University of Alberta

CHALLENGES IN ANALYSIS OF NATURAL SURFACTANTS IN THE OIL SANDS PROCESSING WATER

by

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ABSTRACT

Two major kinds of natural surfactants are released during oil sands extraction: carboxylic acids (naphthenic acids) and sulfonic acids. In this study, commercial surfactants were used as standards to establish the suitable analytical methods with optimized experimental and instrumental parameters. High performance liquid chromatography (HPLC) was utilized in the work to separate individual surfactants in the mixture. For their identification and quantification, naphthenic acids were evaluated by electrospray ionization mass spectrometry (ESI – MS), while sulfonic acids were done by evaporative light scattering (ELS). The developed methods were then extended to the analysis of natural surfactant in oil sands process and tailings water.

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I dedicate this thesis to my parents.

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LIST OF ABBREVIATIONS

CAD	Collision-activated dissociation
CE	Collision energy
CHWE	Clark hot water extraction
CUR	Curtain gas
DCHA	2, 2-Dicyclohexylacetic acid
DCM	Dichloromethane
DP	Declustering potential
ESI	Electrospray ionization
FTIR	Fourier-transform infrared
GC	Gas chromatography
GS1	Nebulizer gas
GS2	Auxiliary gas
HPLC	High performance liquid chromatography
IHE	Interface heater
IS	Ionspray voltage
LA	Lauric acid
LC	Liquid chromatography
M	Mole
MA	Code of an oil sands ore
MCH	1-Methyl-cyclohexnane carboxylic acid
min	Minute

mM	Milli mole
MS	Mass spectrometry
MTBSTFA	N-methyl-N-(t-butyldi-methylsilyl)trifluoroacetamide
NA	Naphthenic acid
NAs	Naphthenic acids
ppm	Parts per million
PW	Process water
RP	Reversed phase
SPE	Solid phase extraction
TPCH	*trans*-4-Pentlycyclohexane carboxylic acid
µL	Micro liter
wt%	Weight percent
v/v	Volume / volume

Chapter 1 Introduction

1.1 Alberta Oil Sands

With declining reserves of conventional crude oil and increasing global demand for oil, oil sands, as a non-conventional resource of oil, become increasingly important. Oil sands deposits in Canada locate in the Athabasca Basin of north-eastern Alberta and Saskatchewan, occupying a total area of 140,200 square kilometers [1]. These deposits are the third largest oil reserves in the world after Saudi Arabia and Venezuela [1], which provides a promising and secure energy supply to North America. Alberta has 171.3 billion barrels of proved reserves that include 169.9 billion barrels of non-conventional crude bitumen and 1.4 billion barrels of conventional crude.

1.2 Recovery Methods

Alberta oil sands are being exploited by means of surface mining techniques and in situ recovery. In commercial practices, surface mining is achieved for oil sands deposits buried less than 65 meters, while in situ recovery is applicable to deposits of more than 200 meters deep [2].

In-situ recovery is a non-upgrading process; that is to extract bitumen from deeper deposits with thermal energy. Steam Assisted Gravity Drainage (SAGD) is one of the commercial in-situ techniques. The process is to reduce the viscosity of bitumen by injecting and circulating the steam down through the

upper horizontal well. The mobilized bitumen in water then drains by gravity to the lower well (oil producer), and is pumped to the surface for further treatment.

Surface mining techniques require removal of overburden material prior to mining oil sands itself. The mined oil sands are processed to extract bitumen by Clark Hot Water Extraction (CHWE) process operating at temperatures above 40 ^{o}C in the extraction plants [3, 4]. This process utilizes caustic (NaOH) to enhance the bitumen recovery by promoting the separation of bitumen from other components of oil sands such as sand, clay, inorganic metals, and organic compounds including indigenous carboxylic and sulfonic surfactants [3-5]. Currently, in Alberta the majority of bitumen production employs surface mining technique, which requires clearing of large area of land, sufficient supply of river water, and giant on-surface facilities. As of December 2009, 1,518 out of 4,800 square kilometers mineable land has been explored in Alberta [1]. In practice, one cubic meter of surface-mined oil sands requires about three cubic meters of river water to process, and produces approximate four cubic meters of fluid tailings that require substantial cost-driven water treatment and reclamation [6].

1.3 Oil Sands Tailings

After bitumen is extracted from surface-mined oil sands by means of CHWE, the resulting fluid tailings are discharged in on-site tailings ponds [7]. The fluid tailings are made up of water, sands, clays, solids, left-over hydrocarbons,

organic compounds, and inorganic salts [8]. The coarse solids settle down very rapidly and form dykes and beaches of tailings ponds. The top layer of tailings ponds is “solid-free” clarified water called tailings water. This water is recycled back to oil sands processing and accounted for up to 90 percent of a company's water use, which significantly reduces the demand of fresh river water [2]. The middle layer contains suspended fine solids, and undergoes very slow settling process that may take three to five years. As of zero discharge policy by the Alberta Environmental Protection and Enhancement Act (1993), over a billion cubic meters of oil sands fluid tailings will be accumulated in on-site tailings ponds by the year of 2020 [9].

1.4 Natural Surfactants

Natural surfactants are produced in the reaction of oil sands with caustic (NaOH), and released into tailings water of tailings ponds. They are known to promote the efficiency of bitumen extraction in Clark Hot Water Extraction (CHWE) by increasing the detachment of bitumen from mineral sands and production of bubbles for flotating bitumen to the froth product. Schramm *et al*. observed that an optimal surfactant concentration in process water led to best bitumen recovery in poor processing oil sands ores. Mikula *et al*. further proved that the optimal bitumen recovery corresponded to the maximized partitioning of surfactants leached from bitumen in the water phase. There are two major kinds of natural surfactants that are speculated to be released: carboxylic type and sulfonic type [4]. Carboxylic type surfactants are termed

naphthenic acids, while sulfonic type refers to sulfonic acids [10]. Naphthenic acids, accounting for as high as 3 wt% in crude oil, are considered as the most environmental threats if left in process water and discharged due to their toxicity [11]. It is reported that naphthenic acids are toxic to aquatic species (lethal concentration LC_{50} < 10%, v / v, in rainbow trout [12]), mammals (lethal concentration LC_{50} = 3.0 g / kg body weight as a symptom of convulsions leading to death [13]), and human (lethal dosage LD_{50} = 11 g kg^{-1} body weight [14]). High concentrations of naphthenic acids in the fresh oil sands tailings ponds water are also verified to undergo a very slow biodegradation process [15]. This makes the water treatment and land reclamation more challenging. In addition, due to the fact that the tailings water in tailings ponds is reused in the oil sands extraction process, the corrosion caused by naphthenic and sulfonic acids in tailings water becomes the major concern to the oil production facilities [16].

1.5 Thesis Objectives

As introduced in Sections 1.1 to 1.4, in order to protect the environment and minimize negative effect of tailings water, it is a must for oil sands companies to be able to evaluate natural-occurring surfactants for the sustainable usage of water and land. To better understand what molecular structures of surfactants, as well as how much of surfactants release into oil sands tailings for environmental monitoring and government regulation, it is critical to have techniques sensitive to distinguish and determine surfactants in tailings water.

This project aims at developing an analytical method to quantitatively characterize and analyze individual natural surfactants (naphthenic acids and sulfonic acids) in the process and tailings water of oil sands extraction. The detailed tasks of this study are as follows:

Naphthenic acids

- Establish a method of high performance chromatography coupled with mass spectrometry (HPLC – MS) with commercially available compounds.
- Apply the developed method to oil sands process and tailings water.

Sulfonic acids

- Develop a method of high performance chromatography equipped with evaporative light scattering (HPLC – ELS)
- Apply the method to oil sands tailings water.

1.6 Thesis Structure

This thesis is divided into four chapters. Chapter 2 concentrates on naphthenic acids analysis. It describes the development of HPLC – MS method with four standard compounds: 1-methyl-cyclohexane carboxylic acid (MCH), trans-4-pentylcyclohexane carboxylic acid (TPCH), lauric acid (LA) and 2, 2-dicyclohexylacetic acid (DCHA). The application of SPE is introduced as a sample preparation strategy when dealing with oil sands process water and

tailings water. Chapter 3 focuses on sulfonic acids analysis. The working parameters of HPLC – ELS method are optimized with the standard compounds: 4-ethylbenzenesulfonic acids and sodium 1-decanesulfonate. The developed method is evaluated with oil sands tailings water. Chapter 4 summarizes conclusions as well as the future work to address significance of this work.

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Chapter 2 Naphthenic Acids

2.1 Introduction

Naphthenic acids (NAs) cover a wide range of aliphatic and alicyclic carboxylic acids found in hydrocarbon reserves (oil sands bitumen and conventional crude oils). The general formula of NAs is $C_nH_{2n+Z}O_2$, where n represents the carbon number and Z indicates the number of hydrogen atoms lost because of cyclization [1]. The Z value is integer (can be zero or negative even numbers, e.g., –2, –4, –6, etc.). Figure 2-1 lists example structures of NAs. The carboxyl functional group (O=C–OH) of NAs is bonded directly with alkyl side chains, single / multiple rings, or single / multiple rings through alkyl side chains [2-4].

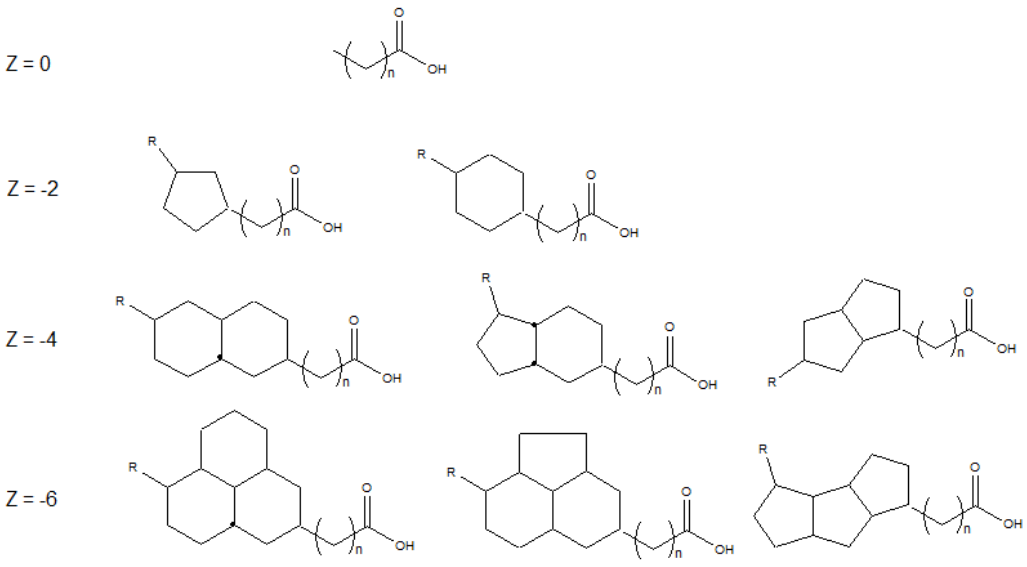


Figure 2-1 Structure of selected naphthenic acids, where R is an alkyl group, and n represents the carboxyl side-chain length.

NAs are weak acids with pKa of 5 to 6. They contribute up to 50% by weight of the total acids in crude oil [5]. NAs are considered as significant environmental pollutants due to their toxicity to aqueous organisms and mammals [6]. NAs naturally exist at concentrations below 1 ppm in North Alberta rivers (e.g., Athabasca River) [7]. However, they are concentrated in the processes of recovering bitumen from mined oil sands as well as recycling tailings water back to extraction. The concentrations of NAs is normally from 40 mg L^{-1} to as high as 120 mg L^{-1} [8]. There are a number of reasons for the high concentration of NAs, including the formation of micelles in aqueous environment during the bitumen flotation, or solubility increase with increasing pH of the processing water [2, 5, 9]. In addition, recent investigations established that the concentrations and complexity of NAs vary with oil sands ores and tailings ponds. The exact chemical make-up of real NAs samples is often unknown [10]. As illustrated above, the qualitative identification and characterization of individual NAs are challenging.

In this work, we employ high performance liquid chromatography to separate a mixture of NA compounds, and electrospray ionization – mass spectrometry (ESI – MS) to identify and quantify these NA compounds. A sample preparation technique – solid phase extraction (SPE) was also discussed and implemented in order to reduce or eliminate the negative impact of interfering species to the NAs signals in oil sands process water as well as tailings water.

2.2 Literature Review

A thorough literature search has revealed that various analytical techniques have been employed for characterization and quantification of naphthenic acids. There are two ways to analyze NAs: determination of total NAs concentrations and characterization of individual NAs. They are discussed and evaluated further in details in the following section.

2.2.1 Determination of Total NAs Concentration

Fourier-transform infrared (FTIR) spectroscopy and gas chromatography – mass spectrometry (GC – MS) after sample derivatization are the two methods that measure the total concentration of NAs in the early stage of studying NAs.

The FTIR spectroscopy is a commonly adopted method for detection of NAs in tailings water due to its easy use in "oil-phase detection" of NAs [11], and is currently used as industry standard method by Syncrude [12]. It involves extraction of NAs from tailings water by liquid-liquid extraction method, followed by measurement of NAs with FTIR. The solvent used in liquid-liquid extraction is dichloromethane (DCM) instead of ethyl acetate to eliminate the tendency of hydrolyzing complex NAs by ethyl acetate [13]. Samples of tailings water are first centrifuged to remove the particles and solids, and then acidified to pH 2 by H_2SO_4, and followed by extraction with DCM in a 1:2 solvent : sample mass ratio at temperatures below 5^oC [13]. The organic phase extracts were concentrated by centrifugation. After reconstitution of NAs extracts with

organic solvent, the samples are ready for FTIR detection and measurement. The infrared absorption bands for both hydroxyl (−OH) and carbonyl groups (−C=O) of carboxylic acids are at frequencies of 3200 to 3600 cm^{-1} and 1700 cm^{-1}, respectively [14]. Grewer *et al*. specified the strong infrared absorption and intensities for monomer and dimer forms of carbonyl groups at frequencies of 1743 and 1706 cm^{-1} [15]. The carbon-hydrogen vibration of carboxylic acids is measured at frequencies of 2850 to 3000 cm^{-1} and 1350 to 1450 cm^{-1} [14]. A previous study reported a 0.5 ppm detection limit of NAs with FTIR [16]. FTIR method is a semi-quantitative method that is based on the IR absorbance of the carboxylic groups to measure the total concentration of naphthenic acids [17]. It usually overestimates the concentration of NAs due to the existence of carboxylic groups of non-NAs in tailings water [11, 16, 17].

The method using conventional GC – MS with derivatization involves multiple steps, including NAs extraction, derivatization, GC separation and MS detection. The pH 2 acidified samples are extracted from chloroform / DCM by liquid-liquid extraction, and then derivatized by N-methyl-N-(t-butyldi-methylsilyl) trifluoroacetamide (MTBSTFA) to the form of methyl-, methyl-tert-butylsilyl-, or tri-methylsilyl-esters [18]. The strategy of NAs derivatization provides thermal stable compounds that can improve chromatography separation and MS detection, enhancing the reproducibility of the results [19]. The total concentration of NAs is easily calculated by integrating the area under peaks in chromatogram. With the GC – MS method, the detection limit was elevated to

approximately 0.01 ppm [16, 20]. However, the GC – MS approach requires extensive sample preparation steps (extraction and derivatization), and cautions have to be taken to avoid the esters hydrolysis [19].

2.2.2 Characterization of Individual NA Compounds

As the rapid development of liquid chromatography technique, the application of high performance liquid chromatography (HPLC) coupling with mass spectrometry (MS) has emerged to be an attractive tool for quantitative determination of certain NAs in a mixture. Pervious researches have established a method of "direct" MS injection, which means there was no LC separation prior to MS. Headley *et al.* suggested in his work that high- and ultra-high-resolution MS are amenable to NAs characterization after comparing against low-resolution MS [19]. Several publications reported direct MS analysis of complex mixture of NAs by high and ultra-high resolution MS [9, 13, 21]. However, there were some technical difficulties present in the "direct" analysis. (1) NAs are not ionized with equal efficiency without LC separation so that not all NAs can be sufficiently resolved by high throughput MS. (2) Ion suppression generated by both analytes and matrices would significantly decrease the detection sensitivity. For example, in a mixture of NAs, only some NAs with high concentrations and / or high ionization efficiencies could be preferentially ionized and detected if no separation was performed before MS source. Matrix, such as metal cations, other surfactant species, and other neutral product etc., may also suppress NAs signals during ionization. Therefore, prior to MS

detection, sufficient separation of the NAs in the sample mixture is required in the study.

2.2.2.1 High Performance Liquid Chromatography (HPLC)

HPLC is a separation technique based on differential partition and adsorption of analyte interacting with stationary phase packed in a column. The surface chemistry of stationary phases, usually modified silica, determines the separation mechanisms within the column. In analysis and identification of an individual NA in a mixture, the most common type of columns used is reversed phase (RP) column. The separation mechanism includes following: NAs molecules are first adsorbed onto non-polar functional groups of stationary phase, such as C8 and C18, through hydrophobic forces; and then desorbed and eluted by modified organic solvents (mobile phase) when applied to column. With different component of the mobile phases (usually called "gradient" as for reversed phase – the ratios of organic modifier (e.g. methanol) increases as time increases), adsorbed molecules with different hydrophobicity will be desorbed at different time. The characteristic retention time of NAs reflects their property difference. It is well illustrated by Wang *et al.* that gradient HPLC elution method was able to separate inorganic salts from the acids without any sample pre-treatment (e.g., extraction step). Therefore, LC technique can be directly coupled with MS for NAs analysis. The species other than interested would be eliminated, which significantly increases the selectivity of the method [11].

2.2.2.2 Mass Spectrometry (MS)

MS is a state of art analytical technique providing high sensitivity, resolution, and selectivity. It analyzes charged species (ions, molecules or atoms) with mass to charge ratio. The mass resolution is from 1 Dalton to 0.0X Dalton depending on the instrumentation. The analyte species are first ionized and vaporized in the region of mass spectrometer ion source. Those ions are then sorted and separated in a mass analyzer, such as quadrupole or ion trap. The separated ions are measured and converted to a mass spectrum.

2.2.2.2.1 Ionization Method – Electrospray Ionization (ESI)

Electrospray ionization (ESI) is a common ionization technique for MS which produces highly charged fine droplets directly from a liquid medium at atmospheric pressure in an electric filed [22]. It encompasses three processes as described by Tang *et al* [23] and schematically shown in Figure 2-2: (1) Formation of charged droplets through an electrospray tip under high electric fields; (2) Shrinkage of charged droplets due to solvent evaporation by flowing drying gas (e.g., Nitrogen); and (3) Formation of gaseous ion "emitted" from charged liquid droplets flowing to a mass analyzer under high potential. Electrospray ionization is able to continuously produce multiply charged ions with the mass range below 2500 Da [24]. However, it has more stringent requirements for salts and other contaminants due to competition for either the limited surface space or limited charge available on ESI [25].

There are two operating ion modes in ESI: positive (protonated) and negative (deprotonated) ion mode. In the analysis of NAs, negative-ion mode is widely used. That means NAs are detected in the form of deprotonated ions. The negative-ion mode offers several advantages: (1) NAs are weak acids that are relatively easy to lose hydrogen ions (H^+); (2) The negative-ion mode produces relatively little fragmentation of the deprotonated ions, which gives relatively clean spectra [21]; and (3) It also gives greater sensitivity of detecting carboxylate anions [19].

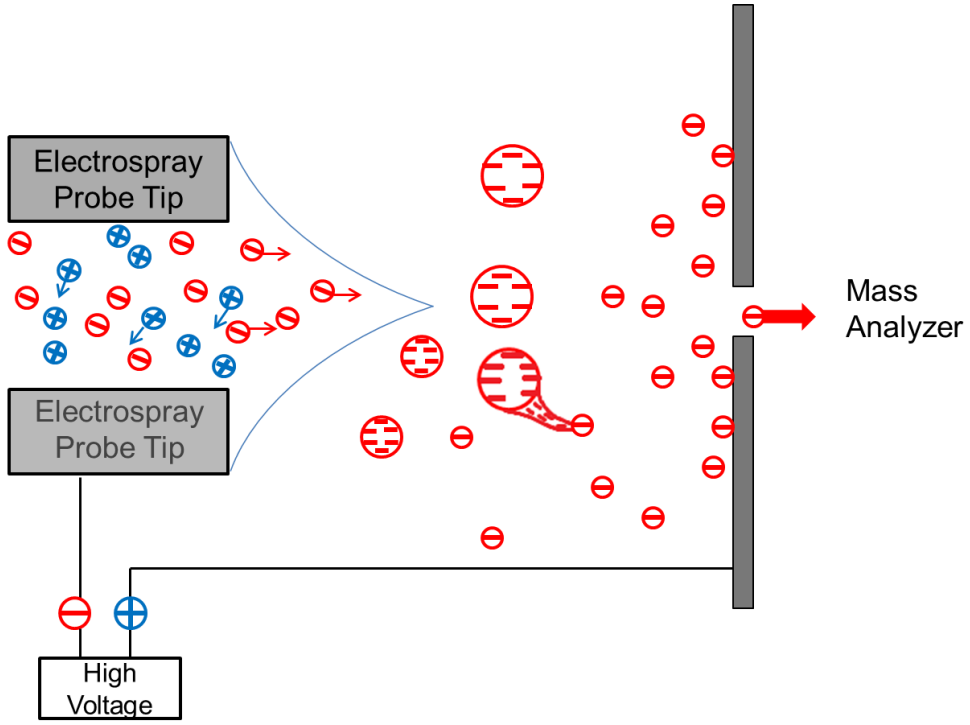


Figure 2-2 Process of electrospray ionization (ESI) in negative ion mode

2.2.2.2.2 Mass Analyzer – Triple Quadrupole and Ion Trap

Triple Quadrupole

Triple quadrupole mass analyzer consists of three quadrupoles (Q_1, Q_2 and Q_3) in series. Each quadrupole is composed of two pairs of opposing cylindrical rods that electrically connected (Figure 2-3). A radio frequency (RF) and direct current (DC) voltage are applied to the pairs of rods, and continuously varied to select the ions of interest (based on mass-to-charge ratio). The ions of interest having stable trajectories travel down the quadrupole and reach the detector. The rest of ions are deflected, and collide on the rods. Quadrupole has two important characteristics that make it most widely used. (1) As large amount of ions can be removed effectively, quadrupole can be used as mass filter; (2) By applying RF-only voltage, quadrupole is able to scan and transmit ions of all m/z values. This feature makes quadrupole serve as a lens to focus and transmit ions without required filtering. Thus, it can be combined with ion trap and function as collision cells in QTRAP® LC/MS/MS mass spectrometer.

Ion Trap

An ion trap mass analyzer consists of a ring electrode and two end-caps (Figure 2-4). When electric potential is applied, a hyperbolic electric field is created inside the chamber. The ions from ESI (source region) are introduced to the hyperbolic field, and sequentially ejected from the trap to the detector. The ion trap has an advantage of accumulating, fragmenting and analyzing ions in one

chamber, but at different times. This approach is to significantly increase its scanning sensitivity compared to the triple quadrupole [26].

QTRAP® LC/MS/MS

The QTRAP® LC/MS/MS system is a hybrid mass spectrometer that combines the advantages of triple quadrupole and ion trap mass analyzers within the same platform. As described above, there are Q_1, Q_2 and Q_3 in the triple quadrupole. In QTRAP, the Q_3 region can be operated either as a quadrupole mass filter or as a linear ion trap. This hybridization offers several advantages over either a conventional triple quadrupole or a conventional ion trap: higher ions trapping efficiencies, higher resolution, and higher ion capacity [26].

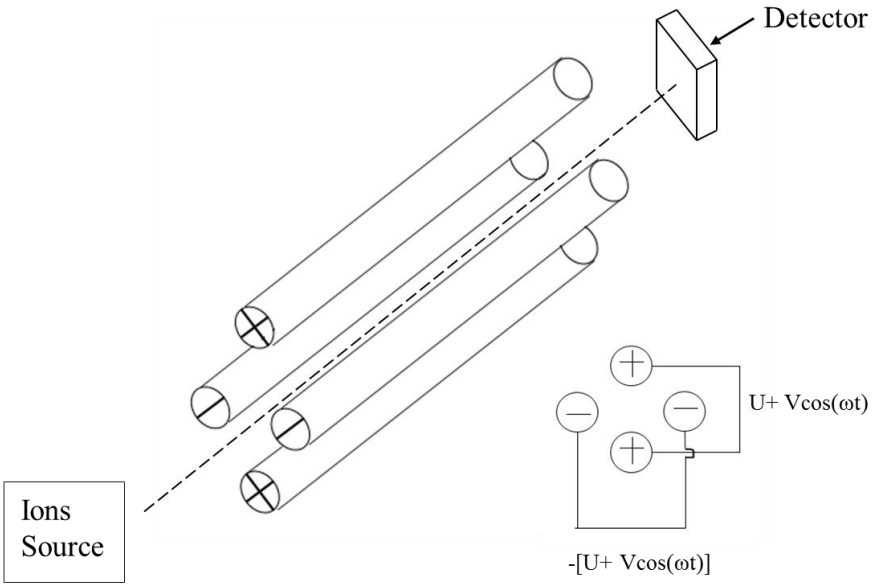


Figure 2-3 Schematic representation of the quadrupole mass analyzer.

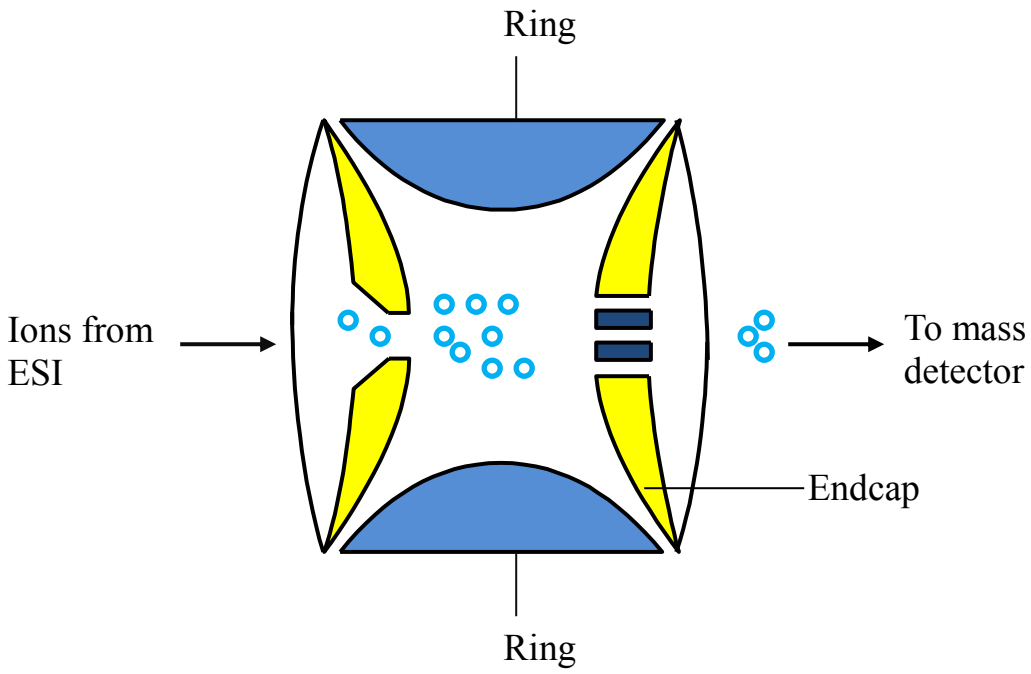


Figure 2-4 Schematic of ion trap mass analyzer.

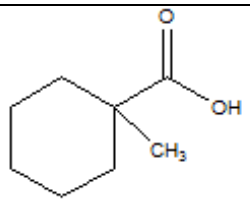
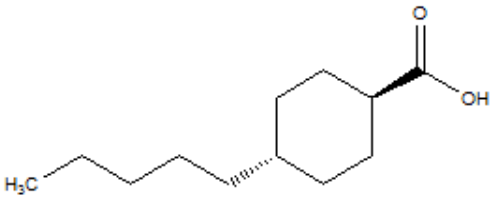
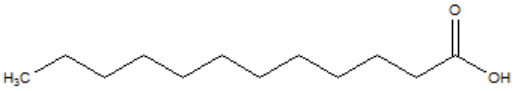
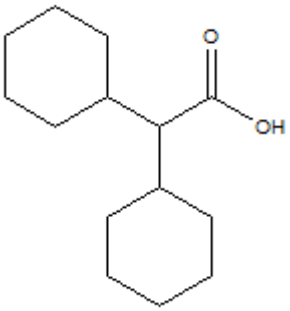
2.3 Experimental

2.3.1 Chemicals and Reagents

Except otherwise noted, all experiments were carried out at pH 7. Four individual commercial available NA standard compounds were considered as model NAs ($C_nH_{2n+Z}O_2$) for method development and validation. They are 1-methyl-cyclohexane carboxylic acid (MCH, Sigma Aldrich), lauric acid (LA, Sigma Aldrich), *trans*-4-pentylcyclohexane carboxylic acid (TPCH, Sigma Aldrich), and 2, 2-dicyclohexylacetic acid (DCHA, Sigma Aldrich).Their structures and molar mass are given in Table 2-1. Regent grade sodium hydroxide (Fisher Scientific), acetic acid (Sigma Aldrich) and sodium hydroxide (Fisher Scientific) were used as pH modifiers. Optima® grade methanol and water (Fisher Scientific), and ammonium acetate (Sigma Aldrich) were used as HPLC mobile phase.

The Oil sands ore (MA) received from Syncrude Canada Ltd. was selected in this study. It was stored in dark at –30^{o}C to minimize aging effect. The compositions were analyzed by Dean Stark, and listed in Table 2-2. Process water (PW) was used to extract bitumen from oil sands. It was from Aurora Mine of Syncrude Canada Ltd with ion concentrations listed in Table 2-3.

Table 2-1 List of NA model compounds studied.

Model Compounds	Molar Mass (amu*)	Structure
1-Methyl-cyclohexane carboxylic acid (MCH)	142.1	 n = 8, Z= –2
trans-4-Pentylcyclohexane carboxylic acid (TPCH)	198.2	 n = 12, Z= –2
Lauric acid (LA)	200.2	 n = 12, Z= 0
2,2-Dicyclohexylacetic acid (DCHA)	224.2	 n = 14, Z= –4

*amu: atomic mass unit

Table 2-2 Composition of MA oil sands ore (wt%).

Feed	Hydrocarbons	Solids	Fines*	Water
Oil Sands	**8.2**	**83.5**	**15.3**	**8.3**

* Fines are defined as weight percent of mineral solids finer than 44 microns.

Table 2-3 Electrolyte concentration in Aurora process water (ppm).

	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}	HCO_3^{-}
Process Water	**34.6**	**18**	**19**	**565**	**336**	**35.3**	**371**	**583**

2.3.2 Preparation of NA Standard Compound Stock Solutions

The stock solutions of 100 ppm standard NAs were prepared in different composition of methanol / water mixture. A set of standard solutions with concentrations of 5, 10, 15, 25 ppm was then prepared by diluting the stock solutions.

2.3.3 NAs in Real Sample

2.3.3.1 Collection of Tailings Water

Tailings water was generated from oil sands processed in process water. The laboratory extraction tailings water was obtained by batch floatation using a Denver cell. A schematic diagram of the modified laboratory Denver cell used

in this study is shown in Figure 2-5. Five hundred grams of oil sands along with 900 mL of processing water (with caustic addition) were placed in one liter flotation cell connected to a thermal water bath at a set temperature of 45^{o}C. The agitation was set at 1500 rpm to condition the slurry without aeration for 5 minutes. After conditioning, air at 150 mL min^{-1} was introduced into the slurry for 10 minutes, liberated bitumen to the froth on the top of the slurry, leaving the solids and water in the cell at the bottom. The middle aqueous phase, so called tailings water, was then collected.

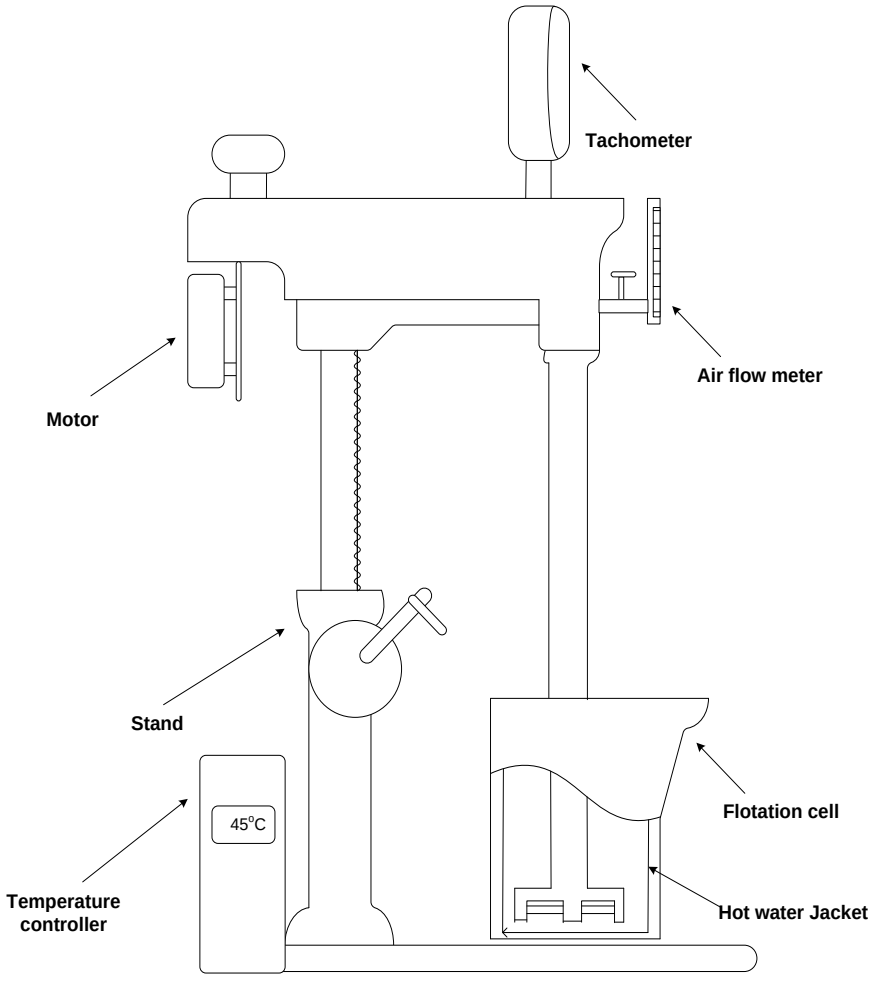


Figure 2-5 Schematic diagram of Denver Cell.

2.3.3.2 Preparation of NAs in Real Sample

NAs are rich in oil sands tailings water. After settling the collected tailings water for 24 hours at room temperature of 20^{o}C, it was centrifuged at 11,500 rpm for 30 minutes, and filtered through 0.1 µm filters three times. The tailings water after removal of solids / fine was sampled and mixed with various ratios of methanol.

2.3.4 Solid Phase Extraction

Solid phase extraction (SPE) is a sample preparation technique to extract, purify and concentrate analyte compounds from liquid mixtures. Compared with liquid-liquid extraction method, SPE offers many advantages, such as complete phase separation, less solvent / time consumption, automation, etc. In this study, the application of SPE was to reduce the amount of potential interfering substances present in real samples that could deteriorate HPLC separation and MS detection.

SPE of NAs in real samples was performed on a 24-port vacuum manifold using Phenomenex® Strata™-X-AW (3 mL / 30 mg, 33 µm, weak anion-exchange) SPE cartridges as shown in Figure 2-6. The SPE cartridge is a short open tube column containing solid sorbent material. The sorbent material has suitable chemical structure (Figure 2−7) that well retains weak acidic compounds in three different interaction mechanisms: weak anion exchange, $\pi - \pi$ bonding,

and hydrophobic interaction. The effective parts of the structure are shown in red in Figure 2-8. The procedure of SPE is schematically summarized in Figure **2-9** and described in details as follows.

(1) Conditioning: Condition the sorbent of Strata™-X-AW cartridge by passing 1 mL of methanol. By doing this, the functional groups of sorbent material are solvated.

(2) Equilibrating: Equilibrate with 1 mL Milli-Q water. The role of equilibration is to maximize the efficiency and reproducibility of analyte molecule retention, and minimize the amount of impurities that will be washed off at the stage of eluting analyte acids [27].

(3) Loading: Adjust sample pH to 7 with acetic acid, and load 2 mL of sample solution to the conditioned and equilibrated cartridge. The acid molecules will be absorbed on the sorbent material, while impurities will not be retained and washed through the column with the solvent under the vacuum.

(4) Washing: Wash cartridge with 2 × 500 µL of 25 mM ammonium acetate, followed by 1 mL methanol to remove the last trace of impurities.

(5) Eluting: Elute acids with 2 × 500 µL 5% NH_4OH in methanol, and collect in a 2 mL sample tube.

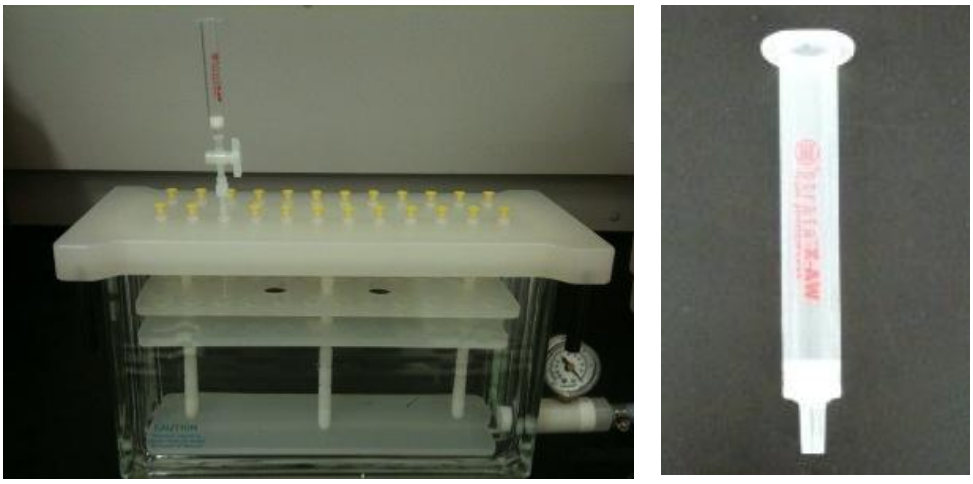


Figure 2-6 Schematic diagram of an SPE experiment and Phenomenex® Strata™-X-AW cartridge.

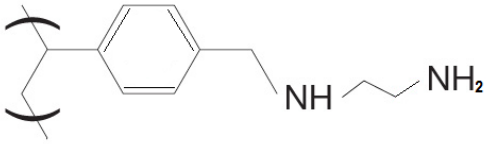


Figure 2-7 Chemical structure of Strata™-X-AW sorbent.

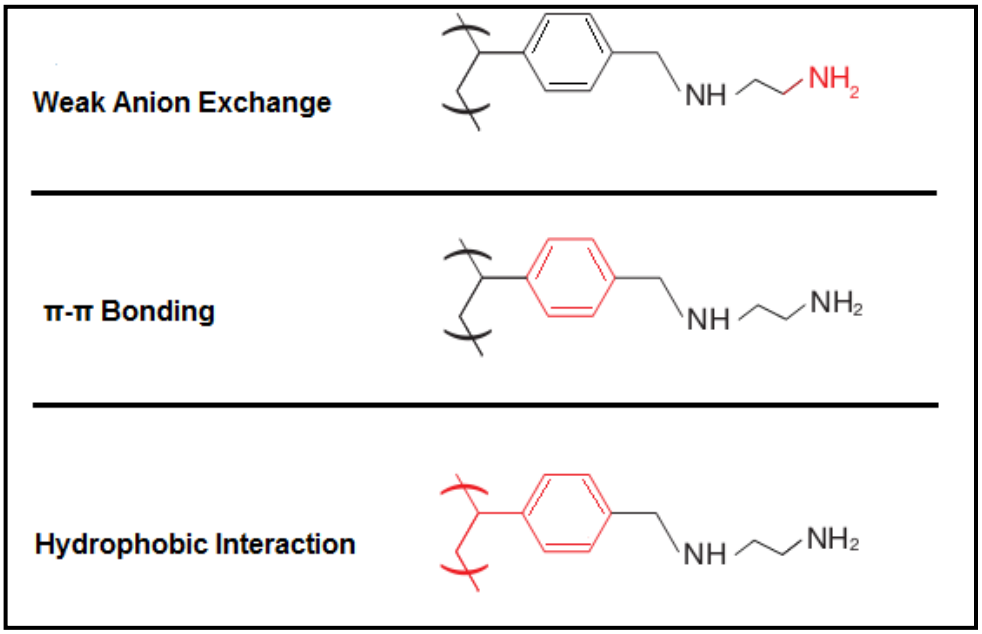


Figure 2-8 Three mechanisms of sorbents to retain weak NAs, shown by red structures.

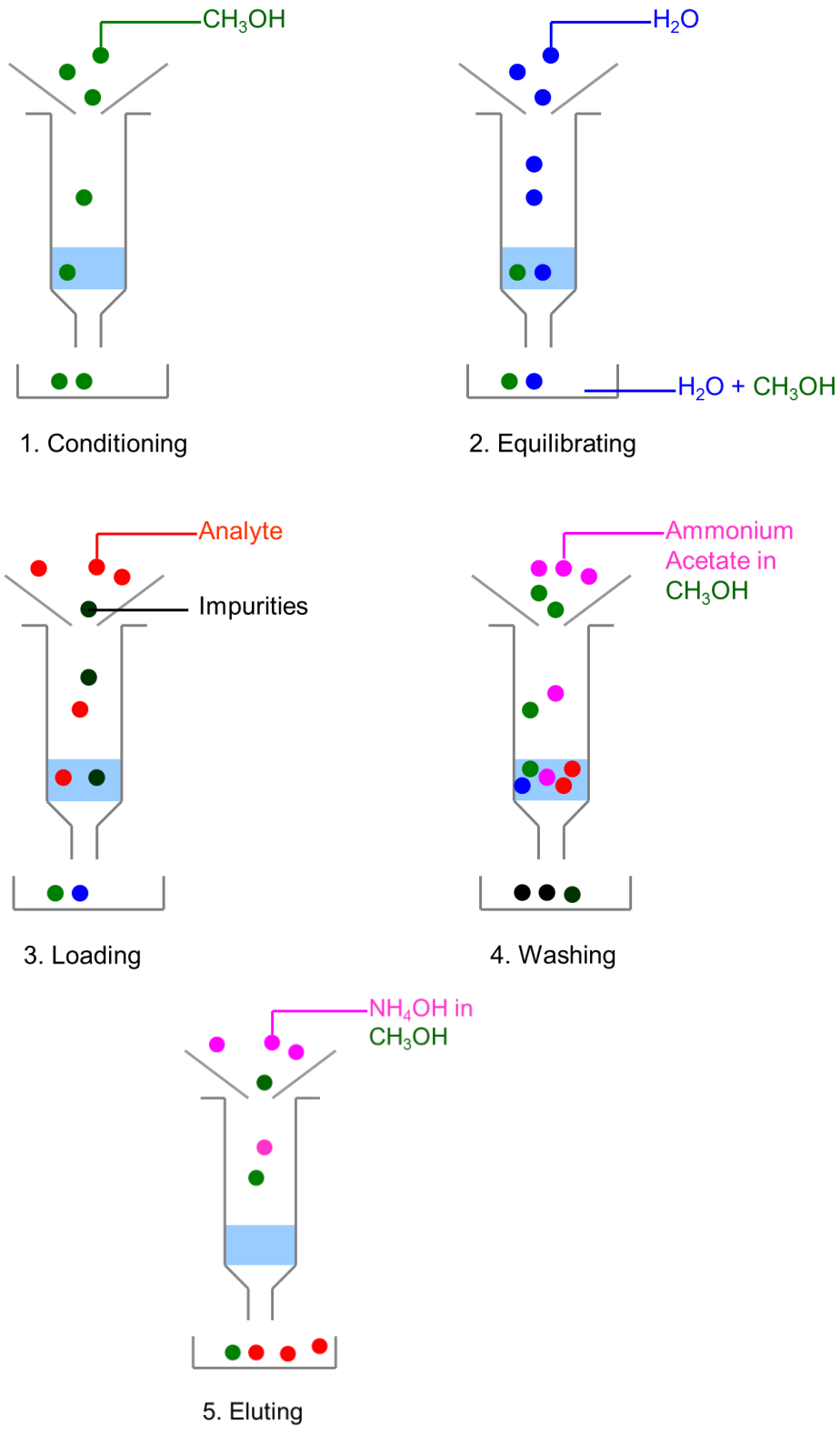


Figure 2-9 Diagram for solid phase extraction.

2.3.5 Liquid Chromatography

Chromatographic separation in this study was carried out on Agilent® 1290 Infinity LC system consisting of autosampler, column compartment and binary solvent pump. The LC system is given schematically in Figure 2-10. The mobile phase used was (A) 5% methanol and 10 mM ammonium acetate in Optimal®-grade water, and (B) methanol. The gradient elution started by maintaining 30% B for 6 minutes, increasing to 100% B over a period of 44 minutes, and back to 30% B holding for 10 minutes to re-equilibrate the column and clean the sample injection needle before next sample injection. The total run time was 60 minutes per sample. Two microliter of a sample aliquot was injected into the reversed phase column, Zorbax® Eclipse XDB C8, with a size of 2.1 × 150 mm and 5 µm particle sidze. The sample was separated and eluted at a flow rate of 250 µL min^{-1}. The use of gradient elution removed most of inorganic salts in the first five minutes of the run, which significantly reduced the chances that inorganic salts enter MS and block the electrospray probe [11].

2.3.6 Electrospray Ionization – Mass Spectrometry (ESI –MS)

Quantitative analysis of NAs was conducted on 4000 QTRAP® LC/MS/MS System (Applied Biosystems, Foster City, CA, USA) equipped with a Turbo V™ ion source given in Figure 2-11. The mass spectrometer was operated in negative electrospray ionization (ESI) mode with enhanced MS full scan (m/z 50 – 800) at a rate of 1000 Da s^{-1}. The deprotonated NAs were detected over the

concentration range of 0 to 25 ppm (e.g., NAs: $R–CO_2H \rightarrow R–CO_2^- + H^+$). Typical mass spectrometer conditions are listed as follows: curtain gas (CUR), 10.0 L min^{-1}; collision-activated dissociation (CAD) gas, high; ionspray voltage (IS), –4500.0 V; source temperature, 500°C; nebulizer gas (GS1), 40 L min^{-1}; auxiliary gas (GS2), 30 L min^{-1}; interface heater (IHE), on; declustering potential (DP), –45.0 V; collision energy (CE), –10.0 V. The total duty cycle was 1.162 s. Data were collected in profile mode and interpreted by Analyst 1.5 Software (Applied Biosystems).

Figure 2-10 Agilent® 1290 Infinity LC.

Figure 2-11 ABSciex QTRAP® 4000.

2.4 Results and Discussion

2.4.1 Column Selection

Four NA standards were chosen as model compounds for this study because they are well defined and commercially available. They also represent a high degree of specificity (different value of m and Z to represent various molecular structures of NAs). NAs are polar and non-volatile compounds. For this type of compounds, the reversed phase column is best fit for liquid chromatography separation. In this work, reversed-phase bonded Zorbax® Eclipse XDB C8 (Agilent) was selected over Zorbax® Eclipse Plus C8 (Agilent). According to Wang *et al*. [11], Zorbax® Eclipse Plus C8 (Agilent) has previously been used and proved to have an excellent separation, reduced peak tailing, and negligible cationic effect in analyzing NA as compared with Aquasil C18 (Thermo) and

Hydro-RP C18 (Phenomenex). However, XDB C8 was a more amenable column, and offers more advantages over Plus C8: lower cost, wide usable pH range (2 – 9), excellent retention and selectivity for mixtures of polar and moderate polar acidic compounds, and lower operating backpressures which provide longer column lifetime.

All four standard compounds were loaded to XDB C8 column, and their chemical composition was determined with the molecular weight detected by the mass spectrometer. It proved that XDB C8 column does not retain these four standard NAs as no specific masses were found in MS spectrum of the blanks (90% methanol solution) before and after running NA standards. The elution order and retention time of four standard compounds from HPLC are listed in Table 2-4. The results in this table indicate that the column selected is able to effectively separate these compounds within a reasonable time period. Even though LA and DCHA are eluted closely from column at 34.32 and 34.35 minutes, the mass spectrometer detector is able to distinguish them by their different molecular weight.

Table 2-4 Retention time of four standard compounds.

Standard Compounds	**MCH**	**TPCH**	**LA**	**DCHA**
Ion Detection [M–H] (amu*)	141.1	197.2	199.2	223.2
Retention Time (minute)	11.91	31.26	34.32	34.35

*amu: atomic mass unit

2.4.2 Optimization of Pre-column Loading Condition

A mixture of methanol and water (v/v) was used as solvent to dissolve NAs. In order to effectively dissolve NAs prior to injection into the column, the pre-column loading condition was examined to evaluate methanol concentration that would give a higher detection signal. It was found that all four standard compounds were completely soluble in more than 75% methanol - water (v/v) mixture prior to being loaded to the column. Therefore 80%, 90% and 100% (v/v) methanol concentrations of the mixture were selected to optimize the HPLC pre-column loading condition. Figure 2-12 shows the HPLC pre-column loading condition of standard compounds dissolved in 80%, 90% and 100% (v/v) methanol solution. The general trends show that standard compounds dissolved in 100% (v/v) methanol solution have the lowest peak areas due to the use of the reversed phase column. A reversed phase column is usually packed with modified silica beads (stationary phase) which have hydrophobic interaction with analytes. Methanol is a strong eluent to the reversed phase column because it would break the van der Waals force between analyte and stationary phase. Even though the column was equilibrated at 30% methanol, the higher amount of methanol in the sample would “disturb” this equilibrium so that not 100% of analytes would be retained on the column and eluted off later for MS detection. Thus the responded peak areas in 100% methanol solution are lowest. As compared with 100% (v/v) methanol solution, standard compounds in 80% and

90% (v/v) methanol loaded in the column give similar results of larger peak areas. However, 90% methanol loading condition of TPCH standard compound shows more symmetric peak shape as shown in Figure 2-13. In addition, it is known that there are hundreds of NAs, some of NAs require a higher volume ratio of methanol to be dissolved, and all NAs are completely soluble in 100% methanol [11]. In order to widely apply the method to future analysis of other NA compounds, 90% (v/v) methanol was selected as pre-column loading condition for the study. All the experiments in the following sections were performed by using 90% methanol to dissolve the standard compounds, unless otherwise mentioned. It should also state that pH of sample solutions has no impact to the analysis technique as 90% methanol (organic solvent) utilized can completely dissolve standard NAs even though they precipitate in aqueous phase at lower pH.

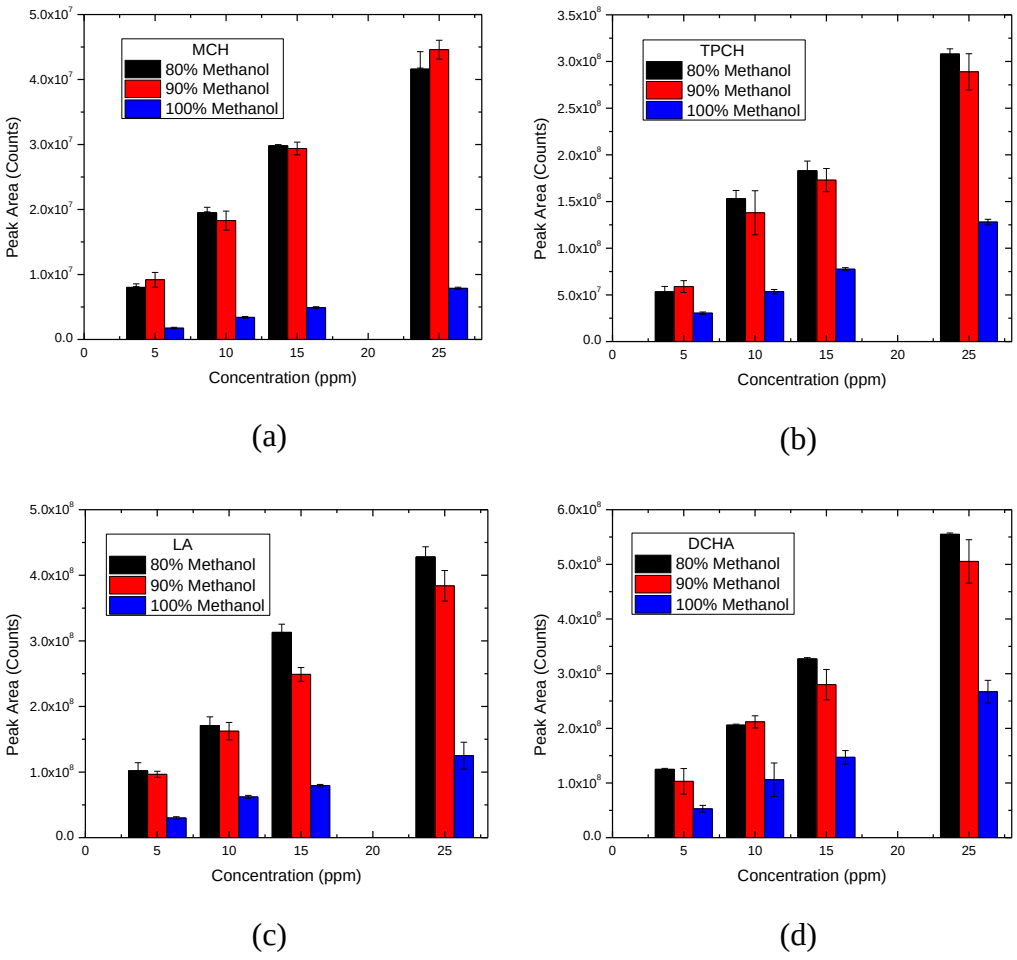


Figure 2-12 Signal intensity of HPLC column loading condition of (a)1-methyl-cyclohexane carboxylic acid (MCH); (b) *trans*-4-pentylcyclohexane carboxylic acid (TPCH); (c) lauric acid (LA); (d) 2,2-dicyclohexylacetic acid (DCHA) in 80%, 90% and 100% methanol solutions.

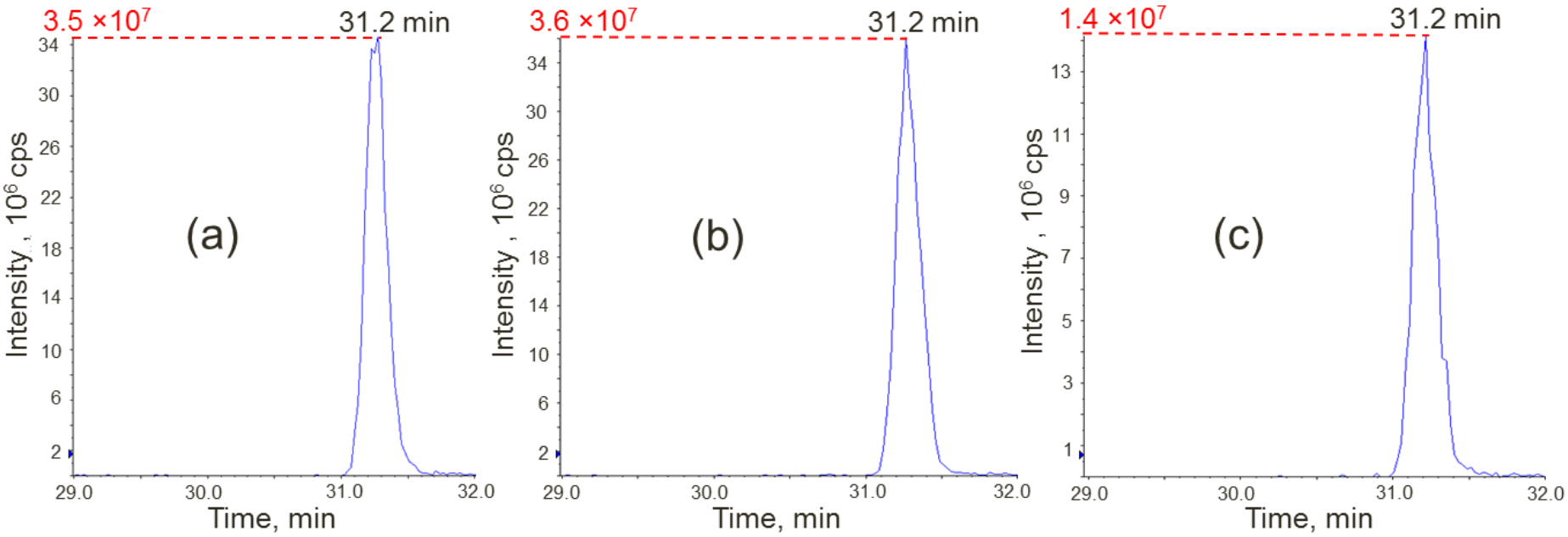


Figure 2-13 Mass spectra of TPCH extracted at elution time of 31.2 minute, dissolved in (a) 80% methanol, (b) 90% methanol and (c) 100% methanol.

2.4.3 Mixture and Individual Analysis in Milli-Q Water

NAs in tailings water are a complex mixture of surface active natural carboxylic acids. To determine whether we can identify and determine NAs in a complex mixture or in tailings water, all four standard compounds were mixed together and analyzed. The results were compared with those obtained in individual NA solutions.

Figure 2-14 shows that peak areas of both individual and mixture solutions agree within error, which indicates that there is no significant difference to run the standards in the individual condition or the mixing condition. The results suggest the absence of any interactions between the standard compounds or the method is insensitive to those interactions if they do exist. The finding here suggests that the standard calibration curve can be made using solutions of NAs mixture, which will reduce the man powder for preparation of individual NA standard solutions, and minimize contaminants and / or sample losses, improving reproducibility. Since each sample run in HPLC – MS takes about one hour, effective use of the instrument time becomes very important. Most importantly, the real NAs samples are always a mixture of hundreds of NAs. Therefore, a mixture of NA standards was chosen for the subsequent analysis.

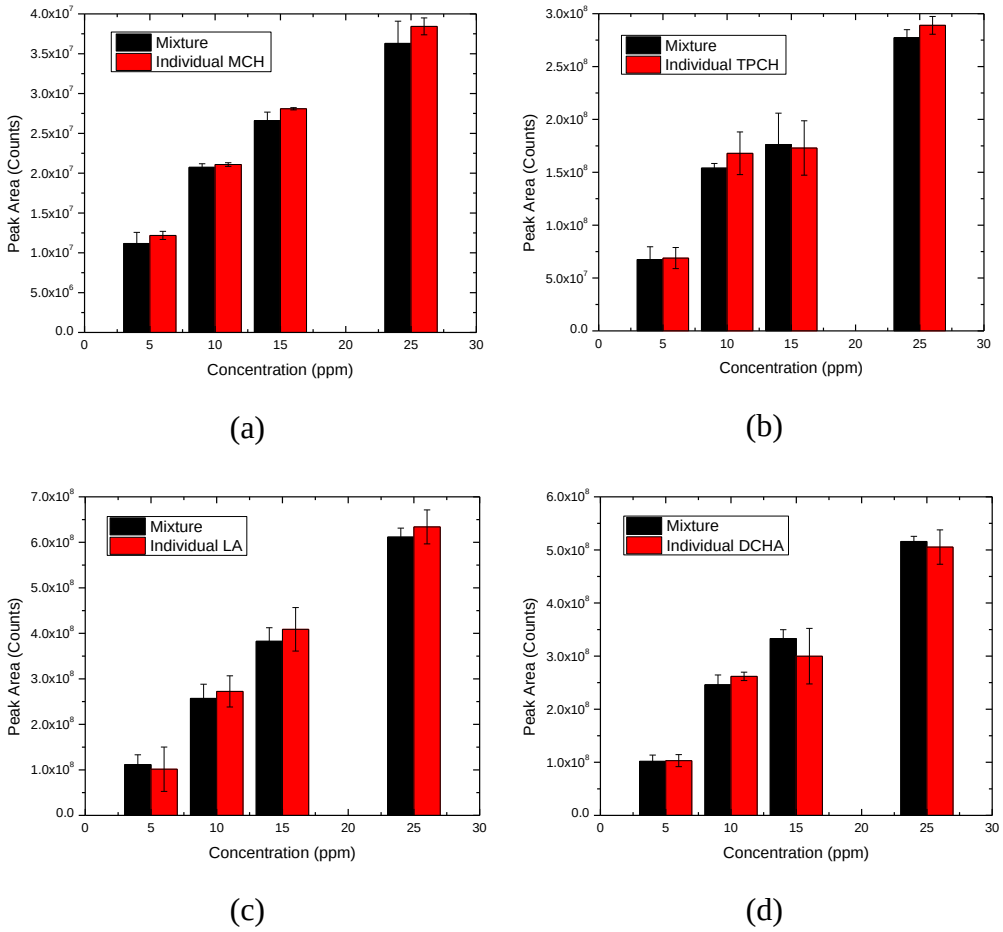


Figure 2-14 Signal intensity of mixture and individual NAs solutions. (a) 1-methyl-cyclohexane carboxylic acid (MCH); (b) *trans*-4-pentylcyclohexane carboxylic acid (TPCH); (c) lauric acid (LA); (d) 2, 2-dicyclohexylacetic acid (DCHA).

2.4.4 Counter Ions Effect

In water-based bitumen recovery process, oil sands are processed with caustic (NaOH) in process water. Both oil sands and process water usually contain magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions. However, mass spectrometry is a well-known technique that high concentration of inorganic salt in the sample will significantly reduce the intensity of signals. To examine the effect of salts in samples on MS signal, a specific amount of magnesium (Mg^{2+}) and calcium (Ca^{2+}) was intentionally added to the mixture of standard compounds, and their signal intensities were compared with those without the addition of counter ions. The concentrations of Mg^{2+} and Ca^{2+} prepared were 18 ppm and 40 ppm, respectively, which are the typical ion concentrations in laboratory generated oil sands tailings water. The signal intensities obtained from pure standard solutions and from solutions containing the given concentration of salts were compared in Figure 2-15. It is evident that Mg^{2+} and Ca^{2+} have no effect on the signal of the standard compounds.

It should be stated that the negative ESI mode of MS is unable to detect the calcium and magnesium dimmers formed with NA ions because these dimmers are all positively charged. The general chemical structures of calcium and magnesium dimmers are given in Figure 2-16. It appears that the negatively charged NA ions are not easy to bond with calcium and magnesium cations as the HPLC mobile phase of ammonium acetate provides a large amount of ammonium cations (NH_4^+) that compete with calcium (Ca^{2+}) and magnesium

(Mg^{2+}) cations to bond with NAs anions. As a result, their binding eliminates the formation of calcium and magnesium NA dimmers in the solution, and hence the interference with the analysis of NAs.

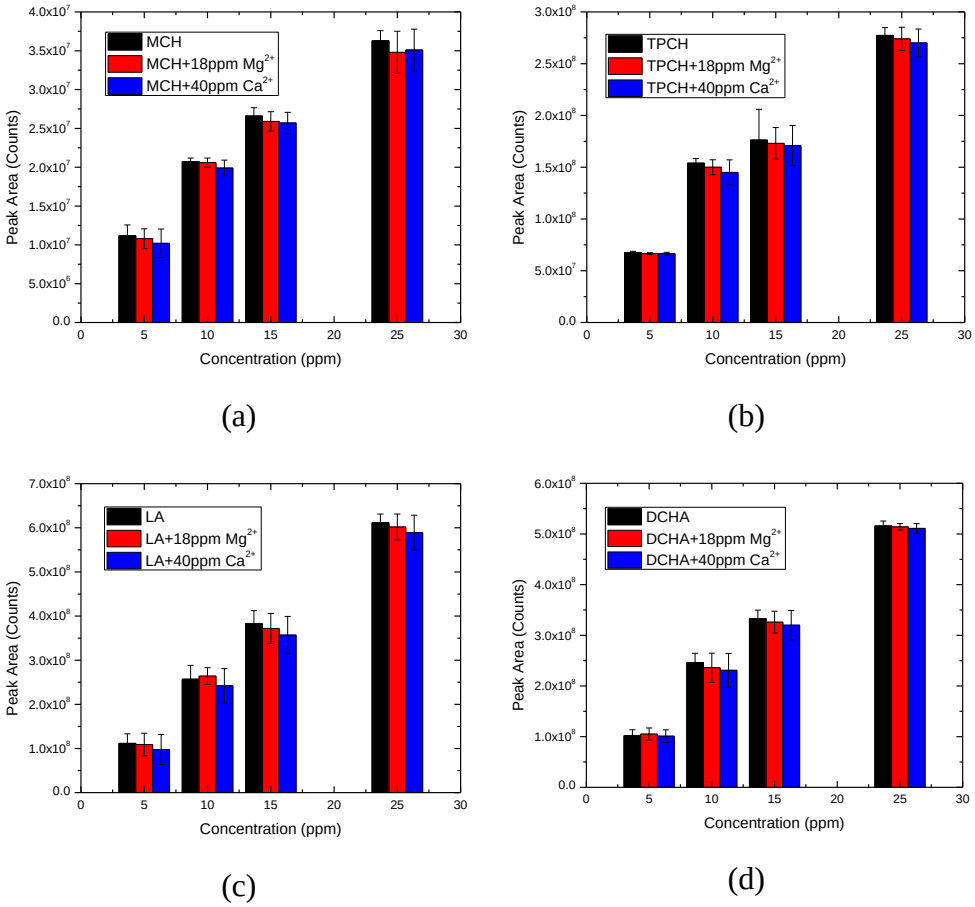


Figure 2-15 Effect of $Mg^{2+}$and Ca^{2+} on analysis of standard NAs. (a) 1-methyl-cyclohexane carboxylic acid (MCH); (b) *trans*-4-pentylcyclohexane carboxylic acid (TPCH); (c) lauric acid (LA); (d) 2, 2-dicyclohexylacetic acid (DCHA).

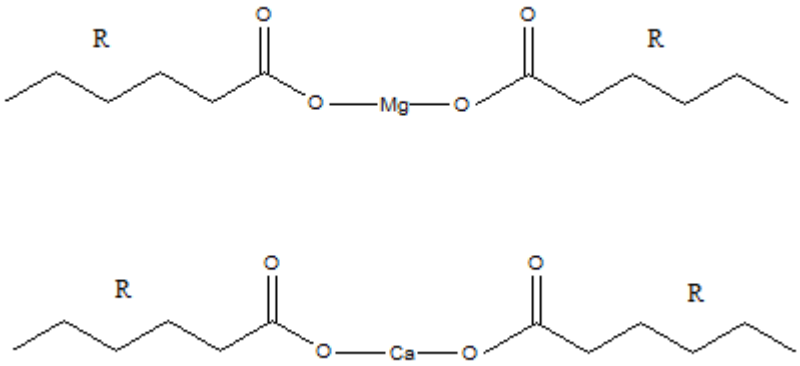


Figure 2-16 Chemical structure of dimmers formed by calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations with anionic NAs ($R–COO^{-}$) in solution.

2.4.5 Effect of Process Water

So far we only tested the situation that standard compounds were dissolved in the mixture of pure HPLC grade methanol and pure Milli-Q water. However, in the industrial oil sands processing, river water is utilized as liquid medium to extract bitumen from oil sands. NAs are released into the process water during this process. It is well known that the process water before and after extraction contains a large number of anionic surfactants other than naphthenic acids (e.g., sulfonic-functional surfactants) [28], counter ions and other unknown ionic species. The existence of those ions may cause major difficulties in quantitative analysis of NAs with ESI – MS, as they could substantially affect the performance of the method (e.g., linearity, dynamic range, reproducibility, and accuracy) by possible ion suppression [29]. Ion suppression refers to as a phenomenon that the probability of detecting analyte

ions in MS is reduced by the presence of other ions dominating the mass spectrum in a mixture [30]. In this case, other surfactants might have strong tendency to interfere with the detection of naphthenic acids molecules in MS, and could possibly suppress their response signals in the ionization process, resulting in poor performance of MS. Therefore, the presence of ion suppression was carefully considered and evaluated in this study. Figure 2-17 shows mass spectra of standard compound TPCH dissolved in the methanol / Milli-Q water solution and methanol / process water solution. The MS peak shape in both solutions stays the same, but the peak height is relatively low in the methanol / process water solution. (It is noted that process water itself (blank) also was analyzed by HPLC – MS, but no MS signal for the mass of TPCH was obtained, which means there was no TPCH in my process water sample). Full range calibration curves for four model compounds dissolved in the solution of Milli-Q water in 90% methanol (pure solvent) and process water in 90% methanol (matrix solvent) are shown in Figure 2-18. It is not surprising that the response of each compound in terms of peak area is higher in pure solvent system than in matrix solvent system. The slopes of calibration curves for both pure and matrix systems differ from each other. These findings confirm our speculation that the process water in which the standard NAs were prepared has a negative effect on MS signal detection, possibly because of ion suppression. The signal degradation could come from both MS and HPLC.

ESI in MS

(1) The presence of non-volatile surfactants/materials at the micelle formation concentration inhibits the formation of analytes droplets through the co-precipitation of analytes, and reduces the efficiency of ionization process by preventing analytes droplets from reaching their critical radius required for gas phase ions to be emitted [31].

(2) Large amount of other ions in process water would compete with analytes ions for either the limited surface space or limited charge available on ESI.

HPLC column

(1) The matrix has a negative effect on column adsorption and partition process, which reduces the separation efficiency of LC.

(2) It is known that HPLC column has a capacity correspondence to the size (diameter and length) of the column. Non-interest molecules would compete for the adsorption sites availability with target compounds, thus reducing the adsorption effectiveness of the interested analytes.

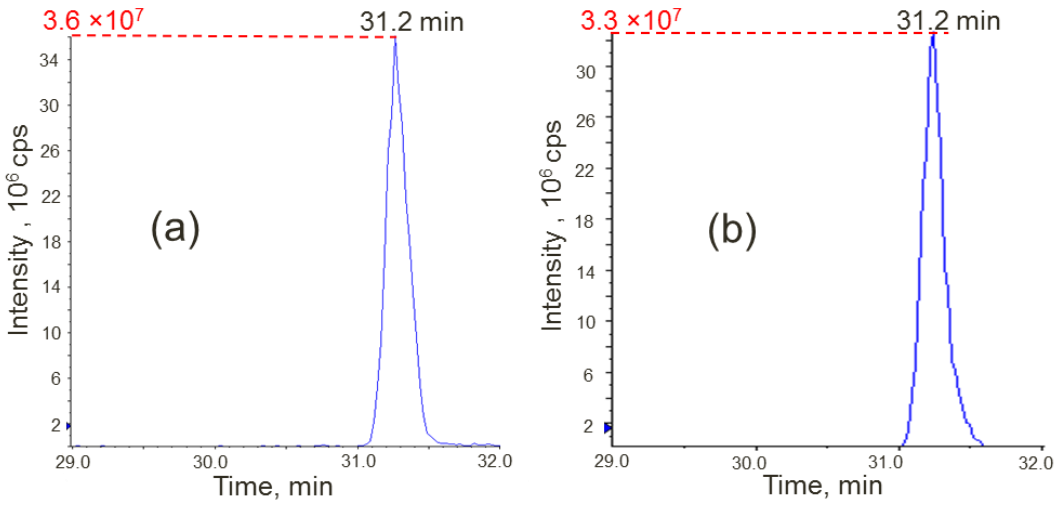


Figure 2-17 Mass spectra of TPCH extracted at elution time of 31.2 minute, dissolved in the mixture of 90% methanol and (a) Milli-Q water, (b) process water.

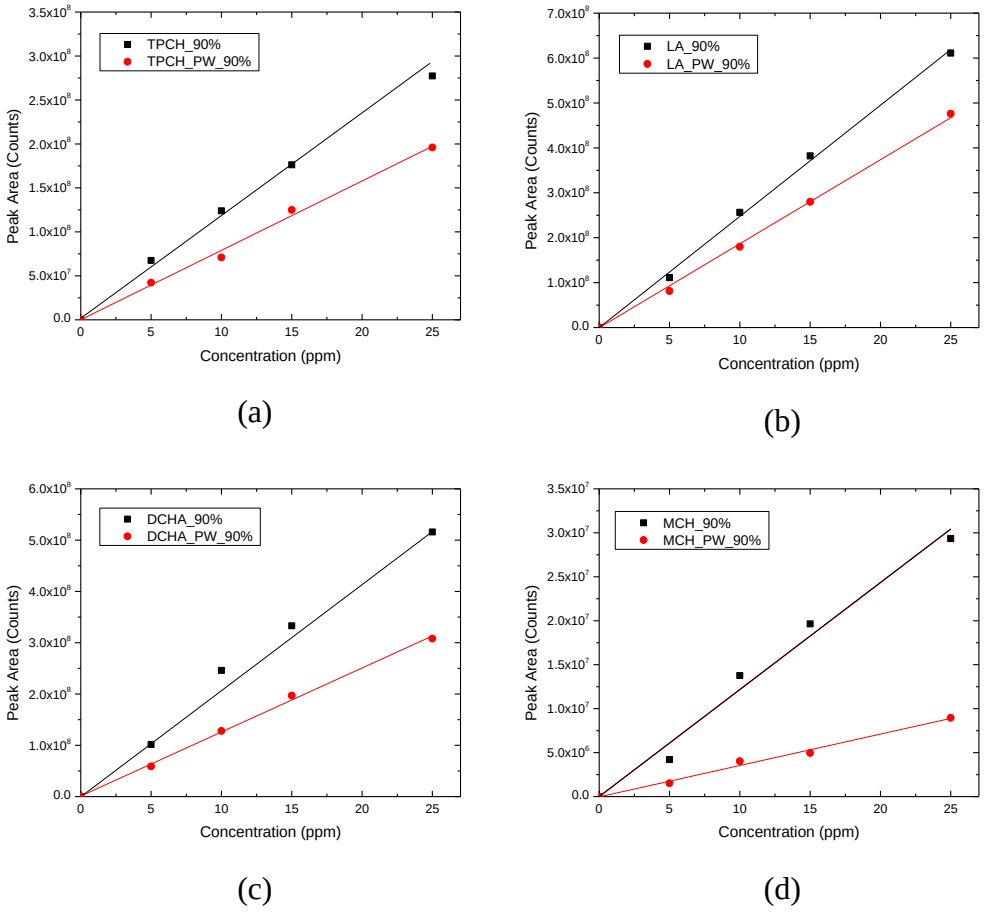


Figure 2-18 Comparison of standard curves of NA standard compounds in pure solvent (Milli-Q water in 90% methanol, Blank) and matrix solvent (process water in 90% methanol, Red) systems: (a) *trans*-4-pentylcyclohexane carboxylic acid (TPCH); (b) lauric acid (LA); (c) 2, 2-dicyclohexylacetic acid (DCHA); (d) 1-methyl-cyclohexane carboxylic acid (MCH).

2.4.6 Solid Phase Extraction

As discussed in Section 2.4.5, the components in process water degrade the signal performance of standard NA compounds. However, process water is a sample system that mimics the real water sample for NAs analysis. To improve the signal performance with process water, pre-analytical protection technique is tested. The objective is to protect the more expensive HPLC column by removing the permanently adsorbed molecules before loading. In addition, the use of the pre-analytical column protection is also to ensure a stable performance of MS probe by preventing plugging of high salts. Either guard column or solid phase extraction would achieve this requirement. Guard column usually is a short column that has similar packing material as the analytical column. An SPE cartridge would have a wide variety of packing choice, and additional enrichment function. Permanently adsorbed compounds would be removed by both guard column as well as SPE cartridge. Considering the complexity of the sample, SPE was chosen because of its high selectivity and enrichment function. Solid phase extraction (SPE) was performed on samples prior to being loaded onto HPLC – MS. As discussed in Section 2.3.4, SPE is a sample preparation technique that effectively removes the unwanted interfering species from sample of interest.

A mixture of standard compounds dissolved in process water with 90% methanol (5, 10, 15, 25 ppm) was extracted using SPE procedure summarized in Section 2.3.4. In brief, the cartridges were first conditioned with 1 mL of

methanol, followed by equilibration with 1 mL Milli-Q water. Two milliliters of sample aliquot adjusted to pH 7 were loaded, and drawn through the cartridge under vacuum suction at a rate of 2 mL min^{-1}. The cartridge was then rinsed with 2 × 500 µL 25 mM ammonium acetate, followed by 1mL methanol to remove the last trace of impurities, and allowed to sit under vacuum for 15 minutes. The adsorbed NAs were finally eluted using 2 × 500 µL 5% NH_4OH in methanol. The eluted extract was evaporated to dryness in a Savant SpeedVac concentrator system (Global Medical Instrumentation, Ramsey, Minnesota), and then reconstituted in 2 mL 90% methanol in water solution.

The performance of SPE treatment was shown in Figure 2-19. It is obvious that the signal degradation caused by process water is recovered to varying degree as shown by the blue line being closer to black line of the pure solvent system for TPCH, LA and DCHA. For MCH, the slope of SPE treated samples is increased compared to untreated samples. However, it is still much lower than the pure solvent system. It is interesting to note that all SPE calibration curves show very good linearity.

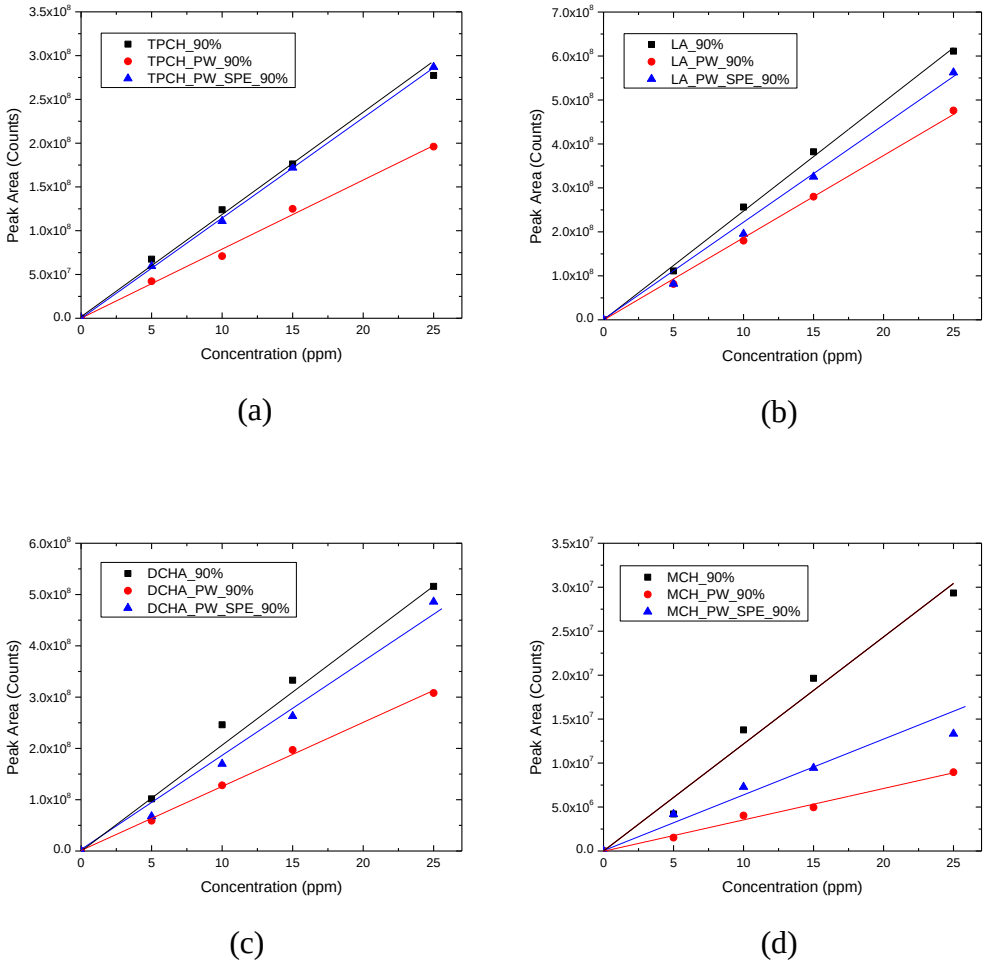


Figure 2-19 Comparison of standard curves under different preparation conditions: Blank line, NAs prepared in pure solvent; Red line, NAs prepared in process water; Blue line, NAs prepared in process water followed by SPE sample pre-treatment. (a) *trans*-4-pentylcyclohexane carboxylic acid (TPCH); (b) lauric acid (LA); (c) 2, 2-dicyclohexylacetic acid (DCHA); (d) 1-methyl-cyclohexane carboxylic acid (MCH).

2.4.7 SPE Application

To further challenge the developed method, tailings water samples were used with SPE method to test its extraction efficiency. Depending on oil sands extraction conditions, tailings water may contain more unknown species and contaminants. There are two tailings water samples used in this study:

Sample 1: tailings water produced from extraction of MA oil sands ore provided by Syncrude Ltd. with 0.03% caustic addition. This tailings water is referred to as MA003.

Sample 2: tailings water produced from extraction of MA oil sands ore provided by Syncrude Ltd. with 0.7% caustic addition. This tailings water is referred to as MA07.

The NA extraction efficiency is expressed as spike recovery (R%), where R% is expressed as:

$$\mathrm{R}\% = \frac{C\,spiked - C\,unspiked}{C\,nominal} \times 100\% \qquad \mathbf{(2-1)}$$

where

C_{spiked} is the concentrations of NAs detected in the spiked sample

$C_{unspiked}$ is the concentration of NAs detected in the un-spiked sample

$C_{nominal}$ *is* the known concentration of NAs added during the spike

The SPE recovery for four different standard compounds is given in Table 2-5, Table 2-6, Table 2-7 and Table 2-8. The commonly acceptable recovery for a method to be considered effective and usable is in the range of 80 to 120 percent (± 20% of the nominal). The recovery of TPCH and LA in tailings water of both MA003 (103% for TPCH and 92% for LA) and MA07 (108% for TPCH and 96% for LA) are all in this range, while those of DCHA in MA07 (75% recovery) and MCH in both MA003 (64% recovery) and MA07 (62% recovery) were lower than the acceptable level. The low recovery of MCH remains unknown because both TPCH and DCHA have similar molecular structures as MCH. Therefore, SPE sample treatment could correct matrix effect caused by both process water and tailings water to certain extend. However, the fact that one out of four model compounds gives lower recovery means that under-detection of some NAs concentration would happen.

Table 2-5 SPE recovery of TPCH in 90% methanol.

	MA003		MA07	
Spike Concentration (ppm)	0	15	0	15
Peak Area (Counts)	0	1.77E+08	0	1.86E+08
Concentration Calculated (ppm)	0	15.43	0	16.21
Concentration Recovered (ppm)		15.43		16.21
Recovery Rate (%)		103		108

Table 2-6 SPE recovery of LA in 90% methanol.

	MA003		MA07	
Spike Concentration (ppm)	0	15	0	15
Peak Area (Counts)	2.41E+06	2.99E+08	3.12E+06	3.13E+08
Concentration Calculated (ppm)	0.17	14.03	0.18	14.61
Concentration Recovered (ppm)		13.86		14.43
Recovery Rate (%)		92		96

Table 2-7 SPE recovery of DCHA in 90% methanol.

	MA003		MA07	
Spike Concentration (ppm)	0	15	0	15
Peak Area (Counts)	6.63E+05	2.68E+08	7.80E+05	1.95E+08
Concentration Calculated (ppm)	0	14.74	0	11.25
Concentration Recovered (ppm)		14.74		11.25
Recovery Rate (%)		98		75

Table 2-8 SPE recovery of MCH in 90% methanol.

	MA003		MA07	
Spike Concentration (ppm)	0	15	0	15
Peak Area (Counts)	1.33E+05	6.75E+06	2.49E+06	6.62E+06
Concentration Calculated (ppm)	0	9.55	0	9.26
Concentration Recovered (ppm)		9.55		9.26
Recovery Rate (%)		64		62

2.5 Conclusions

The feasibility of the HPLC – MS method to determine NAs was studied using four NA standards: MCH, TPCH, LA, and DCHA. Column loading condition was investigated to determine the optimal methanol concentration for both dissolving the sample and producing a higher MS signal. The capability of NAs analysis in a mixture using HPLC – MS was proved in this study. The effect of commonly existing calcium and magnesium ions in the water sample on quantitative analysis of NAs was investigated. It is shown that with the application of SPE sample treatment, the signal degradation caused by process water (as well as tailings water) could be improved to varying degree, depending on the type of NAs. The efficiency of SPE was also investigated with spike recovery methodology. The SPE sample preparation strategy is suggested to remove interferences with mass analysis caused by other impurities, which can otherwise lead to an under-estimation of analytes' concentration and decreased sensitivity. However, the current study is limited to a few available NA standards for the hundreds of individual naphthenic acids present in oil sands mixture. Therefore, this method would need to be further studied with more standard NAs and understand the interactions interferences, to fully establish calibration protocols of unknown species.

Reference

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Chapter 3 Sulfonic Acids

3.1 Introduction

Sulfonic Acids are a group of organic acids having a general formula of RSO_3H, where $–SO_3H$ is the functional group. Sulfonic acids are strong acids, and their acidity is similar to that of the sulfuric acid [1]. Using the method of foam fractionation and spectroscopic characterization, sulfonic acids were first found in tar sands in 1960s from the waxy material by Bowman *et al* [2]. The sulfonic acids are often produced in the form of sulfonate salts during the tar sands and/or oil sands processing by reaction with NaOH. Schramm *et al* in 1987 [2] identified that aliphatic sulfonate salts have hydrocarbon chains with more than five carbons. Owing to the fact that long carbon chains of sulfonic acids have very low biodegradability and high persistency in the environment [3-5], there is an upsurge of interest to characterize and quantify sulfonic acids. The most straightforward method to measure sulfonic acids is titration [6]. The titration method is easily accessed in both laboratory and industrial scales. ASTM D 4711 – 89 (2009) is a standard titration method for alkylbenzene sulfonic acids [7]. However, titration method is limited by its high degree of specificity, and only applies to linear or branched alkylbenzene sulfonic acids. Fourier-transform infrared (FTIR) spectroscopy is a common spectroscopic method to evaluate sulfonic acids. It is achieved by detecting the infrared absorption of sulphur-oxygen groups at the frequency of 1020 cm^{-1} [8]. Thus,

FTIR method reports as the total concentration of sulphur-oxygen groups in the sample by integrating the peak area under the hump. Owing to the fact that there are sulfonyl hydroxide groups ($–SO_3H$) of non-sulfonic acids in oil sands, the integration of the peak under the hump in the spectra could result in over estimation of total concentration of sulfonic acids in oil sands tailings water. In addition, the FTIR method is not designated to retrieve individual sulfonic acids information. On the other hand, gas chromatography (GC), a conventional chromatographic method, provides the possibility to identify and determine the individual sulfonic acids. However, the characteristic of low / non volatility of sulfonic acids limits the GC application to the free sulfonic acids. In addition, GC method usually requires more extensive sample preparation steps e.g., derivatization, which would be problematic because of the strong acidity of sulfonic acids [9, 10].

In the industrial field, a fast and relative inexpensive technique is always preferable. A modern separation technique, liquid chromatography (LC), would fulfill this requirement. It is known that linear alkylbenzenesulfonates (LAS) are the salts of alkylbenzenesulfonic acids. It has been proved that high performance liquid chromatography (HPLC) is the most suitable method for the determination of LAS due to its excellent separation efficiency and low detection limit (2.39 ppm) [11]. Therefore, in this work we utilized the high performance liquid chromatography (HPLC) to separate individual sulfonic acids without samples derivatization, equipped with an evaporative light

scattering (ELS) detector. This method was also applied to oil sands tailings water.

3.2 Instrumentation

Evaporative light scattering detector favors the detection of non-volatile compounds. The detection process (Figure 3-1) involves three stages:

(1) Nebulization: The eluent from HPLC column enters the nebulizer, passes through the nebulizer needle, mixes with nitrogen gas flow, and sprays as droplets;

(2) Mobile Phase Evaporation: The droplets stream passes through a temperature controlled evaporator tube where the mobile phase solvent is evaporated and removed;

(3) Optical Detection: The dried analyte particles scatter light in the optical chamber. The scattered light is detected and converted to electrical signal.

Evaporative light scattering detector is required to run at elevated temperature in the process of nebulization and evaporation to increase signal to noise ratio, and run at low gas flow to control baseline noise.

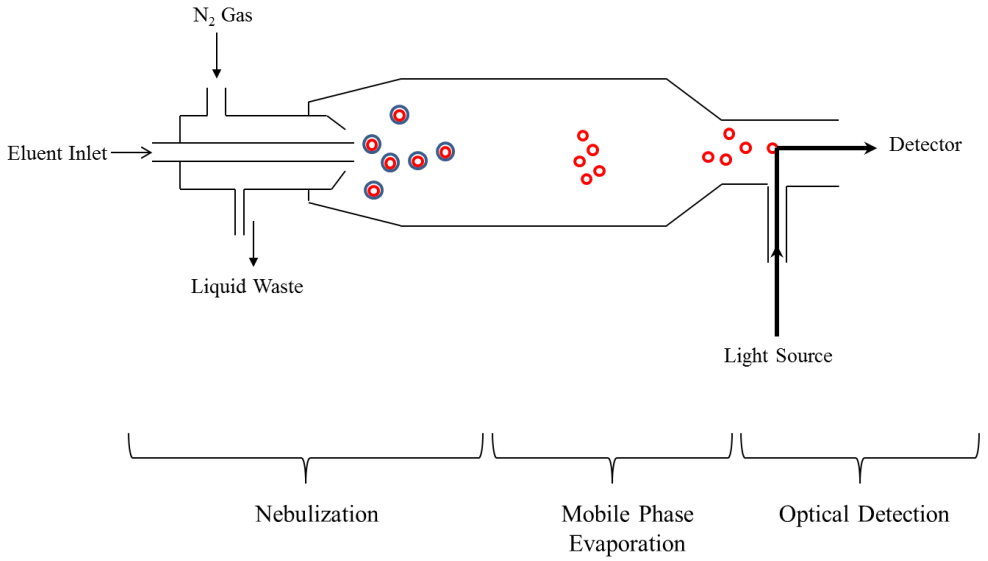


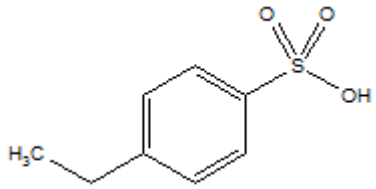
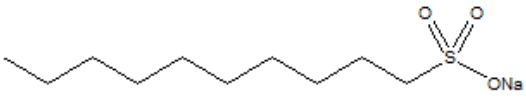
Figure 3-1 Evaporative light scattering detector.

3.3 Experimental

3.3.1 Chemicals and Reagents

Except otherwise stated, all experiments were carried out at pH 3.5 to keep standards in the acid form. In this study, two standard compounds of sulfonic acids were employed in method development. They are listed in Table 3-1 as 4-ethylbenzenesulfonic acid (Sigma Aldrich) and sodium 1-decanesulfonate (Sigma Aldrich), which represent aromatic and aliphatic sulfonic acid, respectively. Optima® grade acetonitrile (Fisher Scientific), ammonium acetate (Sigma Aldrich) and water were used as HPLC mobile phase. Reagent grade sodium hydroxide (Fisher Scientific) and acetic acids (Sigma Aldrich) or hydrochloride (Fisher Scientific) were used as pH modifiers.

Table 3-1 Standard compounds of sulfonic acids.

Model Compounds	Structure
4-Ethylbenzenesulfonic acid	
Sodium 1-decanesulfonate	

3.3.2 HPLC – ELS

HPLC – ELS analyses were performed with Dionex UltiMate® 3000 liquid chromatography equipped with an evaporative light scattering detector from Polymer Laboratories (PL – ELS 2100), as shown in Figure 3-2. Dionex UltiMate® 3000 consists of a binary pump, auto-sampler and column compartment. The chromatographic separation was carried out in an Acclaim™ Surfactant column (460 × 250 mm, 5 µm particle size). The mobile phase used was: (A), 10 mM ammonium acetate (NH_4Ac) in Optimal®-grade water; and (B), Acetonitrile. The gradient elution starts from 15% B and increases to 75% over a period of 15 minutes, holds for 10 minutes at 75% B, and then drops to 15% B followed by 9.9 miniutes equilibration and 0.1 minutes initiation. The total run time is 35 minutes per sample. One hundred microliter of sample aliquot was injected onto the surfactant column, separated and eluted at a flow rate of 300 µL min^{-1}. Detection was accomplished with PL

– ELS 2100. The EIS settings were 50^{o}C of evaporator temperature, 30^{o}C of nebulizer temperature, and 140 kPa of the nitrogen carrier gas pressure for nebulization. Data acquisition, analysis and reporting were done by Chromeleon 6.8 chromatography data system.

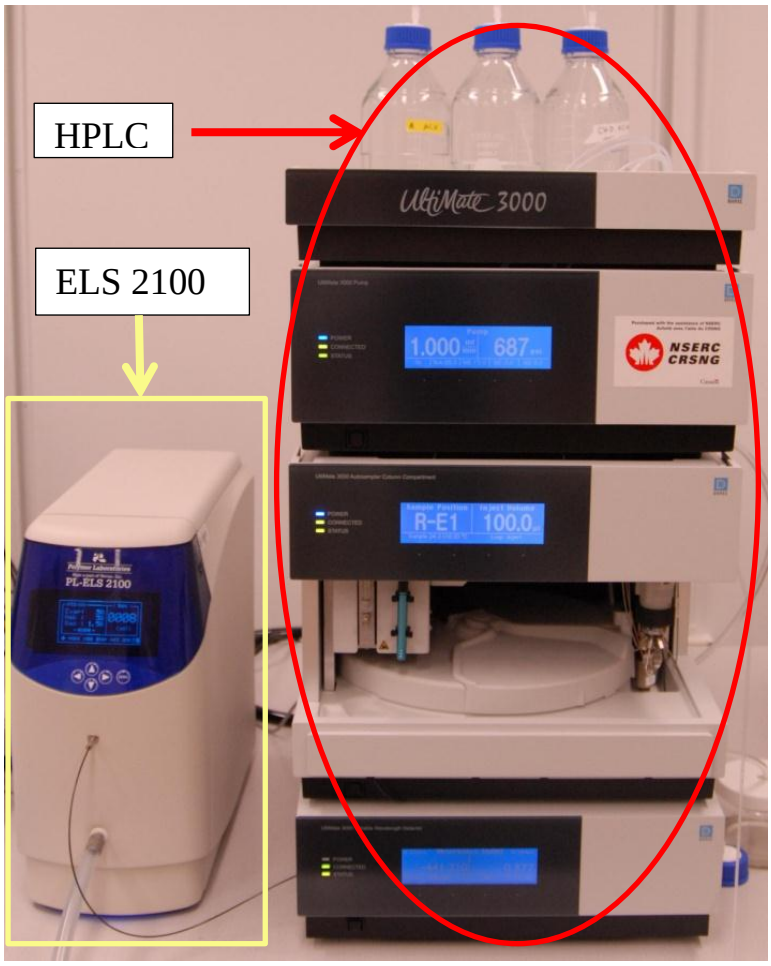


Figure 3-2 HPLC and PL – ELS 2100 Detector.

3.3.3 Sample Preparation

3.2.3.1 4-Ethylbenezensulfonic Acid Spiked in Tailings Water

4-Ethylbenzenesulfoinc acids dissolved in Milli-Q water and tailings water to make sets of standard solutions at concentrations of 0, 5, 10, 25, and 50 ppm, respectively.

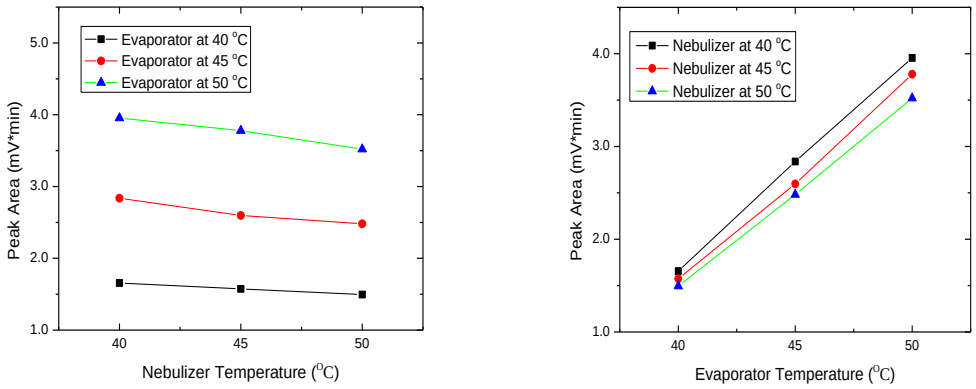
3.3.3.2 Total Organic Carbon (TOC)

One process water sample and three lab-synthetic tailings water samples were selected for TOC analysis in this work. Each sample was acidified to pH 3.5, and the acidified solutions were filtered to remove precipitates prior to TOC analysis.

3.4 Results and Discussion

3.4.1 Effect of Evaporator and Nebulizer Temperature

PL – ELS 2100 was employed as detector of HPLC in this study. To optimize the sensitivity of its detection, the operative temperature of both nebulizer and evaporator were investigated to achieve the best performance. The standard compound of 4-ethylbenzenesulfonic acid was utilized to achieve this goal.



(a) (b)

Figure 3-3 Effect of temperature on signal of detector PL – ELS 2100 with the 4-ethylbenzenesulfonic acid concentration of 25 ppm in Milli-Q water.

As shown in Figure 3-3(a), at the same evaporator temperature, peak areas decrease slightly with the increase of nebulizer temperature. In Figure 3-3(b), peak areas at the same nebulizer temperature are shown to increase with the increase of evaporator temperature. It can be concluded that PL – ELS 2100 should be operated at higher evaporator temperature but lower nebulizer temperature. However, the lowest nebulizer temperature cannot be below 25^{o}C due to requirement of water evaporation in the detector. Therefore, the optimized nebulizer temperature was set at 30^{o}C. With the nebulizer temperature set at 30^{o}C, evaporator temperature was also investigated at higher temperatures of 60 and 70^{o}C. The results are shown in Figure 3-4. The peak area increases with increasing evaporator temperature. However, as shown in Figure 3-5, asymmetrical peak shape was observed in higher evaporator temperature and electronic noise increased significantly as increasing

evaporator temperature. Therefore, the evaporator temperature is selected at 50^{o}C to compromise intensity and noise.

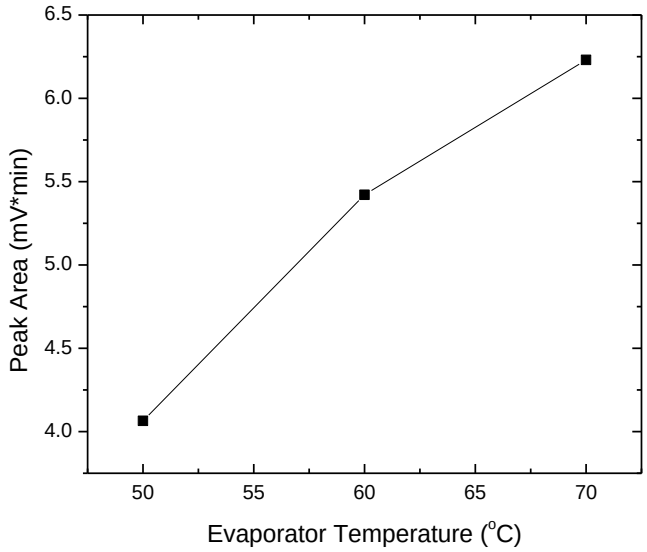


Figure 3-4 Effect of evaporator temperature on signal of PL – ELS 2100 at the optimized nebulizer temperature of 30°C.

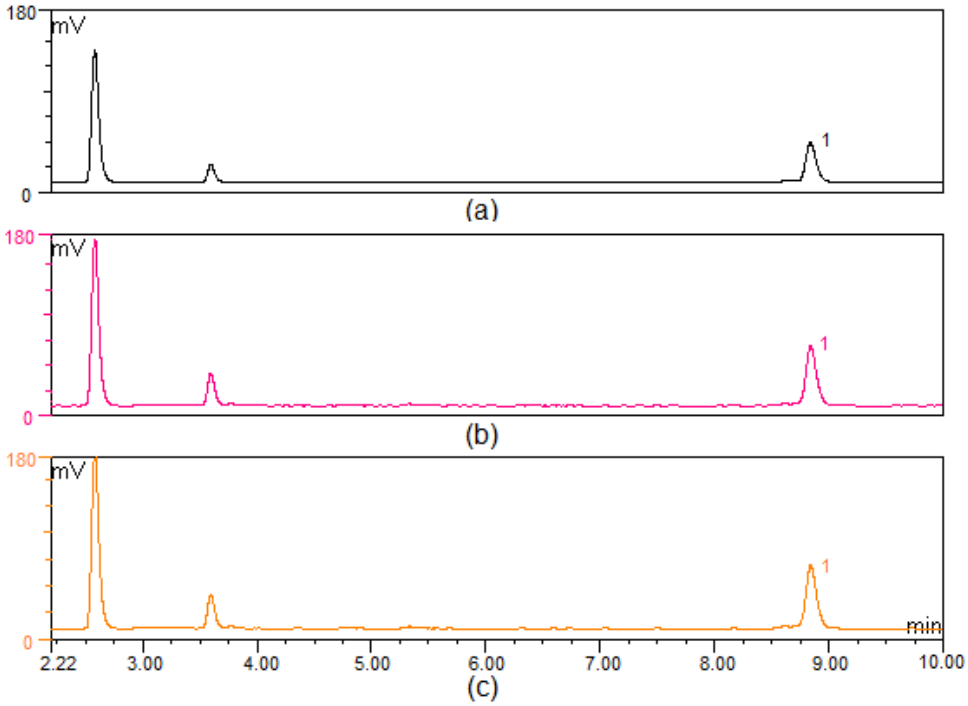


Figure 3-5 HPLC – EIS chromatogram of 4-ethylbenzenesulfonic acid (peak "1") at different sets of nebulizer / evaporator temperatures. (a) 30°C / 50°C; (b) 30°C / 60°C; (c) 30°C / 70°C.

3.4.2 Calibration of Individual Standard Compounds

It is well known that retention time is specific to compound property and column of chosen. Baseline separation of compound peaks is a critical chromatographic parameter to show the ability of separation of compounds. Table 3-2 lists the retention time of both 4-ethylbenzenesulfonic acids and sodium 1-decanesulfonate dissolved in Milli-Q water. Their calibration curves conducted from 5 ppm to 50 ppm at pH 3.5 is given in Figure 3-6. The calibration curve was drawn between peak intensity (peak area) of compounds versus analyte concentration. PL – ELS 2100 detector typically does not linearly response to analyte concentration; instead, exponentially related to concentration with excellent coefficients of 0.99738 (4-ethylbenzenesulfonic acids) and 0.99787 (sodium 1-decanesulfonate) [12-14].

Table 3-2 HPLC retention time of two standard compounds.

Standard Compounds	**4-Ethylbenzenesulfonic acid**	**Sodium 1-decanesulfonate**
Retention Time (minutes)	8.80	15.74

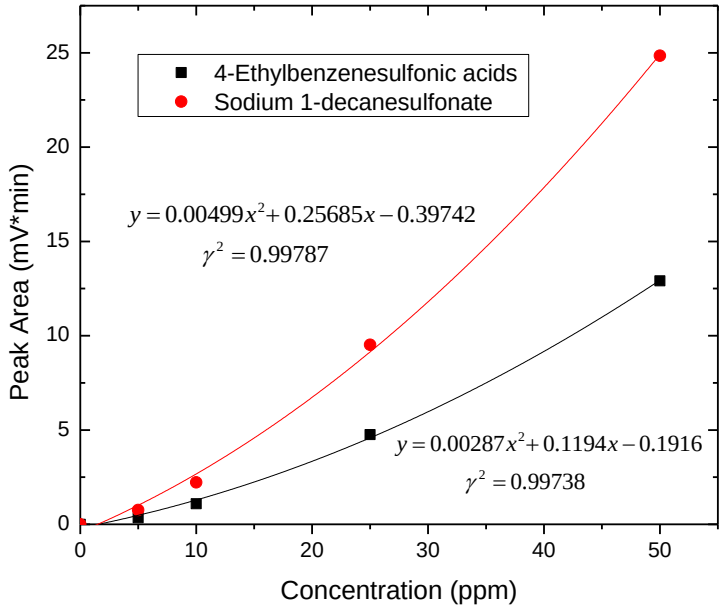


Figure 3-6 Calibration curves for 4-ethylbenzenesulfonic acid and sodium 1-decanesulfonate.

3.4.3 Mixture of Standard Compounds

To understand if there is any possible interaction existing between the standard compounds which could affect the accuracy of individual analyte concentration, the interference of 4-ethylbenzenesulfonic acid and sodium 1-decanesulfonate was studied in a mixture. Figure 3-7 shows ELS spectrum obtained from individual compounds and the mixture. Apparently, there is no significant change in peak height of the 4-ethylbenzenesulfonic acid; however, a slightly decreased peak height of sodium 1-decanesulfonate was observed. Figure 3-8 gives the difference of peak areas of both standard compounds with and without mixing. It is evident that 4-ethylbenzenesulfonic acid is not interfered by other compounds, while the peak intensity of sodium 1-decanesulfonate is

significantly suppressed by an average of 30% by 4-ethylbenzenesulfonic acid. The degree of suppression for sodium 1-decanesulfonate in the mixture is listed in Table 3-3. Therefore it is possible that the aliphatic sulfonic acid would be under-estimated in the mixture where the real sample is always in a mixture system.

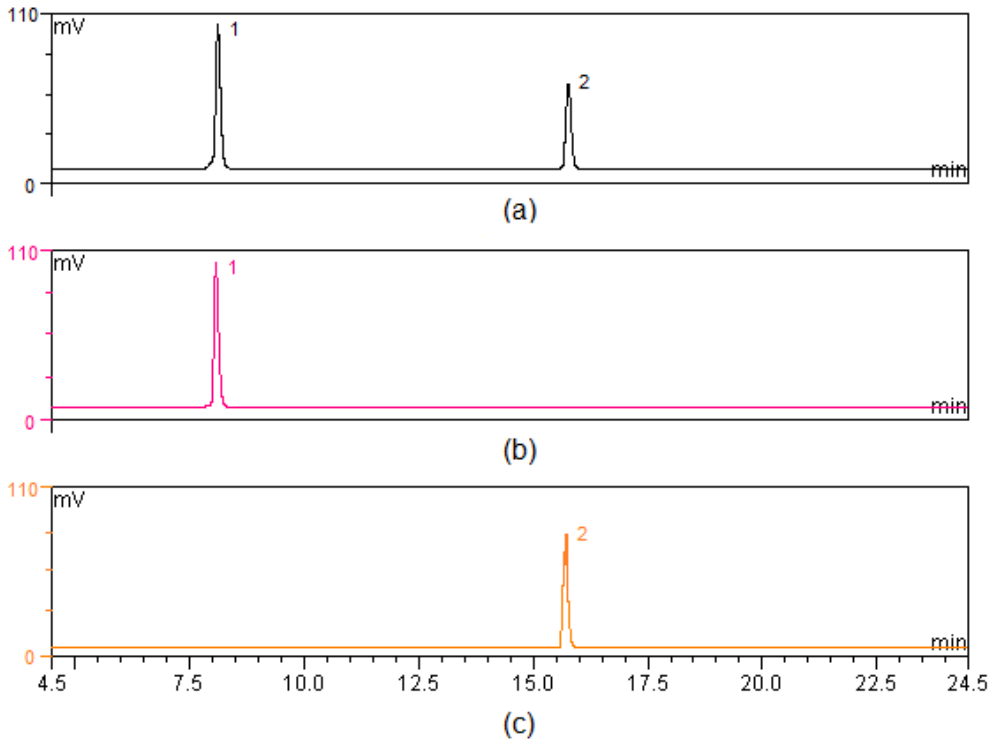
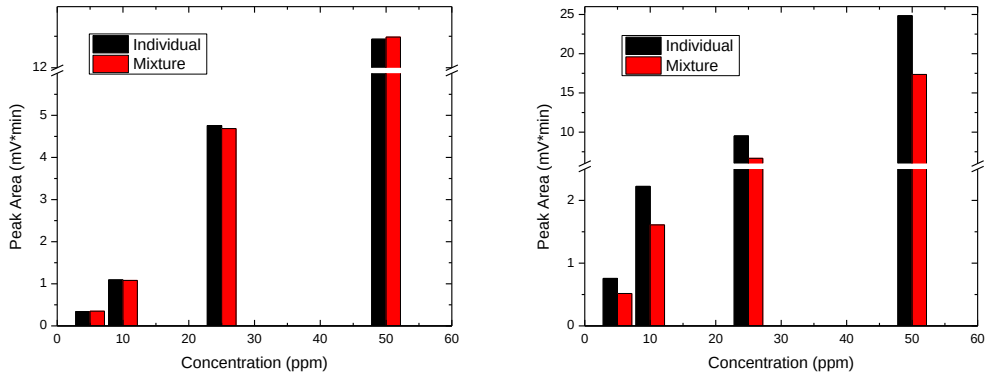


Figure 3-7 HPLC chromatograms of 4-ethylbenzenesulfonic acid (peak "1") and sodium 1-decanesulfonate (peak "2") (a) Mixture of two compounds both at 50 ppm; (b) Only 4-ethylbenzenesulfonic acid at 50 ppm; (c) Only sodium 1-decanesulfonate at 50 ppm.



(a) (b)

Figure 3-8 Intensity of two standard compounds detected from individual analyte or mixture (a) 4-Ethylbenzenesulfonic acid; (b) Sodium 1-decanesulfonate.

Table 3-3 Interference on sodium 1-decanesulfonate in the mixture.

Concentration (ppm)	**Peak Area (mV*min)**		**Suppression Rate (%)**
	Individual	**Mixture**	
0	0	0	
5	0.76	0.52	32
10	2.22	1.61	28
25	9.52	6.67	30
50	24.84	17.35	30

3.4.4 Tailings Water and Standards Spike

Tailings water was loaded into HPLC with ELS detector; however, there is no peak shown in spectrum except high peak intensity of inorganic ions (Ca^{2+}, Mg^{2+}, etc.) before 5 minutes of elution time as shown in Figure 3-9. As mentioned in Section 3.4.3, 4-ethylbenzenesulfonic acid was very stable and its peak intensity was not affected by sodium 1-decanesulfonate. Therefore, 4-ethylbenzenesulfonic acid was selected to spike the tailings water. The recovery as defined in Eq. (2-1) is calculated and listed in Table 3-4. The recovery is found to range from 82% to 102%, which indicates that the method can accurately detect 4-ethylbenzenesulfonic acid. The results also suggest that 4-ethylbenzenesulfonic acid in the tested tailings water is lower than detection limit of the method.

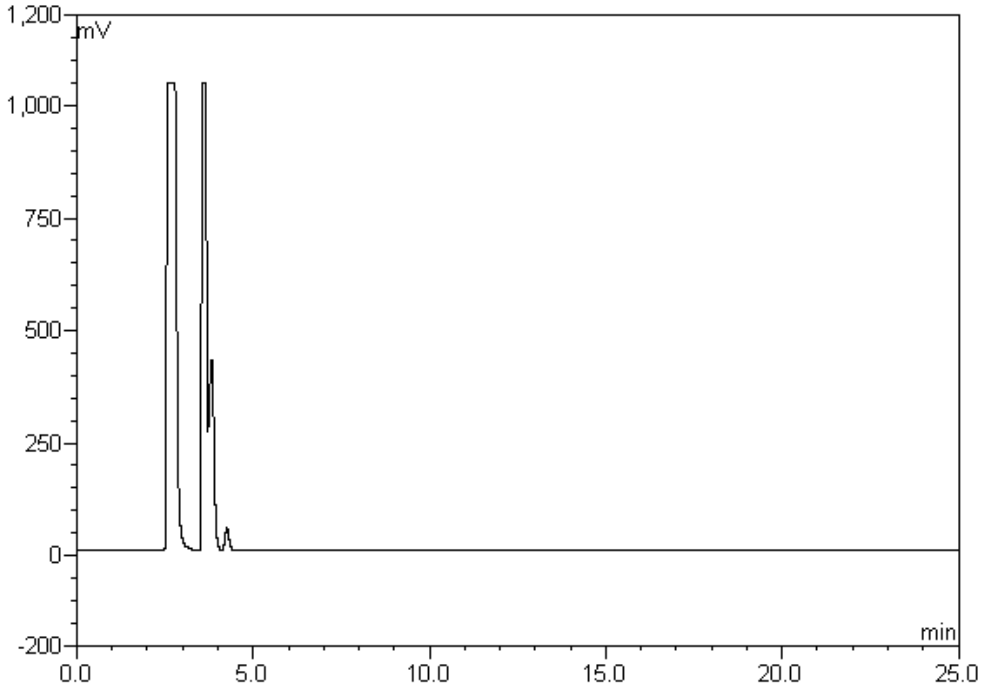


Figure 3-9 HPLC chromatogram of tailings water.

Table 3-4 4-Ethylbenzenesulfonic acid spiking tailings water.

Spike Concentration (ppm)	Peak Area (mV*min)	Calculated Concentration (ppm)	Recovery (%)
0	0	0	
5	0.37	4.27	85
10	1.08	8.80	88
25	4.75	25.62	102
50	12.88	49.82	100

3.4.5 Total Organic Carbon

Sulfonic acids are strong acids with the similar acidity to the sulfuric acid. It is reported that they present in the form of acids at pH lower than 3.5 [1].

Tailings water produced from oil sands processing is rich in surfactants:

naphthenic acids and sulfonic acids. As investigated in Section 3.4.4, no sulfonic acids were detected in the real sample of tailings water except the high level of inorganic ions. However, when same tailings water sample spiked with 4-ethylbenzenesulfonic acid, the method showed acceptable recovery of the surfactant. Thus a concern is raised to whether there are any sulfonic acids existing in tailings water at pH 3.5.

Total organic carbon (TOC) analyzes "the amount of carbon bound in an organic compound". As discussed in Chapter 2, naphthenic acids are classified as weak acids, and constitute the most surfactants in tailings water. Table 3-5 compares the varied TOC concentration at different pH values of tailings water and process water. For all the tailings water samples no matter what concentration of NaOH was added at the beginning of sample preparation, after pH was adjusted to acidic condition (pH 3.5), the TOC concentration were decreased. It is assumed that naphthenic acids fully precipitate out of aqueous solution at pH 3.5. As pH decreases, naphthenic acids start precipitating, and are completely removed at pH 3.5. Sulfonic acids are then considered to contribute to the rest of carbon concentration. Based on the above assumption, Figure 3-10 plotted the TOC concentration versus the amount of NaOH added in tailings water. It is found that TOC for both high and low pH would be plateaued at higher level of NaOH addition. Therefore, we can estimate the concentration of naphthenic acids from the top region only (shown at the top of the figure with red color) and the concentration of sulfonic

acids (bottom region), respectively, in the tailings water. However, when pH equal or less than 3.5, any soluble organic compounds other than sulfonic acids will also have contributions to the TOC analysis, which means TOC method always over-estimates the concentration of sulfonic acids because the method itself measures only "the amount of carbon bound in an organic compound".

Table 3-5 TOC results vary with source of tailings water and pH values.

	pH	TOC (ppm)
Process Water	3.5	41.0
	8.1	59.0
0.05% NaOH Tailings Water	3.5	48.4
	9.5	93.5
0.1% NaOH Tailings Water	3.5	56.1
	10.2	112.8
0.5% NaOH Tailings Water	3.5	64.3
	12.4	121.6

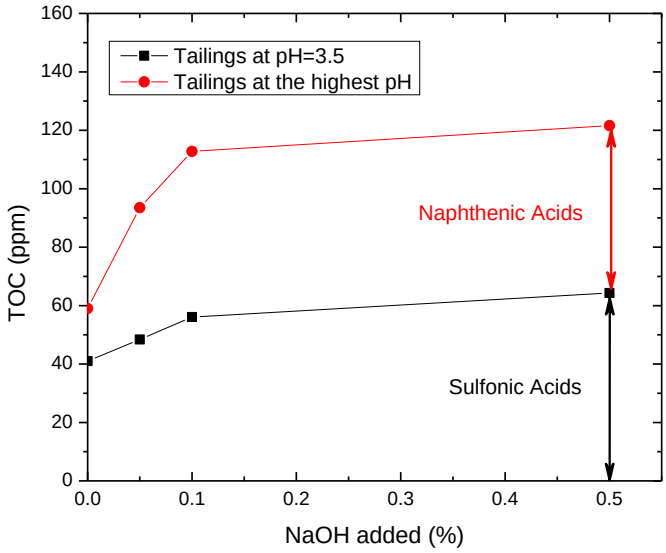


Figure 3-10 Schematics of calculating concentrations of both sulfonic acids and naphthenic acids

3.5 Conclusions

The high performance liquid chromatography with evaporative light scattering detector (HPLC – ELS) has been employed to analyze 4-ethylbenzenesulfonic acid and sodium 1-decanesulfonate in water. Critical operational parameters were investigated to achieve the best performance for this particular analysis. It was found that the aliphatic sulfonic acid was most likely to be underestimated if there was aromatic sulfonic acid presented in the sample. On the other hand, the aromatic sulfonic acid can be accurately detected regardless of analyte was individual components or in a mixture with aliphatic sulfonic acids. The tailings water sample was analyzed using this method. It was found that the concentration of both 4-ethylbenzenesulfonic acid and sodium 1-

decanesulfonate in the process water was below detection limit of HPLC – ELS. Owing to the fact that aliphatic sulfonic acids could be underestimated, it is very difficult to determine whether any sulfonic acids exist in tailings water or were simply below the detection limits (hundreds of sulfonic acids in water samples, but individual one with very small amount that below the detection limits). Although TOC results showed high concentration of carbon in water samples, it might due to organic compounds other than sulfonic acids or contribution of all kinds of sulfonic acids. However, it is worth noting that HPLC – ELS could become an alternative method to determine and identify 4-ethylbenzenesulfonic acid and sodium 1-decansulfonate.

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Chapter 4 Conclusions and Future Work

4.1 Conclusions

Scientific efforts have been made to identify and quantify individual natural surfactants released into oil sands tailings water. Two major groups of natural surfactants, naphthenic acids and sulfonic acids, are analyzed separately by different methodologies. The common instrument of these methodologies is high performance liquid chromatography, a faster and simpler technique compared to FTIR and GC. However, both methods have a certain degree of specificity for specific surfactants.

Naphthenic Acids

An improved HPLC – MS method has been developed to separate a mixture of four NA standards and to measure the amount of each component. The linearity obtained by this method is sufficient for quantification. The advantage of this method is that 90% methanol loading condition significantly enhanced the signal intensity compared with previous studies that utilized 100% methanol. Effect of water chemistry, such as calcium and magnesium ions, on surfactant analysis was examined and proved to have negligible impact for the developed method, because of the gradient elution of HPLC and negative operating mode of MS. SPE was introduced to the work to pre-treat real oil sands samples and showed noticeable enhanced sensitivity against un-pretreated samples due to sample pre-purification and enrichment. The

outcome of this study confirms the feasibility of using SPE as alternative sample preparation strategy.

Sulfonic Acids

This work has demonstrated the utilization of HPLC – ELS for determination of 4-ethylbenezenesulfonic acid (aliphatic sulfonic acids) and sodium 1-decanesulfonate (aromatic sulfonic acids) at pH 3.5. It has demonstrated that aromatic sulfonic acids can be accurately detected despite the interference for aliphatic sulfonic acids. Therefore the method is considered amenable for identifying aromatic sulfonic acids.

4.2 Future Work

To make HPLC – (MS or ELS) more practical, accurate, and effective for industrial monitoring, the following recommendations are proposed for future study.

Naphthenic Acids

1. Internal standards can be used in the method to compensate for the instrumental variability and matrix effects. The choice of internal standards could be compounds that are isotopically labeled naphthenic acids or naphthenic acids that for sure not present in the real sample.
2. The current method has 60 minutes HPLC runtime which is long for industrial standard. Use of rapid resolution column from Agilent could

significantly reduce the run time without sacrifice of HPLC separation resolution.

3. As impurities in samples were eluted off the sorbent of Strata™-X-AW SPE cartridges, the removed impurities can be characterized by various techniques. This would help us understand the interference of impurities to my analysis.
4. Different types of SPE cartridges can be explored to see if they could provide a better sample extraction efficiency, especially to the standard of MCH.
5. Dilution of sample solutions may be required to decrease the concentration of matrix that interferes with ESI – MS analysis. However, on the other hand, sensitivity could be increased by less dilution of the post SPE extract, for example, reconstituting the dried extract to 100 µL instead of 2 mL. Therefore, final reconstitution factor would be balanced between matrix effect and detection limit.
6. The tailings water was obtained from the processing of Syncrude MA ores. The present study could extend to other kinds of tailings water to give a full blueprint of the suitability of method.

Sulfonic Acids

1. More commercially available aliphatic and aromatic sulfonic acids could be examined and analyzed by the developed methodology.

2. The effect of metal cations, such as calcium and magnesium, to the detection of sulfonic acids can be further studied.
3. Due to the various properties of oil sands ores and its subsequent tailings water, those tailings water could also be applied to this method to test the presence of sulfonic acids.