# On-Site Sampling and Determination of Aliphatic Amines in Industrial Waste Water using SPME

by

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# AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

# Abstract

In any oil production company, one of the problems that is faced on a daily basis and which sometimes hinders the operation is corrosion. In the presence of dissolved oxygen in the water inside any vessel, tank, or pipeline, the oxygen attacks the steel to form iron oxides, and this result in corrosion of the steel. To prevent this, corrosion inhibitors are added to the oil and gas streams. These chemicals are based on aliphatic amines, which are soluble in water, to form a film to coat the steel and prevent it from the oxygen attacks.

As a chemist in the laboratory, filming amines residuals should be monitored and optimized in order to make sure the system is protected against corrosion and that no excess chemical remains. This is classically done by lengthy liquid-liquid extraction of filming amines followed by colorimetric determination using spectrophotometry of the extract. SPME is an easy, rapid, and solvent free extraction technique which can be easily coupled with GC for separation and quantification, and is a good candidate to be used for this job.

In this thesis, an introduction about corrosion problems and how to control and monitor them in the oil and gas industry will be shared, as well as a literature review about various methods used to determine amines in different matrices, followed by a description of the SPME procedure, including its theory, modes, fibers, and method development procedures.

A flow-through system was used to simulate the process of flowing streams in pipelines during oil production and to provide unlimited sample volumes, which contributes

to simplifying the calculation of the distribution constant between fiber and solution. Two different agitation methods were compared, which are stirring and sonication, in order to optimize the extraction time profiles of analytes.

A method was developed to determine amines, using a flow-through system at the lowest detection limit possible. Different parameters were examined such as variation of pH, salt addition, and sand addition. It was found that the pH of the solution has to be adjusted in order to get better sensitivity for the desired analytes.

Finally, in-fiber kinetic calibration was used to calculate the concentration of solutions at a short extraction time. This was possible by applying the dominant desorption approach using the same analytes as standards in the fiber. The experiment was successful in shortening the extraction time from 3 hours to 20 minutes, with less than 20% variation in concentrations between the actual and the calculated.

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Last but not least, to my employer Saudi Aramco for their sponsorship of my degree and putting their trust on me, also to my advisor Mrs. White for her support, advice, and kindness.

# Dedication

I dedicate this thesis to my parents for their emotional support overseas, to my lovely wife for her patience to be away from her parents for me, for all the stress she took to look after my children when I am busy in my lab, and for her encouragement to me to complete my work. Also I dedicate this work to my two sons Musaed and Khaled.

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# Chapter 1

# Introduction

## 1.1 Corrosion

Corrosion is one obstacle faced by many industries such as oil, water desalination, and power generation. It is a result of a set of spontaneous reactions of any materials with the surrounding environment.[1] There are many real life examples of materials deteriorating when exposed to certain environments. Wood rots as a result of exposure to moisture in the presence of microorganisms and iron rusts when exposed to water in the presence of oxygen.

Corrosion in the oil industry could be responsible for operational upsets like the unscheduled shutdown of a facility. Leaks caused by corrosion in a pipeline or vessel might contaminate the environment or cause serious personal injuries to workers. Companies are sparing no efforts to control corrosion starting from the point of design of facilities through until actual operation.[2]

### 1.1.1 Cost of Corrosion

Safety in the workplace, health of workers, and the surrounding environment are negatively influenced by corrosion, which also impacts the financial status of operating companies.[2] Many countries have considered this seriously and conducted studies on the cost of corrosion. Countries like the United States, United Kingdom, Japan, Australia, India,

and China have come to the conclusion that corrosion is costing each nation 1 to 5 % of its gross national product (GNP).[2]

In 2001, a study for the cost of corrosion in the US economy was conducted and it was found to cost a total of $137.9 billion/year, which contributes to approximately 3.1 % of United States' GNP.[2]

### 1.1.2 Corrosion Mechanism

Corrosion of metallic materials (pipeline, vessel, or tank) is an electrochemical process that requires the presence of an electrolyte (water and dissolved species) to be reduced while iron is oxidized.[3] At the anode, oxidation of free metallic iron from the steel surface occurs to produce ferrous ions ($Fe^{2+}$) as per the following half reaction:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

Dissolved gases from the stream (e.g. oxygen, carbon dioxide, and hydrogen sulfide) act as the cathode of the cell, which is responsible for the reduction reaction. In the case of oxygen, the half reaction is:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

The overall reaction of both half cells results in the formation and precipitation of iron hydroxide, which is insoluble in production streams:

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$$

In the presence of excess oxygen, iron will further be oxidized from $Fe^{2+}$ to $Fe^{3+}$ producing iron oxide as per the following reaction:

$$2Fe(OH)_2 + ½O_2 \rightarrow Fe_2O_3 \cdot (H_2O)_2$$

The flow of the electrons from the anode (surface of the steel) to the cathode (species in the solution) will result in metallic loss leading to corrosion.[1,4] By having both half cells running smoothly, the corrosion current will continue to oxidize iron from the steel and ferrous ions will continue finding their way out by precipitation. The reaction will continue indefinitely unless it is controlled or prevented.[1,3]

### 1.1.3 Methods for Corrosion Control

Corrosion cannot be totally stopped but it can be minimized and controlled and there are many methods for corrosion control in the oil industry.[1]

#### 1.1.3.1 Cathodic Protection

Cathodic protection (CP) is a method of controlling the corrosion of steel by reversing the role of the anode, which is the surface of the steel, and makes it the cathode. This could be accomplished by applying a direct current from an external anode that is attached to the body of the steel.[1] The external anode is another metal like aluminum or zinc, which will sacrifice by losing its electrons.[3]

#### 1.1.3.2 Protective Coatings

The corrosion of steel or other metals by water can be prevented by the application of protective coatings, which are typically organic polymers like polypropylene.[1] For maximum effectiveness, the coating must be of sufficient thickness and strength to prevent the water from contacting the metal. It should be uniform and continuously cover the internal surface of pipeline or vessel.[3]

#### 1.1.3.3 Oxygen Scavengers

Oil field water systems should be designed to eliminate contact of the water with air. Injection water systems, hydrotesting operations, and acid stimulation jobs should be free of oxygen to prevent corrosion.[3] The removal of oxygen could be performed by adding oxygen scavengers, which are reducing agents such as sulphites and hydrazine.[1]

#### 1.1.3.4 Materials Selection

Corrosion resistant materials like stainless steel are an alternative to carbon steel in some severe environments where corrosion exists with carbon steel.[3] Copper alloys, nickel-based alloys, and non-metallic materials are all possible choices as well.[1] Plastic-based materials like fiberglass and polyvinyl chloride (PVC) are used in low pressure flowlines and storage tanks.[1]

### 1.1.3.5 Corrosion Inhibitors

Corrosion inhibitors are a group of chemicals that are added to industrial systems to stop or slow down electrochemical corrosion reactions on metal surfaces. These chemicals actually coat the surface of the metal by adsorption from the aqueous phase solution or dispersion in the oil phase.[1] Corrosion inhibitors are classified into two main categories, either inorganic or organic.

The inorganic corrosion inhibitors are used mainly in utility systems such as cooling water, which makes them the most widely used type of inhibitor.[3,4] They are crystalline salts of chromates, silicates, phosphates, and molybdates.[1] Chromates are found to act best against corrosion in the recirculation of water for cooling of combustion engines and rectifiers.[4] Nitrites are best to be used in cooling water systems because they do not interfere with ethylene glycol that is added as antifreeze liquids.[4] Zinc salts precipitate on the metal surface to coat it and protect it against corrosion.[1]

In the oil and gas industries, organic corrosion inhibitors are used. These are mixtures of organic compounds that act as surfactants.[1,3] They consist of a hydrocarbon chain that is attached to a strongly polar functional group, usually an amine.[1] The polar head is adsorbed on the metal surface of the pipeline and the hydrocarbon chain, which is hydrophobic is attracted by the oil phase in the stream.[1] This distribution results in the formation of a thin oily layer on the inner surface of the pipeline, that provides a barrier to keep the corrosive water away from the metal surface.[3,4]

### 1.1.3.6 Types of Organic Corrosion Inhibitors

Most organic corrosion inhibitors used in the oil and gas industry contain at least one nitrogen functional group to act as the polar side to be adsorbed on the metal surface. Following are some common organic corrosion inhibitors with their structures:

Imidazolines: They are the most widely used class of organic corrosion inhibitors for general corrosion. Some types of imidazoline-based corrosion inhibitors are resistive to tough operational conditions at elevated temperatures under high pressure.[3]

Quaternary Ammonium Salts: This class of corrosion inhibitors is mostly used in combination with other groups and rarely used on its own. They are characterized by the ability to act as biocides, which prevents bacterial growth and bio-films from forming.[1,3]

Amides: Derivatization of fatty alkyl amines to amides gives another set of organic corrosion inhibitors which is not widely used because of their potential to negatively interfere with the oil water separation process. Other amides derivatized by acylation of amino acids are highly biodegradable and are useful to the separation process.[1,3]

Fatty Amines: The last class here is fatty amines, which are the most frequently used organic corrosion inhibitors in the oil and gas industry.[1,4] The hydrocarbon portion of amines could be a long chain alkyl, cyclic, or aromatic group. When introduced to the system, the amine portion is attached to the metal surface and the hydrocarbon portion forms an oily film that prevents corrosion attacks.

## 1.2 Sample Preparation

The fundamental step of any analytical procedure is the sample preparation, which involves cleaning the sample matrix and transporting the target analytes to a more suitable matrix for instrumental analyses.[5,6] This is very crucial because it leads to the achievement of better detection limits as compared of not having this step.[5] Before obtaining any samples for analyses, sample preparation and a separation technique should be considered. The target analyte and the expected concentration govern the separation technique.[7] The classical sample preparation method for organic pollutants was the solvent extraction prior to analysis, which was then replaced with solid phase extraction (SPE).[5,7,8] Excessive use of organic solvents, which are costly and harmful to the environment, as well as extended time elapsed in the extraction process are two disadvantages associated with these traditional techniques.[8]

### 1.2.1 Determination of Filming Amines Using SPE

SPE is an exhaustive extraction technique, requiring a sorbent – usually polymer-based, such as styrene/divinylbenzene copolymer and polyamide resin – to extract all the organic material from the sample. Kusch and coworker have used SPE and derivatization to determine amines in water boilers at power plants.[9] Approximately 10 mg of the investigated amine standard was dissolved in a solvent, and 100 µL of the derivatization reagent trifluoroacetic anhydride (TFAA) was added. Then, the vial was sealed and placed in

an ultrasonic bath and agitated for 15 min at 60°C. After that, the excess solvent and derivatization reagent were evaporated with nitrogen, and the resultant derivative was dissolved in a solvent and separated in the GC using different detectors: FID, nitrogen-phosphorous detector (NPD) and mass spectrometer.[9] Also, electron impact ionization (EI), positive chemical ionization (PCI), and negative chemical ionization (NCI) mass spectra of the derivatives were presented.[10,11] This method was applied successfully for the identification of filming amines used as corrosion inhibitors in water boilers of power plants. The method achieved low detection limits, but it required the use of a large amount of solvent.

### 1.2.2 Direct SPME Analyses of Short Chain Amines

Short chain amines C3 to C6 were successfully extracted using direct solid phase microextraction (SPME) from air using commercially available fibers polydimethylsiloxane (PDMS), polyacrylate (PA), and carbowax-divinylbenzene (CW-DVB) by Pan.[12] The concentration of the standard solution used was 25 ng/mL containing different short amines. The flame ionization detector (FID) used was not able to detect methylamine and ethylamine. It was found that comparing the three fibers used, CW-DVB has the best extraction recovery among those tested, likely forming hydrogen bonds through the hydroxyl groups present in the polymer surface with the amine group.[12]

One successful derivatization reagent for amines is pentafluorobenzaldehyde (PFBAY), which converts amines to imines. The derivatization can be performed in the presence of acetonitrile and water, which will result in high sensitivity and better chromatographic resolution. PFBAY can only react with primary amines and previous studies have shown that PA was the best SPME fiber coating to extract the derivatives compared to others like CW-DVB.[12]

### 1.2.3 Measurement of Fatty Amine Using Electrochemiluminescence

The electrochemiluminescence (ECL) technique has been utilized in the measurements of residuals of ethoxylated fatty amines used in offshore drilling operations as a corrosion inhibitors. This technique is based on a process through which highly reactive species are generated from stable precursors at the surface of an electrode, and react with one another, producing light. Fatty amine ethoxylates that have tertiary amines were used as a co-reactant in the ECL sequence since they could form a radical in the reaction process.[13]

The detection limit of this method was found to be in the range of 5 to 50 mg/L. Sodium hypochlorite at high pH was used to oxidize the tertiary amine group, which then resulted in the formation of the rhodamine-excited state. The mechanism of the reaction is similar to that of the following tri-*n*-propylamine:

$$Ru(bpy)_3{}^{2+} - e^- \rightarrow Ru(bpy)_3{}^{3+}$$

$$C_9H_{21}N - e^- \rightarrow [C_9H_{21}N^{\cdot}]^+ \rightarrow [C_9H_{20}N]^{\cdot} + H^+$$

$$C_9H_{20}N^{\cdot} + Ru(bpy)_3{}^{3+} \rightarrow * Ru(bpy)_3{}^{2+} + Products$$

Where: $*Ru(bpy)_3^{2+}$ is the electronically excited species capable of undergoing emission

bpy is 2,20'-bipyridine

$C_9H_{21}N$ is tri-n-propylamine

This technique has some advantages, such as the reagents' solubilities in a variety of solvents, its low detection limits (≈$10^{-18}$ M), and the fact that it can be easily adapted for field work.[13]

### 1.2.4 Colorimetric Determination of Filming Amines

The effectiveness of the organic corrosion inhibitors should be evaluated by monitoring their residuals in the system. The concentrations of the chemicals are frequently monitored at the outlet of the plant to confirm that an optimum dosage was applied right from the beginning.

The classical method for that is the colorimetric determination of water soluble filming amine corrosion inhibitors by the reaction with bromocresol purple.[14] Briefly, most water soluble filming amines react with bromocresol purple in a specific buffered medium to form a yellow complex, which is soluble in chloroform. The excess dye of the yellow

complex is extracted and the dye is removed with a pH 4.2 buffered wash. The chloroform layer is extracted with a pH 9.7 buffer solution forming a highly colored violet complex. The absorbance of this complex is measured at 595 nm with a spectrophotometer and compared against calibration standards.

This is a lengthy and tedious job that requires many extraction steps using many buffer solutions as well as the establishment of a calibration curve prior to working with every set of samples. A rapid, easy, one step, and solvent free method is required to assist in quick, precise, and effective decision-making.

## 1.3 Solid Phase Microextraction

Solid phase microextraction (SPME) is a sample preparation technique that was introduced in the 1990s by Professor Janusz Pawliszyn and developed in his research lab at the University of Waterloo.[6,8,15,16,17] This technique, which can be used in the extraction of gases, liquids, and solids, has many advantages over other conventional extraction techniques like SPE and liquid-liquid extraction (LLE).[16,18,19] SPME reduces the impact of harmful organic solvents to both humans and the environment.[15,16,19] It is a rapid, simple, inexpensive technique that can be portable or automated and requires only small sample volumes.[7,15,16,19] Another advantage is that SPME can easily be coupled with separation instruments such as gas chromatographs (GC).[7,16,19] Other techniques such as high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) can also be coupled but not as easily as with GC.[16]

### 1.3.1 Principle of SPME

SPME is based on the partitioning of the analyte in between the sample and a fused silica fiber coated with a stationary phase.[8,15,16,17,18] The coating of the fiber is normally either a liquid or solid polymeric sorbent.[8,15,16] The fiber should be exposed to the sample for a predetermined time, then the analyte will be adsorbed on the fiber coating until an equilibrium is established between both of them depending on the distribution coefficient.[8,16,17] The thermal desorption of analytes from the fiber coating is conducted

simultaneously with the introduction of the fiber into a GC injector for separation and quantification.[6,15,16,17,18] SPME has been successfully used in many applications especially in the field of organic environmental pollutants such as pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic compounds (PAHs), and volatile organic compounds (VOCs).[15,16,17]

### 1.3.2 SPME Modes

Two common modes of SPME are the direct immersion of the fiber in the sample and the exposure of the fiber to the headspace of the sample. In the direct immersion mode, the fiber is immersed in the sample, which is usually gas or liquid, and the liquid should be clean to prevent damage to the fiber. In the headspace SPME, the fiber is exposed to the vapor above the sample, which could be liquid or solid.[6,7,16] The headspace mode is recommended over the direct mode for volatile samples for two main reasons: faster extraction caused by the higher diffusion coefficient of the gas, and longer life time of the fiber because it is not in contact with the sample matrix.[6,7]

### 1.3.3 SPME Theory

The amount of analyte extracted by the coating of the fiber at equilibrium is directly proportional to the concentration of the analyte in the sample matrix.[16,17,20,21] This can be presented mathematically by the following equation:[20]

$$n_e = \frac{K_{fs} V_f V_s}{V_s + K_{fs} V_f} C_0$$

Where: $n_e$ is the amount of analyte

$C_0$ is the initial concentration of the analyte

$K_{fs}$ is the distribution coefficient

$V_f$ is the volume of the fiber coating

$V_s$ is the volume of sample matrix

For large volume samples where $V_s \gg K_{fs} V_f$, as in the case of field sampling of air or lake water, the sample volume may be neglected, which leads to the following equation:[20,21]

$$n_e = K_{fs} V_f C_0$$

From the above equation, the extracted analyte is directly proportional to its initial concentration in the matrix regardless of the sample volume.[16,20,21]

### 1.3.4 SPME Fibers

Fiber selection is one of the keys for achieving higher selectivity for the targeted analytes.[16] Only limited types of fibers are available commercially by Supelco. These cover a relatively good range of polar and nonpolar compounds.[8,16] Other coatings are being developed in-house by research groups.[16,19]

### 1.3.4.1 Commercially Available Fiber Coatings

The fiber core could be a fused silica, stableflex, or metal coated with thin layer of sorbing material with a thickness of 5 to 100 µm. SPME coatings can be classified according to their polarity, coatings type, or coating thickness.[22] The most common sorbents used are polydimethylsiloxane (PDMS) and polyacrylate (PA). PDMS is nonpolar and used mainly for the extraction of nonpolar compounds like VOCs, PAHs, and BTEX. Polar organic compounds, such as triazines and phenols, are best extracted with PA and polyethylene glycol (PEG).[5,6,8,16,22]

Table 1.1: Commercially available SPME fibers and their applications[16,22]

| Fiber Coatings | Film Thickness | Applications |
|---|---|---|
| Polydimethylsiloxane (PDMS) | 7, 30, 100 µm | Nonpolar organic compounds such as some VOCs, PAHs, and BTEX |
| Polyacrylate (PA) | 85 µm | Polar organic compounds such as triazines and phenols |
| Polyethelene glycol (PEG) | 60 µm | Very polar and work better in hydrocarbon or aromatic solvents |
| Polydimethylsiloxane/Divinylbenzene (PDMS-DVB) | 65 µm | Bipolar, aromatic hydrocarbons and small volatile analytes such as solvents; air analysis |
| Carboxen/Polydimethylsiloxane (CAR-PDMS) | 85 µm | Bipolar, VOCs and hydrocarbons |
| DVB/Carboxen-PDMS | 30, 55 µm | Bipolar with wide range of molecular weight analytes |

#### 1.3.4.2 Custom-Made Fiber Coatings

Research groups are working on the development of new fiber coatings capable of extracting highly polar compounds from water matrices.[16,19] The need for a new structure with more sample capacity leads to the development of the sol-gel technology.[6,19] It is a process of chemically binding organic polymers such as PDMS to the inorganic silica forming a cross-linked network providing higher sample capacity, higher thermal stability, more polarity, and lower detection limits.[5,15,19,23]

### 1.3.5 SPME Device

The SPME holder is a syringe-like device modified so that it can accommodate the fused silica fiber, which has a cylindrical shape to fit inside the stainless steel needle. The fiber is mounted on the plunger of the syringe for easy exposure and retrieval of the fiber. This arrangement protects the fiber from damage especially during the piercing of the septum of the vial or the injector of the GC as well as preserving the sample.[6,7,8]

### 1.3.6 On-site Implementation

One of the advantages of SPME is the easy coupling with GC for separation and quantification.[5,7,15] GC is a powerful separation technique with high efficiency and capability of coupling with many kinds of detectors.[7] An automated fiber injection system was later

introduced, which increased applications of SPME-GC in research and industrial laboratories.[15,19]

Most of these applications are conducted in the laboratory and only a few are performed in the field. The need for eliminating storage and transportation of the sample from the field to the lab was highlighted for cases where immediate corrective action was required.[21]

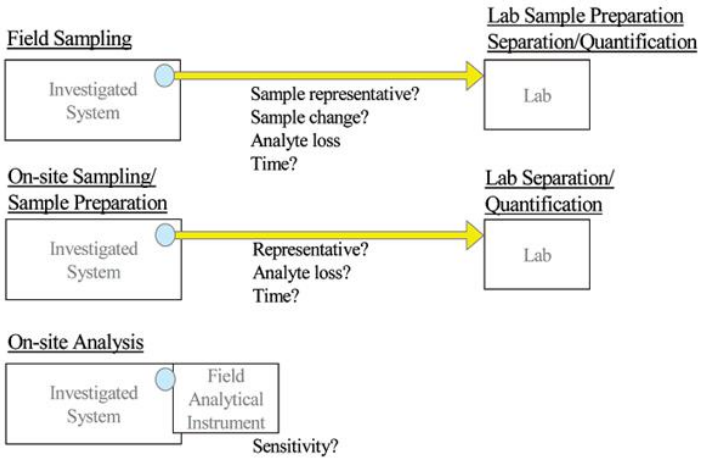


Figure 1.1: Advantages of onsite implementation[18]

On-site implementation of SPME provides accurate, precise, and faster analytical data that is helpful in environmental monitoring, medical investigations, and in vivo sampling (see Figure 1.1).[21,24]

### 1.3.7 Derivatization

One of the interesting approaches to improve extraction and selectivity of SPME is by introducing a derivatization step that converts highly polar compounds to their less polar derivatives.[15,17,19,25] Other issues associated with some analytes, such as high hydrophilicity, high reactivity, high volatility, and thermal instability, could be resolved with derivatization as well.[19,23,25] Derivatization leads to increasing the recovery of the analytes, enhancing the method selectivity and sensitivity, and improving the detection limit when combined with GC.[15,17,19,24,25]

There are three modes of combining derivatization with SPME (see Figure 1.2). Direct derivatization in the sample matrix has the most published research work; it is simply performed by adding the derivatizing reagent directly to the sample and then exposing the SPME fiber to the derivatives to extract them.[15,17,25]

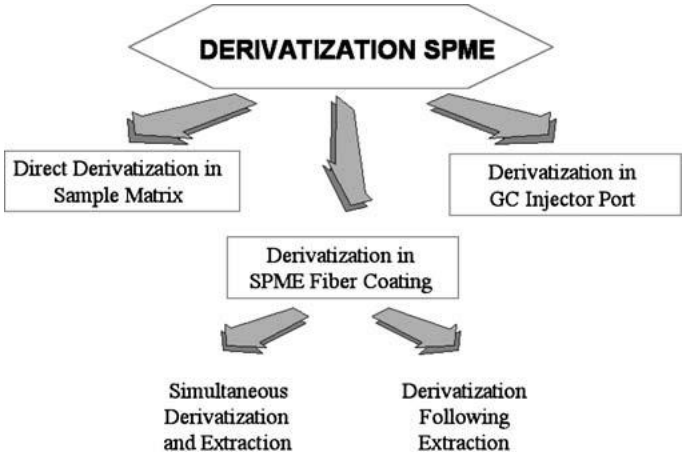


Figure 1.2: SPME derivatization approaches[20]

Derivatization in the SPME fiber coating, which is referred to as on-fiber derivatization in much of the literature, is the most advantageous derivatization technique and is performed by loading the derivatization reagent to the fiber before exposing the fiber to the analyte (see Figure 1.3). It is a powerful combination of extraction and derivatization in one step, which might be useful for onsite analyses. [15,17,24,25]

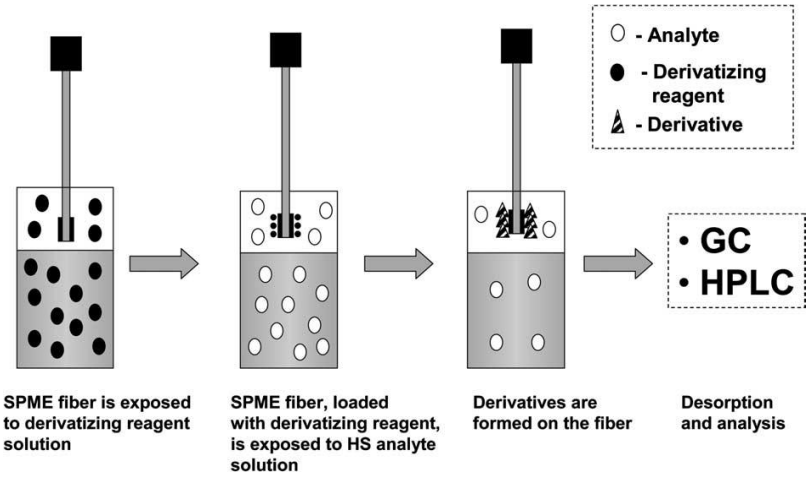


Figure 1.3: On-fiber derivatization[14]

## 1.4 Thesis Objective

The current practice to determine corrosion inhibitor residuals is liquid-liquid extraction of filming amines followed by colorimetric determination using a spectrophotometer. The solvent extraction process is a lengthy procedure, and requires a significant amount of solvent as well as intensive labor. Exposure to too much solvent has a negative effect on both human health and the environment when it is disposed of.

SPME is a rapid, easy, and environmentally-friendly sample preparation technique that is easily coupled to GC, a powerful separation instrument, leading to a higher sensitivity. It can be implemented onsite, which makes it perfect for real-life sampling, especially when immediate corrective action is required.

The objective of this work is to develop and optimize an SPME method for the analysis of aliphatic long chain amines from a solution that has a similar matrix to that of industrial waste water. A flow-through system is used to generate a standard water solution at a constant flow rate in order to simulate flowing streams in pipelines. Finally, dominant desorption kinetic calibrations are used to shorten the analysis times and make the method practical for onsite testing.

### 1.4.1 Target Analytes

The targeted analytes are a group of aliphatic long chain amines that are used as organic corrosion inhibitors for the protection of pipelines in the oil and gas industry. They

mainly consist of octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, as well as others. These chemicals are manufactured and mixed together in certain compositions as per the engineering standards and the kind of water associated with the oil production. A typical composition can be found in the following table:

Table 1.2: Composition of Armeen C[26]

| Chemical | Formula | Composition |
|---|---|---|
| Octylamine | $C_8H_{17}NH_2$ | 7% |
| Decylamine | $C_{10}H_{21}NH_2$ | 6% |
| Dodecylamine | $C_{12}H_{25}NH_2$ | 48% |
| Tetradecylamine | $C_{14}H_{29}NH_2$ | 19% |
| Hexadecylamine | $C_{16}H_{33}NH_2$ | 9% |
| Octadecylamine | $C_{18}H_{37}NH_2$ | 3% |
| Others | - | 7% |

The above table contains the composition of a chemical with the commercial name Armeen C which is produced by Akzo Nobel Chemicals Ltd. (Mississauga, ON). The general formula of the composition of Armeen C is shown below:

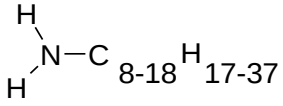


Figure 1.4: Formula of Armeen C[26]

To work in the development of the method, three of these chemicals were ordered separately from Aldrich (Oakville, ON). The three amines are decylamine, dodecylamine, and tetradecylamine, which actually make up 75% of the composition of Armeen C as per

the table above. The following table contains some chemical and physical properties of these three amines:

Table 1.3: Chemical and physical properties of target analytes[27,28,29,30]

| **Chemical** | **Formula** | **CAS #** | **M. W.** (g/mol) | **Boiling Point**/°C | **$pK_a$** | **Solubility** (g/L) | |
|---|---|---|---|---|---|---|---|
| | | | | | | **@ pH 7** | **@ pH 10** |
| Decylamine | $C_{10}H_{21}NH_2$ | 2016-57-1 | 157.3 | 221 | 10.64 | 554 | 3.3 |
| Dodecylamine | $C_{12}H_{25}NH_2$ | 124-22-1 | 185.3 | 259 | 10.63 | 120 | 0.70 |
| Tetradecylamine | $C_{14}H_{29}NH_2$ | 2016-42-4 | 213.4 | 291 | 10.62 | 28 | 0.16 |

### 1.4.2 Sample Matrix

Corrosion inhibitors are water-soluble chemicals that work as surfactants, since they have a polar hydrophilic end attached to a long chain hydrocarbon. The industrial water associated with the oil during production is highly saline, with total dissolved solids (TDS) of more than 50,000 mg/L. It also contains some suspended solids like sand particles which should not exceed the limit of 5 mg/L and size of 0.45 µm as per the engineering standards.

# Chapter 2

# Flow-Through System for the Determination of Aliphatic Amines and Selection of Proper Agitation Method

## 2.1 Introduction

### 2.1.1 The Importance of Sample Volume

The selection of the proper sample volume is crucial in the development of an SPME method, because the mass extracted from the sample is dependent on the sample volume.[22,31] However, when the sample volume is large, as in the cases of air or lake sampling, the amount extracted by the fiber becomes independent of the sample volume which makes it suitable for field sampling and onsite analyses.[32,33] Equations showing these relationships were shared in the previous chapter.

To make use of this simple approach, a flow-through laboratory water system was used to simulate the flowing streams in pipelines and provide large sample volumes. A liquid chromatography (LC) pump capable of generating stable flow rates ranging from 0.01 to 9.99 mL/min was used to deliver solutions to a modified 40 mL vial that is connected to a waste container through Teflon tubes (see Figure 2.1).

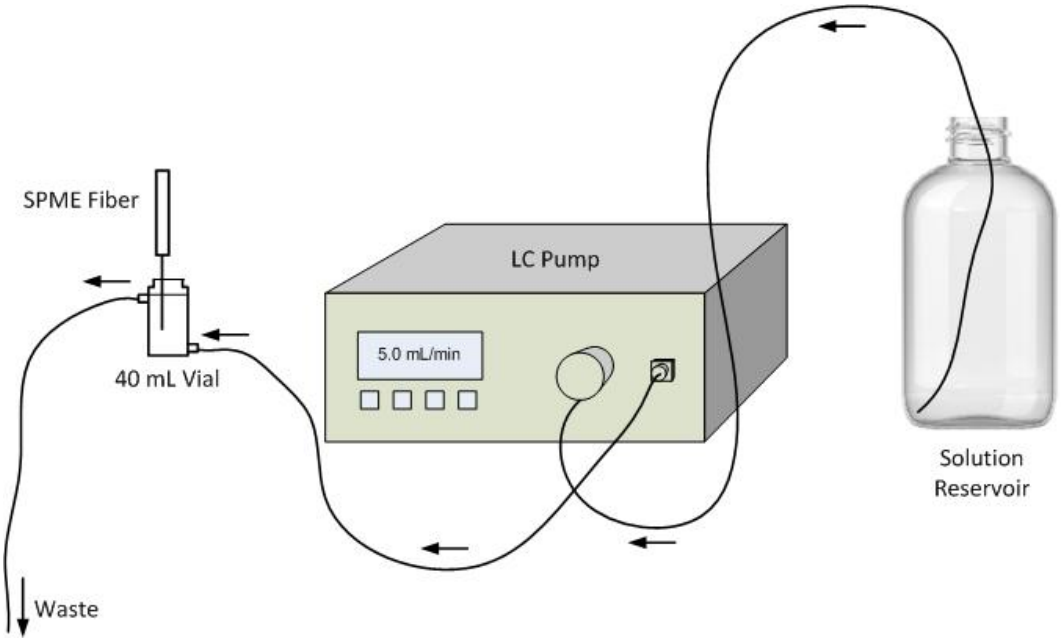


Figure 2.1: Schematic of the flow-through standard amines solution system

### 2.1.2 Agitation

Agitation is required to facilitate rapid extractions, which help in transporting the analytes from the bulk of the solution to the vicinity of the fiber. Choosing the best agitation method can help in reducing the time needed for the analytes to reach equilibrium.[22,33]

There are numerous of agitation techniques available that can be used for SPME extraction, such as magnetic stirring, needle vibration, vial moving, flow-through stirring, and sonication. At high sample flow rates, the flow-through system can offer the best agitation; however, care must be taken to eliminate any source of contamination and to ensure a constant sample flow rate, which will require some additional equipment.[22]

Sonication is another powerful agitation technique which can lead to a shorter extraction equilibration time, but the heat produced by the probe can lead to heating the sample and lowering the extraction efficiency.[22]

## 2.2 Experimental Section

### 2.2.1 Material and Chemicals

Decylamine ($C_{10}H_{21}NH_2$), dodecylamine ($C_{12}H_{25}NH_2$), and tetradecylamine ($C_{14}H_{29}NH_2$) were purchased from Aldrich (Oakville, ON). HPLC grade methanol was used to make standards and was purchased from Caledon Laboratories Ltd. (Georgetown, ON). NANO-pure water that was used in the preparation of samples was obtained from Barnstead Ultrapure Water Systems (Dubuque, IA). Helium, nitrogen, and hydrogen were obtained from Praxair (Waterloo, ON) and were of ultra-high purity. High purity air was generated in the lab using a Whatman Zero Air Generator (Haverhill, MA).

For the agitation experiment, an XL-2000 Sonicator was obtained from Qsonica (Newtown, CT), which was capable of producing power up to 20 W. 3/8" Fisherbrand TFE starburst stirring bars were used for normal agitation with a stirrer at speed of 1000 rpm and were obtained from Fisher Scientific (Ottawa, ON). The LC pump that was used in the generation of flow through system was isocratic digital pump and was obtained from Chrome Tech. Inc. (Apple Valley, MN).

The 100 μm thickness PDMS coating fibers and holder assemblies used were purchased from Supelco (Oakville, ON) and were conditioned as recommended by the manufacturer. Graduated clear glass bottles (1 L) were used to prepare the solutions and were obtained from Cole-Palmer (Montreal, QC). Hamilton syringes that were used for standard preparation and injection were purchased from Hamilton (Reno, NV). Screw top

amber glass vials (40 mL) with PTFE/silicone septa were used for the standards preparation and were obtained from Supelco (Oakville, ON).

### 2.2.2 Instrumentation

A Varian CP-3400 GC equipped with a flame ionization detector (FID) obtained from J&W Scientific (Mississauga, ON) and an Optic 2 programmable-temperature vaporizing (PTV) injector obtained from ATAS GL (Veldhoven, Netherlands) was used for all experiments. The carrier gas was helium maintained at a pressure of 15 psi, and the detector gases flow rates were set to 300 mL/min for air, 25 mL/min for nitrogen (make-up gas), and 30 mL/min for hydrogen. A 1.0 mm i.d. insert liner capable of handling injections of less than 3 µL was used for both SPME and liquid injection and was obtained from ATAS GL (Veldhoven, Netherlands).

The column used was a Restek Rtx®-5Sil MS (5% diphenyl/95 % dimethylsiloxane) phase, and its dimensions were 15 m x 0.25 mm ID with 0.25 µm stationary phase thickness, which was purchased from Chromatographic Specialties (Brockville, ON). For the instrument method, the initial oven temperature was 50°C for 2.5 min, then ramped up to 280°C at the rate of 40°C/min. The injector temperature was programmed for solvent injection from 50°C to 270°C with a rate of 600°C/min and was kept at 270°C for the fiber desorption, and the detector temperature was held at 300°C.

### 2.2.3 Flow-Through Standard Water Generating System

The previously-described setup was used to generate the standard aqueous solution of amines. The flow rate of the LC pump was set at 5.0 mL/min. Solutions with a concentration of 0.1 μg/mL, prepared by adding 0.2 mL of 500 μg/mL methanolic amines mixture to 1 L of nano-pure water, were prepared in a 4 L bottle. The pump was then operated for several hours to allow the system to equilibrate before starting the extractions. Extracted masses were calculated from solvent injection calibration curves, and concentration of the amines mixture in the system was confirmed by liquid-liquid extraction.

## 2.3 Results and Discussion

### 2.3.1 Extraction Time Profile

Although the flow-through system provides a good means of agitation, magnetic stirring was used as well in order to assist in the agitation process, by placing the 40 mL sampling vial on a stirrer with a speed of around 1000 rpm. Then, in order to establish the extraction time profile, the fiber was exposed to the flowing stream in the 40 mL sampling vial for variable times, starting from 1 min up to 300 min. Extraction at each time was repeated three times and relative standard deviation was calculated, which was in the range of 5%. Following are charts showing the extraction time profiles:

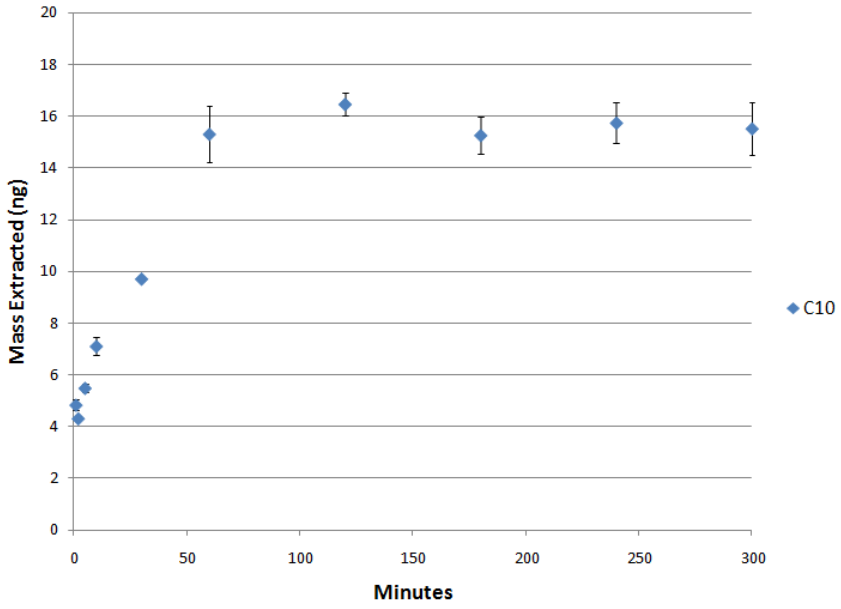


Figure 2.2: Extraction time profile of decylamine from flow-through system that contains amines mixture from 1 to 300 min

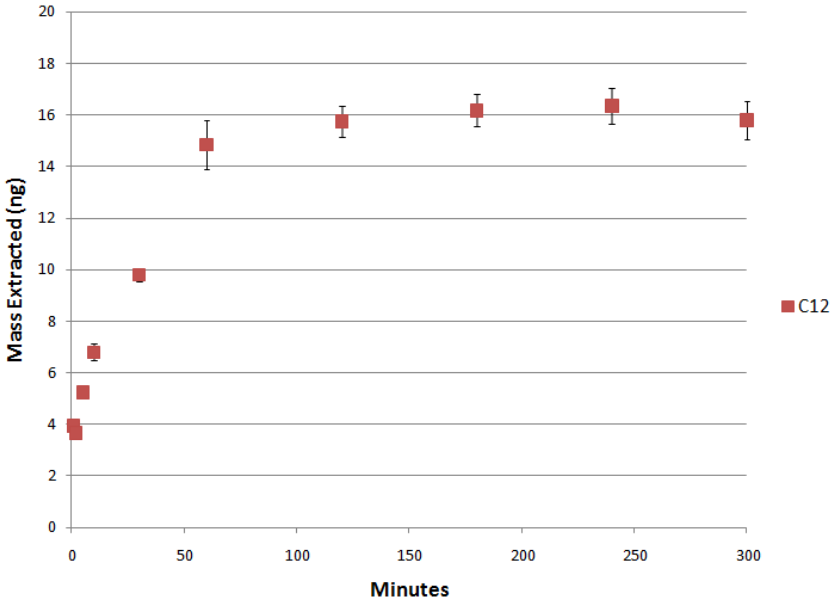


Figure 2.4: Extraction time profile of dodecylamine from flow-through system that contains amines mixture from 1 to 300 min

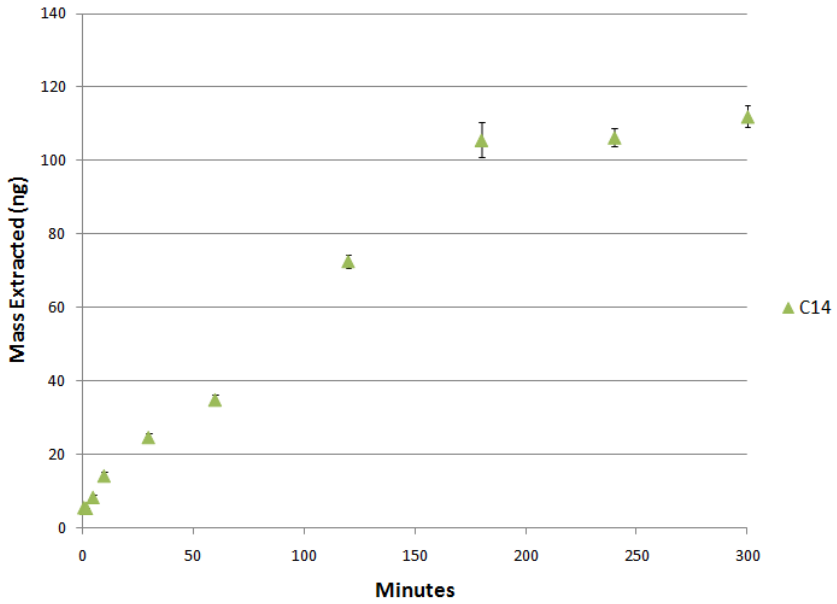


Figure 2.3: Extraction time profile of tetradecylamine from flow-through system that contains amines mixture from 1 to 300 min

From the charts above, it can be estimated visually that decylamine needed 60 min to reach equilibrium, dodecylamine needed 120 min, and tetradecylamine took 180 min, which is a long extraction time. All desorptions were carried out at 270°C for 5 min.

Following is a chromatogram to show peak shapes at different extraction times:

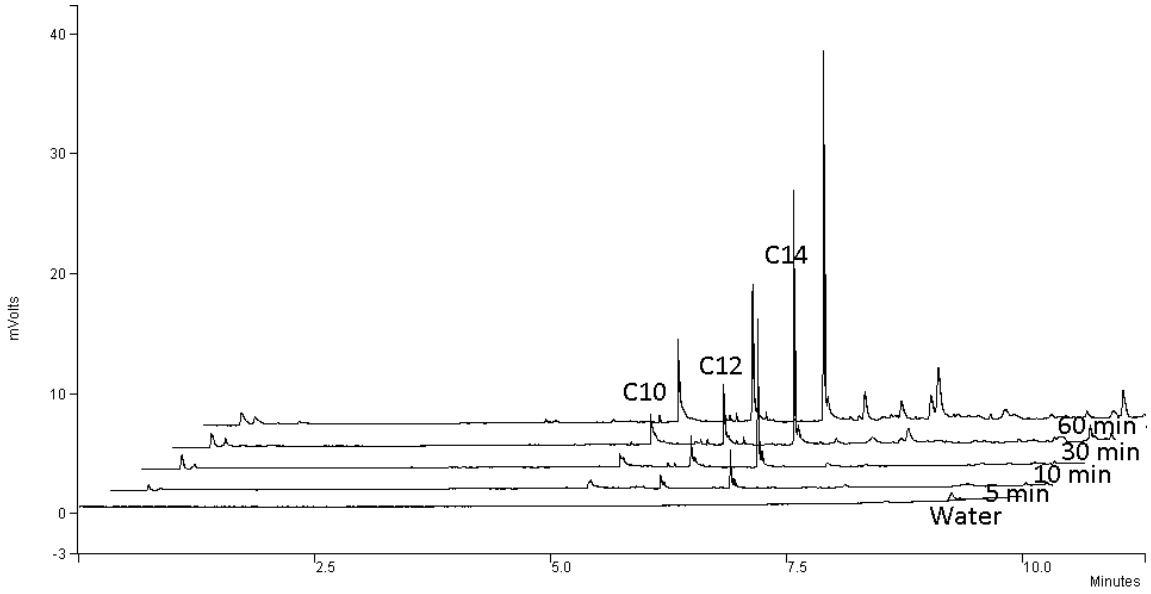


Figure 2.5: Chromatogram of different peaks of different amines at different extraction times

### 2.3.2 Sonication vs. Stirring

Another means of agitation (sonication) was introduced to help in shortening the equilibration time. Probe sonication produces a high power resulting in the possibility of solution heating which might reduce the extraction efficiency, but with the flow-through system, the solution is self-cooled.[22]

There are some other limitations of using the probe sonication approach: the high decibel noise associated with its operation, which is above Occupational Safety and Health Administration (OSHA) recommended exposure levels, and the fear of damaging the fiber coating by the power of agitation.

The same setup was used, and the probe sonication was used at a power of 10 W, instead of the magnetic stirring, with extraction times starting from 1 min up to 60 min, for the reasons mentioned above. The probe was placed inside the 40 mL sampling vial such that the tip of the probe was just below the surface of the solution and with a distance of 1.5 cm from the exposed fiber in order to protect the fiber coating from damage that might occur from the power of the sonication.

Extractions were repeated three times at different extraction times in order to build the extraction time profile, with RSD in the range of 5%. The following charts show a comparison between the results obtained from both experiments:

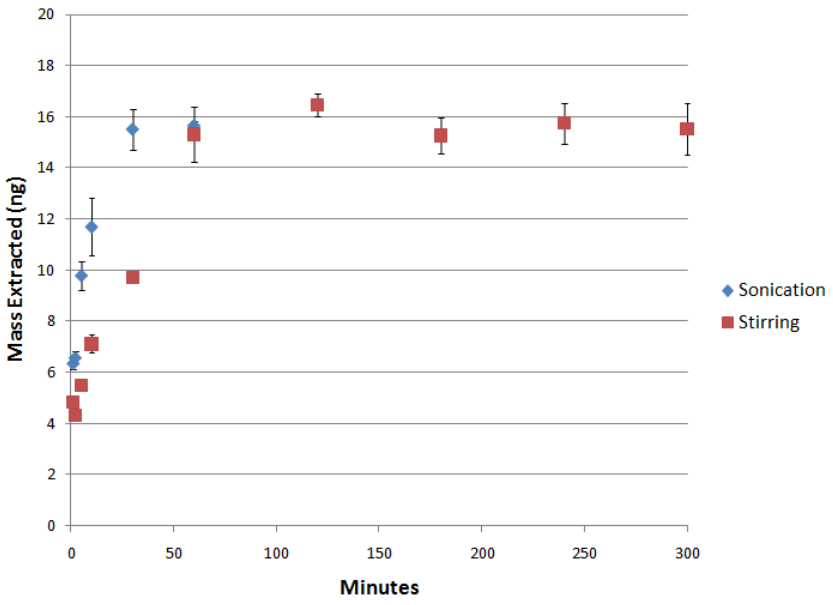


Figure 2.6: Comparison of extraction time profiles of decylamine using two different agitation techniques

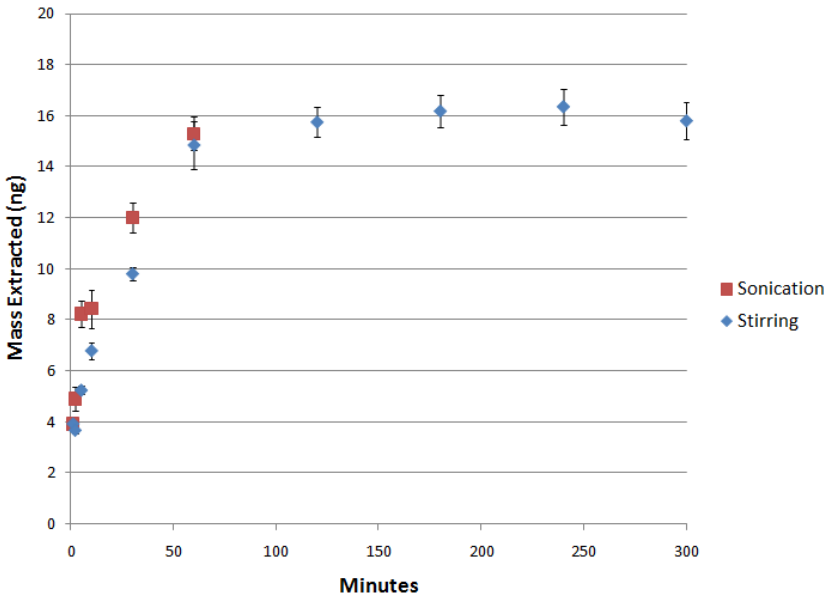


Figure 2.7: Comparison of extraction time profiles of dodecylamine using two different agitation techniques

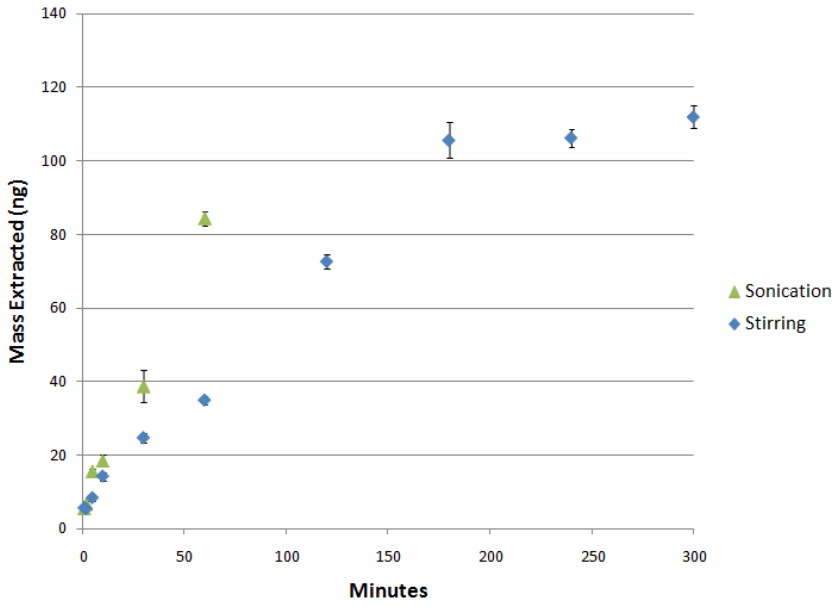


Figure 2.8: Comparison of extraction time profiles of tetradecylamine using two different agitation techniques

It is clear from the above charts that using the probe sonication to assist in the agitation of the sample while extracting helped in reducing the time needed for analytes to reach equilibrium. For decylamine, equilibration time was reduced by about 30 min compared to magnetic stirring. Little improvement was observed for dodecylamine. Finally, for the tetradecylamine, about 80% of equilibrium extraction was in 60 min, compared to the 180 min required for full equilibration with stirring.

Overall, it can be said that sonication is a powerful means of agitation, and if combined with the flow-through system, equilibration time can be significantly shortened. The limitations with using sonication, as described earlier, were the heat generated and the high decibel noise associated with its operation. The heat could be reduced by the flowing

streams, and the decibel noise can be controlled by using a special box designed by the manufacturer of the device in order to minimize the sound. The box can fit the probe and the vial, but was not able to accommodate the setup that was shown in Figure 2.1.

### 2.3.3 Variation of Fiber to Probe Distance

In an effort to have shorter equilibration times for targeted analytes using probe sonication, the fiber was brought as close as possible to the probe head. This could cause more rapid solution agitation, which should help facilitating the mass uptake by the fiber. The more rapid movement of the solution with respect to the fiber, the more analytes present in the solution exposed to the fiber coating, and the closer the system to perfect agitation.[22]

The extraction time profile experiment was carried out for all analytes with the fiber at the new position with respect to the probe head. The results were compared to those previously obtained with the fiber being away from the probe head. The temperature of the solution was monitored and was kept as low as possible, around 28°C, by modifying the flow rate of the LC pump which was set to 8 mL/min. The fiber coating was monitored as well under the microscope for any possible damage caused by the vigorous agitation of the sonication. Figure 2.9 shows the two positions that were tested.

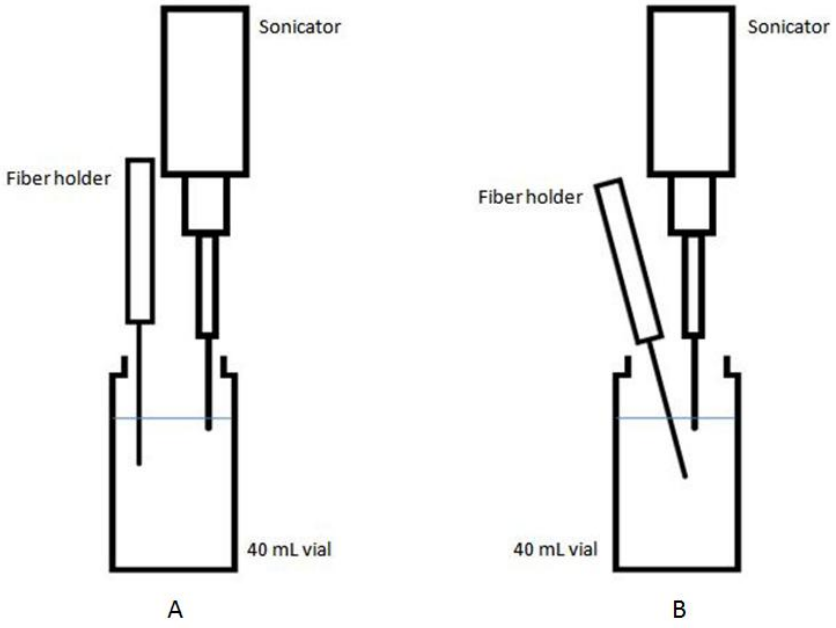


Figure 2.9: The two tested sonicator positions. (A) Having the probe at a distance of ~1.5 cm, and (B) having the probe at a distance of ~0.5 cm

It was noticed that bringing the fiber closer to the probe did not help in reducing the equilibration time, which suggests that the sonication at ~1.5 cm away from the fiber was enough to agitate the solution and give all analytes access to the fiber coating. If true, placing the probe closer or increasing the agitation of the solution will not help in reducing the extraction time.

Shown below are three charts comparing extraction time profiles of the sonication with the two positions from the fiber.

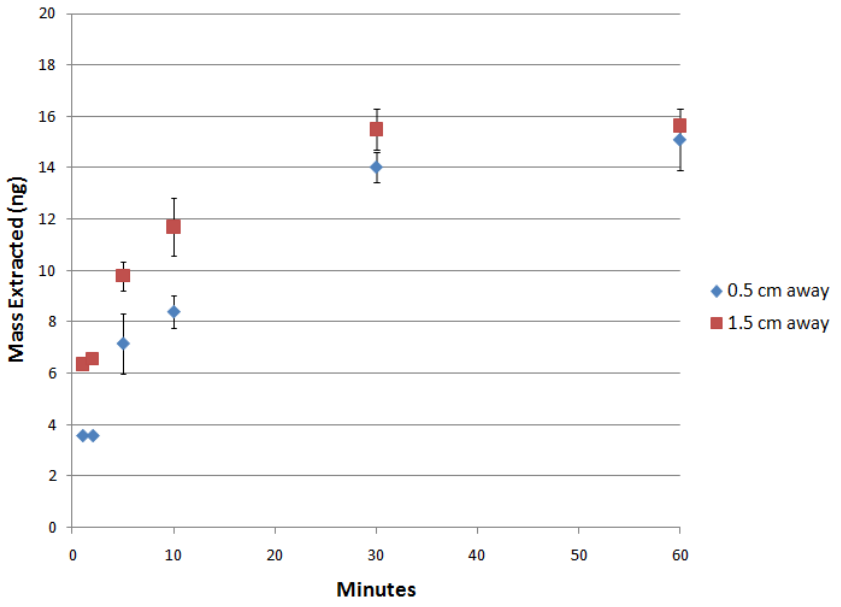


Figure 2.11: Comparison of extraction time profiles of decylamine using sonication with two different probe positions

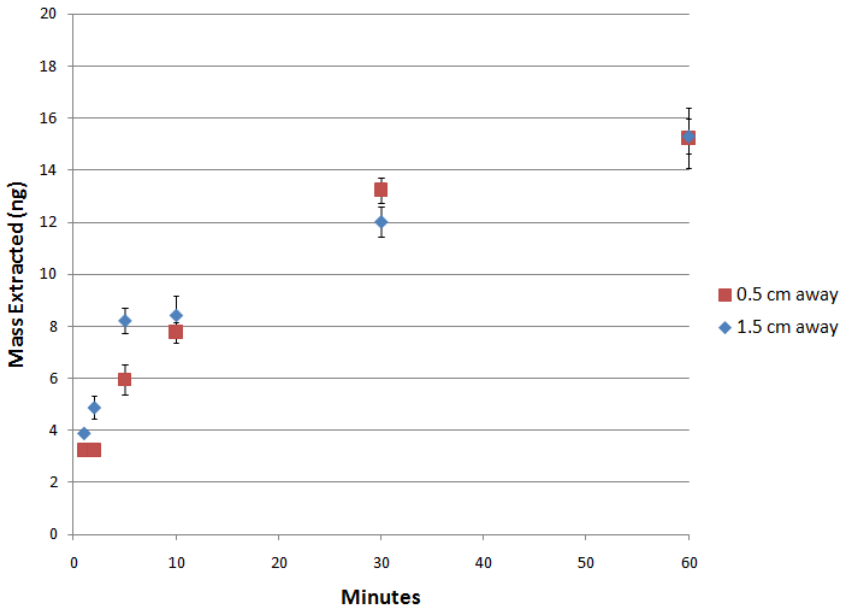


Figure 2.10: Comparison of extraction time profiles of dodecylamine using sonication with two different probe positions

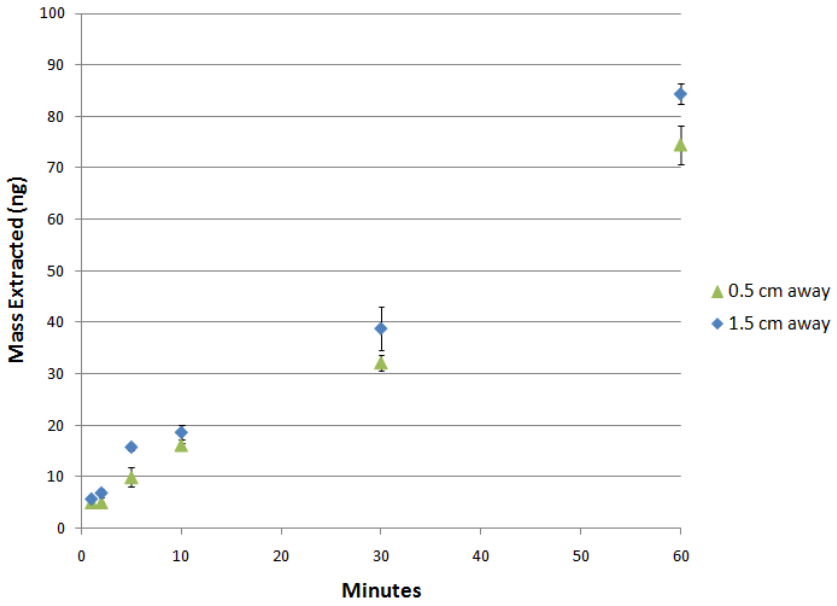


Figure 2.12: Comparison of extraction time profiles of tetradecylamine using sonication with two different probe positions

## 2.4 Conclusion

The sample volume is one of the key parameters in calculating the concentration of samples using SPME. When the sample volume is much higher than the volume of the extraction phase, the calculation of the distribution constant between the fiber and sample becomes much simpler. Also, finding the best agitation method for a certain application is crucial in maintaining a shorter equilibration time. In this chapter, a flow-through system was used to produce large volumes of solutions for extraction in order to develop a method more relevant to field sampling and to minimize the loss of analytes due to adsorption on vessel surfaces. Equilibration time profiles for the analytes were determined using stirring and were compared to another powerful agitation technique, sonication. Sonication was very helpful in reducing the extraction time, but it has three major problems: the heat produced during agitation, the decibel noise which is harmful to human ears, and possible damage to the fiber coating.

# Chapter 3

# SPME Method Development for the Analysis of Aliphatic Amines using the Flow-Through System

## 3.1 Introduction

In this chapter, SPME method development for the determination of aliphatic amines will be discussed using the flow-through system to generate a standard solution that contains the targeted analytes. The system should simulate the actual process of flowing streams in pipelines and provide unlimited volumes of solution, which will help in calculating the fiber/water distribution constant. The distribution constant will be utilized later in the determination of unknown solution concentrations.

Many method development parameters were optimized, including extraction time profile, solution pH, solution ionic strength, sand content, and desorption conditions. The main factor in this experiment was the pH adjustment, which, when increased from 7 to 10, the amount extracted substantially increased. This was mainly because of the fact that amines are of basic nature, so at higher pH, more analytes will exist in the non-ionic form which can be extracted by the fiber coating. On the other hand, at low pH, a large portion of the analytes will be ionized and will not be extracted by the fiber coating.

## 3.2 Experimental Section

### 3.2.1 Chemicals and Materials

Sodium chloride (NaCl), sodium carbonate ($Na_2CO_3$), and sodium hydrogen carbonate ($NaHCO_3$) that was used to modify the solution matrix were purchased from Supelco (Oakville ON).

The rest of chemicals and materials are described in section 2.2.1.

### 3.2.2 Instrumentation

It is the same as described in section 2.2.2.

### 3.2.3 Preparation of Standards and Samples

To prepare the amines mixture, approximately 50 mg each of decylamine, dodecylamine, and tetradecylamine were dissolved in 25 mL of methanol in order to prepare 2000 µg/mL stock solutions. This was diluted with methanol to 500 µg/mL to prepare the working solutions. All samples used for the SPME method development were prepared by adding 0.2 mL of the 500 µg/mL amines mixture into 1.0 L of water, resulting in a 0.1 µg/mL amines solution.

### 3.2.4 Solvent Injections of Amines Mixture

In order to calculate the masses extracted by the SPME fiber coating, detector response should be calibrated by direct solvent injection into the instrument and building a calibration curve from which the masses can be calculated. To do so, a series of standard solvent solutions ranging from 5 to 500 μg/mL containing amines mixtures were used to establish the calibration curves to be used for the calculations of the mass extracted from aqueous samples by the fiber.

Each standard (1 μL ) was injected into the instrument for separation and quantification, which was repeated three times for every standard with relative standard deviation (RSD) ranging from 0.12 to 3.69%. Figure 3.1 shows the calibration curves obtained, along with their corresponding equations.

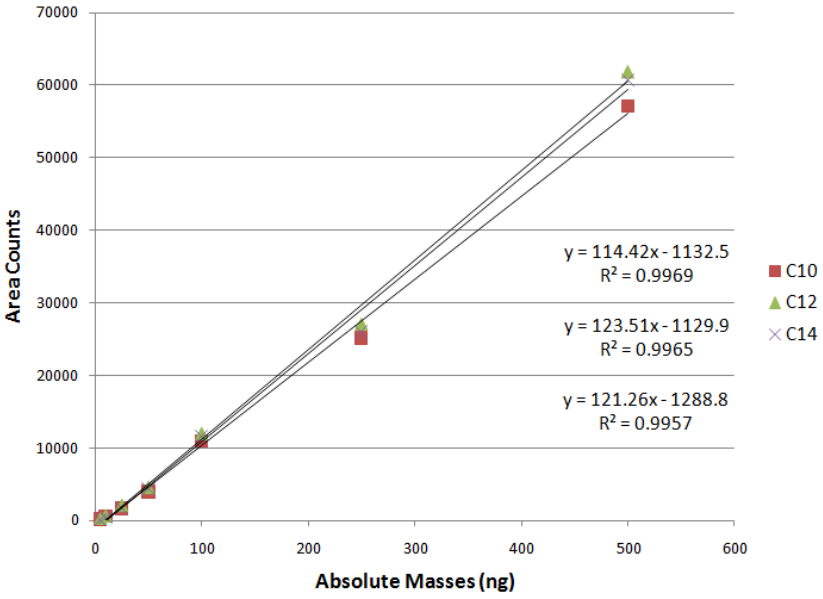


Figure 3.1: Solvent injection calibration curves for decylamine, dodecylamine, and tetradecylamine

### 3.2.5 SPME Mode Optimization

There are two modes of SPME: direct immersion (DI) of the fiber in the sample, and exposure of the fiber to the headspace (HS) above the sample. HS is preferable for volatile and semivolatile analytes, with the advantage of preventing the fiber from direct contact with the sample matrix, which could cause damage to the fiber. DI is used for non-volatile analytes with high boiling points because the portion of the analyte in the headspace is minimal.[22,33] In this study, DI was chosen for all extractions, as the boiling points of the studied analytes ranged from 220 to 290°C.

### 3.2.6 SPME Fiber Selection

PDMS is a non-polar liquid polymer coating which is suitable for a wide range of analytes, since it has similar composition to most of the capillary columns used in GCs.[22,33] A 100 µm thickness PDMS coating was chosen for this study, since it is the universal coating and suitable for non-polar compounds. The polarity of amines is reduced with the increase in the length of the hydrocarbon chain.[12]

## 3.3 Results and Discussion

### 3.3.1 SPME Optimization

SPME is an equilibration process, so experimental conditions must be carefully optimized in order to achieve quantitative results. A number of factors were investigated to optimize the extraction of the amine mixtures using PDMS coating in DI extraction mode. These factors were: the extraction time profile of analytes, the effect of ionic strength on extraction, selection of sample pH, desorption time profile, linearity of the method, and the method limit of detection (LOD).

The solution was prepared by adding 200 mL of 500 µg/L standard solution to waster. Then all of these factors were optimized for the amine mixture using the flow-through system to flow the solution at rate of 5 mL/min. All extractions were performed in triplicate and relative standard deviations were recorded.

### 3.3.2 Extraction Time Profile

Extraction time profile was determined to be 180 min and described in section 2.3.1.

### 3.3.3 Selection of Sample pH

Amines are bases which are easily protonated in neutral water and so become ionized. So, the pH of the solution should be adjusted in order to convert all species to their

neutral form. This can be approached by alkalizing the solution to a pH two units above the $pK_a$ values of the analytes in order to assure that the dominant species in the solutions are neutral. [22,33,34] In the case of the analytes under study, the $pK_a$ values are around 10.60 (see Table 3.1), so a pH adjustment should be made to approximately 12.60. However, extracting from solutions with extreme pH conditions, whether low or high, could damage the fiber coating.

The aliphatic amines are weak bases and have general formula of ($RNH_2$) and when put in solution they react with water and take up one proton to form the conjugate acid ($RNH_3^+$). The equilibrium between both species in solution could be expressed by the following equation:[35]

$$RNH_3^+ + H_2O \leftrightarrows RNH_2 + H_3O^+$$

The acid dissociation constant is expressed as follows:

$$K_a = \frac{[RNH_2][H^+]}{[RNH_3^+]} = \frac{K_w}{K_b}$$

Rearranging the equation to prepare it for the next step to be:

$$[H^+] = K_a \cdot \frac{[RNH_3^+]}{[RNH_2]}$$

Taking $-log$ both sides results in the following:

$$pH = pK_a + log\frac{[RNH_2]}{[RNH_3^+]}$$

The following table summarizes ratio of amines/conjugate acids and their impact on the $pH$ and $pK_a$ relationship:

Table 3.1: Ratio of amines/conjugate acids and their impact on pH and $pK_a$ relationship

| $\frac{[RNH_2]}{[RNH_3^+]}$ | $log\frac{[RNH_2]}{[RNH_3^+]}$ | $pH = pK_a + log\frac{[RNH_2]}{[RNH_3^+]}$ |
|---|---|---|
| 100/1 | 2 | $pH = pK_a + 2$ |
| 10/1 | 1 | $pH = pK_a + 1$ |
| 1/1 | 0 | $pH = pK_a$ |

From the above table, choosing the pH to be two units above the pH will result in amines to be 99% the dominant species in the solution. But when pH and $pK_a$ have the same value, then amines will be present in the solution with same ratio as their conjugate acid.

The used fiber coating in this experiment is PDMS, which can handle solutions with pH in the range of 2 to 11, as per the manufacturer's recommendations. The pH was chosen to be 10, one unit below the upper pH limit, to prolong the life of the fiber coating.

Table 3.2: $pK_a$ values of the targeted analytes (decylamine, dodecylamine, and tetradecylamine)[30]

| **Analytes** | **$pK_a$** |
|---|---|
| Decylamine | 10.64 |
| Dodecylamine | 10.63 |
| Tetradecylamine | 10.62 |

The buffer solution was prepared by mixing 0.025 mol/kg of sodium carbonate ($Na_2CO_3$) and 0.025 mol/kg of sodium hydrogen carbonate ($NaHCO_3$), which resulted in a buffer solution with a pH of 10 at room temperature.[30]

Solutions were prepared by adding the amine standard mixture into water without pH adjustment and compared with a buffered solution that has the pH of 10. In both cases, solutions were prepared in bulk and the system was allowed to equilibrate before the start of extraction. Figure 3.2 shows a comparison between both cases.

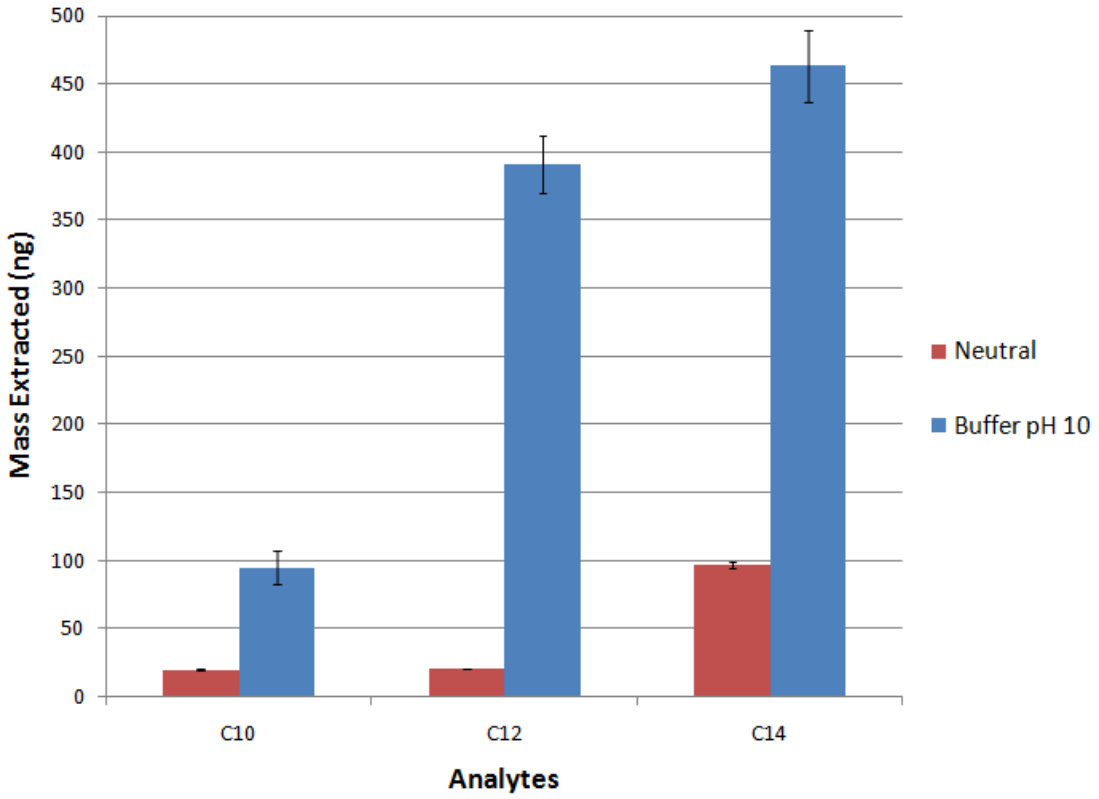


Figure 3.2: Comparison of extracted masses of different amines from neutral solution and pH-adjusted solution

It can be clearly seen that the amount extracted at a pH of 10 was substantially increased as compared to that of the neutral conditions. This is because more analytes were in the non-ionic form at a pH of 10 as compared to that of neutral conditions, so more analytes were available for extraction by the fiber coating. pH adjustment was carried out for the rest of the experiments.

### 3.3.4 Ionic Strength Optimization

When salt is added to the solution, the ionic strength is increased resulting in decreasing the solubility of the organic analytes and improving the sensitivity of the method. This is due to the fact that aqueous solutions prefer to solvate salts rather than organic matters which will result in enhancing the release of analytes from the sample and make them available for extraction by the fiber coating. The addition of NaCl was chosen to adjust the ionic strength of the solution which is the most often used salt.[22]

The concentration of the salt was chosen to be 5% NaCl which is the range of the salt present in the oil production waste water. This amount of salt was added to the buffered solution in order to examine the effect of combining pH adjustment and salt addition on the efficiency of extraction.

In all experiments, solutions were prepared by adding the same amounts of analytes to water, resulting in the same concentration, which was 0.1 µg/mL of the amines mixture. The system was allowed to run 12 hours to reach a steady state and to equilibrate before starting extractions. Extractions were carried out for 3 h, which is the equilibration time as determined earlier in chapter 2.

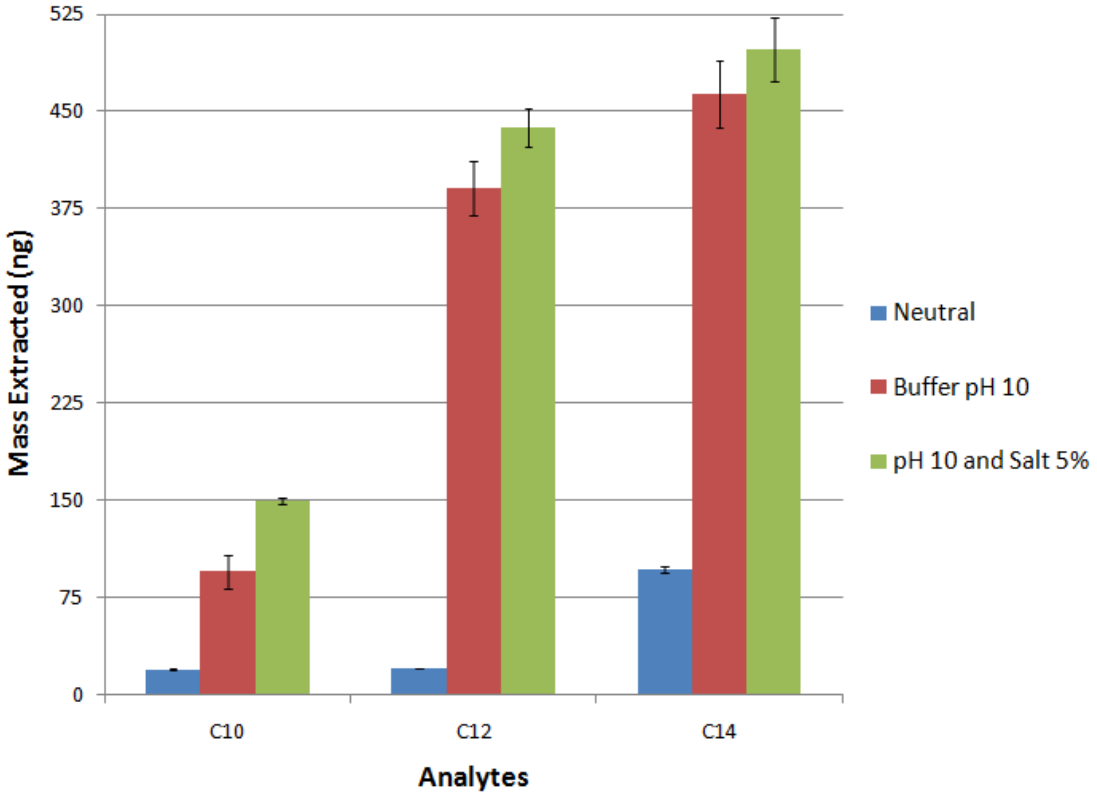


Figure 3.3: Comparison of extracted masses of different amines from neutral solution, pH 10 solution, and pH 10 solution with 5% NaCl

From Figure 3.3, it can be clearly seen that adding the NaCl salt to the pH-adjusted solution did not significantly enhanced the extraction efficiency, as compared to adjusting pH only without any salt added for dodecylamine and tetradecylamine. However, there was some enhancement in the amount extracted for decylamine.

### 3.3.5 Sand Effect Experiment

Since sand and suspended sediments are present in real samples, it was necessary to examine the binding effect of analytes on sand particles. It is known that any additional phases in the solution might compete for analytes with the extraction phase, resulting in a decrease of the extraction efficiency of the target analytes.[22]

This experiment was designed to examine this assumption by adding 5 mg/L of sand particles, which is the maximum allowable sand content in waste water, to the solution. These particles were added to the pH-adjusted solution, which contained 5% NaCl, and allowed to mix properly overnight before starting extraction.

This experiment was necessary to study the possible loss of analytes due to binding to the sand particles. From Figure 3.4, it can be seen that there is a slight variation between the amount extracted with the presence of sand and without the presence of sand.

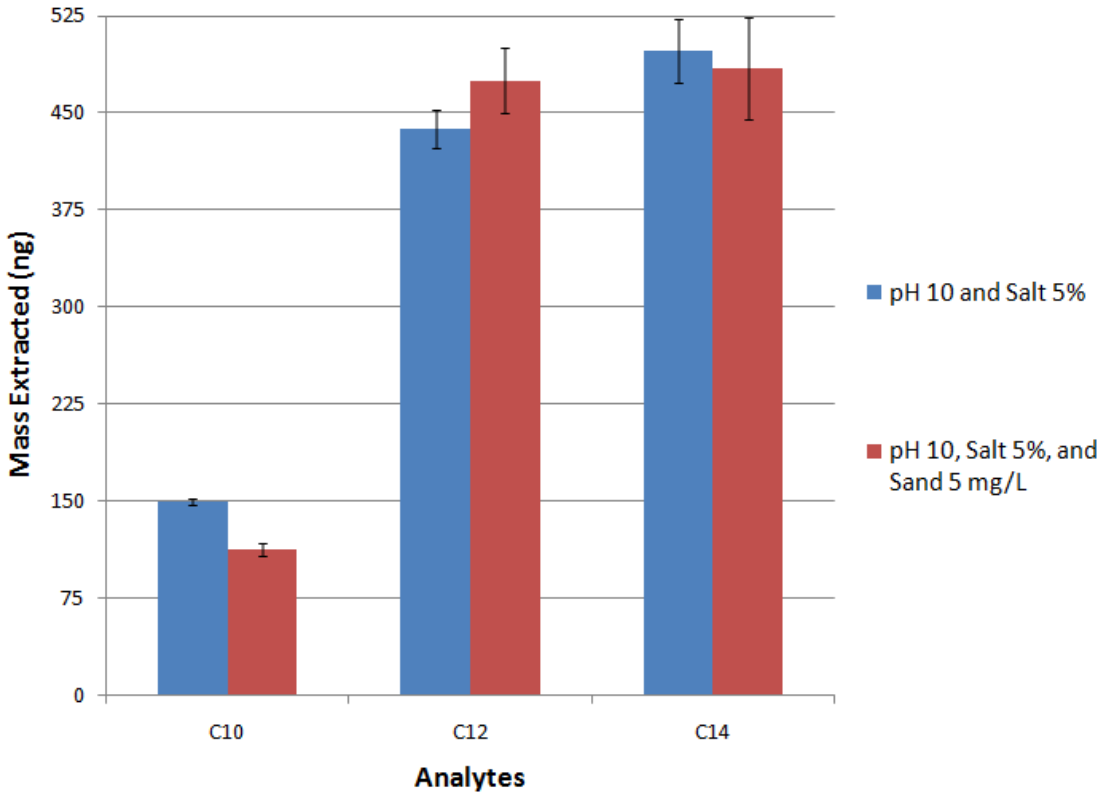


Figure 3.4: Comparison of extracted masses from pH 10 solution with 5% NaCl and pH 10 solution with 5% NaCl and 5 mg/L sand

In the case of decylamine, around 15% of analytes were lost during extraction, with RSD of 2.5 to 4.4%. For dodecylamine and tetradecylamine, variations were much less than that of decylamine. 3 to 8% variations were noticed, with RSD in the range of 3.3 to 8.1% so these variations are not likely significant. A possible reason for the bigger loss in the case of decylamine is because it has a shorter chain length and hence is more polar, which leads to possible losses due to binding to existing surfaces in the solution.

### 3.3.6 Desorption Conditions Experiment

Thermal desorption of extracted analytes into the GC injector ports is affected by many factors, like carrier gas flow rate, injector temperature, and desorption time. The higher the temperature, the more efficient and quicker the release of analytes from the fiber into the GC column is. This is mainly because the gas/coating distribution constant is decreased when the temperature is increased resulting in lowering the affinity of fiber coating to keep the analytes and therefore they are promptly released into the GC column.[22]

The carrier gas was maintained at a constant pressure of 15 psi, and no flow rate control was possible due to the fact that the Optic 2 injector has no carrier gas flow rate control, and so only carrier gas pressure can be controlled. The other two parameters were varied at four different desorption conditions: two different desorption temperatures, 250°C and 270°C, and two different desorption times, 2 min and 5 min.

All experiments were carried out at the optimized conditions, which are: a buffered solution with 5% NaCl for 3 h extraction time. All extractions were done in triplicate, and after each desorption the fiber was placed back into the GC injector for 5 min to further desorb any carryovers of analytes that might not desorbed in the first place. Also, to clear the fiber memory and make it ready for the next extraction.

From Figure 3.5, It was found that 5 min of desorption at 270°C was the optimum desorption condition for this method, where more than 95% of the analytes were transferred into the column with minimum carryover of less than 5%.

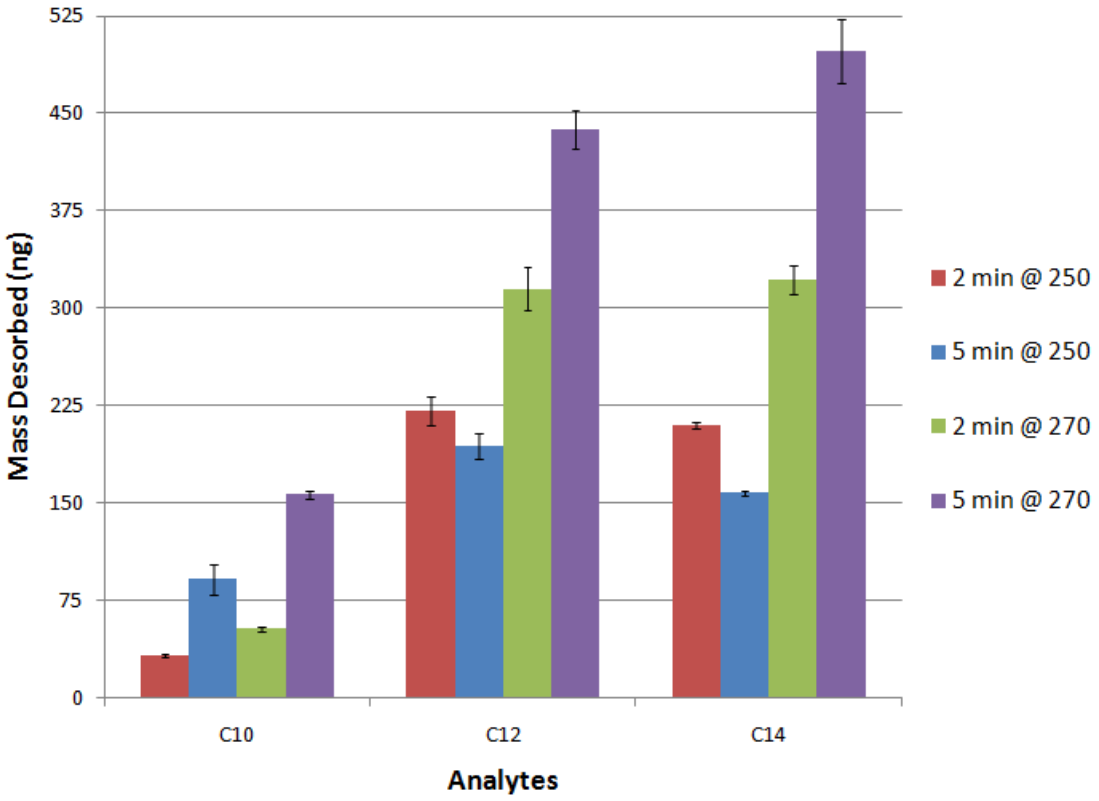


Figure 3.5: Comparison of desorption conditions at 2 min at 250°C, 5 min at 250°C, 2 min at 270°C, and 5 min at 270°C

The carryover experiment was carried out by desorbing fibers for the second time after each initial desorption to calculate how much analytes remain on the fiber. This was

performed at desorption temperature of 270°C for 5 min. the following chart shows the carry over amount which was less than 5%.

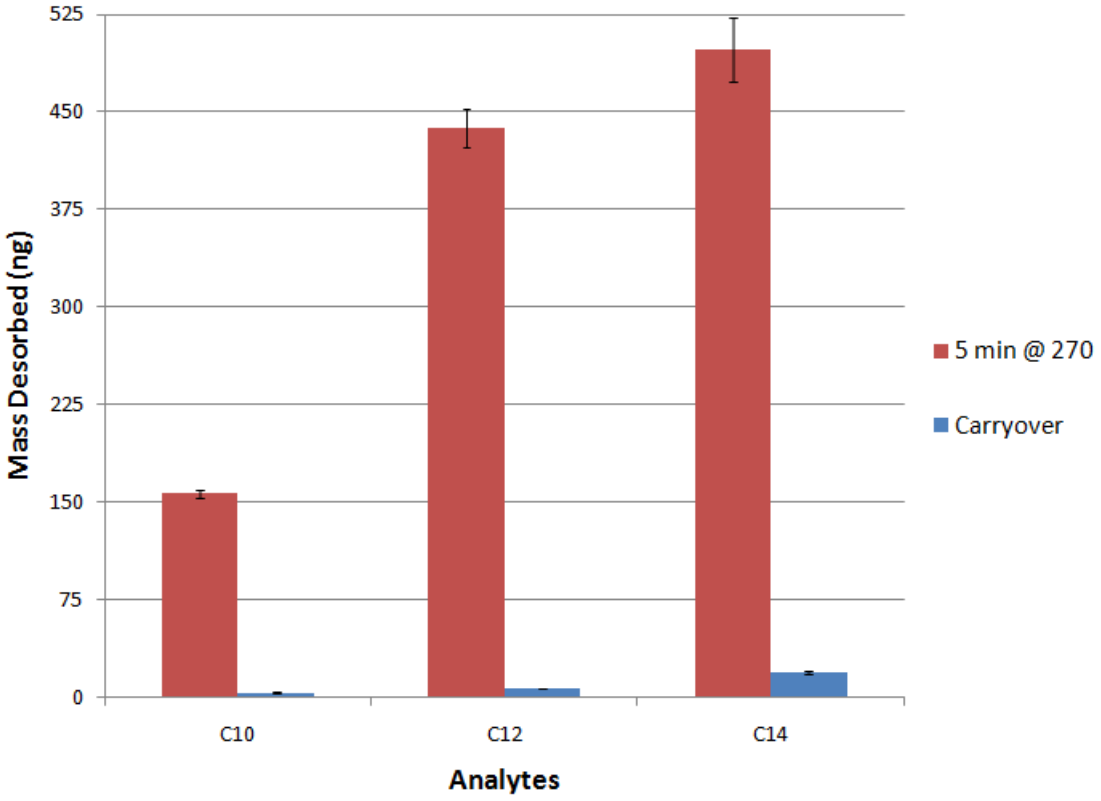


Figure 3.6: Carryover results for desorption at 270°C for 5 min

### 3.3.7 Linear Range and Limit of Detection

The linearity of the PDMS coating to extract amines was determined by the analyses of a set of diluted solutions from the original concentration, which was 0.1 µg/mL using the optimized conditions. 5, 10, 25, and 50 ng/mL were used for this experiment in order to

establish the linear curve. Each concentration was prepared separately and allowed to run for couple of hours in the system until it reached a steady state before starting extractions. Each extraction was performed in triplicate, and RSD was calculated.

Table 3.3: Linearity of the method with calculated LOD

| **Compound** | **Fiber linear range** (ng/mL, FID) | **$R^2$** | **RSD %** | **LOD** (ng/mL) |
|---|---|---|---|---|
| Decylamine | 5 – 100 | 0.9967 | 2.0 – 4.5 | 0.8 |
| Dodecylamine | 5 – 100 | 0.9992 | 3.3 – 5.3 | 1.3 |
| Tetradecylamine | 5 – 100 | 0.9976 | 1.2 – 5.0 | 1.0 |

The limit of detection (LOD) of the detector is generally defined as the lowest amount of analyte that could provide a signal three times the background noise of the blank. It can be calculated mathematically by running at least 7 extractions of a blank or the lowest concentration that could be detected, and then a standard deviation of these runs is calculated and the limit of detection would be 3 times the standard deviation. For that purpose, a solution containing 1 ng/mL of amines mixture was prepared, and the experiment was carried out at optimized conditions. Calculated LODs are listed in Table 3.3.

## 3.4 Conclusion

In this chapter, a method was developed for the extraction of decylamine, dodecylamine, and tetradecylamine from water, using a flow-through system. The various method development parameters were carefully studied and compared in order to get the optimum conditions for extraction. It was found that the pH of the sample has to be adjusted to 10 to have approximately equal ratios of dissociated and un-dissociated amines in the solution. This is because of the fact that the fiber coating extracts only analytes in the un-dissociated form. Sand addition was performed to analyze the possible losses of analytes due to the presence of another extraction phase. It was found that some analytes might be lost if the sample contained certain amounts of sand, likely due to binding of analytes to it. The limits of detection of the three analytes were calculated from 7 extractions of a sample contacting 1 ng/mL of amines, and tabulated above.

# Chapter 4

# In-Fiber Standard Kinetic Calibration for Shorter On-Site Analyses of Aliphatic Amines

## 4.1 Introduction

### 4.1.1 Calibration of SPME by Liquid Injection

To calculate the absolute mass injected into the instrument, liquid injection of known concentrations should be carried out in order to develop a calibration curve in which all area counts can be converted to masses. There are many factors that should be taken into account, like size of the liner, the presence of wool in the liner, and the injector temperature program. A comparison of different scenarios was described in the literature which indicated that a smaller liner ID, with wool packed inside, will result in the best mass transfer into the column.[36]

### 4.1.2 External Standard Calibration

This is one of the traditional calibration methods mostly used for laboratory analyses and sometimes on-site as well. This method is simple and widely-used in SPME calibration by preparing a number of known standards and using SPME for extraction and introduction into the instrument. To use this method, all conditions must be the same for all standards as

well as the unknown sample. Conditions like extraction time, agitation speed, sample temperature, and sample matrix should be controlled.[37]

The simplicity of this method makes it preferable for on-site analyses, especially for gaseous samples, which require a shorter equilibration time. For aqueous samples, this might not be the perfect calibration method since it requires longer equilibration, as in the case of aliphatic amines (3 hours extraction time), and so may not be feasible for field analyses.[22]

This method was also widely used in the calculation of the concentration of the analytes in the flow-through system, which is required to calculate the fiber/solution distribution constant. Different concentrations are prepared with the same matrix modification and extraction/desorption conditions, and from the calibration curve produced, the concentration of a sample of the effluent of the flow-through system can be calculated.[37,38]

### 4.1.3 In-Fiber Standardization

This kind of kinetic calibration is based on the desorption of an internal standard on the fiber coating in order to calibrate the extraction of the target analytes from the sample matrix.[39] Traditionally, the standard is delivered to the sample matrix, which is not practical for on-site sampling; however, in the in-fiber standardization approach, the standard is loaded onto the extraction phase and desorbed into the solution. It utilizes the fact that

absorption and desorption of analytes onto and from an SPME fiber coating are mirror images of each other under the same agitation conditions.[40] Radioactive or deuterated internal standards might be used, but they may be either expensive or not available. The target analytes can be used instead, allowing desorption to calibrate for the absorption.[41]

The absorption of any analyte onto an SPME liquid coating fiber can be theoretically described by the following equation:[20]

$$n = n_0[1 - exp(-at)]$$

Where $n$ is the extracted amount of the analyte at time $t$

$n_0$ Is the extracted amount of the analyte at equilibrium

$a$ is a constant describing the rate of absorption/desorption equilibrium, which depends on mass transfer coefficient, distribution coefficient, and the type of fiber coating[39]

Similarly, the desorption of analytes from an SPME liquid coating fiber into the solution can be theoretically described by the following equation:

$$Q = q_0 exp(-at)$$

Where $q_0$ is the preloaded amount of analyte into the fiber

$Q$ is the amount of the analyte remaining in the fiber after desorbing the fiber into the solution from time $t$[20]

Both equations can be rearranged to express the symmetry of the absorption and desorption of the analyte onto and from the SPME fiber coating.[20]

$$\frac{n}{n_0} = 1 - exp(-at)$$

The left side of the equation represents the fraction of the analyte absorbed on the fiber after time $t$, and the fraction of the analyte remaining on the fiber after desorption for time $t$ can be expressed by:[20]

$$\frac{Q}{q_0} = exp(-at)$$

When $a$ in both equations has the same value, the sum of both equations should equal to 1 at any absorption/desorption time $t$ as follows:[20]

$$\frac{n}{n_0} + \frac{Q}{q_0} = 1$$

The above equation is true for liquid polymer SPME coatings like PDMS and PA because analytes are absorbed by the fiber coating. It was reported previously that when the amount of the standard preloaded onto the fiber is very high, pre-equilibrium desorption of the analyte into the sample matrix is dominant and extraction is insignificant.[41] By preloading a much higher amount of the analyte onto the fiber than the amount that the fiber could potentially extract and then desorbing the fiber into the solution for short times, the amount of analyte that the fiber can extract at equilibrium can be calculated by knowing how much analyte is extracted by the fiber coating for shorter times by rearranging the above equation to be:

$$n_0 = \frac{nq_0}{q_0 - Q}$$

Then, by knowing the $K_{fs}$ value, the initial concentration of the solution can be calculated by the following equation:

$$C_0 = \frac{n_0}{K_{fs}V_f}$$

This approach is very helpful for on-site sampling, providing rapid analyses combining sampling and sample preparation in one step without the bother of external calibrations.

### 4.1.4 Loading Techniques

There are four standard loading techniques that were evaluated previously by Zhao et al. From those, direct transfer from the syringe onto the fiber was chosen for this experiment.[40] This technique was performed by transferring 1 µL of the methanolic standard solution onto the SPME fiber coating and waiting for the full volatilization of the solvent in air at room temperature before desorbing the fiber either into the GC injector or the flowing solution. This technique is preferred for low volatility compounds, as the loss of standards due to vaporization should be limited. It has the advantages of simplicity, good reproducibility, and ease in adjusting the concentration of the loaded standards.

## 4.2 Experimental Section

### 4.2.1 Chemicals and Materials

1.5 mL Fisher brand micro-centrifuge tubes were used for LLE and were purchased from Fisher Scientific (Ottawa, ON).

The rest of chemicals and materials are described in section 2.2.1.

### 4.2.2 Instrumentation

It is the same as described in section 2.2.2.

### 4.2.3 Predominant Desorption for Waste Water Analysis

The waste water of oil production has a salt content of 5% with a neutral pH. So this experiment was carried out using the same conditions of the waste water. By knowing the potential extraction efficiency of the fiber from the solution at equilibrium, the concentration of the preloaded analytes was chosen to be 1 μL of 10,000 μg/mL. The direct transfer of analytes from the syringe into the fiber technique was chosen based on the reasoning described earlier. Waiting time for the solvent content in the standard to evaporate was 5 min and was kept constant for all desorptions. The preloaded amount was verified by desorbing the fiber into the GC port for quantification prior to desorption in the flowing solution which contains the amines mixture. All extractions were repeated five

times using the same fiber for both extraction and desorption. The pre-equilibrium extraction time was chosen to be 20 min, and the same time was set for the preloaded analytes to desorb in the flowing solution. Desorptions and extractions were performed at the same time. LLE was performed in order to calculate the actual concentration of the amines in the solution, and was done several times throughout the experiment.

It is worth mentioning here that the actual maximum allowable concentration of these analytes in industrial waste water is 5.0 μg/mL.

## 4.3 Results and Discussion

### 4.3.1 Calculation of Actual Concentration by LLE

Liquid-liquid extraction (LLE) was carried out to exhaustively extract all analytes available in the solution and calculate the actual concentration in the system. The general procedure of LLE extraction of organic compounds from aqueous was taken from EPA 3510C.[42] 500 mL of the effluent of the flow-through system was collected in a 500 mL separatory funnel and was extracted with three 30 mL portions of methylene chloride. The three organic layers were collected in a 125 mL Erlenmeyer flask and were allowed to evaporate in a water bath at room temperature with nitrogen flowing inside the flask. When the volume of the solvent became less than 2 mL, it was transferred into a 1.5 mL micro-centrifuge tube and evaporated to approximately 1.0 mL. The solvent (1 µL) was injected into the GC for separation and quantification.

The following table summarizes the LLE results for all extractions done during the experiments with their average and standard deviation (n=3):

Table 4.1: Actual concentrations of flow-through system confirmed by LLE

| **Analytes** | **LLE 1** (ng/mL) | **LLE 2** (ng/mL) | **LLE 3** (ng/mL) | **Average LLE** (ng/mL) |
|---|---|---|---|---|
| Decylamine | 233 ± 9.1 | 230 ± 8.2 | 210 ± 19 | 224 ± 22 |
| Dodecylamine | 1447 ± 19 | 248 ± 23 | 221 ± 5.2 | 245 ± 31 |
| Tetradecylamine | 191 ± 4.4 | 153 ± 15 | 139 ± 8.2 | 161 ± 17 |

Table 4.1 shows the variation in the concentrations of the analytes throughout the experiment. Concentrations were quite stable for both decylamine and dodecylamine, but decreased for the heavier amine tetradecylamine. This indicates that tetradecylamine might need more time to equilibrate and become stable in the system due to its behavior as a surfactant. Also tetradecylamine tends to stick on the walls of the glass bottles and tubing, which lowers its concentration with time. This variation in the concentration contributes to the high error in calculating the $K_{fs}$ value, and later the predicted concentration form the dominant desorption experiment. This should be prevented by allowing the system to further equilibrate in order for all active sites of the glass to get saturated with the targeted analytes.

### 4.3.2 Calculation of Distribution Constant $K_{fs}$

The equation that relates initial concentration to the amount extracted at equilibrium and distribution constants can be rearranged to calculate the distribution constant after simplifying the equation, knowing that the volume of the sample is much larger than the volume of the extraction phase. The equation can be rewritten into:

$$K_{fs} = \frac{n_e}{V_f C_0}$$

Where $n_e$ is the amount extracted at equilibrium

$V_f$ is the volume of the 100 µm thickness PDMS coating, which is 0.612 µL

$C_0$ is the initial concentration of each analyte confirmed by LLE

The fiber was immersed in the flowing solution for three hours until equilibrium was reached in order to calculate the amount of analytes extracted, which was used to calculate $K_{fs}$ value as per the above equation. The following table summarizes the results obtained for the extractions of amines mixtures with 5% NaCl:

Table 4.2 : $K_{fs}$ values and log $K_{fs}$ of amines

| **Analytes** | $n_e$ (ng) | $C_0$ (ng/mL) | **$K_{fs}$ Value** | **log $K_{fs}$** |
|---|---|---|---|---|
| Decylamine | 16.7 ± 0.1 | 224 ± 22 | 122 ± 12 | 2.1 |
| Dodecylamine | 50.8 ± 5 | 245 ± 31 | 338 ± 54 | 2.5 |
| Tetradecylamine | 543.5 ± 8 | 161 ± 17 | 55144 ± 600 | 3.7 |

Table 4.3: Comparsion of log $K_{fs}$ values at three different solution matrices with log $K_{ow}$ value[43]

| **Analytes** | **log $K_{fs}$** (pH 7, no salt) | **log $K_{fs}$** (pH 7, 5% salt) | **log $K_{fs}$** (pH 10, 5% salt) | **log $K_{ow}$** |
|---|---|---|---|---|
| Decylamine | 2.2 | 2.1 | 3.7 | 3.8 |
| Dodecylamine | 2.4 | 2.5 | 4.2 | 4.8 |
| Tetradecylamine | 3.1 | 3.7 | 5.2 | 5.8 |

From Table 4.3, it can be seen that the partition coefficient increases with matrix modification which indicates that solubility of the amines decreased as well. When adding 5% NaCl, the solubility of the amines decreases due to the fact that the water solvates the salt more effectively than the amines. Also, when adjusting the pH, approximately equal

ratios of dissociated and un-dissociated amines are present in the solution, so more analytes could be extracted by the fiber coating. Table 1.3 in Chapter One shows the solubilities of the all targeted analytes at the two studied pHs, which decreased by two orders of magnitude when adjusting the pH to 10.

### 4.3.3 Dominant Desorption

The in-fiber kinetic calibration relationship that was shared in section 4.1.3 provides the basis for dominant desorption calibration. In the method, the preloaded amount was chosen to be more than 10 times the potential amount of analytes that the fiber could extract. The preloading was carried out by transferring 1 µL of the methanolic solution (using a micro-syringe) that contained 10,000 µg/mL of the amines mixture directly to the exposed 100 µm PDMS fiber and waiting until the solvent completely evaporated, then the fiber was exposed to the flowing solution that contained the amines mixture, and at the same time another fiber was placed in the flowing solution for extraction. Both fibers were left in the solution for 20 min and then removed and injected into the GC for desorption.

To calculate the predicted amount of analyte that could be extracted at equilibrium, the equation should be rearranged to obtain $n_0$ as follows:

$$n_0 = \frac{nq_0}{q_0 - Q}$$

Table 4.4: The different parameters of the equation and the calculated masses

| **Analytes** | ***q₀*** (ng) | ***n*** (ng) | ***Q*** (ng) | ***n₀*** (ng) |
|---|---|---|---|---|
| Decylamine | 6663 ± 338 | 11.2 ± 0.3 | 2108 ± 73 | 16.4 ± 1.5 |
| Dodecylamine | 6301 ± 371 | 16.2 ± 1 | 3714 ± 227 | 39.5 ± 7.9 |
| Tetradecylamine | 5790 ± 367 | 69.6 ± 2 | 4888 ± 255 | 447 ± 224 |

Then, by knowing $n_0$, $C_0$ can be calculated from the following equation:

$$C_0 = \frac{n_0}{K_{fs} V_f}$$

Where $V_f$ is the volume of the 100 µm thickness PDMS coating, which is 0.612 µL

$K_{fs}$ is reported in Table 4.2

Table 4.5: The calculated concentrations of analyte at equilibrium

| **Analytes** | ***n₀*** (ng) | **$K_{fs}$ Value** | ***C₀*** (ng/mL) |
|---|---|---|---|
| Decylamine | 16.4 ± 1.5 | 122 ± 12 | 220 ± 30 |
| Dodecylamine | 39.5 ± 7.9 | 338 ± 54 | 191 ± 49 |
| Tetradecylamine | 447 ± 224 | 55144 ± 600 | 132 ± 68 |

Finally, the calculated $C_0$ can be compared to the actual concentrations of amines that were previously confirmed by the LLE (see Figure 4.1).

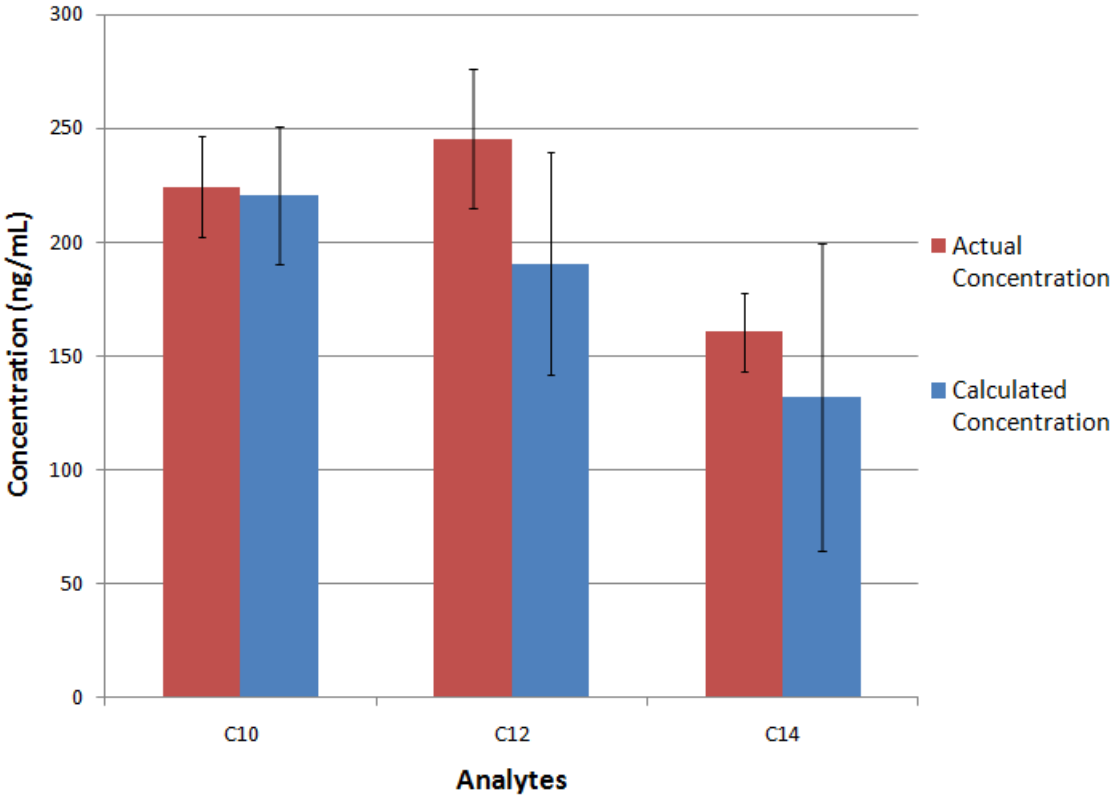


Figure 4.1: Comparison between the actual and calculated concentrations of amines

Tables 4.4 and 4.5 contain averages of data based on 5 replicates and contain standard deviations. The final error was calculated using error propagation formulas, and it is large because there are many sources of error. Errors occur from LLE, equilibrium extraction, $K_{fs}$ calculations, dominant desorption, and concentration calculation.

## 4.4 Conclusion

In this chapter, kinetic calibration using an in-fiber standardization technique was used to shorten analysis time and predict the concentration of the solution. The technique was previously proven in the literature, and it is suitable for field sampling and onsite analyses. The initial concentrations of amines were calculated from LLE, and the $K_{fs}$ value was calculated. Then, a dominant desorption experiment was used to predict the amount extracted at equilibrium without the need to wait for equilibrium to be reached. From there, the initial concentration was calculated and found to fall within 20% or less than the original concentration. This variation is acceptable when it is known that analysis time was shortened from 3 hours to 20 minutes.

# Chapter 5

# Conclusions

This work has successfully demonstrated the use of SPME sampling method for the determination of the concentration of aliphatic amines using the flow-through system. The first part of the studies, focused on applicability of equilibrium SPME method for batch to batch sample analyses in the laboratory. Various parameters such as effect of pH and salt concentration were optimized in order to improve overall method sensitivity on a GC/FID instrument.

The second part of the studies demonstrated the applicability of SPME method for onsite field analysis of aliphatic amines. The author proposed the use of a pre-equilibrium dominant desorption SPME method for this work.

Application of the method to the analysis of waste water samples was not captured in this work because of lack of access to crude oil processing waste water. An initial request made to my sponsors (Saudi Aramco) was turned down due to the hazardous nature of the waste water which restricts shipping overseas. However, the pre-equilibrium dominant desorption SPME method can be easily applied to determine the concentration of aliphatic amines in industrial waste water systems.

In order to achieve SPME onsite field analyses, special tubing and a sampling vial will be installed offline from the main waste water pipeline with a controlled valve, as shown in Figures 5.1 and 5.2.

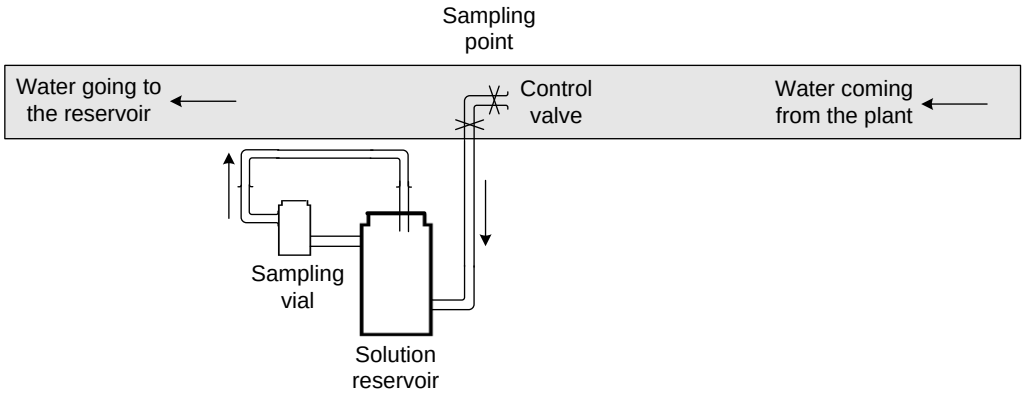


Figure 5.1: The first approach to adjust the pH on-site and the required setup

There are two approaches that can be applied; in the first one (Figure 5.1), the sample water will initially be recycled until the system equilibrates before SPME sampling. For enhanced sensitivity, the pH will be adjusted in the solution reservoir onsite to 10 since this will not affect the main waste water pipeline. SPME extractions and desorptions will be performed in the sampling vial, as indicated in previous chapters.

The second approach (Figure 5.2) will be to pre-determine the pH values of the waste water samples and the corresponding $K_{fs}$ values. The pH range for the industrial waste water is 6.5 to 8.0 and contains 5% salts. With the known $K_{fs}$ values at specific pH, sampling will be performed by first measuring the pH onsite using a hand held portable pH

meter device. The concentration of the aliphatic amines can then be determined for a particular pH of the waste water sample without having to modify the pH of the sample onsite.

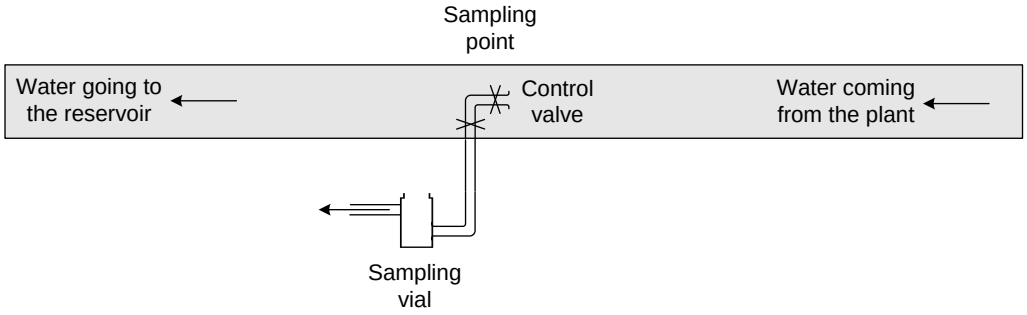


Figure 5.2: The second approach, which does not require pH adjustment

Because of the nature of the industrial waste water and the presence of other organic matters that would interfere with the targeted analytes, more selective detection systems should be used. GC/NPD can be used since it is more selective for nitrogen containing compounds or GC/MS can be used as well. Due to the fact that the analytes are very stable on the fiber after extractions, all fibers will be transported to the laboratory on dry ice for further analyses. This final stage of this work will be completed once the access to the crude oil processing waste water is possible.

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