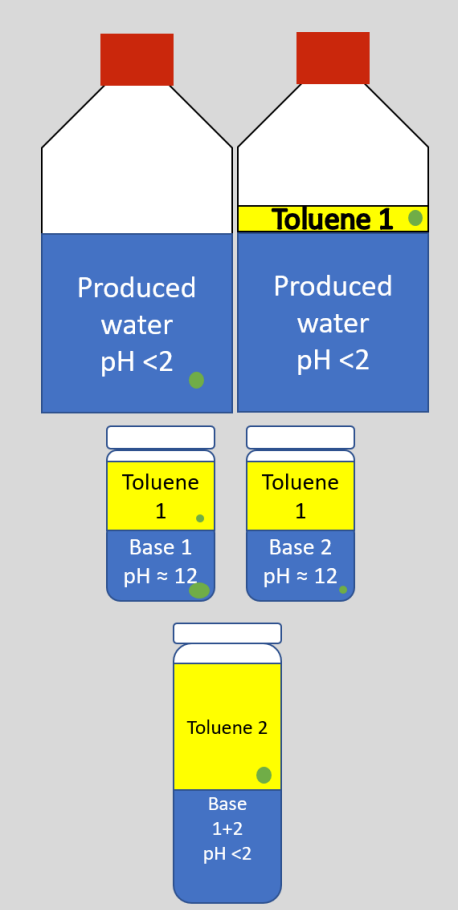


Figure 2.2 Showing the presence of the naphthenic acids in the different extraction steps. Naphthenic acids are shown with a green dot.

2.2.2.2 Spiking

A spiking solution of commercial naphthenic acids mixture in toluene was prepared at 150 000 mg/L.

Four bottles of each produced water sample were spiked with increasing concentrations of spiking solution (prior to the liquid-liquid extraction).

The high concentration of the naphthenic acid in toluene spiking solution was necessary due to the low volume (0.3 mL) which was to be added. The low volume allowed the toluene to be completely dissolved in the produced water, and the naphthenic acids from the commercial naphthenic acid mixture are then dissolved in the same conditions as the naphthenic acids from the produced water. The bottle was stirred for 30 minutes at minimum 1000 rpm with the vortex reaching the bottom of the bottle.

Table 2.2 shows the concentrations of the spiked solutions.

Table 2.2 Concentrations of naphthenic acids in the produced water samples spiked with commercial naphthenic acid mixture. X is the unknown concentration of naphthenic acid in the produced water samples.

	Produced water sample	Spiked produced water sample S1	Spiked produced water sample S2	Spiked produced water sample S3	Spiked produced water sample S4
Naphthenic acid concentration in produced water	X mg/L	X + 9 mg/L	X + 19 mg/L	X + 38 mg/L	X + 56 mg/L
Naphthenic acid concentration in measured sample	X mg/L multiplied with a factor 8	X + 9 mg/L multiplied with a factor 8	X + 19 mg/L multiplied with a factor 8	X + 38 mg/L multiplied with a factor 8	X + 56 mg/L multiplied with a factor 8

2.2.2.2.1 Standard addition method

The method of standard addition is a type of quantitative analysis approach often used in analytical chemistry whereby the standard is added directly to the aliquots of analysed sample. An illustration of the method is shown in Figure 2.3 below.

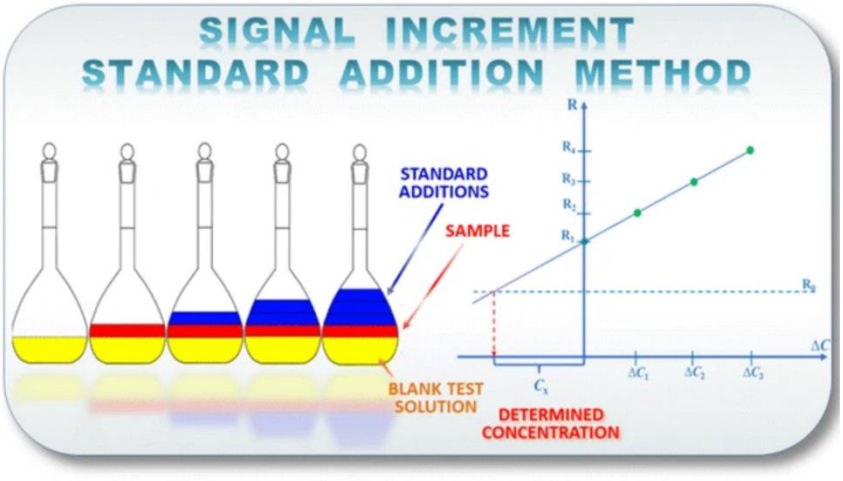


Figure 2.3 The principle of the standard addition method. Standard additions of compounds similar to the sample measured are added in incremental concentrations. Figure from open source reference [77].

This technique is usually used to quantify samples where the sample matrix also contributes to the analytical signal. For this reason the R_0 in the graph is above 0. For the purposes in this report the standard addition method is used to validate the direct measurement of the produced water sample. R_0 would here be the intersection with the x-axis.

2.2.2.3 Derivatization

10 µL derivatization chemical (MTBSTFA + 1% TBDMSCI) was added to 100 µL of oil phase sample giving a >30x excess of derivatization agent and left for 30 minutes to allow the derivatization reaction to complete.

2.2.2.4 GC/MS

The same GC-MS set-up as described in 1.4.2.2.2 was used.

2.2.2.5 GC/FID

GC-FID was set-up as per OSPAR 2005:15.

2.3 Results and Discussion for GC/FID Method Development

The development of the GC-FID method is detailed below. The solvent selection is detailed in Chapter 2.3.1. The use of derivatisation is described in Chapter 2.3.2. The obtained chromatograms are discussed in Chapter 2.3.3.

2.3.1 Selection of Solvent

Pentane is the preferred solvent for GC-FID as it elutes early and quantification for the oil in water measurement starts at C_7. The same column is also used to measure toluene content through BTEX quantification. However, as stated in Chapter 1.4.2.2.1, toluene can be used on GC-FID as it does not pollute later BTEX measurements.

2.3.2 Derivatization for GC-FID

Although the derivatization agent holds additional features with stable fragmentation which are useful in the GC/MS analysis, it is imperative to also derivatize the acids with a derivatization agent for GC-FID analysis. This is due to the impaired chromatographic behaviour of organic acids as they pass through a GC column. Deactivating the polar group with a derivatization agent gives a more volatile and less reactive compound which can readily pass through the GC column.

2.3.3 GC-FID Chromatogram for commercial naphthenic acid mixture

To demonstrate the applicability of GC-FID to quantify naphthenic acid mixtures, 5 toluene solutions with different concentrations of commercial naphthenic acid mixture were prepared, derivatized and measured on GC-FID.

Figure 2.4 shows the chromatogram for one of the toluene solutions with commercial naphthenic acid mixture analysed on GC-FID. First it can be noted that the shape is similar to the shape of the commercial

naphthenic acid mixture chromatogram from the GC-MS shown from phase 1 of the project in the Figure 2.5 below.

Secondly it can be noted that the elution time for the GC-FID is compressed compared to the GC-MS; 6.7 - 8.4 minutes compared to 19 - 41 minutes. The peak furthest to the right is the internal standard chemical, which is not part of the commercial naphthenic acid mixture. The compression of the GC-FID is due to the higher temperature ramp used in the GC-FID. For GC-FID, this ramp-up is possible without loss of accuracy as the detector measures everything that passes through indiscriminately. For the GC-MS, this could lead to lower signal detection as the detector continuously scans for certain masses and if the time interval where the compounds hit the detector is compressed, less of the compounds will be detected in the time window where they elute.

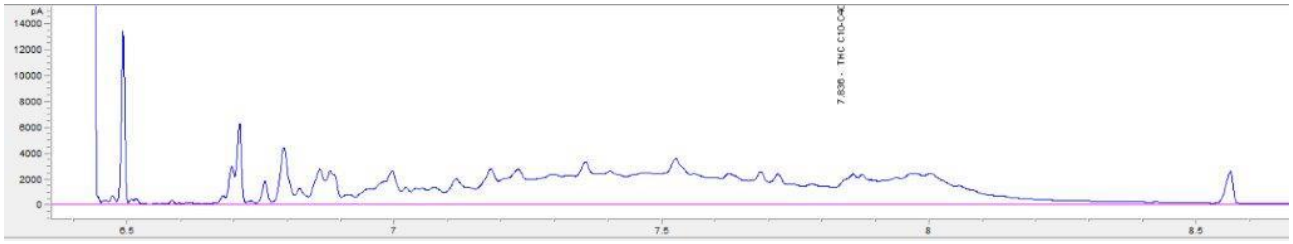


Figure 2.4 GC-FID chromatogram of solution of commercial naphthenic acids in toluene

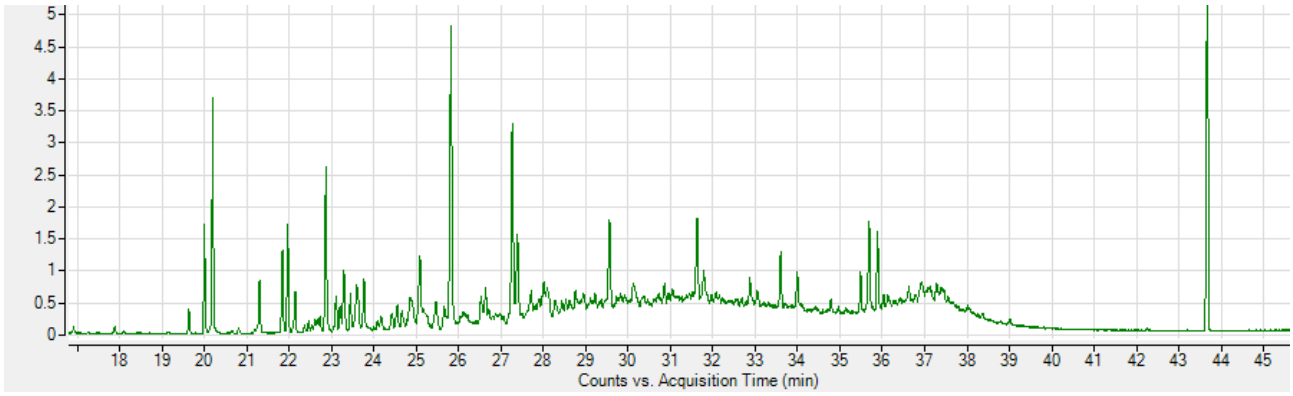


Figure 2.5 GC-MS chromatogram of solution of commercial naphthenic acids in toluene

Unlike the GC-MS, where the detector is not used prior to the solvent peak has passed to preserve the filament, the detector in GC-FID is always on. This results in the large toluene solvent peak seen in the chromatogram below. There is another peak to the left of the toluene solvent, which is likely the derivatization agent.

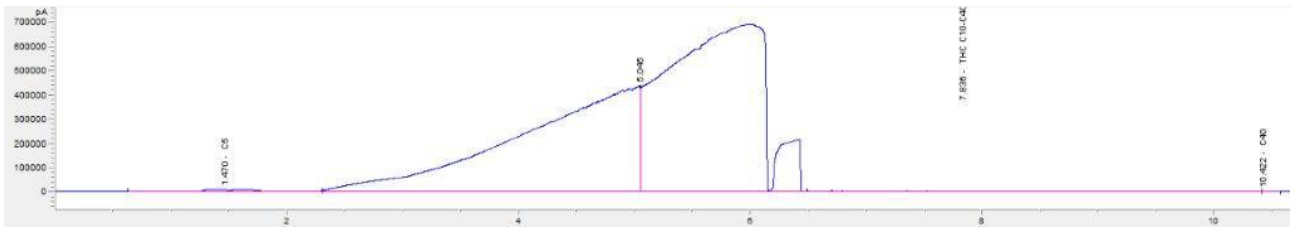


Figure 2.6 GC-FID chromatogram showing the toluene solvent peak

There is a small peak next to the derivatization chemical hump at minute 6.5. This is likely an impurity in the derivatization chemical or simply the catalyst in the derivatization chemical. In Chapter 2.2.1, it can be seen that the derivatization agent MTBSTFA contains 1% TBDMSCl and that the purity is 95%.

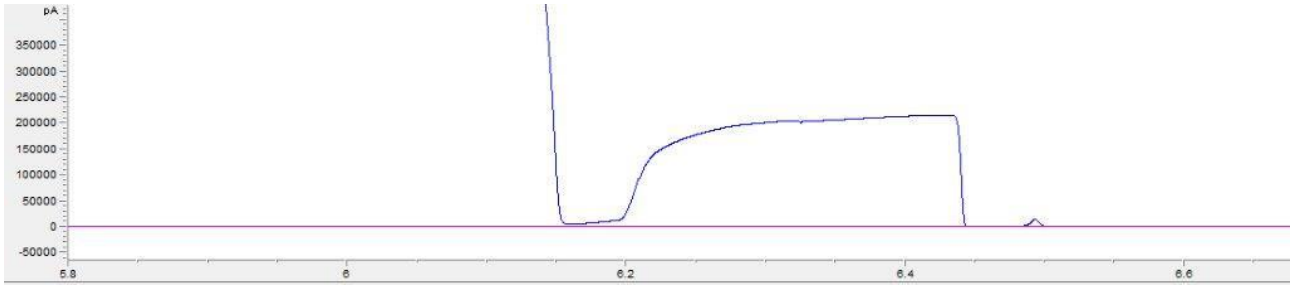


Figure 2.7 GC-FID chromatogram showing a small peak at 6.5 minutes

As the commercial naphthenic acid mixture seems to elute from 6.7 minutes, this peak does not affect the commercial naphthenic acids mixture. Ideally, the peak would disappear upon subtracting the chromatogram of the solvent, derivatization agent and internal standard, from the chromatogram which also contains the commercial naphthenic acid mixture. However, there are small differences in elution time and intensity which makes this subtraction non-ideal. The FID chromatogram of the commercial naphthenic acid mixture after subtraction is shown in Figure 2.8. Here it is clearly shown that the peak at minute 6.5 is not only still there, but there is also a negative peak next to it. This shows the imperfect subtraction for chromatograms. Here again it is shown that the commercial naphthenic acid elutes at minute 6.7 and all of the obtained signal can be correctly integrated from minute 6.7 to 8.5.

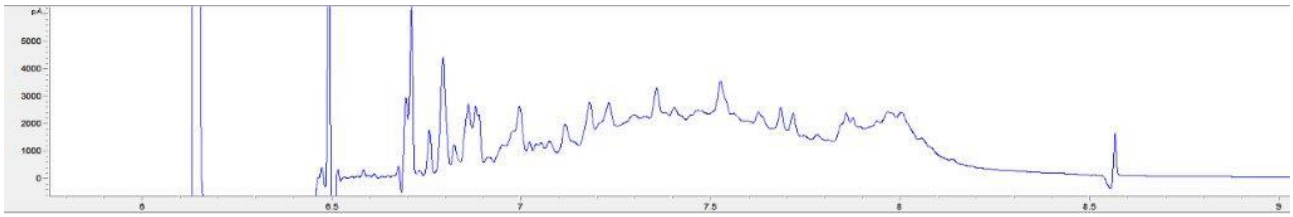


Figure 2.8 GC-FID chromatogram of solution of commercial naphthenic acids in toluene after subtraction

2.3.4 GC-FID quantification of commercial naphthenic acid mixture and single organic acids

Using the integrated signal from the chromatogram, a plot of the area versus the concentration can be made. This was performed for the five concentrations of commercial naphthenic acid mixture in toluene. As shown in Figure 2.9, an linear calibration curve is obtained on GC-FID.

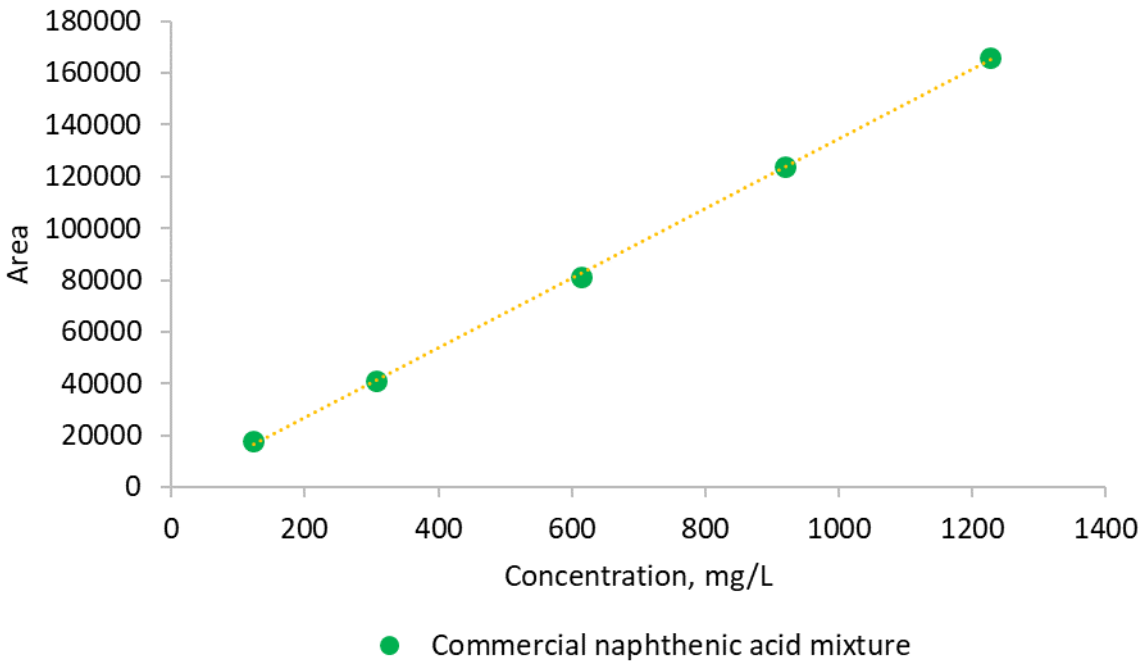


Figure 2.9 Calibration curve obtained for derivatized commercial naphthenic acid mixture in toluene. Here the area is given on the y-axis and the concentration is given on the x-axis.

To compare the results obtained with commercial naphthenic acid mixtures with the signal obtained with single molecules, 5 toluene solutions with different concentrations of 3 single naphthenic acid components were prepared and measured with GC-FID. As shown in Figure 2.10, the signal response to concentration for single naphthenic acid molecular structures is similar to the signal response of commercial naphthenic acid mixtures. This is very different from the GC-MS method, where the structure of the naphthenic acid

molecule and the size of the molecule affects the amount of signal measured for a given concentration of sample.

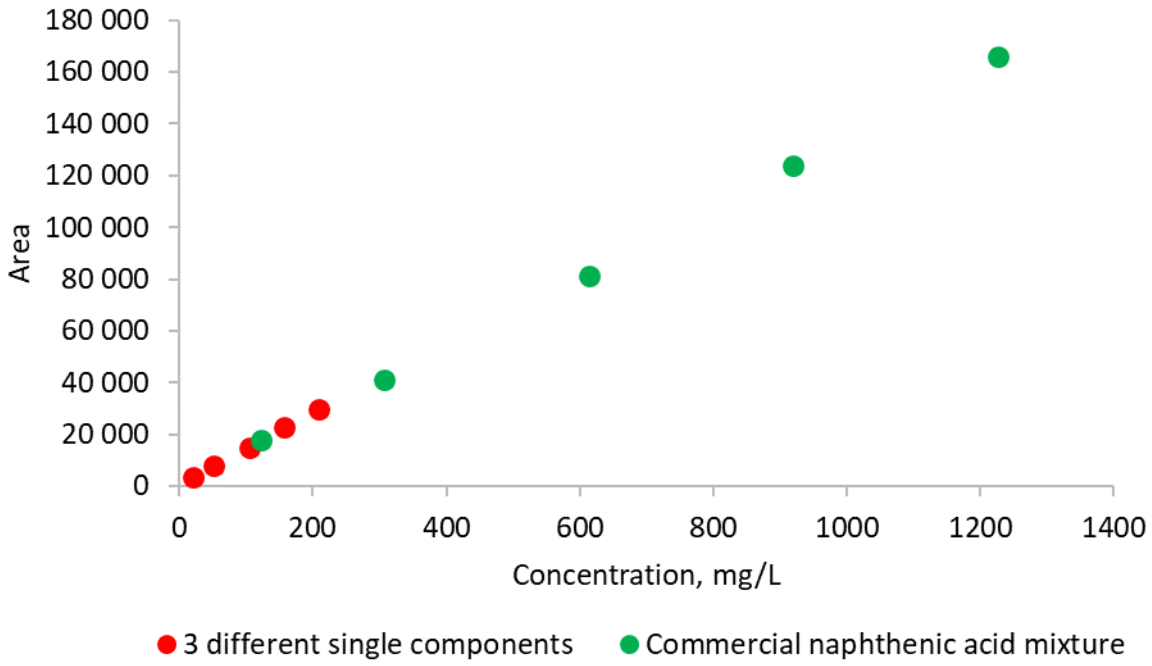


Figure 2.10 Comparison between measured response in GC-FID for commercial naphthenic acid mixture in toluene and toluene solution with 3 different naphthenic acid components. Here the area is given on the y-axis and the concentration is given on the x-axis.

The indifference of the GC-FID method to the composition of molecular structures and sizes in the sample is advantageous as the method is not dependent on that the calibration standard has the same structural and size diversity as the naphthenic acids in the produced water to be measured. Instead of a commercial naphthenic acid mixture, a single organic acid could in theory be used to quantify the content of naphthenic acids in the unknown sample.

Table 2.3 details the concentration of the commercial naphthenic acid mixture and the 3 single components, and compares the actual concentration to the calculated concentration from the calibration curve of these components. It can be noted that the calculated concentrations have a tendency to overestimate the concentration. This is likely due to the inaccuracy in the lower end of the calibration range when using simple linear regression, and the higher noise to signal ratio at low concentration.

Table 2.3 Accuracy of the GC-FID for known samples

	Area	Concentration	Calculated concentration	Calculated concentration vs concentration
Commercial naphthenic acid mixture				

18078	123	134	110 %
41086	307	306	100 %
81437	613	606	99 %
123893	920	922	100 %
166062	1227	1235	101 %
3 different naphthenic acid components			
3450	21	24	117 %
7722	52	55	104 %
14852	104	105	100 %
22642	157	160	102 %
29967	209	212	101 %

2.3.5 GC-FID quantification with mineral oil as a calibration standard

It would be advantageous to link the quantification of naphthenic acids to the oil in water quantification method, as this method is well established in the industry. In the oil in water quantification method described in ISO 9377 part 2, a mixture of two different types of mineral oils is used to calibrate the mass concentration to FID signal curve for hydrocarbons. This method is used to quantify how much oil is in the produced water which is discharged to sea.

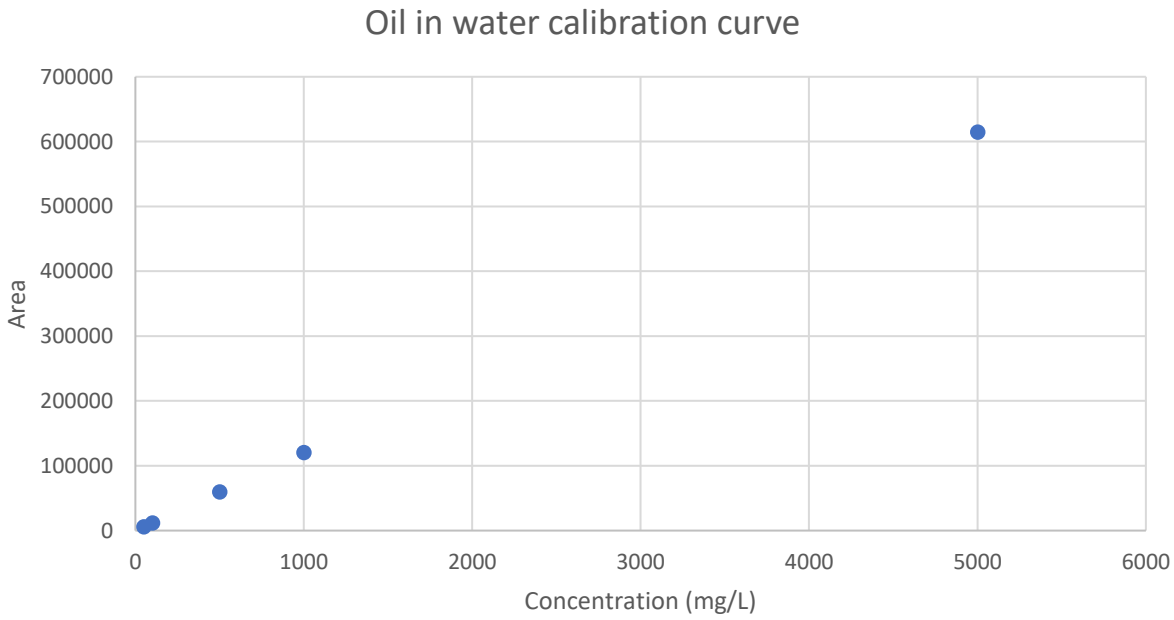


Figure 2.11 Calibration curve for oil in water standards, showing a large linear concentration range.

This mineral oil calibration standard was used to quantify the signal from commercial naphthenic acid mixture and solutions with 3 different naphthenic acid components. Figure 2.12 shows the difference between the

measured and actual quantity when using mineral oil as a calibration standard for the commercial naphthenic acid mixture and the samples with 3 different naphthenic acid components. For higher concentrations of commercial naphthenic acid mixture, the quantity measured when using mineral oil as a calibration standard is 110%. For lower naphthenic acid concentrations, the measured concentration is 20% and even 30% higher than the actual concentration. However, this elevated concentration also occurs when commercial naphthenic acid mixture or the 3 different naphthenic acid components are used as a calibration standard against themselves as shown in Figure 2.12. This is likely due to the inaccuracy in the lower end of the calibration range when using simple linear regression and the higher noise to signal ratio at low concentration.

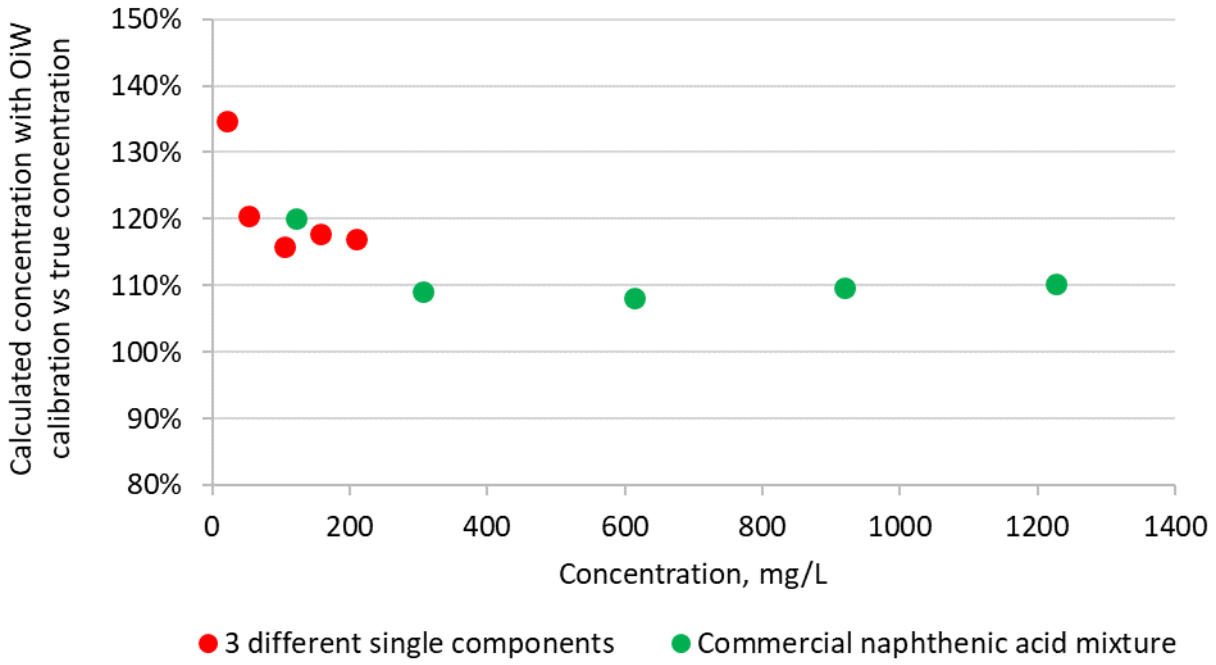


Figure 2.12 Comparison between the measured and actual quantity when using mineral oil as a calibration standard for the commercial naphthenic acid mixture and the samples with 3 different naphthenic acid components. The results are from GC-FID for commercial naphthenic acid mixture in toluene and toluene solution with 3 different single acids.

The 10% higher response in the GC-FID for naphthenic acids when using mineral oil as a calibration standard (hydrocarbons) is not intuitive as the naphthenic acids contain heteroatoms like oxygen, as described in Chapter 1.3.1.3.2. Hydrocarbon molecules where all the carbon atoms are bonded to hydrogen, generally have molar response factors that are equal to the number of carbon atoms in their molecule (the number of ionizable carbon atoms). Organic molecules containing heteroatoms like oxygen tend to have a lower response factor in GC-FID. A simplified insight into the theory here can be taken from Feng, Sun [78]

"When a hydrocarbon compound from the column enters the flame, the following happens in the reducing zone:

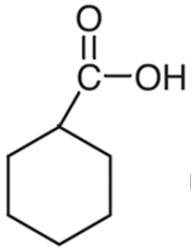
CH radicals are formed from hydrocarbons : (CH) → CH + O.

Formyl cations are formed from CH radicals : CH · → $CHO^+ + e^-$.

The generated ions in the flame will produce a small current, which is proportional to the amount of compound combusted."

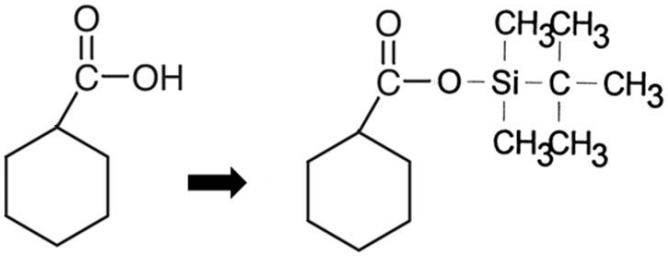
As an example, a simple organic acid can be considered, as shown below.

Cyclohexane carboxylic acid



With C-H bonds giving a signal response in the GC-FID, the organic acid with seven carbon atoms above would have six C-H bonds. The corresponding heptane molecule (C_7H_{16}) would have seven C-H bonds. However the molecular weights of the two compounds are very different, 128 g/mol and 100 g/mol. If a solution of both were measured on GC-FID, active carbons would make out 84% of the mass passing through the FID for the heptane while the corresponding percentage would be 56% for the cyclohexane carboxylic acid. If the solution contained 1 g/L of both compounds and quantifying them on GC-FID using an oil in water calibration, heptane would be measured to 1 g/L while cyclohexane carboxylic acid would register with a concentration of 0.66 g/L. However this does not correlate to the graph in Figure 2.12. Here it is indicated that naphthenic acids are measured to a higher concentration than hydrocarbons.

An important factor to consider at this point is that the naphthenic acids are no longer organic acids upon reaching the detector in the GC-FID analysis. The derivatization step with MTBSTFA attaches a large molecular group to each organic acid molecule as shown in the reaction below.



After derivatization of the acid, there are eleven C-H bonds available for the cyclohexane carboxylic acid. The mass of active carbons to the molecular weight of the original acid is now 103%. The mass passing the FID is higher as a large molecular group is attached after the derivatization. If a solution contained 1 g/L of both compounds and quantifying them on GC-FID using an oil in water calibration, heptane would be measured to 1 g/L while cyclohexane carboxylic acid would register with a concentration of 1.22 g/L. Table 2.4 below illustrates this for a range of acids. Here it is shown that the signal for smaller acids like the cyclohexane carboxylic acid will consistently be measured much higher than the actual concentration in GC-FID when using an oil in water calibration. As the size of the acid molecule increases this effect becomes less pronounced which can be explained by the decreasing relative impact of the inactive and heavy oxygen atoms compared with increasing weight percentage of the carbon atoms in the acid molecule. This effect is marked in green in the table below. At C_{19}, the increased signal is decreased to 109%.

Table 2.4 List of active carbon atoms in hydrocarbon, naphthenic acid and derivatized naphthenic acid molecules. The active carbon atoms gives a signal in the GC-FID.

Number of carbons in molecule	7	8	9	10	11	12	13	14	15	16	17	18	19
Active carbon atoms for hydrocarbons	7	8	9	10	11	12	13	14	15	16	17	18	19
Molecular weight for hydrocarbons	100	114	128	142	156	170	184	198	212	226	240	254	268
Active carbon atoms % of molecular weight for hydrocarbons	84 %	84 %	84 %	85 %	85 %	85 %	85 %	85 %	85 %	85 %	85 %	85 %	85 %
Active carbon atoms for naphthenic acids	6	7	8	9	10	11	12	13	14	15	16	17	18
Molecular weight for naphthenic acids	130	144	158	172	186	200	214	228	242	256	270	284	298
Active carbon atoms % of molecular weight for naphthenic acids	55 %	58 %	61 %	63 %	65 %	66 %	67 %	68 %	69 %	70 %	71 %	72 %	72 %
Active carbon atoms for derivatized naphthenic acids	11	12	13	14	15	16	17	18	19	20	21	22	23
Active carbon atoms % of molecular weight for derivatized naphthenic acids	102 %	100 %	99 %	98 %	97 %	96 %	95 %	95 %	94 %	94 %	93 %	93 %	93 %
Active carbon atoms for derivatized naphthenic acids	7	8	9	10	11	12	13	14	15	16	17	18	19
Calculated concentration with OiW calibration vs true concentration for derivatized naphthenic acids*	121 %	119 %	117 %	116 %	114 %	113 %	112 %	112 %	111 %	110 %	110 %	109 %	109 %
Molecular isomeric formula													
Hydrocarbons C_nH_{2n+2}					Atomic weight	C	H	O					
Naphthenic acids (organic acids) $C_nH_{2n}O_2$						12	1	16					

* This is concentration x divided by (Active carbon atoms % for molecular weight for hydrocarbons) and multiplied by (Active carbon atoms % of molecular weight for derivatized naphthenic acids).

According to the experimental values in Figure 2.12 the overestimation of the concentration of naphthenic acid mixtures is consistently around 110% in the concentration range the GC-FID samples in this project are expected to operate in.

Hence, the mineral oil calibration standard can be used if a correction factor of 110% is used to adjust the measured GC-FID concentrations to compensate for the signal effect. This correction assumption seems to be less accurate for low concentration samples (<300 mg/L), where the difference in signal response seems to be higher. This is likely due to the inaccuracy in the lower end of the calibration range when using simple linear regression.

A further simplification can also be made in the laboratory by adjusting the volume of the added derivatization chemical to 10% of the sample volume. This allows a direct correlation between the concentration of the sample prior to the dilution with derivatization chemical to the measured concentration in GC-FID when using oil in water calibration.

2.3.6 Conclusion

The GC-FID analysis for naphthenic acids was successful. The chromatograms for GC-FID showed a similar but shortened elution compared to the chromatograms obtained with GC/MS. It is essential to derivatize the naphthenic acids to obtain a good elution through the GC column. The results show that naphthenic acids give the same response in GC-FID independent of size and structure. Quantification of naphthenic acids calibrated against mineral oil, shows that the measured concentration overestimates the actual concentration. This is supported by the theory as it should theoretically be upwards of 10% higher according to the theoretical discussion regarding the effect of the derivatization step. Consequently, the oil in water calibration curve was chosen to be used for all further GC-FID quantification with a correction factor of 110% in order to correct for this overestimation between hydrocarbons and derivatized naphthenic acids.

2.4 Results and Discussion for Extraction and Quantification of Naphthenic Acids from Produced Water

An overview of the evaluation is presented below.

Extraction and naphthenic acid quantification of produced water samples (Chapter 2.4).

This evaluation is split in two stages.

First stage (Chapter 2.4.1)
Produced water from four installations were chosen based the naphthenic acid concentration measured in previous NOROG projects. The produced water samples chosen came from installations A F G and J in Table 2.1.

- The liquid-liquid extraction method is used to extract naphthenic acids to an organic solvent to enable analysis on GC (Chapter 2.4.1.1).
- The samples are analysed by GC-MS. The GC-MS chromatograms are analysed and discussed in detail (Chapter 2.4.1.2) and the structural compositions of the naphthenic acids in the produced water is shown (Chapter 2.4.1.3)
- The samples are analysed by GC-FID (Chapter 2.4.1.4). The GC-FID chromatograms are analysed and discussed (Chapter 2.4.1.4.1) and are used to quantify naphthenic acids (Chapter 2.4.1.4.2)

Second stage (Chapter 2.4.2)

The remaining produced water samples were used for this stage. Naphthenic acids were extracted from the produced water with the same procedure used for the four first samples, but this time with added demulsifier.

- Quantification results are presented (together with results from the first samples). The direct measurement method is compared with the method using standard addition with and without correction (Chapter 2.4.2.1).
- 3D plots showing the composition by structure is presented for 2 of the 6 samples (Chapter 2.4.2.2).
- The concentration of naphthenic acid is determined in all samples by GC-MS and compared with the results for GC-FID (Chapter 2.4.2.3).

General

Sub-chapters 2.4.3- 2.4.6 contains evaluations of the issues listed below.

- Accuracy and concentration limits (Chapter 2.4.3)
- Pentane as an alternative solvent to toluene (Chapter 2.4.4)
- Quantification of the larger naphthenic acids (Chapter 2.4.5)
- Potential influence of production chemicals and phenol compounds (Chapter 2.4.6)

2.4.1 Initial tests of the method on produced water samples

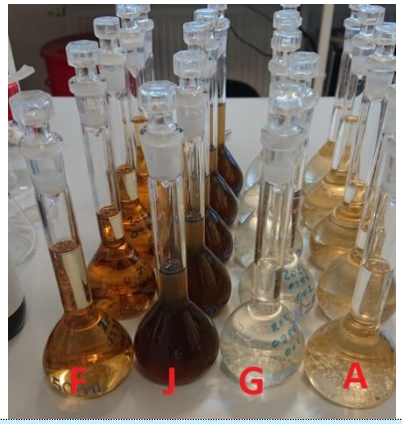
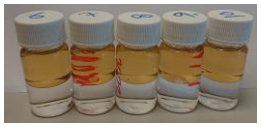
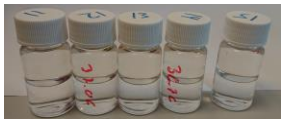
2.4.1.1 Extraction and isolation of naphthenic acids from produced water samples

The quantification method from the first project phase was measuring a naphthenic acid concentration of 100 mg/L to 1500 mg/L for GC-MS. In this project phase the GC-FID concentration range was found to extend to lower concentrations. During the liquid-liquid extraction, the aim was not only to isolate, but also concentrate the naphthenic acids from the produced water to be within this concentration range. Based on the previously reported naphthenic acid content of the produced water from these fields, the extraction volumes were adjusted to increase the concentration 8 times compared to the naphthenic acid concentration in the produced water.

The produced water contains dissolved crude oil components and dispersed crude oil droplets. Upon sampling with pH~6-8 of the produced water, the absolute content of naphthenic acids in the produced water is large compared to the absolute content of naphthenic acids in the crude oil droplets. Acidic crude oils typically contain 0.5 wt% naphthenic acids and <90% of these naphthenic acids (with molecular weights from 150-600 g/mol) are not water-soluble at pH 7. So at pH~6-8, the crude oil droplets in the produced water still have around 0.5 wt% naphthenic acids. However upon sampling the pH in the produced water is lowered to ~2. At this pH the naphthenic acids dissolved in the water will become hydrophobic and migrate to the organic phase inside the oil droplets. If some of these crude oil droplets, attached to the bottle wall or bottom for example, was not captured by the organic extraction solvent, the quantity of naphthenic acids measured after extraction and isolation would not be an accurate measurement of the naphthenic acid concentration in the produced water. Rigorous stirring ensures that all the crude oil droplets at the bottle walls are contacted by the toluene and captured by the method.

The extraction method in the laboratory for these initial tests were documented with pictures to facilitate the interpretation of the obtained results. These pictures are shown in Table 2.5.

Table 2.5 Documentation of the liquid-liquid extraction method through the different extraction steps.

Produced water sample A	Produced water sample F	Produced water sample G	Produced water sample J
After the first extraction step (Step 1 in Chapter 2.2.2.1) from produced water bottles to toluene			
			
	No solids	No solids	
Toluene phases removed from the produced water bottles. (Step 2 in Chapter 2.2.2.1)			
			
After extraction with alkaline (high pH) water (Step 3 in Chapter 2.2.2.1)			
			

As shown in Table 2.5 the water phase in the produced water bottles was not clear after the first extraction step with toluene. The water phase was opaque and the bottles from produced water A and J had a collection of light brown semi solids at the interface between oil and water.

Another noticeable difference is the colour difference of the toluene phase after the first extraction. The toluene from produced water sample J had a dark amber colour, the toluene extract from produced water A and F had a yellow and amber colour while the toluene extract from produced water G had only a yellowish hue. The colour can come from both dissolved components and dispersed oil droplets in the produced water.

The next extraction step was performed with some anticipation, as the liquid-liquid extraction of naphthenic acid solutions with alkaline (high pH) water had caused the formation of stable emulsions in previous projects. Fortunately, the phase separation went effortlessly for three of the four produced water samples. No centrifugation was needed to obtain complete separation. For the fourth produced water sample, J, a stable emulsion was formed in this extraction step. The emulsion did not separate upon centrifugation. A droplet test of the emulsion into toluene and water revealed that it was a water in oil emulsion. For the three produced water samples which did not form an emulsion, the toluene and water phase also separated immediately after the last extraction step with back extraction back into toluene with low pH.

Overall the isolation method was successful for three of the produced water samples (A, F and G). The final sample extract from these three produced water samples were analysed further with GC-MS and GC-FID, the results of which are recorded below.

2.4.1.2 GC-MS analysis

The sample extracts from produced water samples A, F and G were analysed with GC-MS.

2.4.1.2.1 GC-MS analysis of produced water sample A

The resulting chromatograms for produced water sample A is shown below.

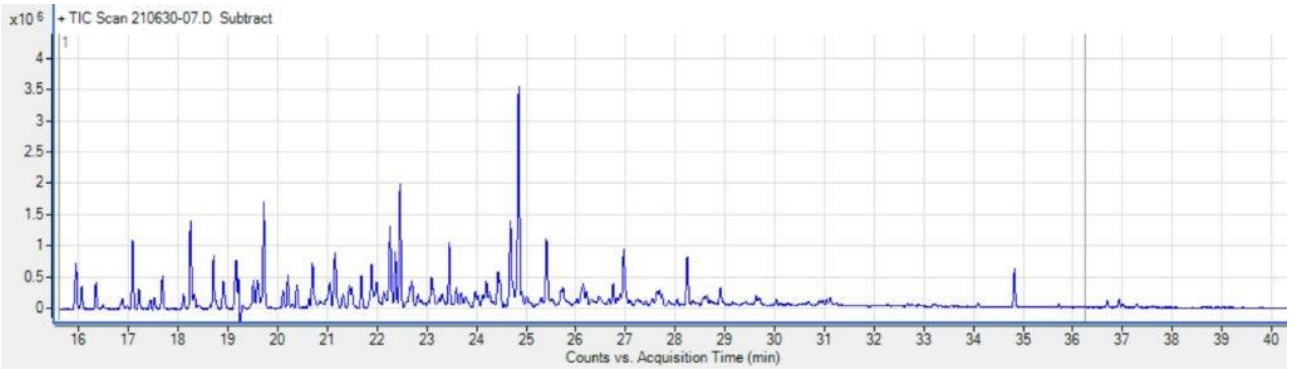


Figure 2.13 Chromatogram of the chemical compounds isolated and extracted from produced water sample A, likely to be naphthenic acids. The sample has undergone derivatization with MTBSTFA. An internal standard 4-(nonyloxy)benzoic acid was added to the sample, but the peak is not shown as it elutes later in the chromatogram. The chromatogram has been subtracted with a "blank" chromatogram for a solvent sample with derivatization agent.

The chromatogram in Figure 2.13 shows the chemical compounds registered from produced water sample A. These compounds are likely to be naphthenic acids. First it can be noted that the compounds elute in discrete peaks which is not the norm for naphthenic acid mixtures. As described in the theoretical chapter, naphthenic acid mixtures often elute as a continuous hump due to the large number of molecules with overlapping boiling point properties. However, for naphthenic acids with low molecular mass i.e. low number of carbon atoms, see Appendix C, there are both fewer structural compositions available, and

fewer structural isomers possible (see Table 1.1). The chemical compounds are therefore still likely to be naphthenic acids given that they are of low molecular weight. It can be noted that the chemical compounds start to elute from the column earlier compared to the compounds in the commercial naphthenic acid mixture ref. Figure 2.8 (GC-FID chapter). Whereas the acids from the commercial naphthenic acid mixture elute from around minute 20 from the GC-MS column, the compounds in the produced water sample A elute from minute 16. The commercial naphthenic acid mixture likely does not contain the small naphthenic acids present in the produced water. Commercial naphthenic acid mixture are caustic extractions of crude oil distillation cuts from a refinery [68] and the light acids in these crude oils have either been lost to the corresponding produced water or desalting water for those crude oils, or the light acids are part of another distillation cut in the refinery which was not used to make the commercial naphthenic acid mixture.

The chromatogram has been subtracted with a "blank" chromatogram for a solvent sample with derivatization agent. This can be seen in minute 19 where a negative signal is obtained. This might be impurities from the derivatization chemical. The sample was only run with derivatization agent, so it is not possible to see if there is a shift in elution time for some of the peaks after derivatization. This would be a crude analysis of if the compound is able to undergo derivatization, which is not possible for hydrocarbons, but possible for compounds like naphthenic acids. However, by looking at the mass spectra of the peaks, more information can be obtained as to which compound has been registered by the mass spectrometer detector.

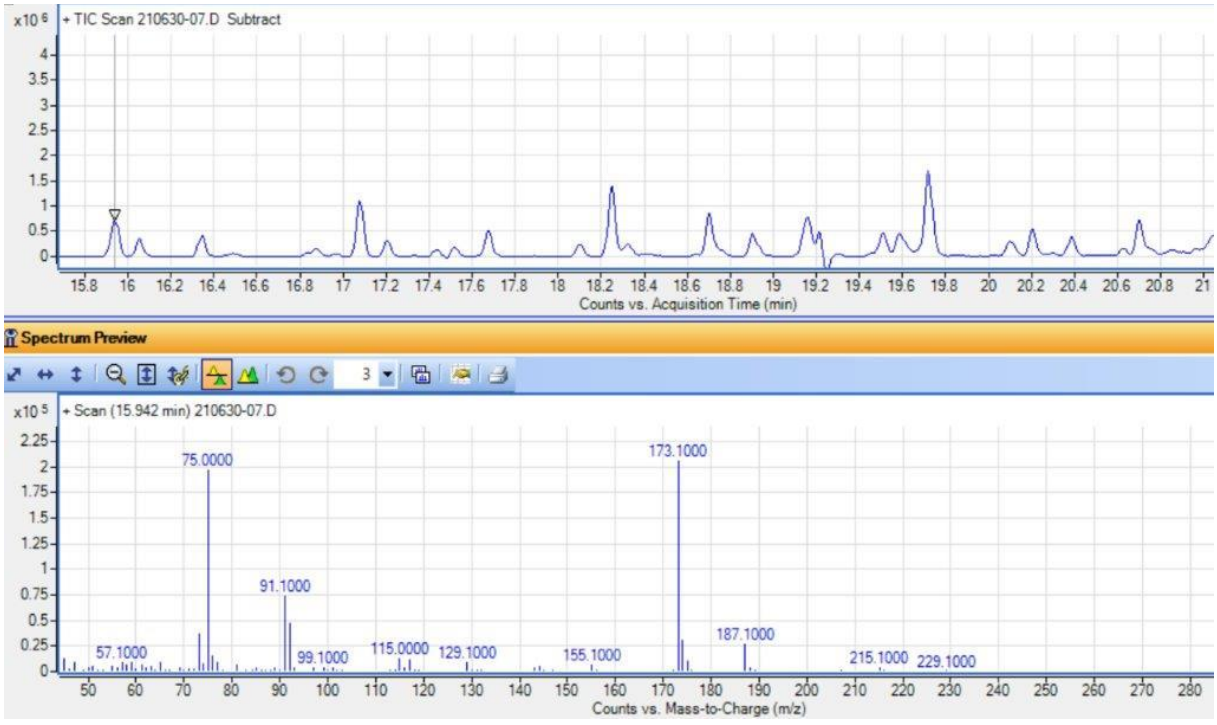


Figure 2.14 Mass spectra for the peak in the chromatogram around minute 16 for chemical compounds isolated and extracted from produced water sample A.

The mass spectra in Figure 2.14 above show the registered masses for the first peak in the chromatogram. The registered mass has a dominant ion at 173 g/mol. By comparing with the table 4.13 in Appendix C, it can be seen that this mass corresponds to a derivatized hexanoic acid, $C_6H_{12}O_2$. It should be noted that the dominant ion adds 57 mass units to the molecular weight of the hexanoic acid molecule. Another

characteristic trait of the derivatized compounds is that the isotopes of silicon and carbon which gives it a couple of signal percentages to the +1 mass isotope, 174 g/mol.

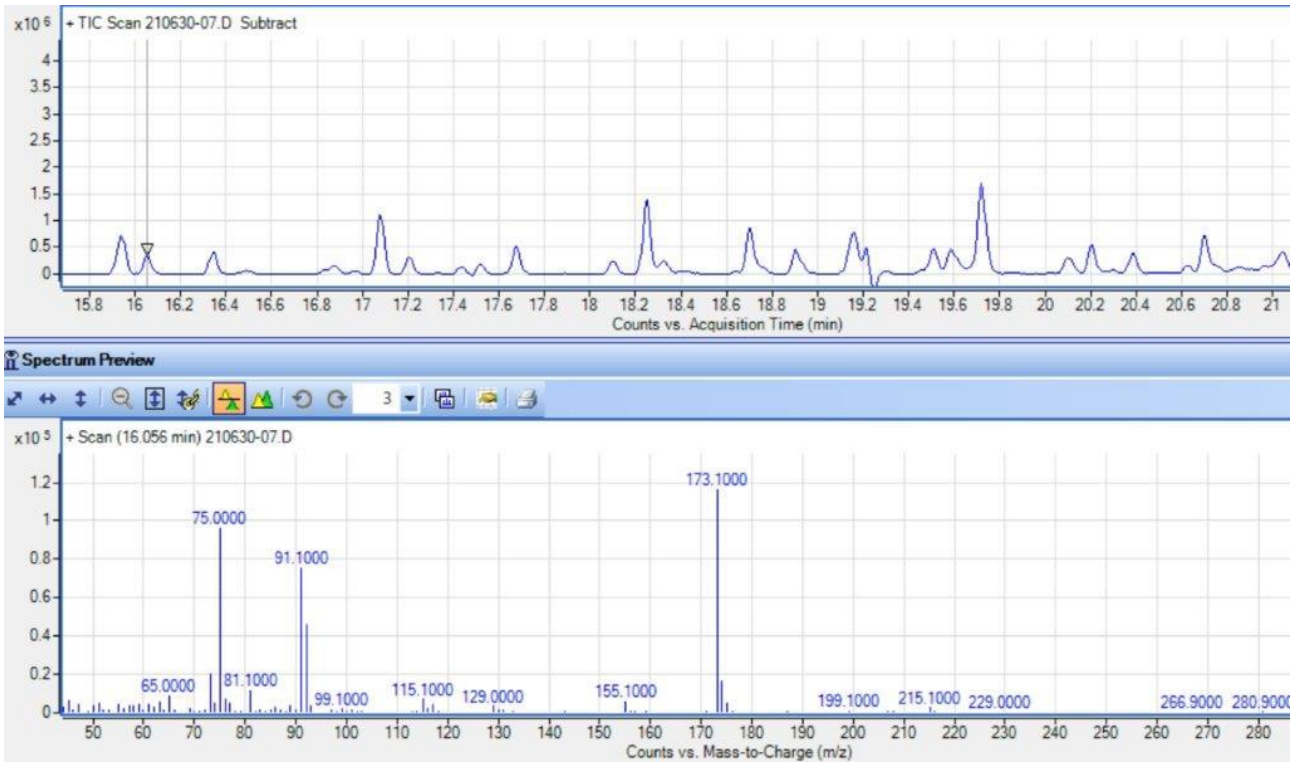


Figure 2.15 Mass spectra for the peak in the chromatogram around minute 16.1 for chemical compounds isolated and extracted from produced water sample A.

The mass spectra in Figure 2.15 above show the registered masses for the second peak in the chromatogram. The registered mass has a dominant ion at 173 g/mol which is again likely to be derivatized hexanoic acid ,$C_6H_{12}O_2$. However, since this compound elutes later in the chromatogram, it is likely that this acid has a different structure compared to the acid that eluted in the first peak. This is the effect which is shown in Figure 1.16 where branched acid molecules elute at a different rate compared to the straight chain acid molecule.

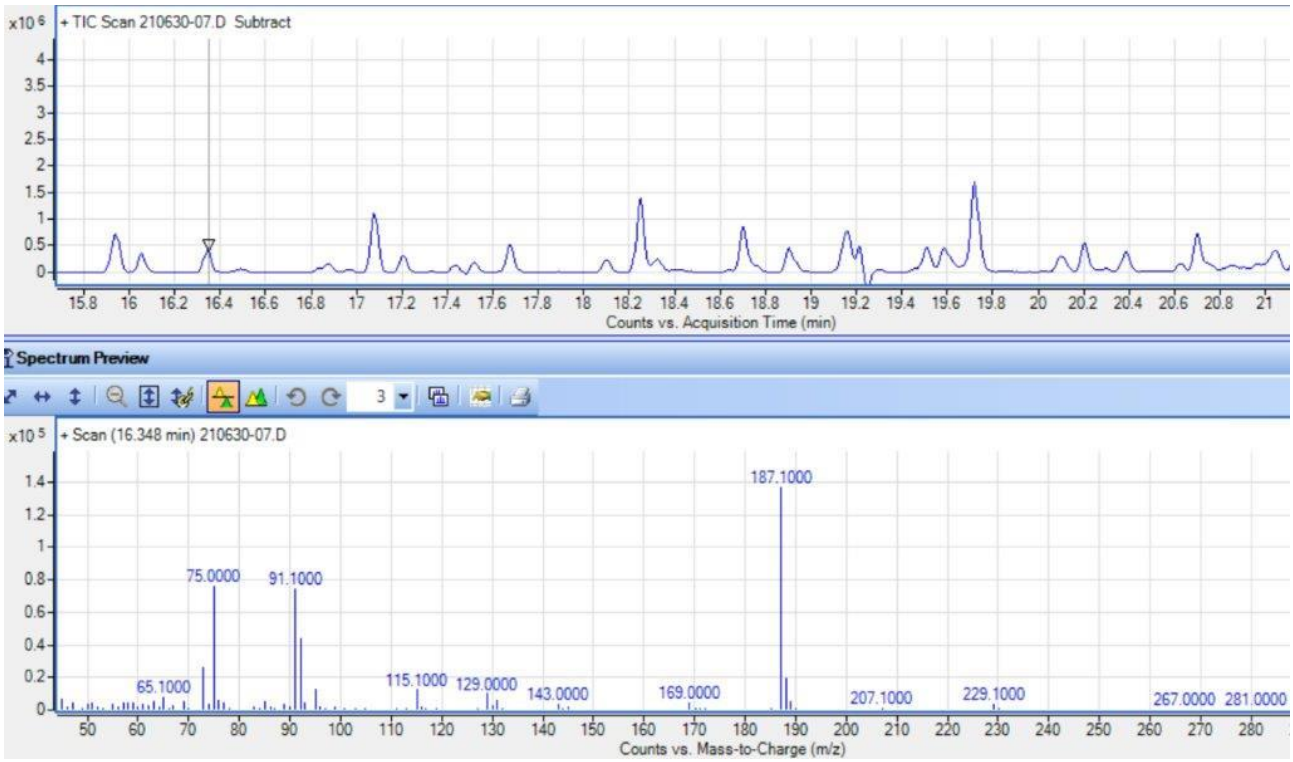


Figure 2.16 Mass spectra for the peak in the chromatogram around minute 16.4 for chemical compounds isolated and extracted from produced water sample A.

The mass spectra in Figure 2.16 above show the registered masses for the third peak in the chromatogram. The registered mass has a dominant ion at 187 g/mol. By comparing with the table 4.13 in Appendix C, it can be seen that this mass corresponds to a derivatized heptanoic acid, $C_7H_{14}O_2$. The next peak at minute 17.1 is again registered with a dominant ion at 173 g/mol which is likely another structural isomer of the hexanoic acid $C_6H_{12}O_2$. The full chromatogram can be linked like this.

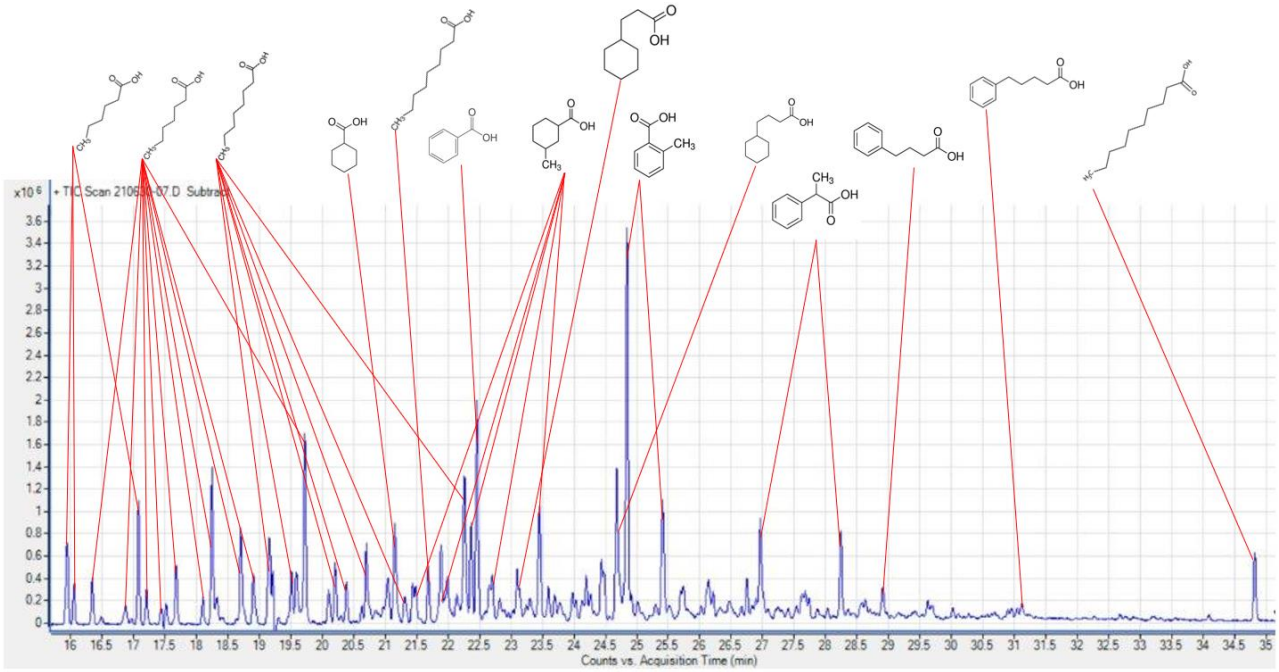


Figure 2.17 Chromatogram of naphthenic acids from produced water sample A. The peaks are identified by their dominant fragment peak which is compared to the structural naphthenic acid isomer in Appendix C.

As described in Chapter 1.4.3.6.3, the GC-MS chromatogram can be processed to only show the signal from certain masses which hit the detector. This is referred to as the extracted ion chromatogram (EIC), different from the total ion chromatogram (TIC). By extracting the masses in Appendix C, the EIC chromatogram can be shown. By viewing the EIC chromatogram over the TIC chromatogram, it can be verified that the shape of the two chromatograms are similar. This similarity confirms that the chemicals compounds which have eluted and gives signal on the GC-MS are able to undergo derivatization. From the extraction and isolation method, these compounds should be naphthenic acids.

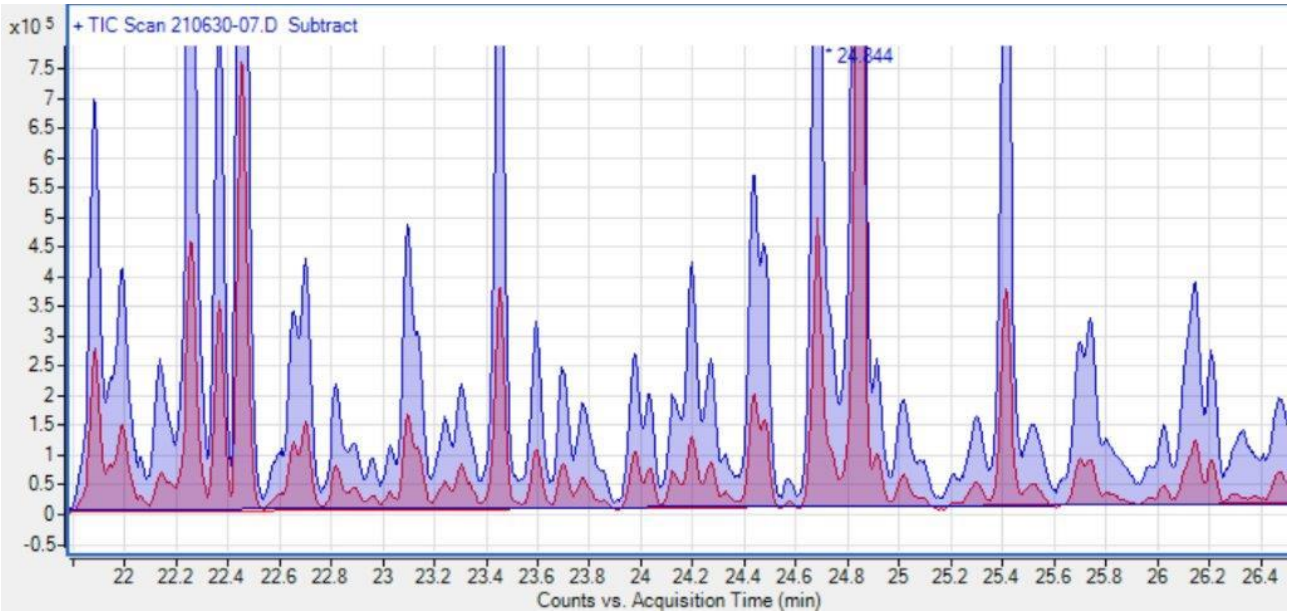


Figure 2.18 Zoomed in Chromatogram showing the EIC and TIC of the chromatogram. The overlap in shape indicates that the substances are able to be derivatized, and through the isolation procedure, these are likely to be naphthenic acids.

By comparing the TIC and EIC it can be demonstrated that the EIC makes up 33% of the TIC signal for produced water sample A. For the commercial naphthenic acid, this number is 31%. Note that this EIC is calculated slightly different than the EIC from phase 1 of the project, here it is manual integration of the whole EIC while the EIC from phase 1 of the project was calculated as the sum of integration of single components.

2.4.1.2.1 GC-MS analysis of produced water sample F

The chromatogram of the chemical compounds isolated and extracted from produced water sample F is shown below.

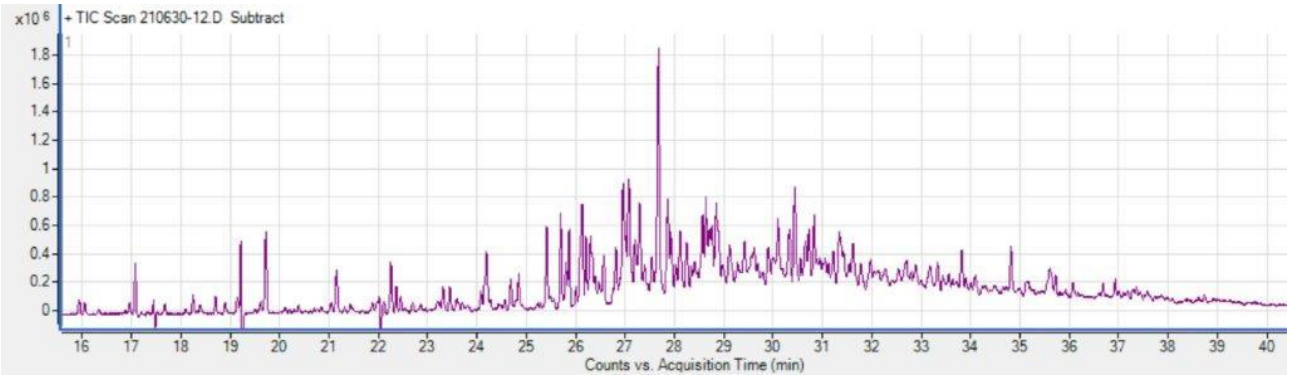


Figure 2.19 Chromatogram of the chemical compounds isolated and extracted from produced water sample F, likely to be naphthenic acids. The sample has undergone derivatization with MTBSTFA. An internal standard 4-(nonyloxy)benzoic acid was added to the sample, but the peak is not shown as it elutes later in the chromatogram. The chromatogram has been subtracted with a "blank" chromatogram for a solvent sample with derivatization agent.

The chromatogram above in Figure 2.19 shows the chemical compounds registered from produced water sample F. These compounds are likely to be naphthenic acids. First it can be noted that the compounds here elute in discrete humps which is the norm for naphthenic acid mixtures, as described in the theoretical chapter. Secondly it can be noted that these compounds elute later in the chromatogram compared to the naphthenic acids from produced water sample A. This points to either structural differences or larger molecule weight which translates to higher boiling points. The chemical compounds are therefore likely to be different from the naphthenic acids in produced water sample A. The chromatogram has been subtracted with a "blank" chromatogram for a solvent sample with derivatization agent. This can be seen in minute 19 where a negative signal is obtained as discussed for the previous produced water sample. By looking at the mass spectra of the peaks, more information can be obtained as to which compound has been registered by the mass spectrometer detector.

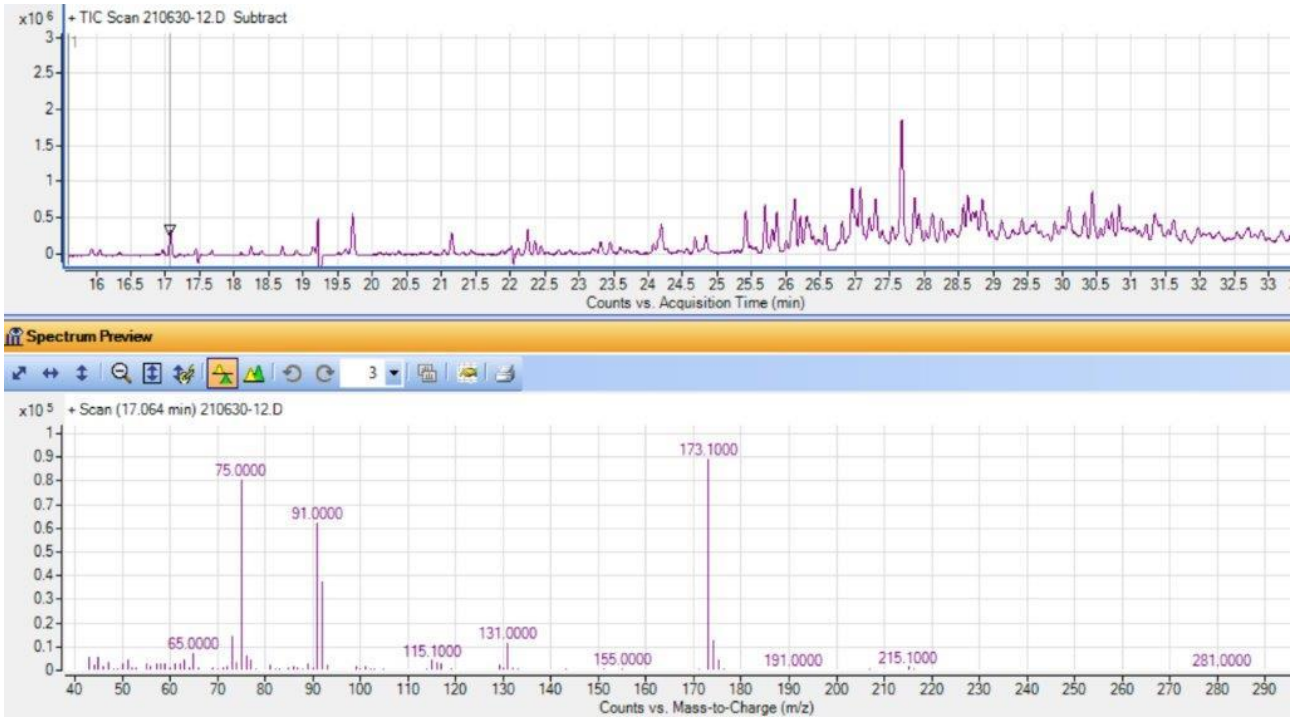


Figure 2.20 Mass spectra for the peak in the chromatogram around minute 17 for chemical compounds isolated and extracted from produced water sample F.

The mass spectra in Figure 2.20 above show the registered masses for the first peak in the chromatogram. The registered mass has a dominant ion at 173 g/mol. This is likely the same hexanoic acid, $C_6H_{12}O_2$ which was registered in the first produced water sample at minute 17. The mass spectra of the peak has the same characteristic trait of the derivatized compounds is that the isotopes of silicon and carbon gives it a couple of signal percentages to the +1 mass isotope, 174 g/mol.

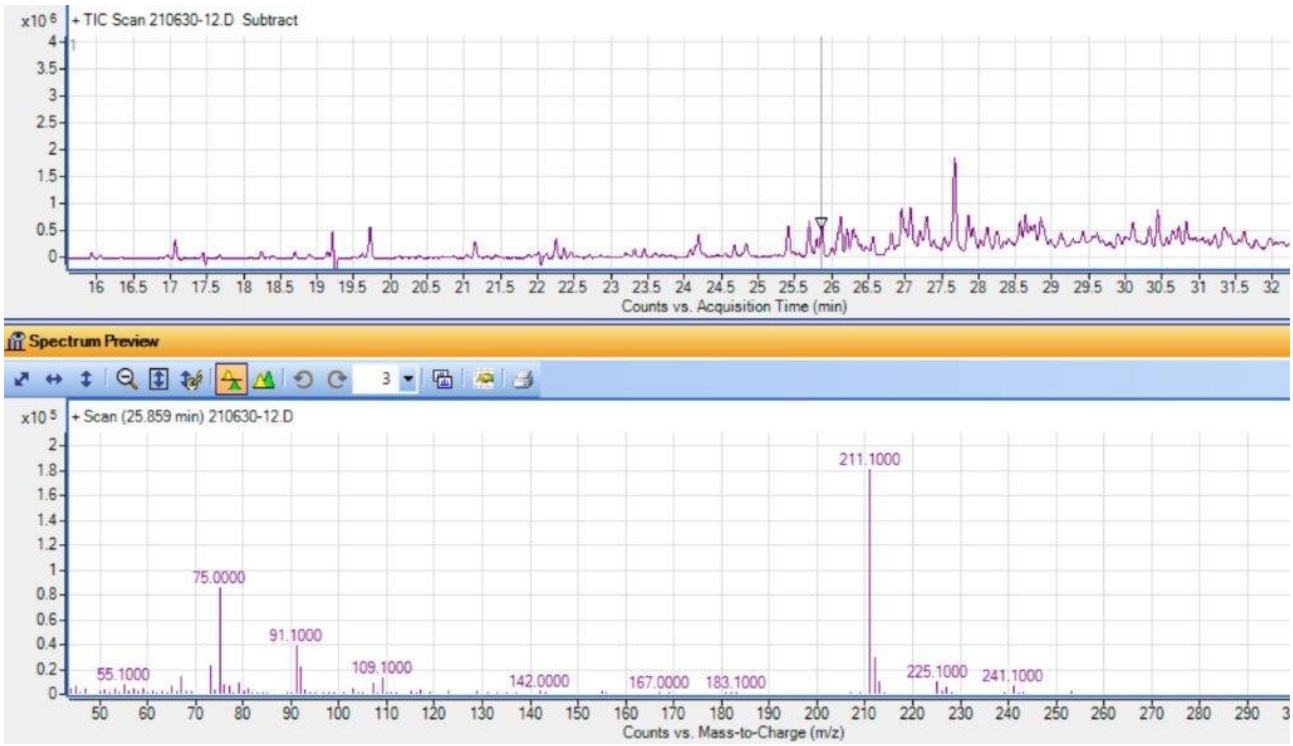
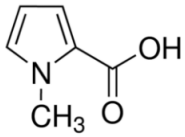
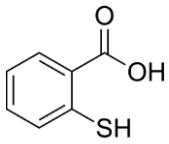
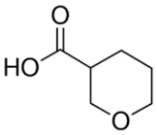
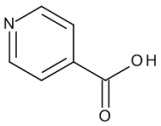
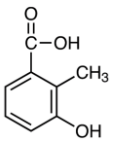


Figure 2.21 Mass spectra for the peak in the chromatogram around minute 26 for chemical compounds isolated and extracted from produced water sample F.

The mass spectra in Figure 2.21 above show the registered masses for a later peak in the chromatogram, at the start of the "hump". The registered mass has a dominant ion at 211 g/mol. However, by comparing with the table 4.13 in Appendix C, it can be seen that this mass does not correspond to any of the possible naphthenic acid structures. This is a limitation of the mass table 4.13 in Appendix C, as it only considers the standard isomer masses with carbon, hydrogen and two oxygen atoms. Naphthenic acids with other heteroatoms like nitrogen, sulphur and additional oxygen atoms in the molecular structure can obtain masses which are not covered by table 4.13. Some examples of these naphthenic acids are shown in the table below.

Table 2.6 Table showing different naphthenic acid structures with heteroatoms in the molecule which are not included in the masses in table 4.13 for naphthenic acids with the formula $C_nH_{2n}O_2$.

Name	Chemical Formula	Structure	Molecular weight	After derivatization [+57 mass units]
1-Methyl-2-pyrrolecarboxylic acid	$C_6H_7NO_2$		125 g/mol	182 g/mol

Thiosalicylic acid	$C_7H_6O_2S$		154 g/mol	211 g/mol
Tetrahydro-2H-pyran-3-carboxylic acid	$C_6H_{10}O_3$		130 g/mol	187 g/mol
4-Pyridinecarboxylic acid	$C_6H_5NO_2$		123 g/mol	180 g/mol
3-Hydroxy-2-methylbenzoic Acid	$C_8H_8O_3$		152 g/mol	209 g/mol

In Table 2.6 above there are multiple naphthenic acids structures with heteroatoms in the molecular structure. These masses are not included in the mass table in table 4.13. It is possible to add these structures as well, however due to the exponential increase in structural combinations for organic molecules, this task can fast become an overwhelming undertaking. Regarding the unknown mass 211 g/mol detected in the chemical compounds from this produced water sample, it can be seen from Table 2.6 that this likely corresponds to thiosalicylic acid, which has a thiol group (-SH) attached to the benzoic acid ring. Like the carboxylic acids, thiols are also a weak acid, hence it likely that this compound with both groups would be captured from the produced water in the extraction and isolation method.

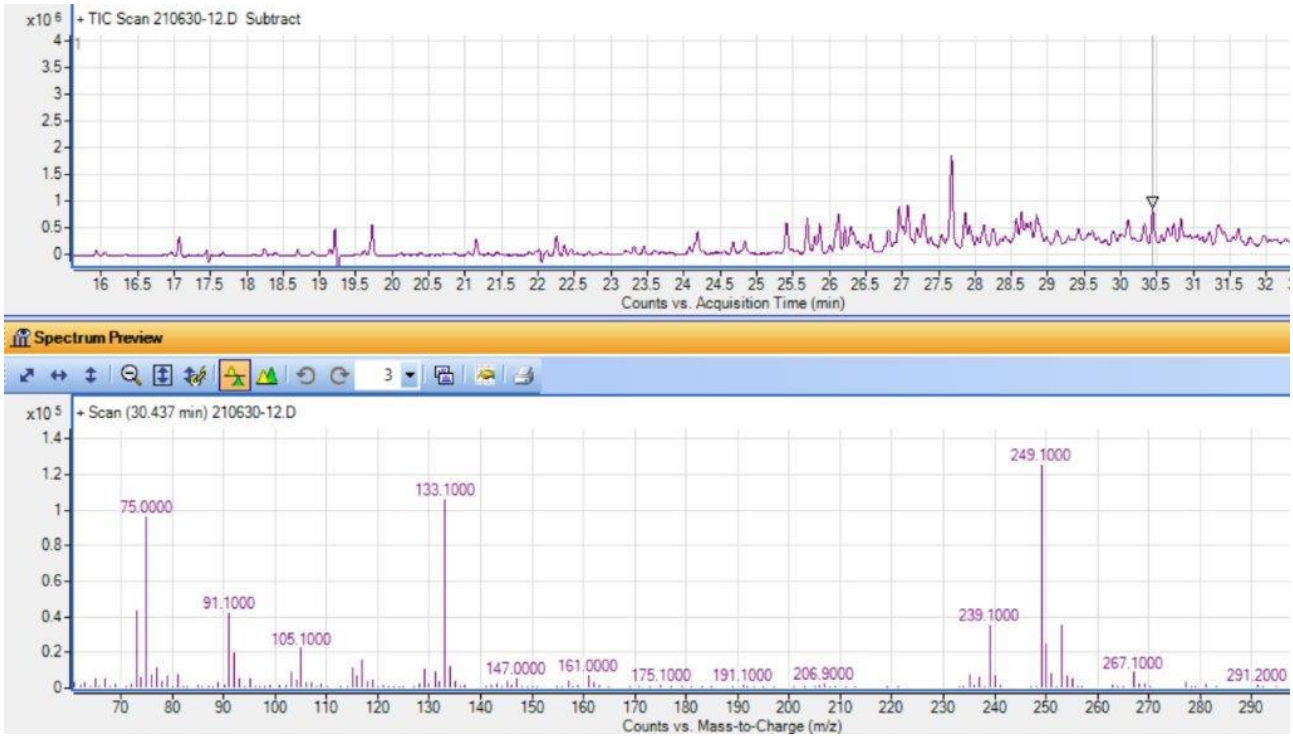


Figure 2.22 Mass spectra for the peak in the chromatogram around minute 30.5 for chemical compounds isolated and extracted from produced water sample F.

The mass spectra in Figure 2.22 above show the registered masses for the peak later in the chromatogram. The registered mass has a dominant ion at 249 g/mol. By comparing with the table 4.13 in Appendix C, this mass corresponds to a derivatized Pentamethylbenzoic acid, $C_{12}H_{16}O_2$. There are also other peaks which elute from the column at this minute, however these are likely not fragments from the C_{12} acid. Rather they are likely to be other naphthenic acid structures which is to be expected as the mass spectrum is now taken from the naphthenic acid hump and not a discrete elution peak.

As described earlier in this chapter, by extracting the masses in Appendix C, the EIC chromatogram can be extracted from the TIC chromatogram. By viewing the EIC chromatogram over the TIC chromatogram, it can be verified that the shapes of the two chromatograms are similar. This similarity confirms that the chemicals compounds which have eluted and gives signal on the GC-MS are able to undergo derivatization. From the extraction and isolation method, these compounds should be naphthenic acids.

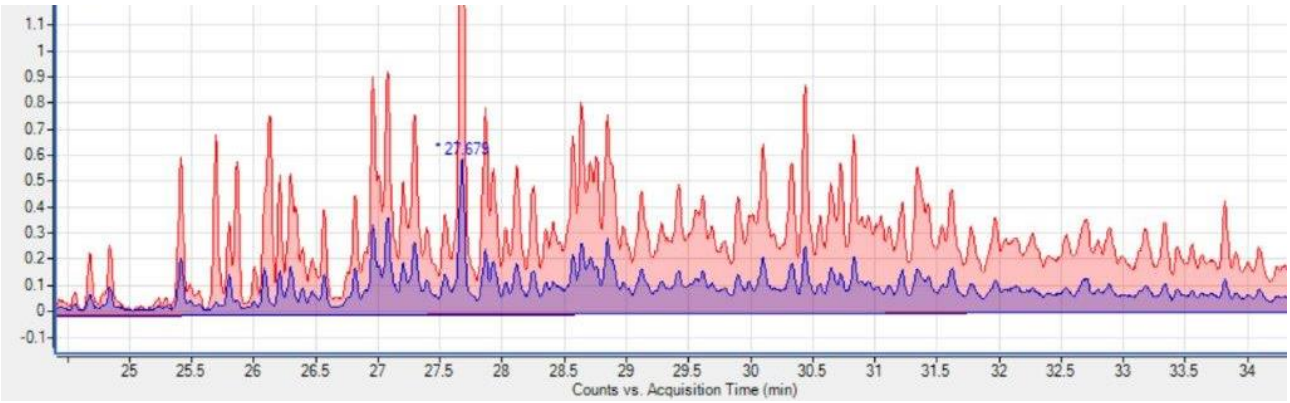


Figure 2.23 Zoomed in Chromatogram showing the EIC and TIC of the chromatogram. The overlap in shape indicates that the substances are able to be derivatized, and through the isolation procedure, these are likely to be naphthenic acids.

By comparing the TIC and EIC it can be demonstrated that the EIC makes up 30% of the TIC signal for produced water sample F. This is very similar to the ratio obtained for produced water sample A and for the commercial naphthenic acid, 33% and 31% respectively.

2.4.1.2.1 GC-MS analysis of produced water sample G

The chromatogram of the chemical compounds isolated and extracted from produced water sample G is shown below.

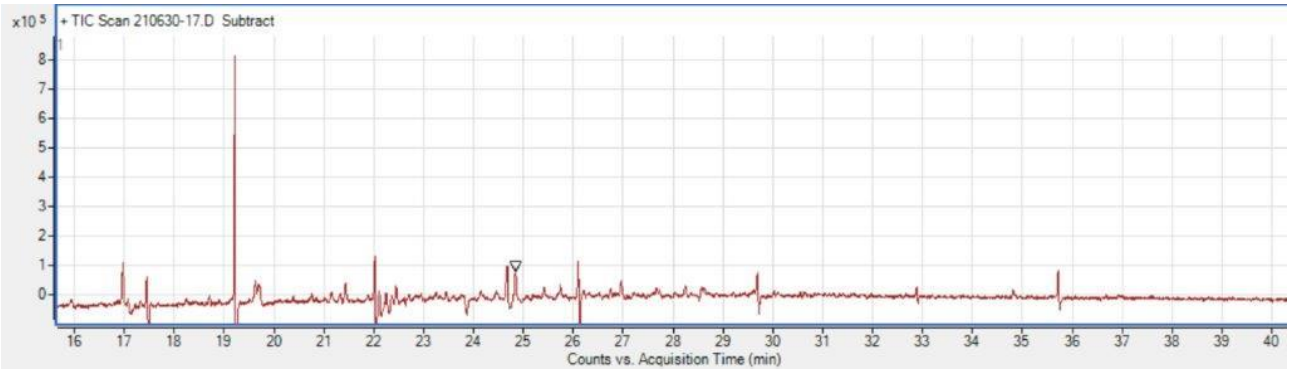


Figure 2.24 Chromatogram of the chemical compounds isolated and extracted from produced water sample G, likely to be naphthenic acids. The sample has undergone derivatization with MTBSTFA. An internal standard 4-(nonyloxy)benzoic acid was added to the sample, but the peak is not shown as it elutes later in the chromatogram. The chromatogram has been subtracted with a "blank" chromatogram for a solvent sample with derivatization agent.

The chromatogram above in Figure 2.24 shows the chemical compounds registered from produced water sample G. First it can be noted that there is almost no signal registered by the GC-MS. Secondly it can be noted that the signal intensity on the y-axis is an order of magnitude lower than the chromatograms for the other two produced water samples. Most of the peaks that can be observed are likely from the solvent, as there are negative signals right next to them. This occurs when the contaminants in the solvent blank does not elute at a completely overlapping time with the contaminants in the solvent used for the sample. Therefore the whole contaminant peak is not subtracted when the solvent blank is subtracted from the sample. This is not visible on the other chromatograms due to the shift in order of magnitude on the y-axis. There are however some peaks without adjoining negative signal which could be naphthenic acids.

2.4.1.3 Structural composition of naphthenic acids from the produced water samples

By allowing the identification of the naphthenic acids present in the produced water samples, three-dimensional naphthenic acid distribution plots can be created. By using the mass tables for naphthenic acid isomers displayed in Appendix C, the signal from one naphthenic acid isomer can be identified and the area% of the integrated chromatographic response of all the naphthenic acid isomers can be calculated.

In Figure 2.25 below, the TIC and the three-dimensional naphthenic acid distribution plot are shown for the two of the produced water samples. In the three-dimensional plots, the number of carbon atoms in the acid is displayed on one horizontal axis while the structure given as the number of rings is displayed on the other horizontal axis. From the three-dimensional plots, the Produced water sample A appears to have mostly saturated naphthenic acids with a few aromatic acids. This is reflected in the shape of the chromatogram with little overlap between the peaks. For Produced water sample F, there is a completely different composition of naphthenic acid isomer distribution with mostly acids with 2, 3 and 4 rings and aromatic acids. The acids with 3 rings is not possible to see in this 3D plot. The chromatogram of the Produced water sample F reflects this composition with a continuous hump of the elution of the naphthenic acids. For Produced water sample G the 3D plot is not included as the signal intensity is too low for any intelligible information to be extracted from it.

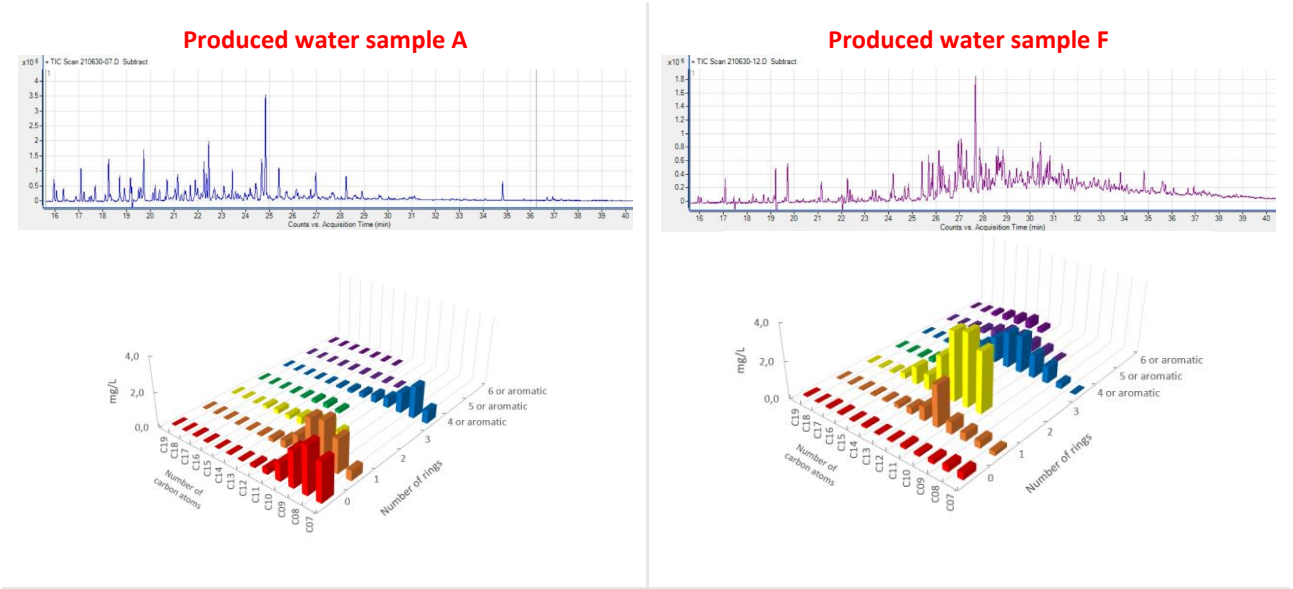


Figure 2.25 Chromatograms and three-dimensional distribution plots for each of the naphthenic acid mixtures

2.4.1.4 GC-FID analysis of the samples

2.4.1.4.1 Analysis of the GC-FID Chromatogram for naphthenic acids from produced water

The same samples were run on GC-FID. The GC-FID chromatogram for produced water sample A is shown in Figure 2.26 below with the GC-MS chromatogram added again in Figure 2.27 for reference. First it can be noted that the elution starts earlier compared to the elution for the commercial acid mixture. Whereas the naphthenic acids in the commercial naphthenic acid mixture eluted after the negative impurity peak in minute 19 for GC-MS and 6.65 for GC-FID, some of the light acids in the produced water sample A, elutes before this impurity peak. However, by counting the peaks, it appears that they elute after the large negative peak at 6.4 minutes in the GC-FID, which is also likely an impurity from the derivatization agent

used. Hence these light acids can also be captured by GC-FID. However, as shown in Figure 2.17 these acids are mainly C_6-C_8 acids and there is already a measurement method to quantify C_1-C_6 organic acids from produced water. To avoid measuring C_6 acids in this quantification method, the GC-FID integration was set to start after the last C_6 acid peak to capture acids from C_7 and upwards. As shown in Figure 2.17 this comes at the expense of two identified C_7 peaks which elute prior to the last C_6 peak however, the loss of these small peaks should have a negligible impact on the overall quantification. As with commercial naphthenic acid mixture, it can be observed that the overall shape of the chromatogram of produced water sample A is similar for both GC-FID and GC-MS although the chromatogram for GC-FID is compressed as it elutes over a shorter time span.

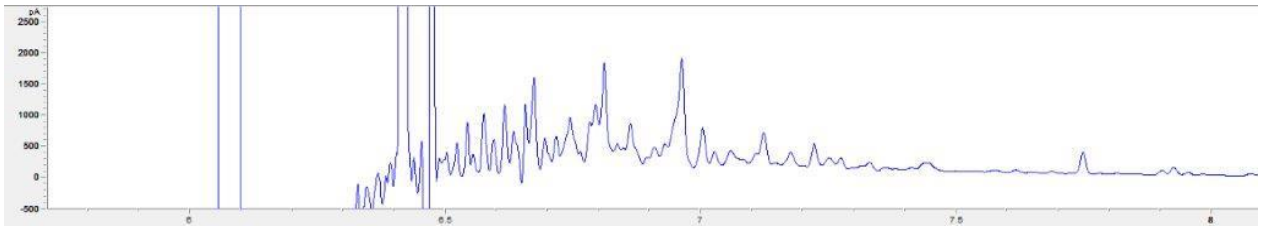


Figure 2.26 GC-FID chromatogram of produced water sample A

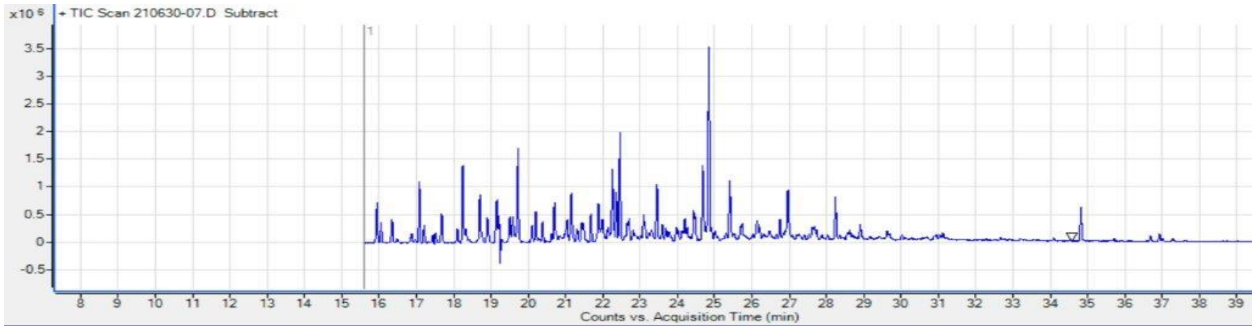


Figure 2.27 GC-MS chromatogram of produced water sample A

The GC-FID chromatogram for produced water sample F is shown in Figure 2.28 below with the corresponding GC-MS chromatogram added for reference in Figure 2.29. As for the produced water sample A it can be noted that the elution starts earlier compared to the elution for the commercial acid mixture here aswell. As for the commercial naphtenic acid mixture and the produced water sample A it can be observed that the overall shape of the chromatogram is similar for both GC-FID and GC-MS although the chromatogram for GC-FID is compressed as it elutes over a shorter time span.

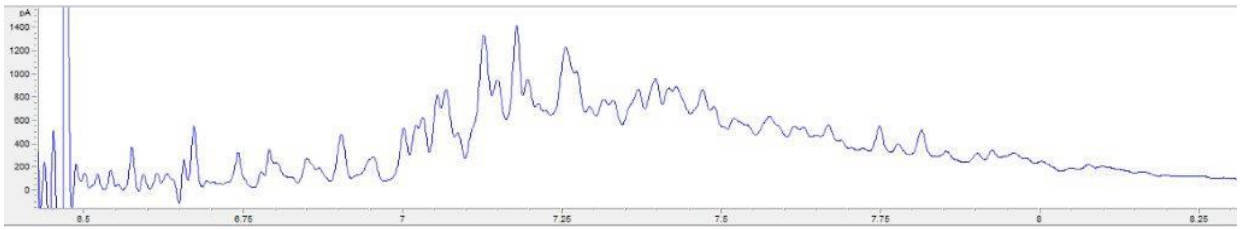


Figure 2.28 GC-FID chromatogram of produced water sample F

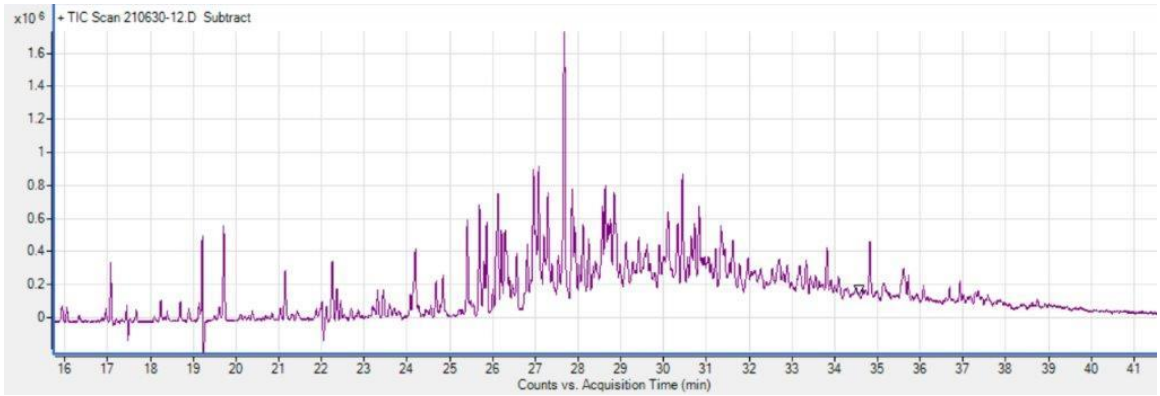


Figure 2.29 GC-FID chromatogram of produced water sample F

2.4.1.4.2 Quantification of naphthenic acids from produced water

After verification that the GC-FID chromatograms have a good overlap with the GC-MS chromatograms and that the GC-MS results verified that the eluting compounds are likely naphthenic acids, quantification with the GC-FID was performed. The isolated and extracted produced water samples from produced water A, F and G were run through the GC-FID and quantified using the oil in water calibration as described in Chapter 2.3. The results are shown in Table 2.7 below.

Table 2.7 Measured concentrations of naphthenic acids in the produced water samples with GC-FID.

	Produced Water Sample A	Produced Water Sample F	Produced Water Sample G	Produced Water Sample J
Naphthenic acid concentration	24 mg/L	41 mg/L	2.8 mg/L	- mg/L*

* The naphthenic acid concentration of this produced water sample was not measured as a stable emulsion formed during the liquid-liquid extraction.

Table 2.7 show that the produced water samples chosen for this initial test have measurable amounts of naphthenic acids in them. Two of the three produced water samples which could be quantified (from A and F) had 24 and 41 mg/L naphthenic acids in them. The third produced water sample, G, had only 2.8 mg/L naphthenic acids.

2.4.1.4.1 Recovery of spike concentration and validation of naphthenic acids quantification by standard addition method

Four out of five bottles of produced water from each field produced water sample were spiked with commercial naphthenic acid mixture before the naphthenic acids were extracted and isolated as described in the method section 2.2.2.2. The added concentration of commercial naphthenic acid mixture is shown in Table 2.2.

Table 2.8 below show the quantification results obtained for the spiked and non-spiked produced water samples. Here the measured concentration for the unspiked produced water sample has been subtracted from the measured concentration of the spiked produced water sample and this number has been compared to the actual spike concentration. The results show that the recovery of the spike concentration is from 65% to 100%.

Table 2.8 Measured concentration of produced water and spike produced water samples with percent recovery of spike concentration.

	Naphthenic acid concentration in produced water A and (recovered spike %)	Naphthenic acid concentration in produced water F and (recovered spike)	Naphthenic acid concentration in produced water G and (recovered spike %)
Produced water sample	24 mg/L	41 mg/L	2.8 mg/L
Spiked produced water sample S1	32 mg/L (89%)	50 mg/L (98%)	8.7 mg/L (76%)
Spiked produced water sample S2	40 mg/L (83%)	55 mg/L (72%)	15 mg/L (74%)
Spiked produced water sample S3	50 mg/L (71%)	72 mg/L (80%)	26 mg/L (70%)
Spiked produced water sample S4	65 mg/L (74%)	79 mg/L (70%)	34 mg/L (65%)

By performing the naphthenic acid quantification on the produced water samples spiked with known amounts of commercial naphthenic acid mixture, the applicability and accuracy of the method can be demonstrated through the standard addition method as detailed in Chapter 2.2.2.2.1.

The naphthenic acid concentrations by direct measurement and the standard addition predicted concentration of the produced water samples are shown in the Table 2.9 below. There is a large discrepancy between the two naphthenic acid concentrations, measured directly and by the standard addition method. This can be explained by the consistently lower concentration measured for the spiked solutions demonstrated by the recovery in Table 2.8. By comparing the theoretical concentrations of the samples with added spike concentration in Table 2.2, to the measured concentration after the naphthenic acids have been extracted and isolated from the produced water in Table 2.8, it is apparent that the measured concentration is lower.

In the standard addition method, a loss of added spike during the experimental method leads to a flatter slope compared to the slope that would be obtained if there was no loss of sample. Consequently a less steep slope leads to a higher predicted concentration of the unknown sample.

Table 2.9 Measured concentrations of naphthenic acids in the produced water samples spiked with commercial naphthenic acid mixture.

	Naphthenic acid concentration in produced water A	Naphthenic acid concentration in produced water F	Naphthenic acid concentration in produced water G
Produced water sample direct measurement	24 mg/L	41 mg/L	2.8 mg/L
Standard addition predicted concentration	35 mg/L	59 mg/L	5.5 mg/L

The commercial naphthenic acid mixture used to spike the concentration have some good features as it contains a broad range of naphthenic acid molecules of relevant size to partition into produced water. However, the commercial naphthenic acid mixture also contains some naphthenic acids which are too large to be water soluble, even at high pH. In other words, in the liquid-liquid extraction step with alkaline (high pH) water, where naphthenic acids move from the oil phase to the water phase, some of the largest naphthenic acids from the spike will not move to the water phase. This is demonstrated in Figure 1.5 a) where some of the Fluka commercial naphthenic acid mixture still remains in the oil phase after alkaline water liquid-liquid extraction at pH 12. This is one drawback of using this commercial naphthenic acid mixture as a spike. However, since these large acids are not water soluble at pH 12, it is very likely that they are not present in produced water, pH around 7-8, hence the effect can be corrected for. To demonstrate this these saturated large acids C_{18}-C_{19} in the commercial acid mixture used have a pK_{wo} of 6.6 [75] and summing up with a pK_a of around 5, it can be calculated that at pH 12 the concentration in oil is 40% of the concentration in water by using equation 7 in Appendix B. At pH 7 the concentration in oil is 40 000 times higher in oil compared to water.

To account for this predictable loss of sample a method correction factor was required. To obtain this method correction factor 4 samples of toluene with increasing concentrations of commercial naphthenic acid mixture were prepared. These toluene samples were to represent the toluene after the acidic liquid-liquid extraction from produced water to toluene had taken place. The toluene samples were extracted and isolated with the liquid-liquid extraction method in the same way that toluene after the acidic liquid-liquid extraction from produced water to toluene.

The figure below shows the GC-MS chromatogram of the commercial naphthenic acid mixture before and after the liquid-liquid extraction. Here is can be observed that much of the signal from minute 35 to 39 has disappeared after the liquid-liquid extraction. This is the signal from the large naphthenic acids present in the commercial naphthenic acid mixture. Comparing these chromatograms to the chromatograms from produced water sample A and F, Figure 2.13 and Figure 2.19, it can be noted that the produced water sample A does not have many large naphthenic acids which elute this late in the chromatogram. Produced water sample F however, has a proportion of its naphthenic acids that elute in this timespan of the chromatogram. However as shown in the Figure 2.25 and Figure 1.27a, the large acids in question are

highly unsaturated for the produced water sample F and saturated for the commercial naphthenic acid mixture. A question arises as to the ability of the method to capture all of these large acids from produced water F, as they could be a limited water solubility at pH 12 like the large acids in the commercial naphthenic acid mixture. As demonstrated in a later chapter this is likely not an issue. Experiments and discussion on the method's applicability for high molecular weight unsaturated compounds is added in Chapter 2.4.5.

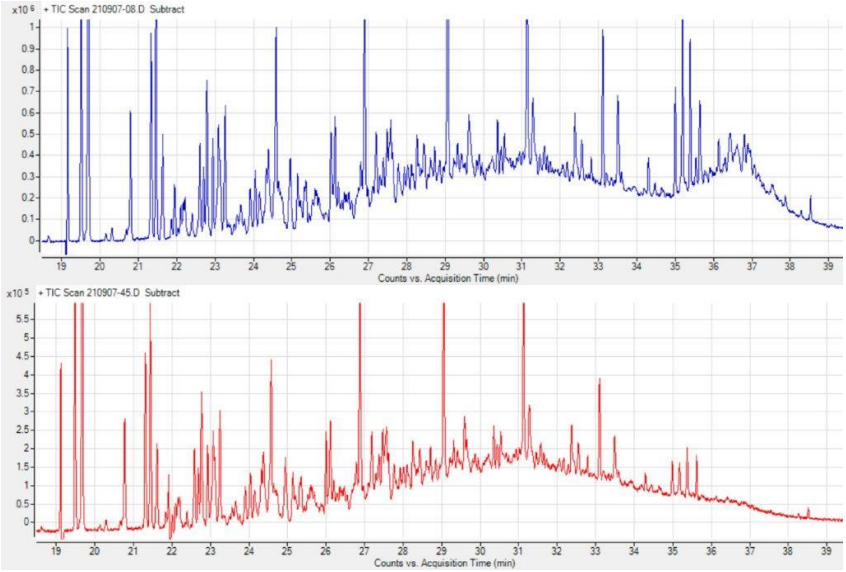


Figure 2.30 Chromatograms of toluene with commercial acid mixture prior to and after the liquid-liquid extraction. The hump from the C_{19} acid at minute 37 is absent after the extraction due to the low solubility in water for high molecular weight saturated acids.

The quantification results are shown in Table 2.10.The measured concentration of the commercial naphthenic acid mixture after the liquid-liquid extraction, is as expected, lower than the concentration prior to the liquid-liquid extraction. The difference between the two concentrations is consistently around 83%. A method correction factor of 0.83 was therefore added to the spike concentration to correct for the sample lost in the liquid-liquid extraction.

Table 2.10 Table listing the actual concentration of the commercial naphtenic acid mixture used as a spike and the measured concentration after liquid-liquid extraction.

	Actual concentration prior to liquid-liquid extraction	Measured concentration post liquid-liquid extraction	Recovery after liquid-liquid extraction
Toluene with commercial acid mixture concentration 1	68	56	82,9 %
Toluene with commercial acid mixture concentration 2	136	115	84,9 %
Toluene with commercial acid mixture concentration 3	273	226	82,8 %
Toluene with commercial acid mixture concentration 4	410	333	81,4 %

The formula for calculating the method corrected spike concentration to be used in the standard addition quantification verification is shown below.

$$Added\ spike\ concentration \cdot 0.83 = \ Method\ corrected\ spike\ concentration$$

As shown in Table 2.11, when the method corrected spike concentration is used in the standard addition method the concentration calculated by the standard addition method has a much better overlap with the direct measurement concentration. For the two samples with the highest naphthenic acid concentration the concentration predicted by the standard addition method is 120% of the direct measurement concentration. For the remaining produced water samples with lower concentration of naphthenic acid, the standard addition method concentration is 161% of the direct measurement concentration.

Table 2.11 Table listing the concentrations of naphthenic acids measured directly with GC-FID or calculated from the standard addition method.

	Direct measurement concentration	Standard addition concentration	Overlap between quantification measurements	Standard addition concentration with method correction factor	Overlap between quantification measurements
Produced water A	24 mg/L	35 mg/L	145%	29 mg/L	121 %
Produced water F	41 mg/L	59 mg/L	145%	49 mg/L	121 %
Produced water G	2.8 mg/L	5.5 mg/L	193%	4.5 mg/L	161 %

The standard addition quantification method can validate that the results obtained through direct measurement are representative of the actual naphthenic acid concentration in the produced water sample. For produced water samples where there is a low concentration of naphthenic acids (<10 mg/L), the method is less accurate than the ones predicted for produced water samples with high concentration of naphthenic acids. As can be seen in Figure 2.12,when the concentration measured by the GC-FID is low, the accuracy of the measurement is as consistent as it is for higher concentrations. There is an eightfold concentration ratio between the sample measured in the GC and the naphthenic acid concentration in the produced water. The solvent sample from Produced water sample A would then have a concentration of 192 mg/L in the GC-FID while solvent sample from Produced water sample G would have a concentration of 24 mg/L in the GC-FID. This can likely be solved by increasing the concentration of the final solvent extract by reducing the volume, i.e. extract sample from 10 mL water with 1 mL solvent instead of equal volumes. The standard addition method is also sensitive to the measured signal from the sample with the highest spike concentration. The recovery of the spike concentration varies as shown in Table 2.8. For the sample with the highest spike concentration the recovery was lower than expected. This loss could be caused by random variation in the first extraction step (stirring with toluene and left standing for 16 hours), where some of the bottles had a collection of light brown semi solids at the interface between toluene and water and the water phase was also still opaque upon extraction of the toluene. Other sources of error are discussed in Chapter 2.4.1.5 below. Loss of sample leads to a less steep curve in the standard addition method and consequently a higher concentration. The consistently higher concentrations calculated from the standard addition method, indicate that there is some loss of sample during the extraction steps. However the discrepancy seems to be small for produced water samples with a higher naphthenic acid concentration (>10 ppm).

As discussed earlier, in Figure 2.25 there are highly different compositions of ring structures for naphthenic acids from field A and F. While the naphthenic acids from field A consists of mainly fatty and 1 ringed acids, the naphthenic acids from field F, consists of mainly 1-3 ringed acids and aromatic or 4 ringed acids. The ability of the method to accurately measure the quantity of naphthenic acids from both of these produced water samples indicates that the method is applicable to produced water with widely different compositions of naphthenic acids.

2.4.1.5 Possible error sources for initial test:

There is likely some loss of sample in the first extraction step (stirring with toluene and left standing for 16 hours). Here some of the bottles with produced water and toluene phase on top had a collection of light brown semi solids at the interface between toluene and water. For some of the produced water bottles the water phase was also opaque at this stage, pointing to very small toluene droplets still present in the water phase. These small droplets would in theory have an interface rich in surface active compounds like naphthenic acids, which still have a certain surface active nature at low pH. The naphthenic acids would then diffuse from the toluene phase on top of the produced water and saturate the surface of the toluene droplets in the water phase below. However, based on the results, this loss of sample is acceptable. As there is loss of sample from the added spike there is likely a loss of sample of the naphthenic acids from the produced water as well.

Uncertainty related to the addition of low volumes (0.3 mL) of highly concentrated spike solution (150 000 mg/L) can have an impact on the apparent recovery. The same spiking volume was added to the toluene in Table 2.10. The consistency between the theoretical and measured results here indicate that the accuracy of the spike volume is sufficient.

A simplification is used in the calculation of the concentration ratio. An assumed density of 1000 g/L for produced water is used, while produced water density can vary between kg 1-1.14/L. Testing for this variable it was observed that changing the density from 1000 g/L to 1100 g/L increased the naphthenic acid concentration by 10% while the standard addition method result remained unchanged.

2.4.1.6 Conclusion for the initial tests:

Despite the apparent extraction challenges regarding opaque water phase and the formation of solids present after the first extraction step, the initial tests demonstrated that the method can be used successfully to quantify the content of naphthenic acids in produced water. The recovery of the spiked concentration is from 65-98%. However, since some of the spike concentration is not possible to recover, the expected spike concentration was adjusted. The measured concentrations of naphthenic acids are similar to the naphthenic acid concentration from the standard addition method. There seems to be less overlap between the two concentrations for produced water sample with the lower naphthenic acid concentration of ca. 3 mg/L. This is likely due to the inaccuracy of the quantification method with GC-FID at low sample concentrations. The recovered spike concentration from the produced water samples varies. This could be caused by uncertainties in the method. However it could also be caused by sample loss in the extraction phase, especially the first extraction step. Emulsion breaker can be added to this extraction step to reduce potential sample loss.

2.4.2 Extraction and quantification method applied to the remaining produced water samples

After successfully demonstrating the method on three of the produced water samples, the procedure was repeated for the remaining produced water samples from field B, C, D, E and i. Emulsion breaker salt was added in the produced water in the first extraction step. In general the water phases were clearer with emulsion breaker, however the produced water samples were not the same as the ones analysed in the initial tests. None of the remaining produced water samples formed a stable emulsion in the alkaline liquid-liquid extraction step as was the case for produced water sample J.

2.4.2.1 Quantification results for the remaining produced water samples

The chromatograms of the remaining produced water samples are not shown. They all have low concentrations of naphthenic acids (<10 mg/L) and have similar chromatograms to produced water sample G in the previous chapter.

The results showing identified concentration of naphthenic acid in the produced water samples are shown in Table 2.12. The results from the initial evaluation are included.

Table 2.12 Identified concentration [mg/L] of naphthenic acid in the produced water samples with comparison of different methods.

Produced water sample	Direct measurement	Standard addition before method correction	Overlap between quantification methods	Standard addition corrected	Overlap between quantification methods
A	24	35	145 %	28.8	121 %
B	2.2	3.3	149 %	2.7	124 %
C	2.4	5.7	234 %	4.7	195 %
D	4.1	4.8	118 %	4.0	98 %
E	1.9	2.7	138 %	2.2	115 %
F	41	59	145 %	49	121 %
G	2.8	5.5	193 %	4.5	161 %
H	1.0	1.4	141 %	1.1	118 %
i	3.2	4.2	134 %	3.5	112 %

Table 2.12 indicate that the direct measurement method using GC-FID with a mineral oil calibration standard gives an accurate concentration for naphthenic acids in the produced water. The discrepancy between the concentration given by direct measurement and the standard addition method is higher for the produced water samples with low concentrations of naphthenic acids (<10 mg/L).

Table 2.13 shows the results of the direct measurements and the standard addition spike concentrations. Here it can be seen that the recovery of the added spike is not 100%, even when the expected loss from liquid-liquid extraction at pH 12 is accounted for. However, for the new samples with added emulsion breaker in the first liquid-liquid extraction step (samples B,C,D,E,H and i), the recovery is higher, indicating an effect of the emulsion breaker. For most of the samples, close to 90% of the added spike concentration is recovered. However, some samples have a spike concentration recovery of as low as 78%. A high loss of spike concentration is reflected in the discrepancy between the concentration from direct measurement and the concentration given by the standard addition method. As there is loss of sample from the added spike there could be a loss of sample of the naphthenic acids from the produced water as well.

Table 2.13 Measured concentrations of naphthenic acids in the produced water samples spiked with commercial naphthenic acid mixture.

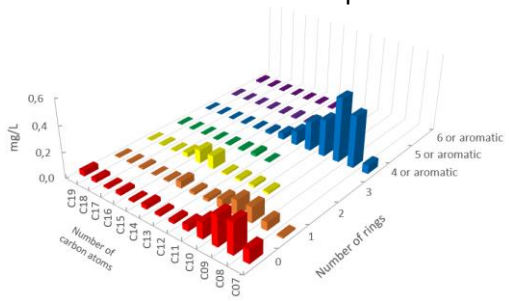
	Naphthenic acid concentration in produced water A		recovered spike % after method correction factor produced water A	Naphthenic acid concentration in produced water B		recovered spike % after method correction factor produced water B	Naphthenic acid concentration in produced water C		recovered spike % after method correction factor produced water C	Naphthenic acid concentration in produced water D		recovered spike % after method correction factor produced water D	Naphthenic acid concentration in produced water E		recovered spike % after method correction factor produced water E
Produced water sample Direct measurement	24	mg/L		2.2	mg/L		2.4	mg/L		4.1	mg/L		1.9	mg/L	
Spiked produced water sample S1	32	mg/L	107 %	9.8	mg/L	94 %	10	mg/L	95 %	11	mg/L	79 %	8.4	mg/L	84 %
Spiked produced water sample S2	40	mg/L	100 %	17	mg/L	94 %	17	mg/L	92 %	19	mg/L	91 %	16	mg/L	87 %
Spiked produced water sample S3	50	mg/L	86 %	31	mg/L	91 %	30	mg/L	89 %	33	mg/L	89 %	29	mg/L	86 %
Spiked produced water sample S4	65	mg/L	89 %	45	mg/L	91 %	39	mg/L	78 %	50	mg/L	91 %	42	mg/L	86 %
corrected standard addition concentration of X	29	mg/L		2.7	mg/L		4.73	mg/L		4.03	mg/L		2.24	mg/L	

	Naphthenic acid concentration in produced water F		recovered spike % after method correction factor produced water F	Naphthenic acid concentration in produced water G		recovered spike % after method correction factor produced water G	Naphthenic acid concentration in produced water H		recovered spike % after method correction factor produced water H	Naphthenic acid concentration in produced water i		recovered spike % after method correction factor produced water i	Naphthenic acid concentration in produced water J	recovered spike % after method correction factor produced water J
Produced water sample Direct measurement	41	mg/L		2.8	mg/L		1.0	mg/L		3.2	mg/L			
Spiked produced water sample S1	50	mg/L	118 %	8.7	mg/L	91 %	7.3	mg/L	83 %	10	mg/L	93 %		
Spiked produced water sample S2	55	mg/L	86 %	15	mg/L	89 %	12	mg/L	81 %	18	mg/L	94 %		
Spiked produced water sample S3	72	mg/L	97 %	26	mg/L	84 %	25	mg/L	84 %	32	mg/L	92 %		
Spiked produced water sample S4	79	mg/L	84 %	34	mg/L	79 %	36	mg/L	83 %	45	mg/L	91 %		
corrected standard addition concentration of X	49	mg/L		4.6	mg/L		1.2	mg/L		3.5	mg/L			

2.4.2.2 Structural composition of naphthenic acids from the produced water samples

3D plots of two of the remaining samples were prepared as shown in Figure 2.31. A stronger concentration was necessary to achieve useful information regarding the composition for these samples. The produced water samples without spike from field D and i were used to prepare a stronger concentration sample by using a lower volume of solvent in the last liquid-liquid extraction step. The final concentration would then be ten times higher. From the MS spectra we see that the compositions of the naphthenic acids are quite different from the composition of the naphthenic acids in produced water A and F. This gives further credibility to the method to work for different compositions of naphthenic acids.

Produced water sample D



Produced water sample i

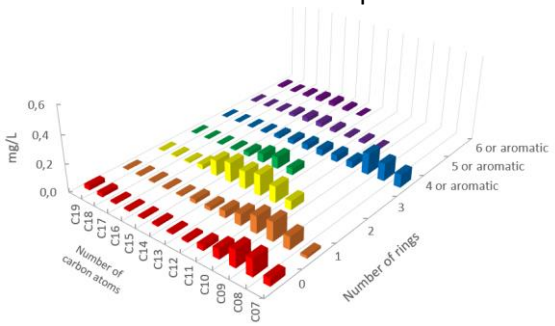


Figure 2.31 Three-dimensional distribution plots for the naphthenic acid mixtures from produced water samples D and i

2.4.2.3 Quantification with GC-MS

GC-MS was also used to quantify the naphthenic acids extracted and isolated from the produced water samples. The calibration curve for the commercial naphthenic acid mixture, Fluka from phase 1 of the project was used to obtain the results below. The GC-FID results are included for comparison.

Table 2.14 Comparison of the naphthenic acid concentration measured on GC-MS and GC-FID.

Produced water sample	Quantification with GC-MS	Quantification with GC-FID	Relative concentration given by GC-FID and GC-MS
A	36	24	149 %
B	2.8	2.2	127 %
C	1.5	2.4	61 %
D	6.0	4.1	145 %
E	2.0	1.9	103 %
F	43	41	106 %
G	2.7	2.8	94 %
H	1.8	1.0	187 %
i	4.5	3.2	143 %
Sample D with 10 times higher concentration from Chapter 2.4.2.2	3.5	3.7	94%
Sample i with 10 times higher concentration from Chapter 2.4.2.2	2.6	2.9	89%

As shown in Table 2.14, the GC-MS quantitative results when using a calibration curve for a commercial naphthenic acid mixture does not match well with the results obtained with GC-FID. For lower concentrations samples this could have be attributed to the accuracy of the GC-MS compared to the GC-FID. For produced water sample A which has a higher concentration of naphthenic acids, there is still a large difference between the two quantification methods. It could be that the bottom-up MS quantification method described in Chapter 1.4.3.6.7 would yield more accurate results. However, due to the promising results obtained with GC-FID quantification, this was not prioritized in this project. GC-MS can indicate if there are compounds which are not supposed to be quantified, like benzoic acid. Then the relative contribution to the chromatogram area could be taken from the GC-MS and the GC-FID response could be adjusted to remove impact from benzoic acid.

2.4.3 Evaluation of the method accuracy and lower limits of detection and quantification

2.4.3.1 Evaluation of the method accuracy

To test the precision and accuracy of the method, parallels were performed for most of the produced water bottles. Pairs of non-spiked and spiked samples of various concentration were used. The spike concentrations for each of the produced water samples were chosen to get a large variation in concentration for the measured samples. The extraction method was further improved by reducing the volume of the last liquid-liquid extraction step by 50% to obtain a stronger concentration for the sample to be measured on the GC-FID. To test reproducibility of a measurement method, the measurement should ideally be performed with as much variation as possible. Different operators, on different days and with

different instrument. The reproducibility in this project was performed with different operators and on different days. The same instrument was used for all measurement. The obtained datapoints are listed in Appendix D in Table 2.30.

To evaluate the accuracy of the method the relative spike recovery for the method can be calculated by the following equation:

Equation 1 *Source EURACHEM, guidelines for accreditation for measurement methods. Fitness of purpose of analytical methods.*

$$R'(\%) = \frac{\bar{x}' - \bar{x}}{x_{spike}} \times 100$$

Where $R'(\%)$ is the relative spike recovery, $\bar{x}'$is the mean value of the spiked sample, $\bar{x}$ is the mean value of the un-spiked sample and x_{spike} is the added spike concentration. As our spike is not 100% recoverable, the correction factor of 83% spike recovery is added to the calculation.

The obtained relative spike recoveries are shown in Table 2.15.

Table 2.15 Relative spike recovery to assess the accuracy of the method

Produced water sample	Mean concentration $\bar{x}$ of the un-spiked sample	Mean concentration $\bar{x}'$of the spiked sample	Spike concentration added corrected with recovery factor 83%	Relative spike recovery
A	26	56	30	101 %
B	2.7	18	16	92 %
C	3.2	18	16	92 %
D	4.8	12	8.3	82%
F	43	84	46	89 %
G	3.4	16	14	92 %
i	3.8	11	7.8	92 %

Table 2.15 shows the relative spike recovery at various concentrations for the tested produced water bottles from produced water A,B,C,D,F,G and i. In general the spike recovery is higher for the samples measured in this chapter compared to the previous chapter in Table 2.13. This is likely due to the higher concentration ratio used during liquid-liquid extraction, which further reduces the GC-FID measurement uncertainty for low concentrations (<300 mg/L). For produced water sample A, the adjusted recovery is 100%, while the recovery for the other produced water samples is around 90% and produced water sample D had a relative recovery of 82%. This is likely due to the difference in sample loss during the first extraction step as produced water from different fields contain different content. However, the opaqueness and solids formation of the produced water bottles are the first extraction step were not documented. Therefore it is not possible to stipulate any correlation to the relative spike recovery. The relative spike recovery results indicate that the results obtained with this measurement method will have a negative bias as some sample is likely lost in the first extraction step from produced water where there was an opaque water phase and

formation of solids. The following liquid-liquid extraction steps in the method will also have a minor impact, as there is always some solubility of compounds in each liquid phase.

To evaluate the precision of the repeated measurements on the non-spiked samples and the accuracy of the repeated measurements on the spiked samples, the data points were collected in a the graph shown in Figure 2.32. For the non-spiked samples, the accuracy cannot be determined as the real concentration is not known. For the spiked samples, the accuracy can be evaluated since the spike concentration added is known.

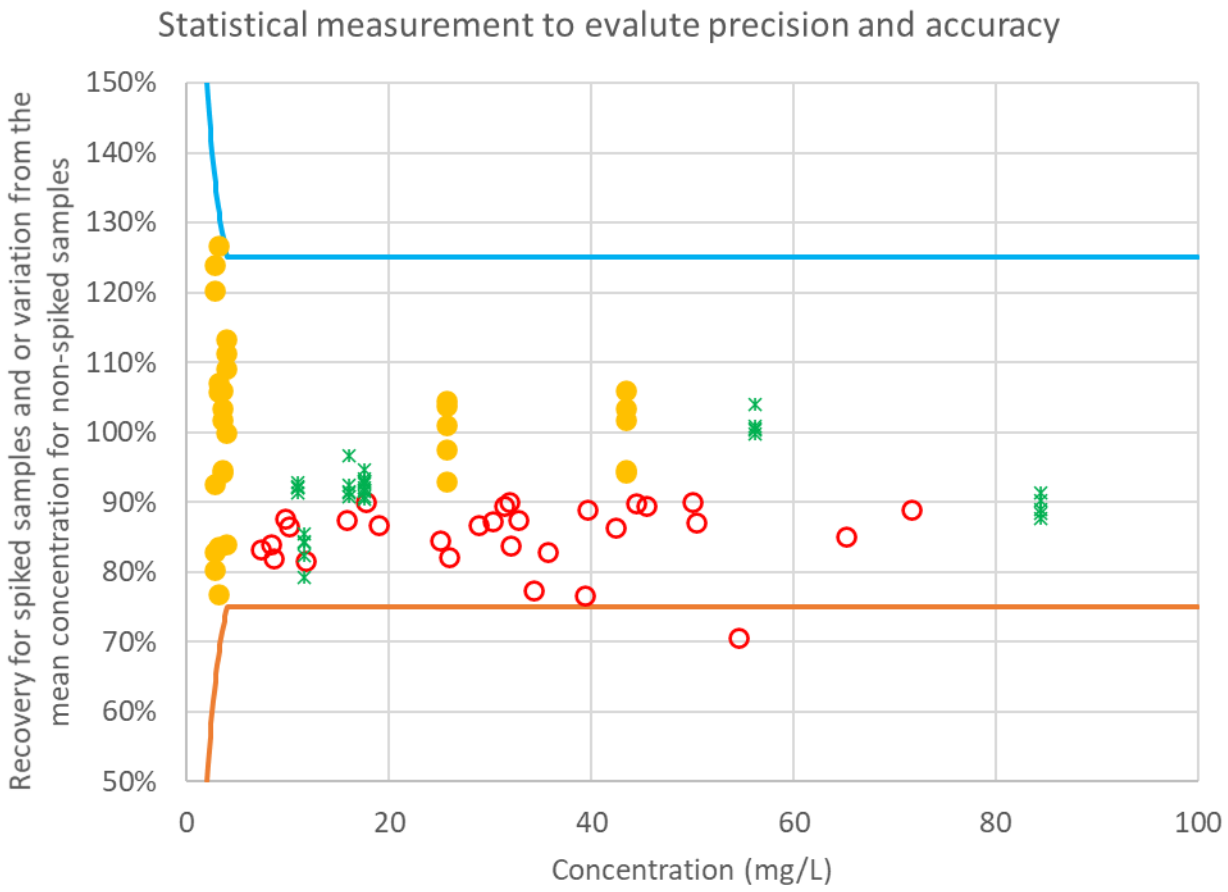


Figure 2.32 Graph showing the data points of the repeated measurements on the non-spiked samples and the repeated measurements on the spiked samples. The y-axis indicates the recovery of the spiked samples (and variation from the mean concentration for the non-spiked samples. The x-axis indicates the concentration. The green crosses show the datapoints for repeated measurements with the same spike concentration and the red dots show the datapoints for single measurements with for various single concentrations. The yellow dots indicate the concentration of the non-spiked samples. The orange and blue lines are the estimated uncertainty of the method adjusted to fit the datapoints for 95% confidence.

Figure 2.32 above shows the measurement accuracy for the spiked samples and the precision of the non-spiked samples. The yellow dots indicate the concentration of the repeated samples of produced water samples without added spike. For concentrations of naphthenic acids above 10 mg/L there is a lower precision compared to the measurements taken on produced water samples with low naphthenic acid

concentration. The precision at lower concentration indicates a lower precision for the measured concentration. This is likely caused by the lower accuracy of the GC-FID calibration curve for lower concentrations as discussed in Chapter 2.3.5 and Figure 2.12. The green crosses indicate the concentration of the repeated samples of produced water samples with added spike. The samples are very similar, which indicating good repeatability for the method with a slight negative bias, likely due to sample loss. The concentration ratio from produced water to the sample entering the GC-FID was 14, i.e. the sample measured has 14 times higher concentration than the concentration in the produced water. With a naphthenic acid concentration in produced water of around 3 mg/L, the measured concentration in GC-FID will be around 42 mg/L. As shown in Figure 2.12 the consistency for GC-FID is lower in the lower concentration range. This concentration ratio can be further increased in further optimization of the method to lower the limit of detection and quantification. For example, the two produced water samples D and i from Chapter 2.4.2.2 were extracted with a concentration ratio of 70. With their measured of around 4 mg/L and 5 mg/L, the measured concentration in the GC-FID is around 280 mg/L to 350 mg/L. As shown in Figure 2.12 there is a high consistency for GC-FID concentration measurements from 300 mg/L and upwards.

Regarding the repeatability of the method, the repeated experiments for the spiked and non-spiked samples, shown in yellow dots and green crosses above, show that the method can deliver consistent results when the method is used by different operators and different days.

To calculate the overall accuracy of the measurement method, the average recovery and standard deviation of the obtained data listed in Appendix D, Table 2.30 is given in Table 2.16 below.

Table 2.16. Table listing the calculated overall accuracy of the measurement method developed in this project.

Average recovery	Standard deviation	Relative standard deviation
94 %	8 %	9 %

95% confidence interval for measurement method Average Recovery ±2 x Relative standard deviation	
Min	76 %
Max	112 %

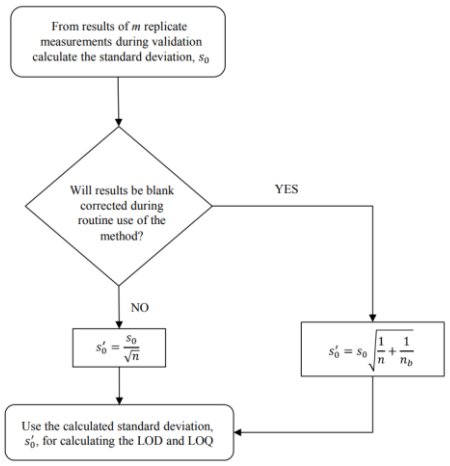
Table 2.16 shows the average spike recovery at various concentrations for the tested produced water bottles. The average recovery is 94% with a relative standard deviation of 9%. The results show that the results obtained with this measurement method can with 95% confidence (2 times relative standard deviation) be viewed to be within 76% - 112% of the true value. The estimated uncertainty for the measurement method is the largest of 1 mg/L or 24%.

2.4.3.2 Evaluation of limit of quantification and detection

To demonstrate the lower limit of quantification and detection for the method, repeated experiments on non-spiked bottles of produced water samples, E and H were performed. To test repeatability of a measurement method, the measurement should ideally be performed with as little variation as possible.

Same operator, same day and with the same instrument. The repeatability in this project was performed as described.

This form of analysis aims to demonstrate the concentrations a which noise can be distinguished from signal for the measurement method. An established method from Eurachem [79] was used to obtain these results. The flowchart for the procedure is shown below.



s_0 is the estimated standard deviation of m single results at or near zero concentration.

s_0' is the standard deviation used for calculating LOD and LOQ.

n is the number of replicate observations averaged when reporting results where each replicate is obtained following the entire measurement procedure.

n_b is the number of blank observations averaged when calculating the blank correction according to the measurement procedure.

Source Eurachem [79].

Table 2.17 Concentrations measured for repeated experiments on produced water samples E and H. The table also show the calculated limit of detection (LOD) and limit of quantification (LOQ) for the method.

Test sample	Produced water sample E	Produced water sample H
1	1.82	0.93
2	1.73	1.24
3	1.88	0.77
4	1.76	0.81
5	1.85	0.87
6	1.82	0.53
n	1.81	0.86
nb	Not applicable	Not applicable
s0	0.055	0.232
s0'	0.023	0.095
LOD	0.07	0.28
LOQ	0.23	0.95

As shown in Table 2.17, the quantitative results for produced water sample E were very consistent. For produced water sample H however, the concentrations are less consistent. There were problems during the extraction method for some of the samples with produced water H. More formation of solids than usual appeared in the first extraction step with toluene and produced water, and an emulsion formed during the extraction with alkaline water. This was not observed for the produced water samples of produced water sample H extracted in Chapter 2.4.2. As there were not enough produced water bottles left to repeat the analysis, the results obtained with produced water sample E are assumed to be representative. The obtained LOD was 0.07 mg/L and the LOQ was 0.23 mg/L.

2.4.3.3 Conclusion for method accuracy and lower limits of detection and quantification evaluation

The method accuracy was calculated to 76% - 112% of the true value. By comparing this to the oil in water OSPAR 2005-15 method for spiked samples, which assumes 80-110%, the measurement method established for naphthenic acids in this project has an equivalent accuracy. The lower level of detection and quantification was only obtained for one of the two produced water samples tested due to extraction problems in the first extraction step. The results show that positive detection for naphthenic acids can be obtained at concentrations as low as 0.07 mg/L and quantification can start for concentrations as low as 0.23 mg/L. Overall the experiments show a good repeatability in that the method can produce robust and similar results with different operating conditions. The method has been accredited by the national accreditation body of Norway.

2.4.4 Pentane as solvent

In the standard oil in water quantification method, pentane is used as the solvent instead of toluene. To check the applicability of pentane as a solvent for the extraction and isolation method of naphthenic acids from produced water, two bottles from all produced water samples were extracted with pentane. The highest spike concentration from Table 2.2 was added to one of the bottles from each set.

After the first liquid-liquid extraction from produced water, the water phase was still cloudy as was the case when toluene was used as the extraction medium. One exciting different was however that the liquid-liquid extraction step with alkaline (high pH) water for produced water sample J, did not yield a stable emulsion as was the case for toluene as the solvent. As a result the naphthenic acids of this produced water sample were now able to proceed to quantification and analysis on GC-FID and GC-MS.

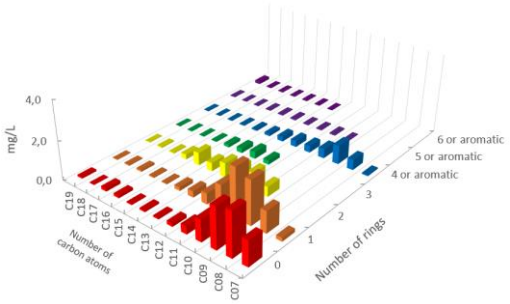
The GC-FID quantification results are shown in Table 2.18 below. First it can be noted that produced water sample J has a low concentration of naphthenic acids, 0.98 mg/L. Secondly it can be noted that the concentration predicted by the standard addition method has a bias towards higher concentrations as was the case with toluene as the solvent. This bias is consistent with sample loss in the first liquid-liquid extraction step from produced water. This could be linked to the number different spike concentrations. In this part only one spike concentration was used, while for the comparisons between direct measurement concentration and standard addition predicted concentration in the previous Chapters, multiple spike concentrations were used. Although the largest spike concentration has the most impact, the difference in number of spike concentrations will alter the results.

Table 2.18 Concentration of naphthenic acid from produced water samples when pentane was used as the extraction solvent.

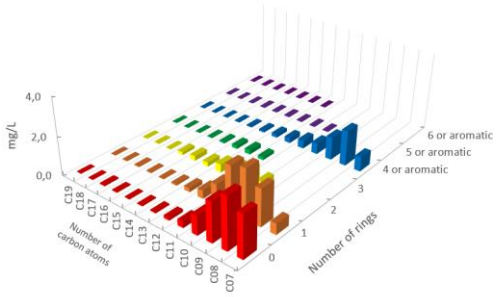
Produced water sample	Direct measurement	Standard addition corrected	Overlap between quantification method
A	19	21	113 %
B	1.5	1.7	116 %
C	1.5	1.8	117 %
D	2.1	2.5	122 %
E	1.4	1.8	127 %
F	39	46	115 %
G	2.0	2.4	121 %
H	0.9	1.1	116 %
i	3.2	3.8	117 %
J	0.9	1.1	122 %

Comparing the naphthenic acid concentrations obtained with pentane as the solvent to the concentrations obtained with toluene as the solvent, it can be noted that the concentrations with pentane are consistently lower. As discussed in the theoretical section from phase 1 of this project, in the Chapter 1.2.4, especially figure Figure 1.6 and in Chapter 1.3.1.2, the polarity of the solvent affects liquid-liquid partitioning of polar compounds like naphthenic acids. At low pH this effect is more prominent for low molecular weight acids which have higher water solubility compared to larger acids. For acids with an aromatic ring the effect will also be more prominent due to their increased solubility in water.

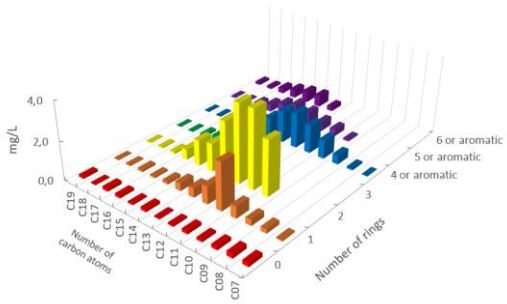
Produced water sample A with pentane as solvent



Produced water sample A with toluene as solvent



Produced water sample F with pentane as solvent



Produced water sample F with toluene as solvent

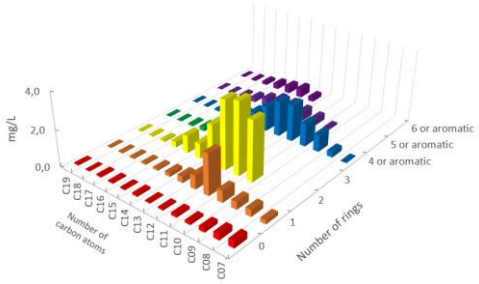


Figure 2.33 3D plots of the composition of naphthenic acids extracted from produced water A and F using either pentane or toluene as solvent

Figure 2.33 shows the 3D plots of the composition of naphthenic acids in extracted from produced water A and F using either pentane or toluene as solvent. At first glance the compositional distributions can appear similar, however detailed comparisons reveal that much less of the low molecular weight acids are recovered in pentane compared to toluene. Table 2.19 below show the detailed comparison between the two solvents where the percentage is given for the signal strength of the acid when pentane was used compared to when toluene was used as the solvent.

Table 2.19 Structural naphthenic acids isomer areas from GC-MS for naphthenic acids extracted from produced water A and F using either pentane or toluene as solvent

Produced water sample A extracted with pentane	19	mg/L	Produced water sample A extracted with toluene	24	mg/L
Number of rings					
C	0	1	2	3	4 or aromatic	5 or aromatic + 1 ring	6 or aromatic + 2 rings
C14							
C13							
C12			109 %				
C11		95 %	92 %		63 %		
C10	87 %	83 %	80 %		66 %		
C09	80 %	68 %			64 %		
C08	65 %	45 %			23 %		
C07	45 %	25 %			6 %		

Produced water sample F extracted with pentane	39	mg/L	Produced water sample F extracted with toluene	41	mg/L
Number of rings					
C	0	1	2	3	4 or aromatic	5 or aromatic + 1 ring	6 or aromatic + 2 rings
C16							
C15			100 %				
C14			127 %	103 %	95 %		
C13			98 %	96 %	87 %		
C12		90 %	88 %	89 %	69 %		
C11		80 %	78 %		53 %		
C10		69 %	64 %		55 %		
C09					37 %		
C08							
C07							

Although toluene seems to capture more naphthenic acids from produced water compared to less polar pentane solvent, a more polar solvent than toluene like dichloromethane for example, could prove to be even better at capturing the low molecular weight acids (C_7 – C_{11}) from the produced water. One of the reasons why toluene was chosen as the solvent in this project was due to the heating step in the derivatization as detailed in Chapter 1.4.2.2.1. In the previous project phase it was also concluded that the heating step was unnecessary, hence there is no longer a rationale for choosing toluene as the solvent instead of dichloromethane in the liquid-liquid extraction.

Regarding produced water sample J, as shown in it Table 2.5 formed a stable emulsion when toluene was used as the solvent and did not form an emulsion when pentane was used as the solvent. Prior to the pentane experiment, it was theorized that this produced water sample had a high concentration of naphthenic acids, which are very surface active and emulsion stabilizing at high pH, or a production chemical with emulsifying properties. With the emulsion free result with pentane and the negligible quantity of measured naphthenic acids, it is now more likely that asphaltenes could be the component which stabilized the emulsion at high pH. Asphaltenes are large surface-active molecules which create a mechanical barrier around water in oil emulsions which prevent them from merging together to bigger droplets and eventually two separate liquid phases. Asphaltenes are also soluble in toluene and insoluble in pentane (by definition). In toluene the asphaltene molecules are free and mobile to arrange themselves at the droplet surface. In pentane the asphaltenes are chunked together in large particles without much ability to populate and rearrange themselves around droplets.

The emulsion stabilizing properties of asphaltenes are also sensitive to the pH of the aqueous phase. The produced water sample J is suspected to hold a high oil in water content due to the dark colour of the solvent phase after the first extraction step from produced water. The emulsion stabilizing effect could also be caused by a production chemical such as an emulsion breaker. If the production chemical used is sensitive by the saturated/aromatic balance of the solvent and the pH of the aqueous phase.

2.4.5 Test range for acids

The method has a limitation when it comes to the recovery of larger naphthenic acids. This is demonstrated by the loss of e.g. the larger acid C_{19} from the commercial naphthenic acid mixture. This was shown earlier in Figure 2.30. In Table 2.20 below the mass spectra for the commercial acid mixture before and after liquid-liquid extraction are compared. Some of the values are above 100% as there are some uncertainties in comparing mass spectra from GC-MS. A broader trend can be observed, for example the signal for the high molecular weight acid C_{19} is only 31% of the signal prior to the liquid-liquid extraction. The low molecular weight acid C_8 also shows a slightly lower recovery after liquid-liquid extraction. This is likely due to the higher solubility of low molecular weight acids even at low pH levels, so some of this acid could be remaining in the water phase from the last acidic extraction step. The naphthenic acids in between C_8 and C_{19} have a good recovery after the liquid-liquid extraction. The overall recovery of 85% is likely due to the high individual concentration of C_{19} in the commercial naphthenic acid mixture.

Table 2.20 Table showing the comparison between the mass spectra of the commercial naphthenic acid mixture before and after liquid-liquid extraction. As mass spectra comparisons have some uncertainties regarding signal strength for different GC-MS analysis, a cut-off was used for some of the naphthenic acid masses with low signal strength. Some of the naphthenic acid isomers show a recovery over 100% for the same reason.

Toluene with commercial naphthenic acid mixture	151	mg/L	Toluene with commercial naphthenic acid mixture after liquid-liquid extraction	128	mg/L	85 %	recovery
C	-00	-02	-04	-06	-08	-10	-12
C19	31 %						
C18							
C17							
C16			99 %				
C15	93 %	97 %					
C14	95 %	109 %	108 %	106 %			
C13	111 %	101 %	104 %	113 %			
C12	102 %	103 %	102 %				
C11	111 %	100 %	105 %				
C10	102 %	106 %					

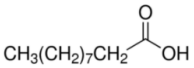
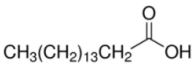
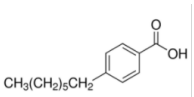
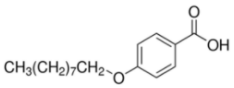
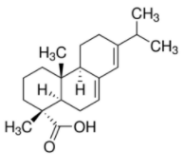
C09	97 %	99 %
C08	87 %	
C07		

Since the method only measures the produced water content after the extraction and isolation method, there is a potential that some large naphthenic acids are present in the produced water will not be detected by the method since the method discriminates against the large naphthenic acids in the commercial acid mixture. However, the produced water usually holds a relatively neutral pH of around 6-8. The liquid-liquid extraction in the method uses a pH of 12 in the organic phase to water extraction. Any naphthenic acids dissolved from crude oil to produced water at pH 8 is therefore likely to also dissolve fully or at least partially into the water at pH 12 in the liquid-liquid extraction step. No such large acids are detected in the 3D chromatograms for the produced water samples A,F,i and D, shown in Chapter 2.4.1.3 and Chapter 2.4.2.2.

The applicability of the commercial naphthenic acid mixture to evaluate expected naphthenic acid recovery from the produced water can be discussed for produced water samples with a prominent composition of aromatic acids. The commercial naphthenic acid mixture was chosen due the broad distribution of naphthenic acid structures; however it does not have much aromatic or 4 ringed acids in it. It could be that aromatic acids in the produced water does not have an adequate recovery, even when toluene is used as the extraction medium. The excellent recovery (90% average) for the added commercial naphthenic acid mixture does not prove that this is not the case, due to the difference in composition.

To verify that the method does not discriminate against larger acids a screening with 5 model acids was performed. The model acids chosen are listed in Table 2.21.

Table 2.21 Table listing the model acids chosen to test for method discrimination for large naphthenic acids in the liquid-liquid extraction.

Name	Isomeric formula	Structure	Molecular weight	
Decanoic acid	$C_{10}H_{20}O_2$		172 g/mol	C10 Z=0
Palmitic acid	$C_{16}H_{32}O_2$		256 g/mol	C16 Z=0
4-Heptylbenzoic acid	$C_{14}H_{20}O_2$		220 g/mol	C14 Z=-8
4-(Nonyloxy)benzoic acid	$C_{16}H_{24}O_3$		264 g/mol	C16 Z=-8
Abietic acid	$C_{20}H_{30}O_2$		302 g/mol	C20 Z=-10

The model acids from Table 2.21 were dissolved in toluene and extracted with the liquid-liquid extraction method. The samples prior to and after extraction were analysed on GC-FID and GC-MS. GC-MS was used solely to match the peak elution time to the acid. The results are shown in Table 2.22 below:

Table 2.22 GC-FID of toluene with 5 model acids comparing the GC-FID signal prior to and after liquid-liquid extraction.

5 model acids in Toluene	Area prior to extraction	Area after extraction in pH 12 water and backextracted to fresh toluene	Comparison of GC-FID values
Decanoic acid	11325	10960	97 %
Palmitic acid	11630	583	5 %*
4-Heptylbenzoic acid	10508	10119	96 %
4-(Nonyloxy)benzoic acid	6203	5709	92 %
Abietic acid	4657	4430	95 %

** Crystallization occurred at the interphase during the extraction with pH 12 water. This might account for the loss of palmitic acid.*

Overall the test with the five model acids shows that large acids with a higher degree of unsaturation will be captured by the method. The inability of the method to capture the saturated C_{19} naphthenic acids from the commercial naphthenic acid mixture can therefore be seen as an artificial limitation, as saturated C_{19} is not likely to be present in the produced water at pH 8 and the unsaturated equivalents of C_{19} which are present in the produced water at pH 8 will be captured by the method. Crystallization occurred at the interphase during the extraction with pH 12 water. This likely accounts for the loss of palmitic acid.

2.4.6 Production chemicals and phenol compounds concern

2.4.6.1 Production chemicals

When moving from experiments where all ingredients were known to a waste stream from a complex processing facility, there was an uncertainty regarding the impact of production chemicals on the extraction, isolation and quantification method. Most of the production chemicals added in upstream processing facilities are oil soluble and are mostly sent with the stabilized crude oil to the refinery. Some of the production chemicals are however water soluble like scale inhibitors, oxygen scavengers and biocides. If these chemicals inhibited some of the same solubility as naphthenic acids, these chemicals would follow the naphthenic acids through the extraction and isolation method. It was expected that these chemicals would present themselves as sharp peaks in the chromatogram, and if they could not undergo derivatization, have an uncharacteristic fragmentation in the GC/MS. Thorough analysis of the GC-MS chromatograms suggests that no measurable amounts of production chemicals are present in the extracted and isolated produced water sample. This is likely to be caused by different solubilities compared to naphthenic acids or the production chemical molecules are too large to vaporize and travel through the column in the GC/MS.

2.4.6.1 Regarding phenols and alkylphenols

A possible source of error can come from phenols and alkyl phenols. These compounds are slightly acidic and are able to be derivatized by the derivatization agent. The phenol content for some produced water installations were quantified by Røe Utvik [80] as listed in Table 2.23 below.

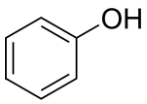
Table 2.23 Content of phenolic compounds from the produced water from 4 different platforms. Table from Røe Utvik [80].

mg/L	Brage	Oseberg F	Oseberg C	Troll
sum all phenols	6	11	11	0,6
phenol	3.5	7	6	0.03
cresol	2	3.5	3.8	0.06
ethylphenol	0.5	0.75	0.95	0.41
propylphenol	0.09	0.13	0.08	0.06
butylphenol	0.02	0.03	0.02	0.02

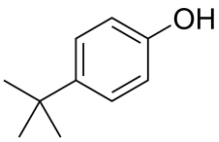
Table 2.23 demonstrate that phenols can be prevalent in produced water. The gathered data suggest that the two smallest phenols, phenol and cresol, are the most prevalent compounds in produced water. This is

likely due to their higher solubility in water compared to molecules with more hydrocarbon like characteristics. For example butylphenol is less water soluble than phenol due to the hydrocarbon tail.

Phenol



Butylphenol



To demonstrate how phenols and other polar compounds in the produced water will distribute themselves during the liquid-liquid extraction, their octanol water partition coefficient can be used along with their pKa. Phenols are weak acids and have a pK_a of around 10 and hence they dissociate in water around this pH. As the project uses toluene and not octanol, the octanol water partition coefficient for phenols can be adjusted to a toluene water partition coefficient through the equation from Leo, Hansch [81]: $K_{toluene/water} = 1.135K_{octanol/water} - 1.777$. The distribution of a monoprotic acid, like phenols or naphthenic acids, in an oil water mixture can be calculated by Equation 7 in Appendix B. The distribution of phenols, thiosalicylic acid (mentioned in Chapter 2.4.1.2.1) and a typical naphthenic acid 4-heptylbenzoic acid (C_{14}) at high and low pH in a toluene water mixture can be calculated by is shown in Table 2.24 below. Here it can be seen that although some of the lighter phenols are lost at low pH, they are mainly toluene soluble and will follow the oil phase at low pH extraction, same as the naphthenic acids. Consequently at high pH the phenols will dissociate and more of them will be in the water phase compared to the toluene phase same as for the naphthenic acids.

Table 2.24 Solubility of various compounds in toluene and water at high and low pH.

Chemical compound	pKa	Log Koctanol/water	Log $K_{toluene/water}$	At pH 2: x times more in water compared to toluene	At pH 12: x times more in water compared to toluene
Phenol	10	1.5	-0.0745	1.18	119
Cresol	10	2	0.49	0.32	32.4
Ethylphenol	10	2.36	0.90	0.12	12.6
Propylphenol	10	3.2	1.8	0.01	1.41
Buytlphenol	10	3.29	1.9	0.01	1.11
Thiosalicylic acid.	3.5	2.39	0.93	0.11	36673301
4-heptylbenzoic acid (C_{14}) (typical naphthenic acid for reference)	5	-	3.8 [42]	0.0002	1600

As demonstrated in Table 2.24 above, the liquid-liquid extraction method can be assumed to capture some of the phenol content of the produced water along with the naphthenic acids. Some of these phenols will have mass ions after derivatization (molecular weight + 57) identical to those of some naphthenic acids. See Appendix C, Table 2.29 for naphthenic acid masses.

Table 2.25 Molecular weight and mass isomer weight in GC-MS after derivatization for phenols and aromatic acids

Chemical compound	Molecular weight	Molecular weight + 57	Naphtehnic acid with the same molecular weight
Phenol	94	151	-
Cresol	108	165	-
Ethylphenol	122	179	Benzoic acid (C7)
Propylphenol	136	193	Toluic acid (C8)
Butylphenol	150	207	Dimethylbenzoic acid (C9)

To evaluate impact from phenols on the quantification of naphthenic acids from produced water, a phenol standard mix and benzoic standard mix were derivatized and analysed with GC-MS. The resulting chromatograms are shown in Figure 2.34 and Figure 2.35 below.

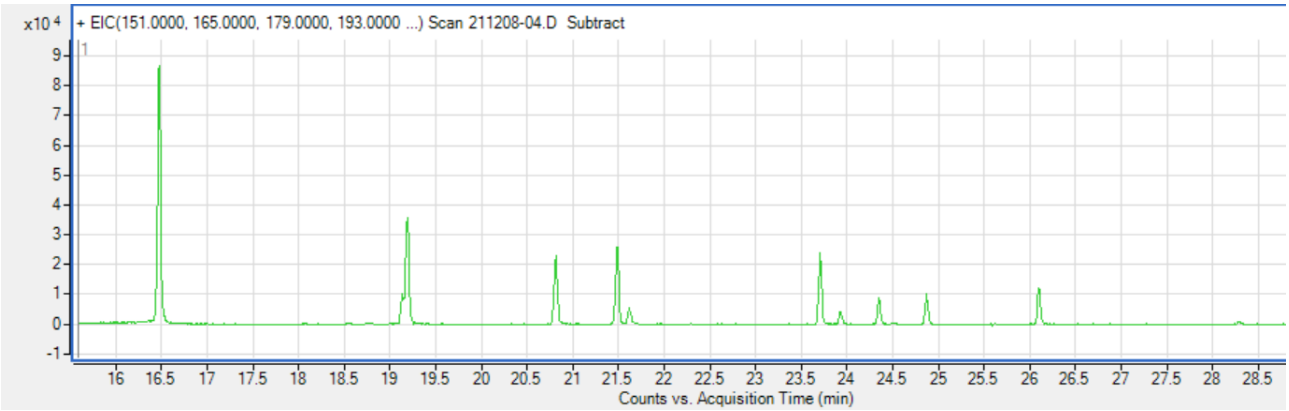


Figure 2.34 Phenol standard chromatogram on GC-MS

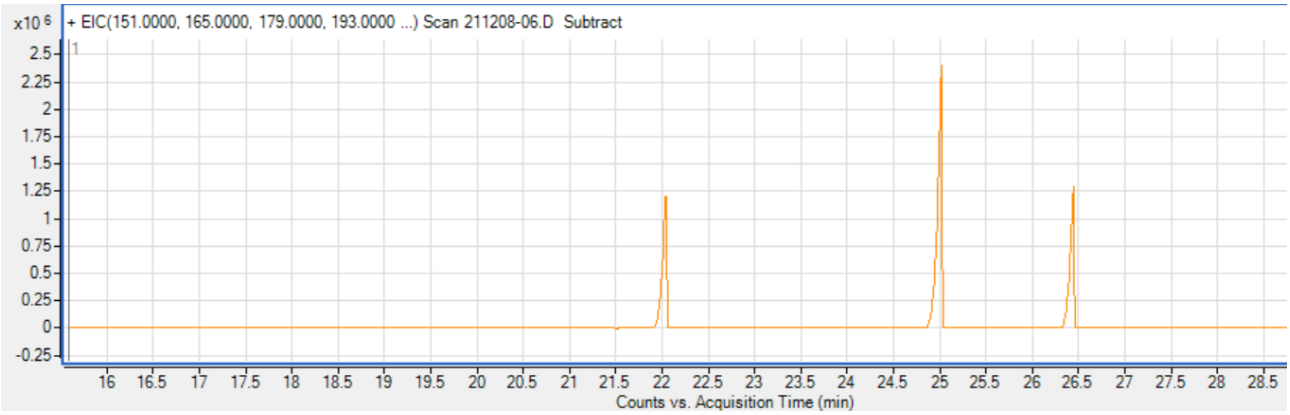


Figure 2.35 Benzoic acid standard chromatogram on GC-MS

As shown in Figure 2.34 and Figure 2.35 above, although the benzoic acids and phenols have overlapping masses when analysed with GC-MS, their elution time through the GC-MS column differs. The first peaks in Figure 2.34 are phenol at minute 16.5 and cresol at minute 19.2. For ethylphenol and benzoic acid which both share the mass 179, the peaks for the structural isomers of ethylphenol elute from the column at minute 20.7, 21.4 and 21.6 in Figure 2.34, while benzoic acid which only has one structure elutes at minute 22 in Figure 2.35. For propylphenol and p-tuloic acid which both share the mass 193, the peaks for the structural isomers of propylphenol elute from the column at minute 23.7, 23.9 and 24.4 in Figure 2.34, while p-tuloic acid which only has one structure elutes at minute 25 in Figure 2.35. For butylphenol and dimethylbenzoic acid which both share the mass 207, the peaks for the structural isomers of Butylphenol elute from the column at minute 24.4 (shared with structural isomer of propylphenol), 24.8 and 26.1 in Figure 2.34, while dimethylbenzoic acid which only has one structure elutes at minute 26.4 in Figure 2.35. Although it appears that the elution time can be used to make a clear distinction between phenols and naphthenic acids, the benzoic acid standard used here only contains three structural isomers. Both toluic acid and dimethylbenzoic acid can have 3 or more structural isomers which have both lower and higher boiling points. This can cause them to be indistinguishable from phenols in the chromatogram.

To evaluate the impact from phenols on the produced water measurements, the EIC of masses; 151, 165,179,193 and 207, was extracted from the chromatogram of produced water A and F. The resulting chromatograms are shown below in Figure 2.36 and Figure 2.37.

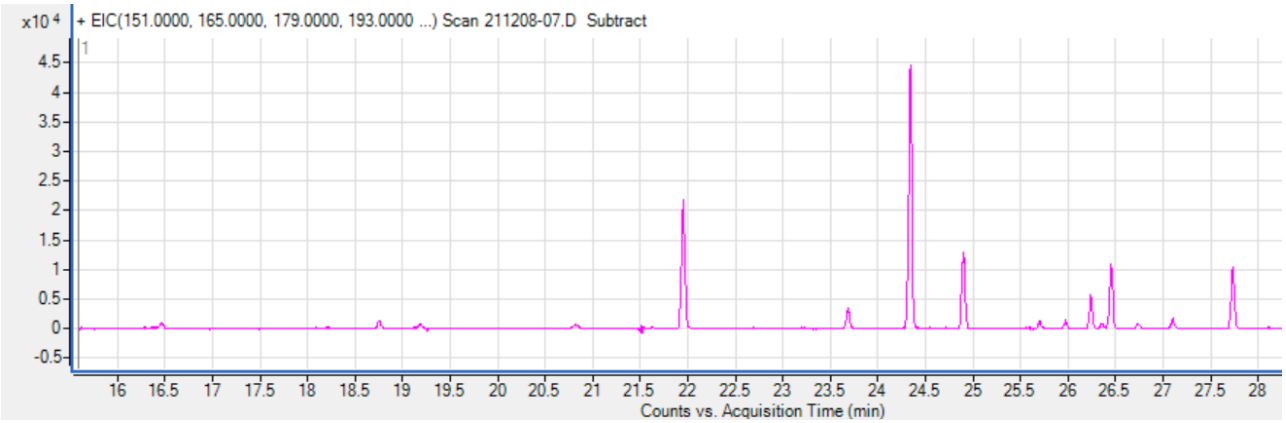


Figure 2.36 Chromatogram EIC of phenolic masses; 151, 165,179,193 and 207 for produced water A

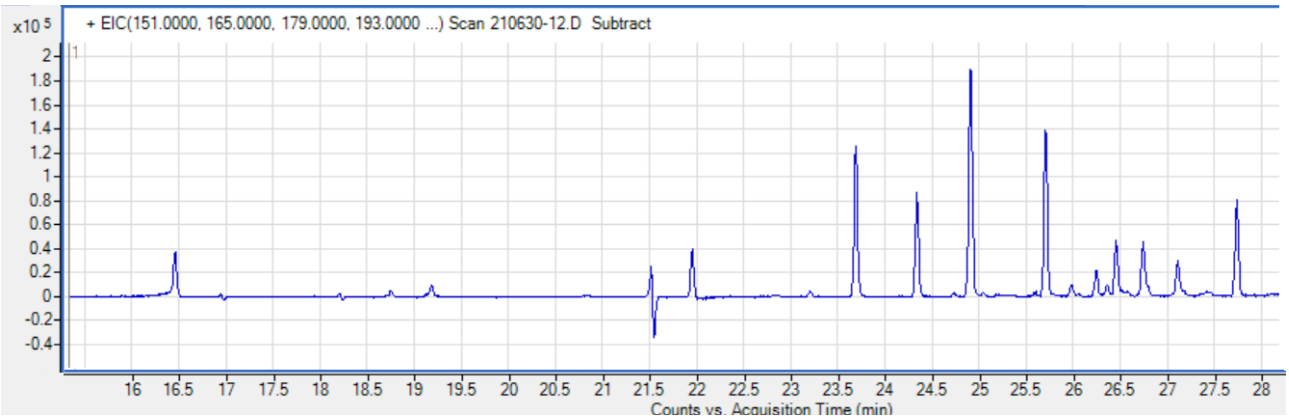


Figure 2.37. Chromatogram EIC of phenolic masses; 151, 165,179,193 and 207 for produced water F

As shown in Figure 2.36 and Figure 2.37 of the EIC chromatograms of potential phenol and naphthenic acid masses, there is a clear phenol signal for produced water sample F at minute 16.5 and faint signals for phenol and cresol in both produced water samples A and F. The peak at minute 22 is clearly benzoic acid as the corresponding phenol has an earlier elution time. The peaks at 23.7 and 24.4 and 24.9 could point towards the presence of propylphenol or butylphenol at the elution time matches. However as mentioned above, it could also be structural isomers of toluic acid (ortho and meta) which have a lower boiling point compared to p-tuloic acid structural isomers of dimethylbenzoic acid.

To assess the likelihood of the compounds being phenols instead of toluic acid and dimethylbenzoic acid, the solubility of the different compounds in toluene and water at high and low pH are given below.

Table 2.26 Solubility of various compounds in toluene and water at high, low and neutral pH.

Chemical compound	pKa	Log Koctanol/water	Log $K_{toluene/water}$	At pH 2: x times more in water compared to toluene	At pH 12: x times more in water compared to toluene	At pH 7: x times more in water compared to toluene
Propylphenol	10	3.2	1.8	0.01	1.41	0.01
Butylphenol	10	3.29	1.9	0.01	1.11	0.01
Toluic acid	5	2.27	0.79	0.16	1621810	16.38028
Dimethylbenzoic acid	5	2.8	1.4	0.039	398107	4.020882

As shown in Table 2.26 toluic and dimethylbenzoic acid at high pH are many times more water soluble compared to their phenol counterparts, propylphenol and butylphenol. Bringing it back to which compounds are likely to be present in the produced water. If the produced water pH is assumed to be around 7, Toluic acid and dimethylbenzoic acid have a water concentration 16 times and 4 times higher than the toluene concentration. For their phenol counterparts, the water solubility at this pH is almost the

same as at pH 2. Crude oil and toluene are not the same solvent, as crude oil is a mixture of saturates and aromatics, however with the orders of magnitude difference in the ratios detailed above, and the similar molecular structure of the two molecule groups, the ratios should remain equivalent for crude oil.

To illustrate this the phenol standard was put through the same extraction procedure as the liquid-liquid extraction. The resulting chromatograms, before and after the extraction are shown in the Figure 2.38 below.

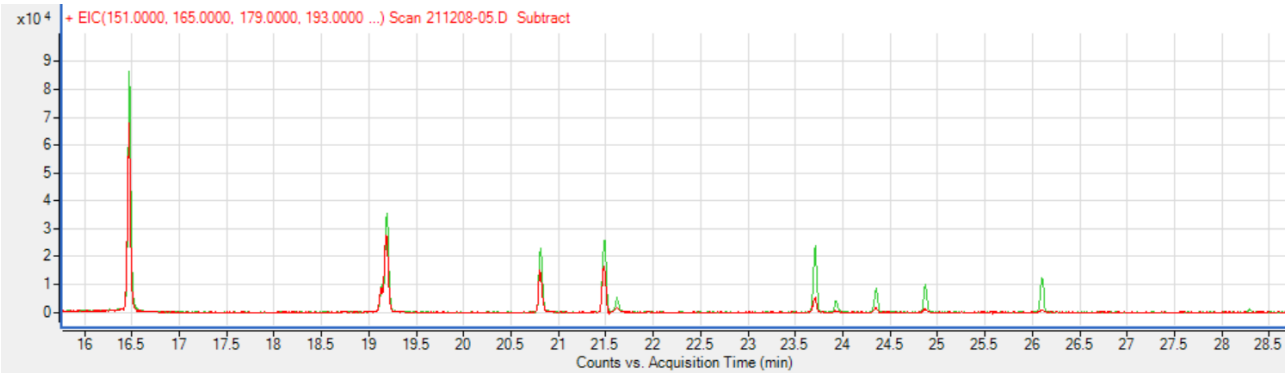


Figure 2.38 Phenol standard chromatogram on GC-MS in green and Phenol standard after liquid-liquid extraction and back extraction using toluene shown in red.

As can be seen in Figure 2.38 of the phenol standard before and after liquid-liquid extraction, the recovery of the three lightest phenols is around 70%. For propylphenol or butylphenol however from minute 23,7 and onwards, the recovery is much lower.

To demonstrate the influence phenolic compounds can have on the produced water quantification measurements, the GC-MS area from phenolic compounds was compared to the GC-MS area of naphthenic masses. This analysis was performed on produced water samples A, F, i and D. As described in Chapter 2.4.1.2.1, the signal response of the other produced water samples was too low to be analysed in GC-MS. Although the naphthenic acid concentration of produced water i and D were low, the signal response in GC-MS could be obtained as these samples were also extracted with an increased concentration ratio during the liquid-liquid extraction as described in Chapter 2.4.2.2. The results of the area comparisons are listed in Table 2.27 below.

Table 2.27 Signal contribution from phenolic compounds for naphthenic acid quantification for 4 produced water samples.

Produced water sample with (naphthenic acid concentration)	EIC area from naphthenic acid masses	EIC area phenols assuming all phenol masses are phenols	Phenol area vs naphthenic acid area	EIC area from naphthenic acid masses	EIC area phenols assuming only verified phenol masses are phenols	Phenol area vs naphthenic acid area
A (26 mg/L)	1955943	293935	15 %	1955943	9034	0 %
D* (4.8 mg/L)	6002695	1634395	27 %	6002695	293372	5 %
F (43 mg/L)	64355025	1782124	3 %	64355025	96365	0%
i* (3.8 mg/L)	4752436	1405901	30 %	4752436	929228	20%

** Produced water sample i and D had a concentration ratio of around 70 in the liquid-liquid extraction method.*

As shown in Table 2.27 above, if all phenol masses are to be counted as phenols and not naphthenic acids, they account from 3%-30% of the measured signal response in GC-MS. As the shape of the GC-MS and GC-FID chromatograms are similar the ratio is assumed to be roughly equivalent for GC-FID. The impact from phenolic compounds appears to be non-negligible, however, as shown Table 2.26 and Figure 2.38 and corresponding text, there is a high likelihood that the signal from masses which could be both propylphenol/butylphenol or toluic acid/dimethylbenzoic acid are almost exclusively different structural isomers of toluic acid/dimethylbenzoic acid. When this is taken into consideration, the phenol signal from verified phenolic compounds can be extracted and compared to the naphthenic acid signal as shown to the right in Table 2.27 above. Here the impact from phenols is negligible for produced water samples A and F. For produced water samples D and i there is still a 5% and 20% impact from phenolic compounds. This signal comes largely from phenol and cresol. The lightest of the two will not be included in the GC-FID as it elutes too early in the chromatogram, see Chapter 2.4.1.4.1. Cresol however, will be counted as a naphthenic acid in GC-FID with the method developed in this project, unless the signal elution time is identified with GC-MS and the corresponding peak area is subtracted in the GC-FID chromatogram. The low concentration of naphthenic acid and relatively high concentration of phenols could be correlated to the pH of the produced water for these fields. If the pH of the produced water is around 5, the phenol concentration and naphthenic acid concentration would be similar as shown in Table 2.28 below.

Table 2.28 Solubility of various compounds in toluene and water at pH 5.

Chemical compound	pK_a	Log $K_{octanol/water}$	Log $K_{toluene/water}$	At pH 5: x times more in water compared to toluene
Propylphenol	10	3.2	1.8	0.01
Butylphenol	10	3.29	1.9	0.01
Toluic acid	5	2.27	0.79	0.32
Dimethylbenzoic acid	5	2.8	1.4	0.07
4-heptylbenzoic acid (C_{14}) (typical naphthenic acid for reference)	5	-	3.8 [42]	0.000317

2.4.6.1.1 Conclusion on the impact of phenolic compounds

Overall the impact from phenols appears to be negligible compared to the naphthenic acid signal for produced water samples with high naphthenic acid concentration (>10 mg/L). For produced water samples with lower naphthenic acid concentration 20% of the measured concentration could be from the phenol content and not naphthenic acids, however, with the higher uncertainty of quantification for low concentration naphthenic acid samples detailed in Chapter 2.4.3.3, this is not a concern for the measurement method in general.

It should be mentioned that with the proper isolation of phenols from other compounds like naphthenic acids, the GC-MS and GC-FID analysis used here with the derivatization agent could prove to be a valid alternative to existing phenol quantification methods. With the concentrated samples for produced water sample D and i, which were extracted with a concentration ratio of around 70, the signal responses for phenol compounds phenol and cresol are clear and quantifiable.

2.5 FTIR

FTIR analysis of naphthenic acids was attempted with (attenuated total reflection) and spectroscopy. On the ATR only, the standard with 150 000 mg/L and the toluene solution with the highest content of commercial naphthenic acid mixture registered with a signal. With spectroscopy it was attempted to use the smallest cuvette available. A weak signal was recorded with pure toluene. As commercial naphthenic acid mixture was added, the signal disappeared. Hence it was decided to focus on the GC-MS and GC-FID instead. FTIR was proposed to validate the presence of naphthenic acids in the samples. This was validated by detailed analysis of the GC-MS chromatograms and spectra instead.

2.6 Cooperation with NIVA and the authors behind the previously published quantification method

In the theory chapter (1.3.1.3.5) and the conclusion of the first project phase (1.4.4) emphasis was put on the naphthenic acid quantification method developed by Samanipour, Reid [71]. Here, a LC-HRMS with ESI

ionization to identify and quantify different naphthenic acid isomer groups across 6 produced water samples. It would have been especially interesting to obtain a sample of the commercial naphthenic acid mixture used in that research, as it had a perfectly distributed concentration of naphthenic acids from C_8 to C_{35} which covered the whole structural spectrum from saturated to acids with multiple ring structures or aromatic rings. The commercial naphthenic acid mixture used in this project contains mostly 0-2 ringed acids from C_8-C_9. It was also of interest to obtain more information of the data analysis behind the results as it did not make clear how the calibration curves for the individual naphthenic acid isomers were made. After the first project phase, contact was initiated with NIVA and Professor Samanipour. Although repeated meetings were held, the authors of the published research were not able to explain to a degree that the participants of this projects could understand, how the simplifications made in their research could justify the published results. Although a sample of the commercial naphthenic acid mixture used in the research was initially agreed to be sent, sadly it turned out that the bottle had been thrown away.

2.7 Conclusions

The second phase of the quantification of naphthenic acids in produced water project was successful.

It was demonstrated that naphthenic acids can be extracted and isolated from produced water.

The GC-MS analysis of the samples demonstrate that the measured compounds are naphthenic acids and that interference from phenols is likely to be negligible. It was not observed any significant interference from production chemicals. With the assurance that the compounds measured are naphthenic acids, the GC-FID quantification method developed in this project can be used to achieve a quantification with a higher accuracy compared to GC-MS.

It was demonstrated that the oil in water calibration correlates with naphthenic acid concentration on GC-FID. The concentrations measured by direct measurement were validated by the standard addition method. The quantification method used for GC-MS in this project phase proved to be less accurate than the results obtained with GC-FID. GC-MS can be used to gain insight of the molecular weight and structural distribution of the naphthenic acids in the produced water. GC-MS can also be used to identify non-relevant peaks and remove their contribution to the total naphthenic acid content if e.g. the content of benzoic acids is not relevant to be included in the naphthenic acid concentration.

The content of naphthenic acids in 10 produced water samples obtained from the Norwegian Continental Shelf ranged from 1 mg/L to 45 mg/L. The method accuracy was calculated to 76% - 112% of the true value. By comparing this to the oil in water OSPAR 2005-15 method for spiked samples, which assumes 80-110%, the measurement method established for naphthenic acids in this project has an equivalent accuracy.

A proposed method is ready to be applied in the industry with defined limit of detection and lower limit of quantification. The method quantifies: Toluene extractable components from pH2 produced water, which can be extracted to a water phase at pH 12 and backextracted to a fresh toluene phase at pH 2. The components must be able to undergo derivatization and elute after n-hexanoic acid on GC-FID adjusted as per OSPAR 2005:15 (including BAM calibration). The method captures acids down to C_7 acids and there is an existing method which captures C_1-C_6 acids.

2.8 Considerations for further work

To further validate the method, it would be of interest to perform a cross validation in cooperation with other laboratories. Applying the method on other fields than the ten fields covered in this project would also be interesting to further test the robustness of the method.

A more polar solvent than toluene like dichloromethane (DCM) for example, could prove to be even better at capturing the low molecular weight acids (C_7-C_{11}) from the produced water. One of the reasons why toluene was chosen as the solvent in this project was due to the heating step in the derivatization as detailed in Chapter 1.4.2.2.1. In the first project phase it was also concluded that the heating step was unnecessary, hence there is no longer a rationale for choosing toluene as the solvent instead of DCM in the liquid-liquid extraction. The use of other solvents than toluene could be a suggestion for further method improvement.

As the commercial naphthenic acid mixture used to gauge the recovery in this project, contains little to no low molecular weight aromatic acids (C_7-C_{11}), the loss of low molecular weight aromatic acids in this method should be evaluated. To perform this evaluation a sample of produced water sample F can be made. Produced water sample F has an acceptable content of aromatic acids. This sample should then be extracted and backextracted with toluene to compare the recovery. The recovery of these acids will then give a better idea of how much is lost in the method when it comes to produced water with a high content of low molecular weight aromatic acids (C_7-C_{11}).

A different spiking chemical could be used. The commercial naphthenic acid mixture can be modified to be 100% water soluble and 100% oil soluble by removing the largest naphthenic acids in the mixture. This can be done by partitioning it at pH 10 and back extracting the water phase to fresh pentane. The pentane would now only contain only the naphthenic acids from the mixture which are 100% water soluble to 100% oil soluble depending on pH. After evaporation of the pentane and a stable weight of the naphthenic acid residue is obtained it can be used to make a new spike solution where no correction factor would be needed for the standard addition verification.

As described in Table 1.3 and the surrounding text, a certain loss of mass from the saturated low molecular weight acids (C_6 – C_8) should be expected during the extraction process due to their solubility in water at low pH levels. By performing multiple extractions and adjusting the GC-FID integration cut-off it should in theory be possible to get a reliable quantification of C_7 acids, which when paired with the standard quantification method for C_1 - C_6 organic acids should truly cover the whole range of organic and naphthenic acids in produced water.

With the proper isolation of phenols from other compounds like naphthenic acids, the derivatization used in this project could prove to be a valid improvement to existing phenol quantification methods. With the concentrated samples for produced water sample D and i, which were extracted with a concentration ratio of around 70, the signal responses for phenol and cresol are clear and quantifiable.

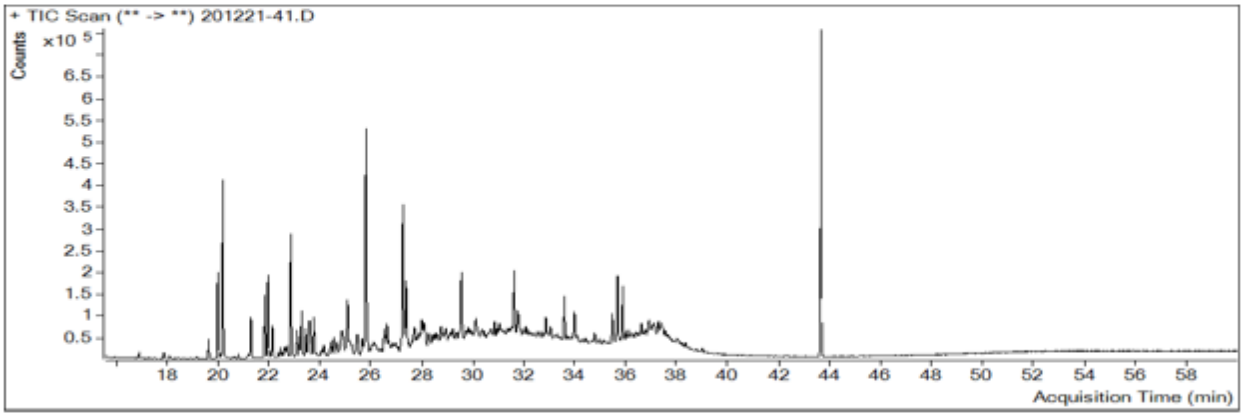
Although GC-MS quantification using commercial naphthenic acid to create a total signal calibration curve, proved to give inaccurate measurements compared to GC-FID, the bottom up GC-MS quantification detailed in Chapter 1.4.3.6.7, could be tested for the spiked and non-spiked produced water samples. If successful, GC-MS analysis can be used to quantify not just the total naphthenic acid concentration, but also the concentration of individual naphthenic structural isomers. This could prove to be useful when calculating the environmental impact factor if the different naphthenic acid structural isomers have different impact factors.

Appendix A. **Examples of how naphthenic acid content in samples can be reported if GC-MS is used in the analysis method.**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Fluka naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **1 473,9** mg/L Calculated molecular weight: **213,4** g/mol



Plot of calculated concentration of groups based on area% and m/z

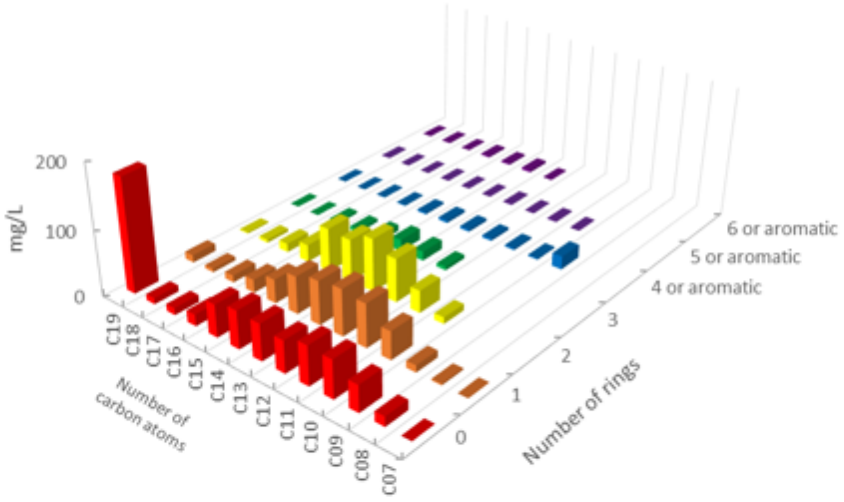


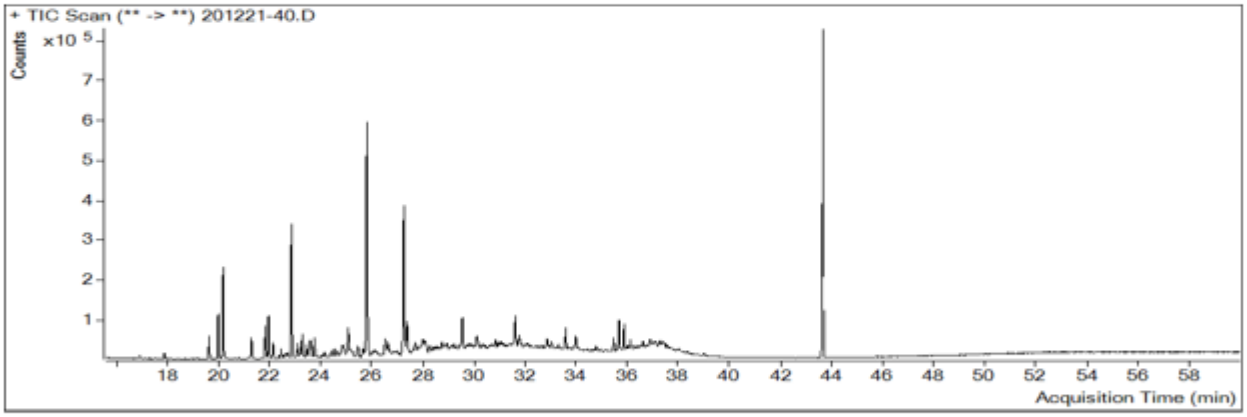
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	0	15	41	58	59	49	56	57	49	18	11	9	175	**597**
1	0	2	11	43	66	71	66	57	36	20	11	6	11	**400**
2				10	34	66	81	64	66	26	13	5	2	**367**
3						6	14	18	10	5	4	0	0	**57**
4 or aromatic			20	2	3	4	4	4	3	1	1	0	0	**42**
5 or aromatic				0	1	0	1	0	0	0	0	0	1	**3**
6 or aromatic							0	4	2	2	0	1	0	**9**
Sum C	**0**	**17**	**72**	**113**	**163**	**196**	**222**	**204**	**166**	**72**	**40**	**21**	**189**	**1 475**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Fluka naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **726,7** mg/L Calculated molecular weight: **212,9** g/mol



Plot of calculated concentration of groups based on area% and m/z

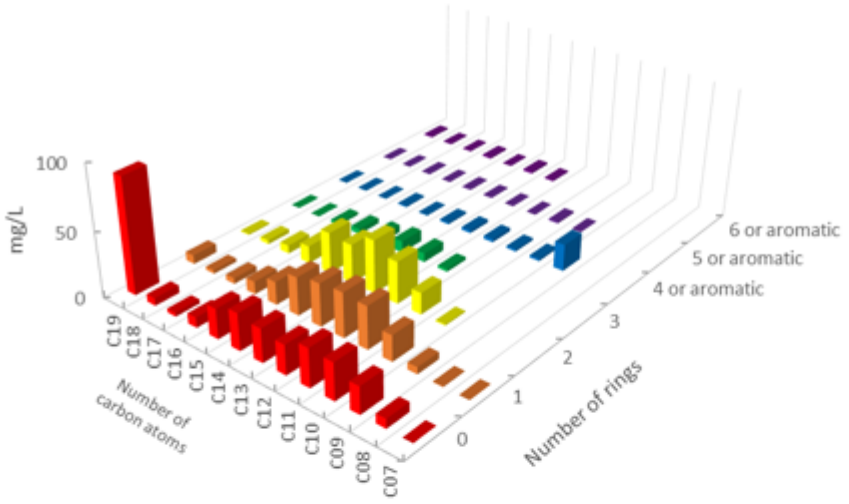


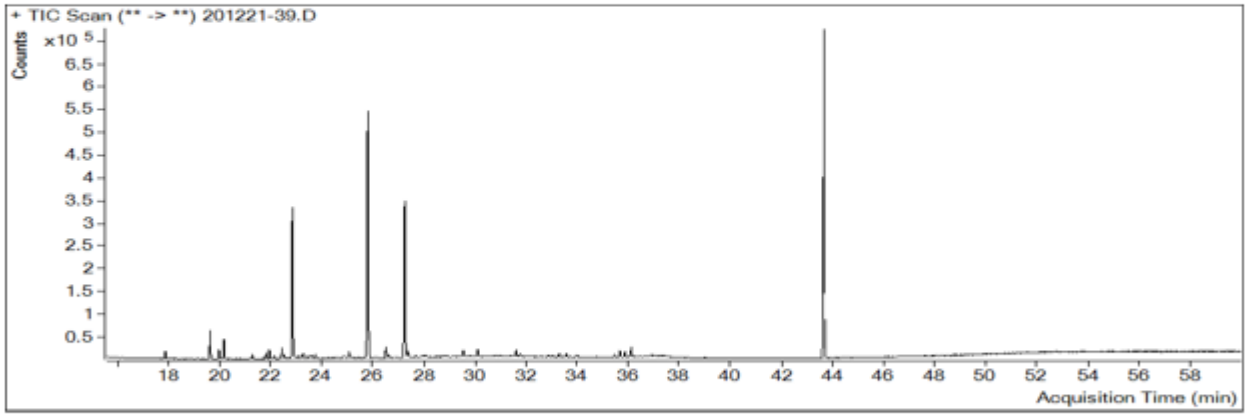
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	0	7	21	28	29	22	25	28	23	8	3	6	89	**289**
1	0	1	5	20	32	34	32	29	17	10	4	3	7	**194**
2				1	16	32	40	29	31	13	6	3	1	**172**
3						2	7	9	6	4	2	0	0	**30**
4 or aromatic			20	2	2	3	2	2	1	1	0	0	0	**33**
5 or aromatic				0	1	0	0	0	0	0	0	0	0	**1**
6 or aromatic							1	2	0	1	0	1	1	**6**
Sum C	**0**	**8**	**46**	**51**	**80**	**93**	**107**	**99**	**78**	**37**	**15**	**13**	**98**	**725**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Fluka naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **174,5** mg/L Calculated molecular weight: **202,0** g/mol



Plot of calculated concentration of groups based on area% and m/z

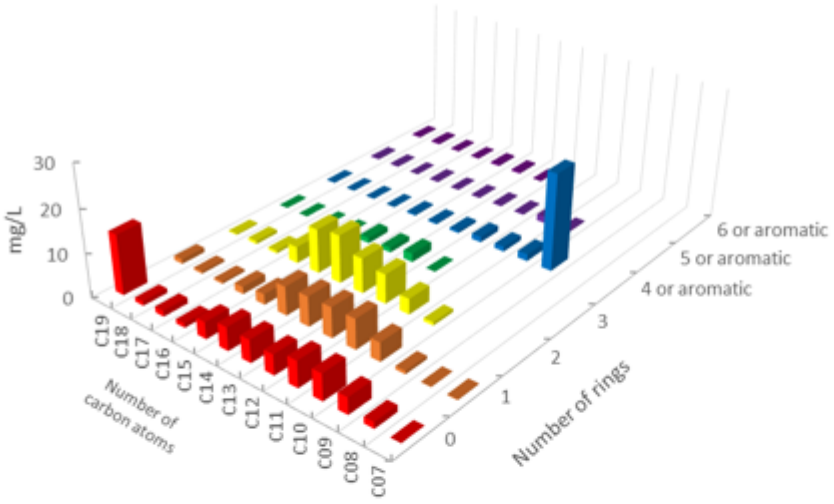


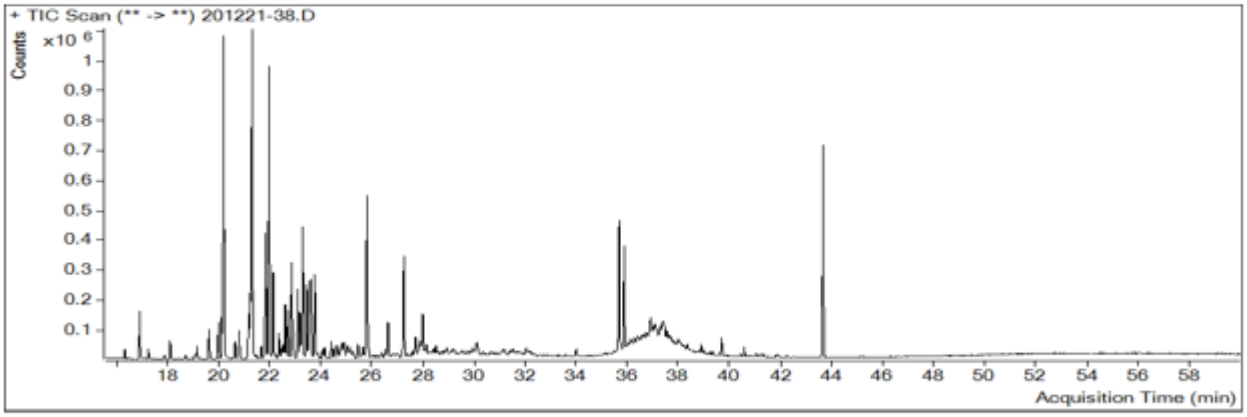
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	0	1	4	6	6	5	5	5	4	1	1	1	14	**53**
1	0	0	1	4	7	7	7	7	2	2	1	1	1	**40**
2				1	4	7	8	11	10	4	1	1	0	**47**
3						0	2	1	1	0	0	0	0	**4**
4 or aromatic			22	2	1	1	1	0	0	0	0	0	0	**27**
5 or aromatic				0	1	0	0	0	0	0	0	0	0	**1**
6 or aromatic							0	0	0	0	0	0	0	**0**
Sum C	**0**	**1**	**27**	**13**	**19**	**20**	**23**	**24**	**17**	**7**	**3**	**3**	**15**	**172**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Acros naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **1 535,2** mg/L Calculated molecular weight: **210,2** g/mol



Plot of calculated concentration of groups based on area% and m/z

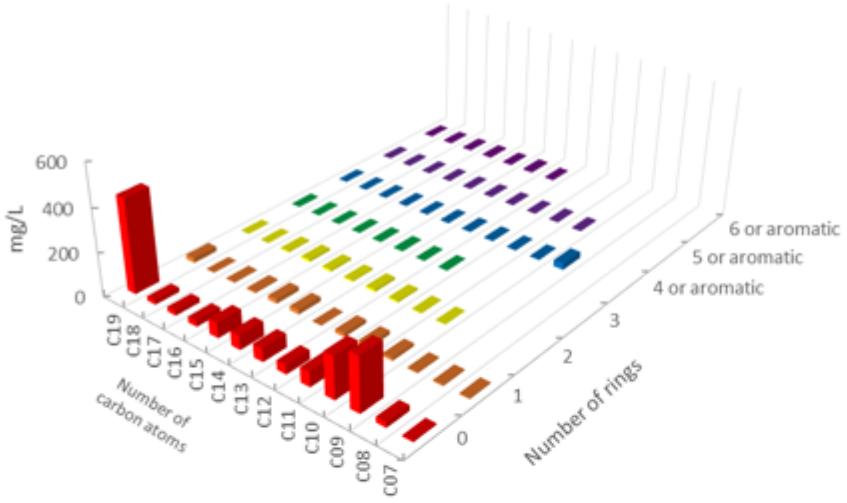


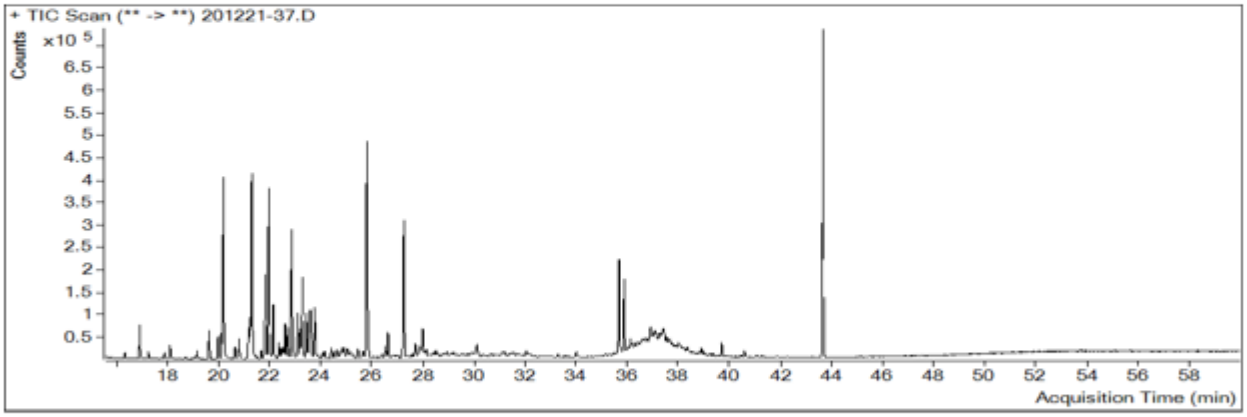
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	6	25	246	191	67	43	62	65	69	27	21	20	433	**1 275**
1	4	5	5	14	18	16	2	21	20	7	4	0	22	**138**
2				2	3	7	11	6	9	10	5	0	0	**53**
3						1	0	3	2	1	0	0	0	**7**
4 or aromatic			29	2	1	2	2	1	0	0	0	0	0	**37**
5 or aromatic				0	1	0	0	1	0	0	0	0	1	**3**
6 or aromatic							1	7	3	5	3	3	1	**23**
Sum C	**10**	**30**	**280**	**209**	**90**	**69**	**78**	**104**	**103**	**50**	**33**	**23**	**457**	**1 536**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Acros naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **685,2** mg/L Calculated molecular weight: **214,3** g/mol



Plot of calculated concentration of groups based on area% and m/z

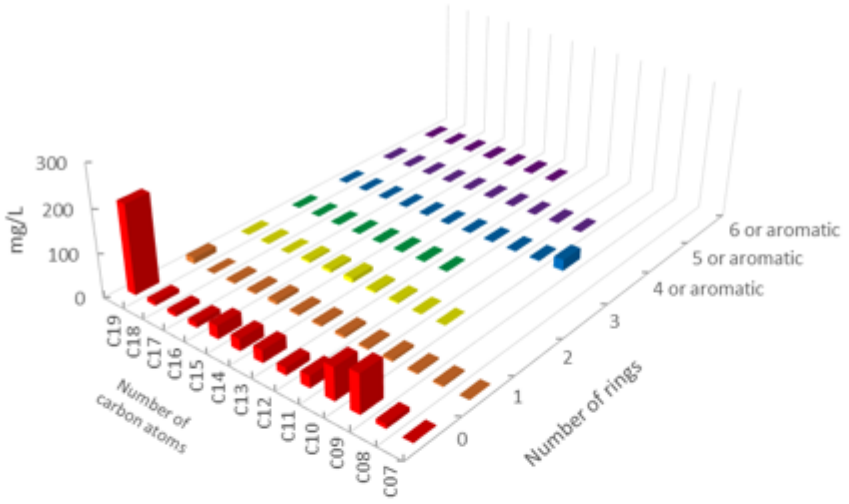


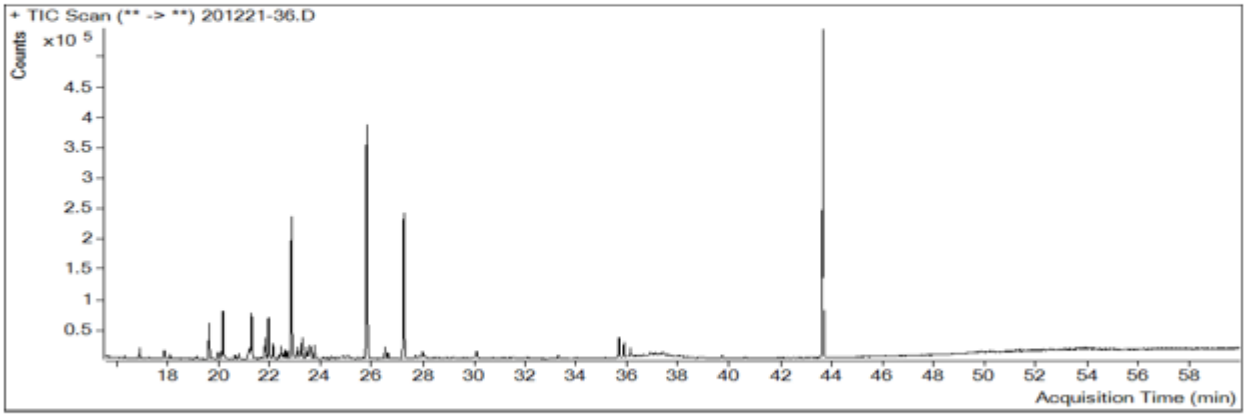
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	1	10	89	74	27	17	29	27	30	12	9	10	206	**541**
1	0	3	3	6	4	6	4	4	8	4	4	0	14	**60**
2				0	1	3	4	10	6	5	0	2	1	**32**
3						0	2	2	1	0	1	0	0	**6**
4 or aromatic			26	2	1	2	1	0	0	0	0	0	0	**32**
5 or aromatic				0	1	0	0	0	0	0	0	0	1	**2**
6 or aromatic							0	3	1	2	1	1	1	**9**
Sum C	**1**	**13**	**118**	**82**	**34**	**28**	**40**	**46**	**46**	**23**	**15**	**13**	**223**	**682**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Acros naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **186,4** mg/L Calculated molecular weight: **202,6** g/mol



Plot of calculated concentration of groups based on area% and m/z

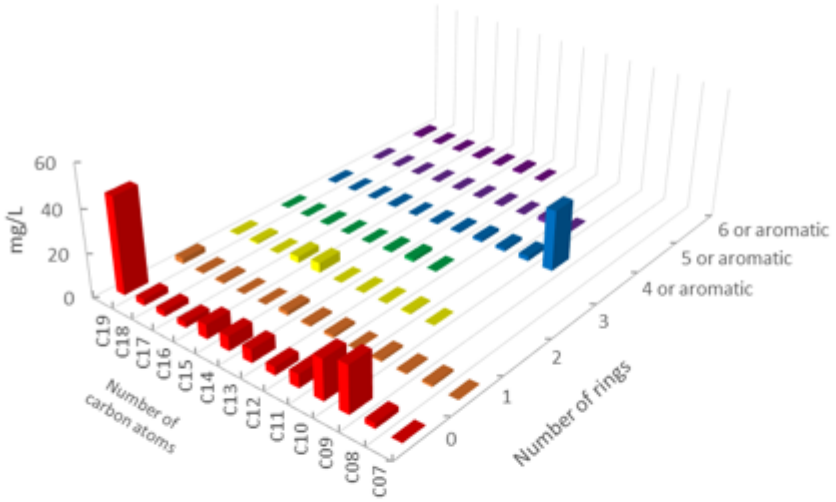


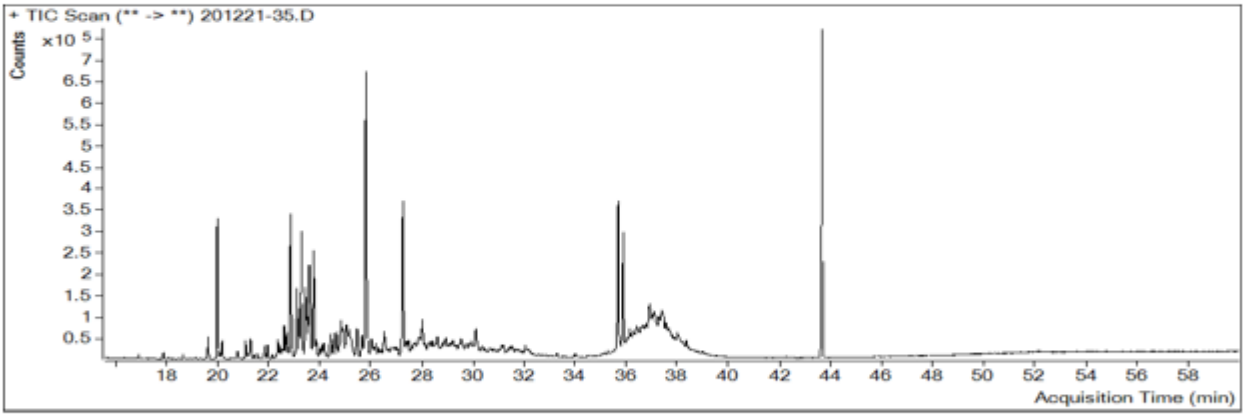
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	0	2	21	18	6	4	6	7	7	3	3	3	45	**125**
1	0	1	1	1	0	1	1	2	0	0	1	1	3	**12**
2				0	0	0	0	0	5	3	0	1	0	**9**
3						0	1	1	0	0	0	0	0	**2**
4 or aromatic			28	2	1	1	1	0	0	0	0	0	0	**33**
5 or aromatic				0	2	0	0	0	0	0	0	0	0	**2**
6 or aromatic							0	1	0	0	0	0	1	**2**
Sum C	**0**	**3**	**50**	**21**	**9**	**6**	**9**	**11**	**12**	**6**	**4**	**5**	**49**	**185**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Sigma naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **992,5** mg/L Calculated molecular weight: **218,4** g/mol



Plot of calculated concentration of groups based on area% and m/z

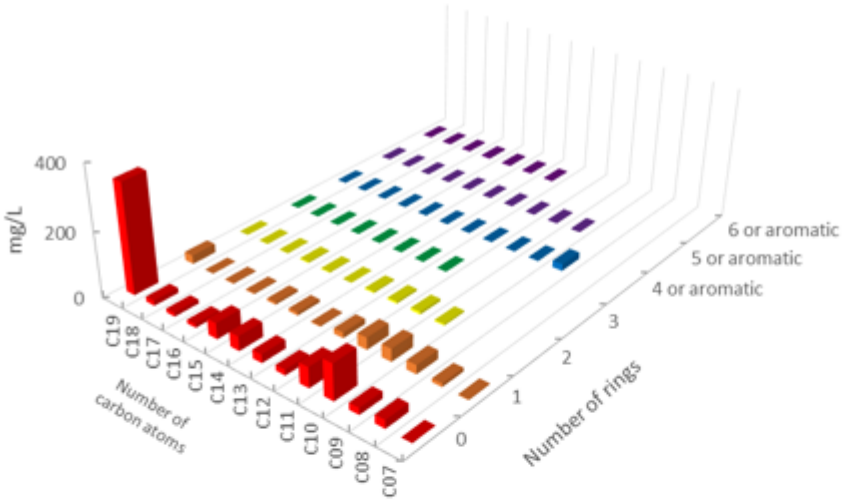


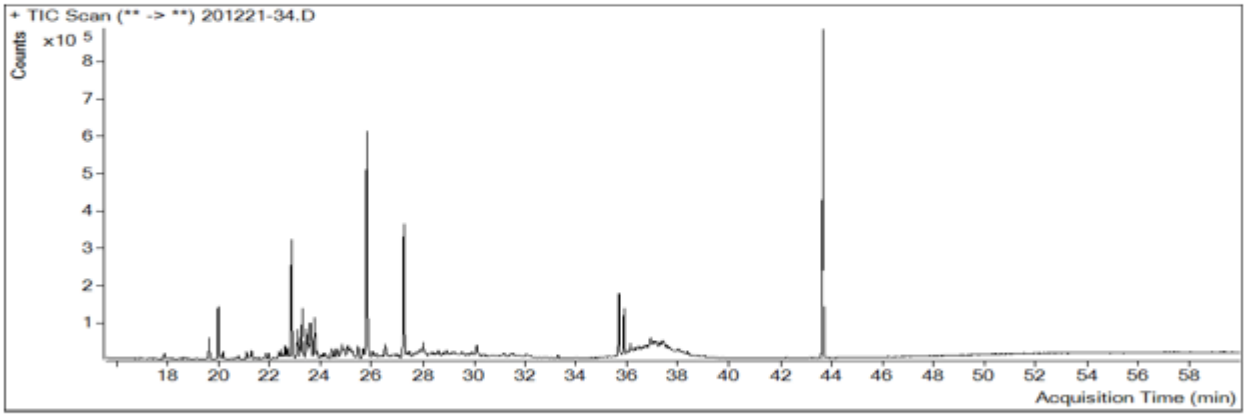
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	1	25	21	109	62	17	26	44	48	12	12	15	339	**731**
1	2	11	27	39	37	17	3	10	7	3	3	1	26	**186**
2				4	8	6	4	0	3	3	1	1	0	**30**
3						0	0	1	1	1	1	0	0	**4**
4 or aromatic			21	2	1	1	1	0	0	0	0	0	0	**26**
5 or aromatic				0	1	0	0	0	0	0	0	0	1	**2**
6 or aromatic							1	3	2	3	2	2	2	**15**
Sum C	**3**	**36**	**69**	**154**	**109**	**41**	**35**	**58**	**61**	**22**	**19**	**19**	**368**	**994**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Sigma naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **437,8** mg/L Calculated molecular weight: **212,8** g/mol



Plot of calculated concentration of groups based on area% and m/z

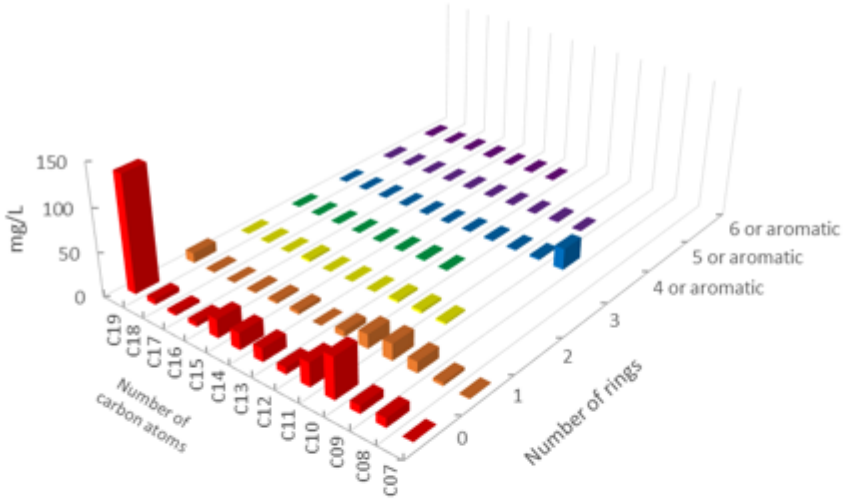


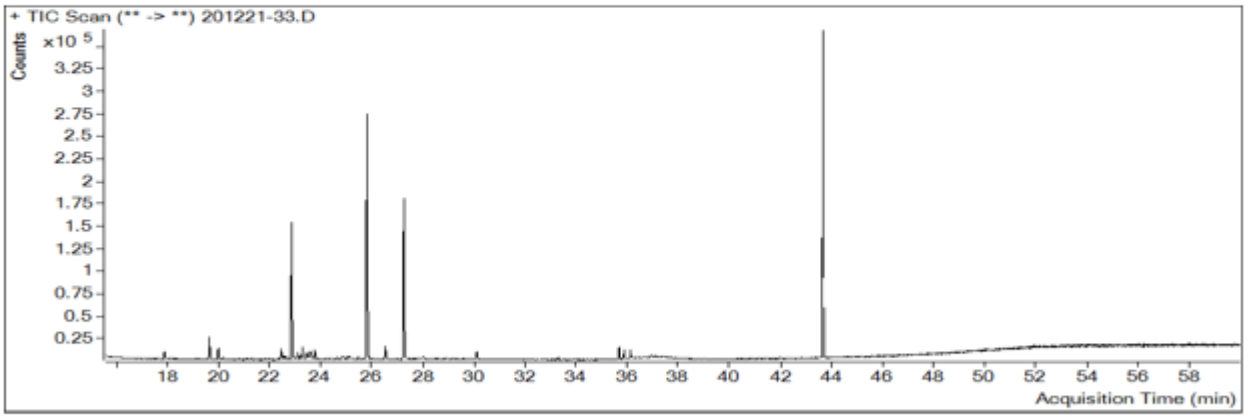
Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	1	10	9	47	27	8	15	19	21	5	3	6	135	**306**
1	1	4	13	19	16	7	0	4	3	1	0	1	11	**80**
2				2	3	2	0	0	0	3	0	1	0	**11**
3						0	1	0	0	0	0	0	0	**1**
4 or aromatic			24	2	1	1	1	0	0	0	0	0	0	**29**
5 or aromatic				0	2	0	0	0	0	0	0	0	1	**3**
6 or aromatic							0	1	0	1	1	0	1	**4**
Sum C	**2**	**14**	**46**	**70**	**49**	**18**	**17**	**24**	**24**	**10**	**4**	**8**	**148**	**434**

Naphthenic acids C7-C19 GC-MS, preliminary report format

Sample name: **Sigma naphthenic acid mixture, derivatized with MTBSTFA**

Measured concentration: **129,7** mg/L Calculated molecular weight: **196,7** g/mol



Plot of calculated concentration of groups based on area% and m/z

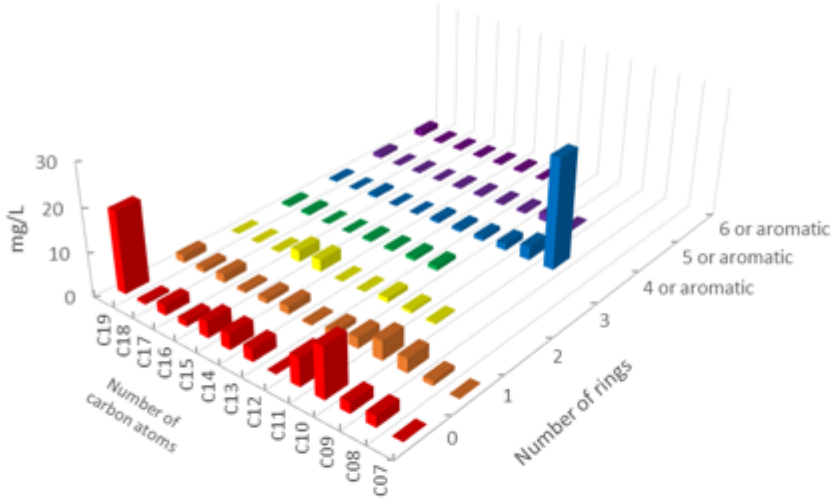


Table of calculated concentration of groups based on area% and m/z

Number of rings	C07	C08	C09	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	# rings
0	0	3	2	12	6	0	3	4	4	1	2	1	19	**57**
1	0	1	3	4	2	1	0	2	1	1	2	1	2	**20**
2				0	1	1	0	0	3	3	0	0	0	**8**
3						1	1	0	0	0	0	1	0	**3**
4 or aromatic			26	3	2	1	1	1	0	0	1	0	0	**35**
5 or aromatic				0	2	0	0	0	0	0	0	0	1	**3**
6 or aromatic							0	0	0	0	0	0	1	**1**
Sum C	**0**	**4**	**31**	**19**	**13**	**4**	**5**	**7**	**8**	**5**	**5**	**3**	**23**	**127**

Appendix B. Equations to calculate naphthenic acid content based on pH

For acids in oil-water systems the partitioning of the non-ionized forms in each phase can be described by,

$$K_{wo,HA} = \frac{[HA]_w}{[HA]_o} \qquad (1)$$

where $K_{wo,HA}$ represent the partition coefficient for an acid. $[HA]_w$ represent the acid concentration in the water phase, and $[HA]_o$ represent the acid concentration in the oil phase. This partition coefficient is independent of the concentration, but consideration should be given as to what species of the compound are being measured, since unaccounted equilibria like dimerization, micellization and hydration can make the measured partition coefficient concentration-dependent [82]. Ionizable compounds like acids require, in addition to the partition coefficient, the dissociation constant in aqueous phase,

$$K_{a,HA} = \frac{[A^-]_w[H^+]}{[HA]_w} \qquad (4)$$

where $K_{a,HA}$ represent the acid dissociation constant, and $[A^-]_w$ is the conjugate base in the water phase.

By accounting for mass balances and excluding other phenomena like micellization, these expressions can be used to obtain expressions for the oil and water concentrations of acids and bases as a function of pH,

$$[HA]_{w,tot} = \frac{[HA]_{o,init}}{\frac{[H^+]}{P_{wo,acid}(K_{a,HA} + [H^+])} + \frac{V_w}{V_o}} \qquad (6)$$

where $[HA]_{o,init}$ represent the initial concentration of acid in the oil phase, and $[HA]_{w,tot}$ represent the sum of dissociated and undissociated acids in the water phase. The terms V_o and V_w denote the volume of the oil and water phase, respectively.

The distribution ratio for compounds which can dissociate in water can be calculated for monoprotic acids with equation 7 [83]. The distribution coefficient accounts for all forms of the compound, both dissociated and undissociated, in the water and organic phase.

$$\log\left(D_{\frac{toluene}{water}}\right) = \log\left(K_{\frac{toluene}{water}}\right) + \log\left[\frac{1}{(1+10^{pH-pKa})}\right] \qquad (7)$$

where $D_{\frac{toluene}{water}}$ represent the distribution of dissociated and undissociated acid in each of the two phases, $K_{\frac{toluene}{water}}$ represents the partition ratio of the undissociated compounds in each phase, pKa represents the dissociation constant of the acid and pH is the water phase pH.

Appendix C. Examples of naphthenic acid masses.

Table 2.29 Mass to charge ratio (m/z) for stable ion fragment of naphthenic acid isomer $C_nH_{2n+z}O_2$ derivatized with MTBSTFA. The stable ion mass fragment obtained with MTBSTFA has a mass of [M+57] where M is the molecular weight of the acid. Some masses are excluded by on the rules set up by Holowenko, MacKinnon [84] except aromatic structures are included here.

	Number of ring structures						
Carbon number (*n*)	0	1	2	3	4 or 1 aromatic ring	5 or 1 aromatic ring and 1 saturated ring	6 or 1 aromatic ring and 2 saturated rings
5	159						
6	173						
7	187	185			179		
8	201	199			193		
9	215	213			207		
10	229	227	225		221	219	
11	243	241	239		235	233	
12	257	255	253	251	249	247	
13	271	269	267	265	263	261	259
14	285	283	281	279	277	275	273
15	299	297	295	293	291	289	287
16	313	311	309	307	305	303	301
17	327	325	323	321	319	317	315
18	341	339	337	335	333	331	329
19	355	353	351	349	347	345	343
20	369	367	365	363	361	359	357
21	383	381	379	377	375	373	371
22	397	395	393	391	389	387	385
23	411	409	407	405	403	401	399
24	425	423	421	419	417	415	413
25	439	437	435	433	431	429	427
26	453	451	449	447	445	443	441
27	467	465	463	461	459	457	455
28	481	479	477	475	473	471	469
29	495	493	491	489	487	485	483
30	509	507	505	503	501	499	497
31	523	521	519	517	515	513	511
32	538	535	533	531	529	527	525
33	552	550	547	545	543	541	539
34	566	564	562	559	557	555	553
35	580	578	576	574	571	569	567
36	594	592	590	588	586	583	581
37	608	606	604	602	600	598	595

Appendix D. Repeated measurements to test the method accuracy

Table 2.30 Parallels of spiked and non spiked samples for produced water experiments performed in Chapter 2.4.3.3. Each row has two samples, one with spike and one without spike. Some pairs of the samples are missing due to laboratory errors during preparation or analysis for either the spiked or non-spiked sample.

	Measured concentration of produced water sample	Measured concentration of produced water sample with spike
A	27	35
A	27	36
A	25	37
A	26	37
B	3.3	19
B	3.4	20
B	2.5	20
B	2.3	19
C	3.4	19
C	3.3	19
C	4.0	19
C	2.6	19
D	5.4	10
D	5.0	9.7
D	5.0	9.8
D	4.5	10
F	45	56
F	46	55
F	41	54
F	44	56
G	3.8	16
G	3.8	17
G	3.9	16
G	2.9	17
i	4.4	9.5

i	4.4	9.3
i	3.7	9.4
i	3.5	9.4

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