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Abstract:

The area of carbon capture solvent degradation with degradation mechanisms is described in this project. Analyses of degraded samples originate from a pilot plant for carbon capture studied and a theoretically chromatographic procedure assessed with respect to the sample analyses. A Dionex DX _500 cation-exchange chromatograph with Dionex IonPac SCS 1 column is used for analysis the samples. The eluent used in this work was 8 mM MSA with 7 % (v/v) ACN.

The main part was to prepare a calibration curve for MEA and show the quality of the calibration curve by calculates the standard deviation. The result shows highest value for standard deviation equal to ±34.187 % and the lowest ±8.346% for 3 mM/l and 0.5 mM/l MEA respectively.

Determination coefficient for calibration curve was 0.9996 with 0.04 % deviation from the perfect fit. Some of the systematic errors in the preparation of calibration curve are quantified.

The calibration curve is used to identify the remaining MEA in the oxidative degradation samples. The analysis of oxidative degraded samples was restricted to MAE and still there are a number of unknown components in the samples.

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Preface

This is the final task of master degree in the second year study in process technology at Telemark University College. This task is a second variation of the primary task which is changed due to personally situation and limitation of time.

To understand this thesis it is necessary to have some knowledge about ion chromatography. All chromatograms and data from this research can be found in a separate appendix on CD.

I would like to thank my supervisor Prof. Klaus-Joachim Jens for his continuous guidance and support throughout the entire time of this project. My sincere gratitude also goes to PhD. Wang Tielin and Nora Furuvik for good advice and help in the laboratory.

Porsgrunn, 08.11.2013

Mojgan Zarsav

Nomenclature

Symbol	Explanation
A	Peak area
A_s	Peak asymmetry
a	Width of peak from centre to left bound
b	Width of peak from centre to right bound
H	Plate height
h	Peak heigth
k_D	Distribution constant
k’	Retention factor
L	Column length
N	Plate number
n	Number of data in the dataset
n_m	Number of molecules in mobile phase
n_s	Number of molecules in stationary phase
Q	Quaternary ammonium
R^2	Determination coefficient
R_s	Resolution
R	Correlation coefficient
s	Standard deviation
t_M	Dead time
t_R	Retention time
t_s	Solute retention
W_s	Peak width
$\bar{x}$	Mean value
x_i	Value of data point number i
σ	Gaussian standard deviation
α	Selectivity factor

Abbreviations	Explanation
ACN	Acetonitrile
CM	Carboxymethyl
CV	Coefficient of variance
DEA	Diethanolamine
DEAE	Diethylaminoethyl
DIPA	Di-2-propanolamine
HEEDA	Ethylenediamine
HEIA	Cyclic urea
HPIC	High Performance Ion Chromatography
IEC	Ion-exchange chromatography
mM	Milli molar
LC	Liquid chromatography
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MSA	Methane sulfonic acid
QAE	Quaternary amino ethyl
RSD	Relative standard deviation
S	Methyl sulfonate
SP	Sulfopropyl
TEA	Triethanolamine
µS	Micro Siemens

Molecular formulas	Name
CO_2	Carbon dioxide
H_2O	Water
NH_3	Ammonia
O_2	Oxygen

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1 Introduction

An introduction to the thesis will be provided in this chapter. Some background information related to this project and the task description will be discussed in this chapter.

1.1 Background

During the past couple of decades in the light of climate change threats due to emissions of greenhouse gasses, capturing of these gases has become an increasingly important research interest. One of the greenhouse gases which are in the center is the carbon dioxide (CO_2) gas that the most significant source of emission of this gas is the fossil fuel. Therefore, researchers and scientist at all world experimenting on the new technologies to control CO_2 emissions and reduce the greenhouse effects and also improve the CO_2 capture technologies that are already in use. There are three major technologies to capture CO_2 from exhaust gases include Post-combustion, pre-combustion and oxy-fuel, which the most well established one in the industry is the post combustion capture .The Post-combustion involves in capturing of CO_2 from flue gas after the combustion while in the pre-combustion $CO_2$is captured from the gas prior to the combustion. In the oxy-fuel capture the oxygen from the air is separated from nitrogen and mixed with the fuel before fed into the boiler unit, due to nitrogen the products after combustion achieve a flue gas stream with high CO_2 concentration and water that water can easily be condensed and separate from the gas and obtained almost a pure CO_2.

Post combustion is the background for this project. This technology can be applied by different kinds of the separation methods such as chemical absorption (solvent scrubbing), adsorption, physical absorption, cryogenics and membrane separation which the most widely used one is the chemical absorption with an amine as absorbent more detailed description about this method can be found in section 2.3. Monoethanolamine (MEA) and aminomethylpropanol (AMP) are examples of amines used as solvent. One of the problems during this separation method is solvent degradation due to the presence of O_2 and CO_2. Due to process economics and performance it is required to understanding the possible MEA degradation pathways and the degradation products for developing MEA oxidation inhibition. Therefore, ion chromatography which is the oldest and widely method can be used to identify products in oxidative degradation samples. In this research Dionex DX _500 ion chromatograph will be used.

1.2 Task description

The main objective of this project work is to use a cation-exchange chromatograph from Dionex to analyses a set of samples of degraded MEA originating from a CO_2 capture pilot plant. The result will be based on experiments in the laboratory with use of cation-exchanger chromatograph. To be able to measure the amount of remaining MEA in the unknown samples, a standard solution of MEA has to be prepared and analyzed and the calibration curve should be made from the results.

The quality of the calibration curve should be shown by calculation of standard deviation. A chromatographic procedure is to be theoretically assessed with respect to the sample analyzed. An introduction to the area of carbon capture solvent degradation will be given.

2 General theory

In this chapter general theory about amines, especially MEA, degradation pathways for MEA with focus on thermal and oxidative degradation will be discussed. In addition error, statistics, calibration methods as area normalization, internal standard, external standard and standard addition will be described.

2.1 Amine types

Amines are organic substances with a nitrogen atom bound to one or more hydrocarbon groups. Amines have a structure reminiscent of ammonia, (see *Figure 2-1.a.)*. There are various amine groups, which can be classified to primary, secondary and tertiary amines depending on the number of alkyl groups attached to nitrogen atom.

In primary amines (R-NH2) nitrogen atom in the ammonia has been bounded to two hydrogen atoms and one organic group, (see Figure 2-1.b) while secondary amines (R-NRH) consist of two organic groups and one hydrogen atom attached to nitrogen atom, see Figure 2-1.c. Monoethanolamine (MEA) is an example of primary amine and diethanolamine (DEA) and di-2-propanolamine (DIPA) for secondary amines. Tertiary amines (R-NR2) are amines wherein all hydrogen atoms in ammonia molecule have been substituted by organic groups, (see Figure 2-1.d). Triethanolamine (TEA) and methyldiethanolamine (MDEA) are most commonly tertiary amine used in the removal of CO_2 from gas streams. [1]

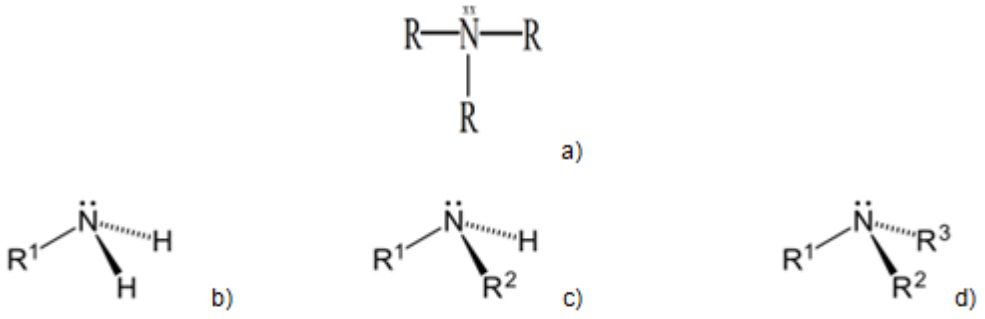

Figure 2-1: Sketch of ammonia a) and primary b), secondary c) and tertiary d) amines.[2]

2.1.1 MEA as a solvent

Among the different alkanoamines which described in the previous section, MEA has been selected for this study. Even though MEA has been used in CO_2 absorption in several years, it has some advantages as well as disadvantages in comparison to other commonly used alkanolamines.

The main benefits of MEA is high removal efficiency due to its lowest molecular weight thus more reactivity toward carbon. Furthermore MEA is a strong base that is the reason why it has quick

reaction rates which give highest purity. MEA has less hydrocarbon loss when processing refinery gas streams because of its low solubility for hydrocarbons. In addition MEA has a low raw material cost.[2]

The chemical structure of MEA is shown in Figure 2-2 and some physical properties of MEA can be found in Table 2-1.

Table 2-1: Physical properties of MEA. [3]

Molar weight [g/mol]		61.09
Vapor pressure, mmHg at 20 ºC		0.36
Solubility in water, % by weight at 20 ºC		Complete
Boiling point [ºC]	760 mmHg	171
	50 mmHg	100
	10 mmHg	69
Freezing point [ºC]		10.5

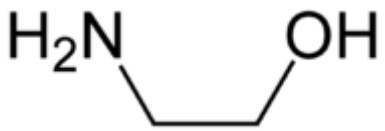

Figure 2-2: Structure of MEA. [4]

2.2 Degradation of MEA

One of the main problems in the CO_2 capture process is degradation of amine in the process, i.e. it cause corrosion in the columns, provide some environmental hazardous degradation products and furthermore succeeds additional costs for both removal degradation products and replaced degraded MEA with make-up steam due to solvent loss [5]. Thus it is quite important to decrease the degradation rates in the CO_2 removal system. Following section will provide the main degradation forms of MEA and those degradation mechanisms in a CO_2 capturing plant.

2.2.1 Thermal degradation

Thermal degradation of MEA occurs at temperatures below 200 ºC with presence of CO_2. An overwive of thermal degradation mechanism of MEA is shown in Figure 2-3. MEA react with CO_2 in to form protonated MEA and MEA carbamate. The carbamate reacts further to 2-oxazolidinone

which with attack of another MEA molecule and CO_2 produce ethylenediamine (HEEDA). The final step in the degradations is reaction between HEEDA with CO_2 and water or MEA molecule and water which forms cyclic urea (HEIA) and Tri- HEIA or AEHEIA respectively. [6, 7]

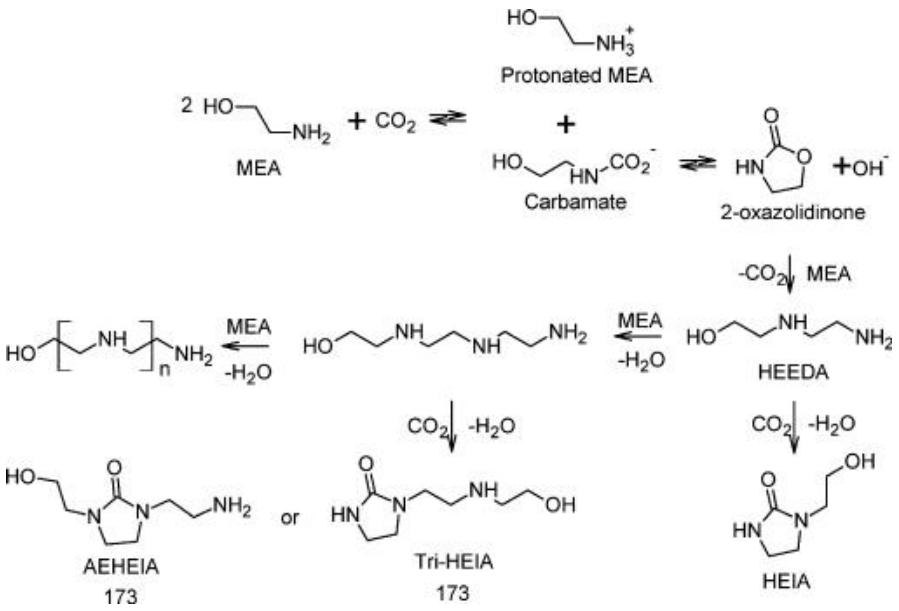

Figure 2-3: Thermal degradation mechanism of MEA. [6]

Janson Davis et al [7] studied thermal degradation of MEA in different temperature, CO_2 loading and MEA concentration. Figure 2-4 illustrates the MEA loss due to increasing temperature from 100 ºC to 150 ºC, while at temperature below 100 ºC thermal degradation of MEA is insignificant.

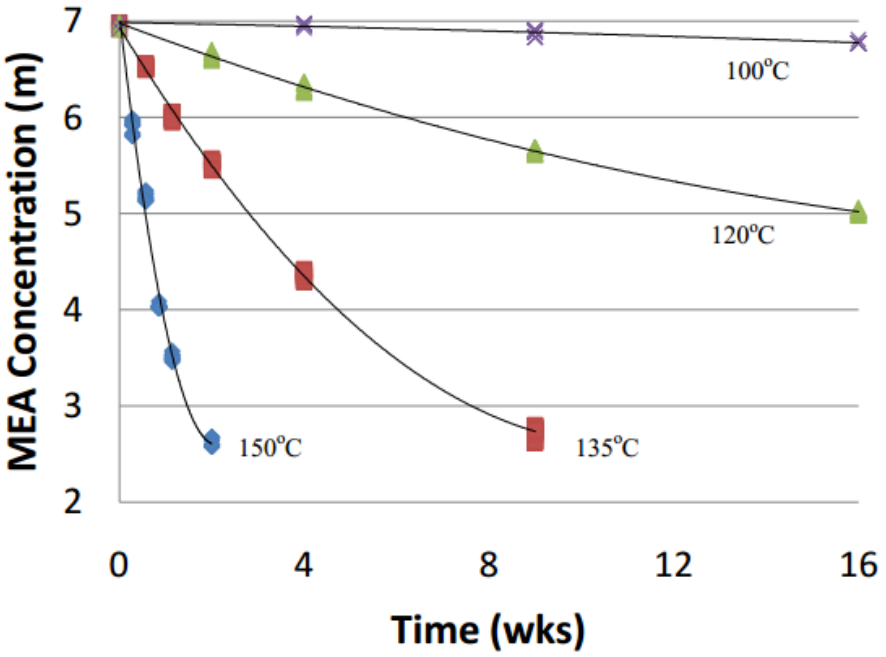

Figure 2-4 : MEA loss as a function of temperature for 7m MEA solutions with a loading of 0.4 moles CO2 per mole amine. [7]

In addition, increasing in MEA concentration (3.5m-11m) and CO_2 loading (0.2-0.5) increase thermal degradation of MEA. Figure 2-5 and Figure 2-6 shows the effect of varying of MEA concentration and CO_2 loading in 135 ºC respectively.

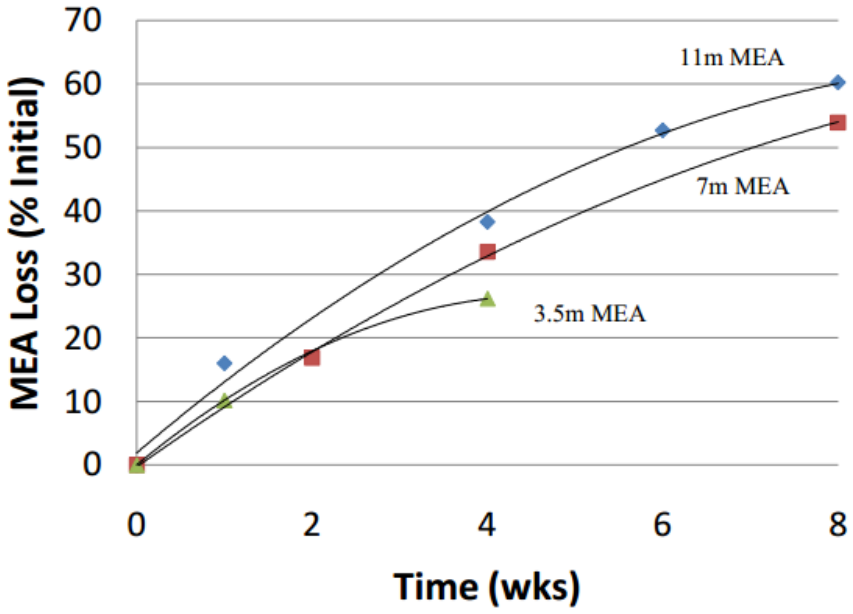

Figure 2-5: MEA loss as a function of initial amine concentration at 135 ºC and a loading of 0.4 moles CO2 per mole amine.[7]

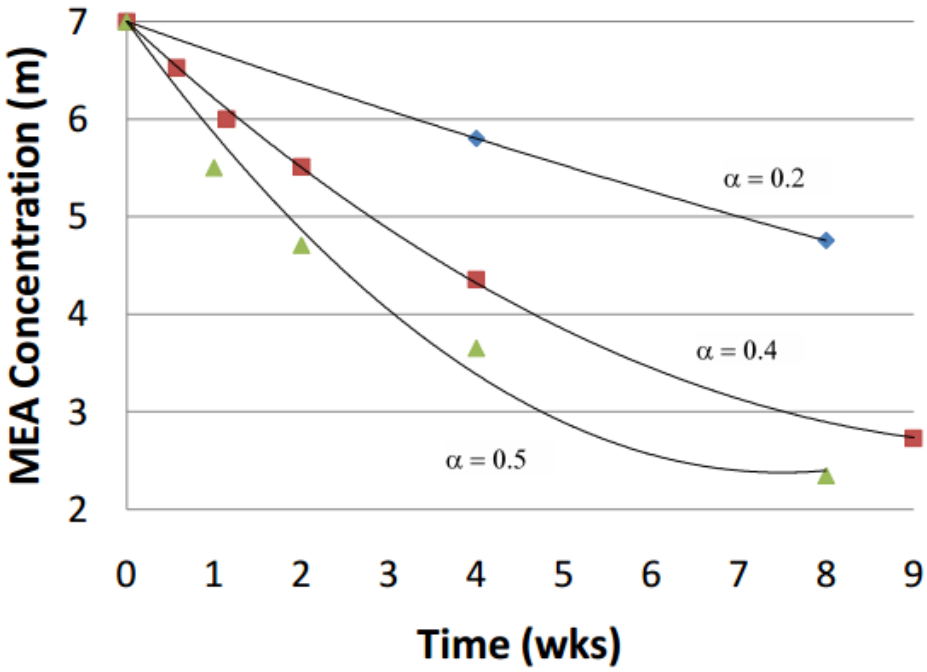

Figure 2-6:MEA loss as a function of CO2 concentration for 7m MEA solutions at 135 °C. [7]

2.2.2 Oxidative degradation

In contrast to thermal degradation ,oxidative degradation optained without presence of CO_2 and high temperature, it takes place when there is presence of oxygen and metal iones in the flue gas. It mainly takes place in the absorber. Supap et al [8] studied oxidative degradation of MEA in a temperature range of 120-170 ºC and a MEA consentration range of 2-11 m at 241-345 kPa oxygen and obtained a 1 and 1.5 values for reaction orders of MEA and O_2. These results displays the more effects of O_2 consentration in oxidative degradiation of MEA than the MEA concentrations . Two different mechanisms (see 2.2.2.1) are given for the oxidative degradiation of MEA that both generate the same products. The typical observed products of oxidative degradation are aldehydes ,organic acids such as acetate, formate, glycolate, acetate, imines, ammonia and nitrosamines [5].

Equation 2-1 and equation 2-2 shows elementary reaction of one MEA molecule with O_2 and relationship between the NH_3 evolution rate and O_2 consumption rate recpectivliy.

$$MEA + \upsilon\, O_2 \rightarrow NH_3 + degradation\ products \qquad Equation\ 2\text{-}1$$

$$NH_3\ evolution\ rate = O_2\ consumption\ rate / \upsilon \qquad Equation\ 2\text{-}2$$

In the degradation measuremnets the O_2 Stoichiometry (υ) is extremtly important. As showen in Table 2-2 acetaldehyde will be formed without O_2 in the reaction and for different degradation products stoichiometry of O_2 is varies from 0.5 to 2.5.[9]

Table 2-2: Oxygen stiochiometry for the formation of various degradiation products.[9]

MEA+υ O_2→NH_3+degradation products	
Products	Stoichiometry (υ)
Acetaldehyde	0.0
Formaldehyde	0.5
Acetic Acid	0.5
Hydroxyacetaldehyde	0.5
Glycolic Acid	1.0
CO	1.5
Formic Acid	1.5
Oxalic Acid	2
CO_2	2.5

2.2.2.1 Oxidative degradation mechanisms

As mentioned previously to kind of mechanisms are provided for oxidative degradation of MEA. The mechanisms were initially suggested by the US Army Research and DevelopmentLaboratories in the 1960s and called elctron abstraction and hydrogen abstraction mechanisms. As shown in Figure 2-7 the electron abstraction mechanism implies the abstraction of an electron from the ione par of the nitrogen. The part in the mechanism with dotted line are proposed by Gary T. Rochelle and susan Chi[10]. The mechanism initiated with a reaction between MEA and a metal ion (Fe^{3+}) and forming an aminum radical that can de-protonates to form an imine radical. The imine radical react with a secound radical to form an imine which further reacts with a H_2O molecule and produse an aldehyde and amonia (see reaction (I) in Figure 2-7). Chi and Rochelle [10] suggested that the imine radical can react with an O_2 (see reaction (II) in Figure 2-7) and form an peroxide radical. This radical could then react with another MEA and result an amino-peroxid which could decompose to an imine and a hydrogen peroxide.

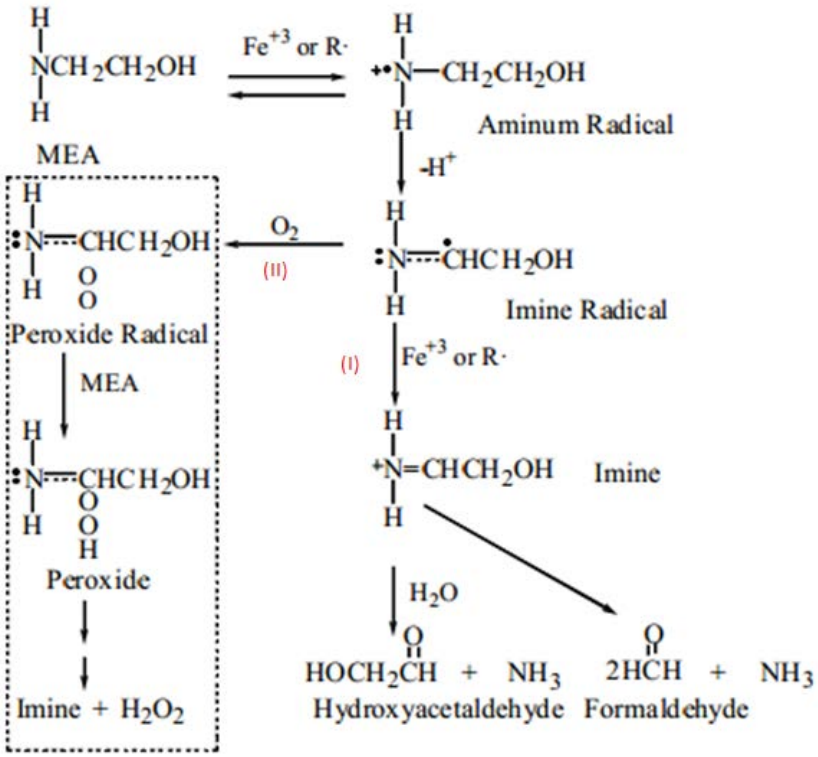

Figure 2-7: Electron abstraction mechanism.[10]

hydrogen abstraction mechanism indicate the abstraction of a hydrogen either from the nitrogen or the α/β-carbon. Hull et al [11] indicate that 73% of the hydrogen abstractions occurs on the α-carbon.

Another study has shown that oxidative degradation of MEA happen via hydrogen abstraction mechanism. In these studies the initiating radicals such as $OH^{\cdot}$, $H^{\cdot}$, e^{-} (aq) created from ionization radiation to degrade aqueous solutions of amines. The hydrogen abstraction mechanism proceeded in a alkaline solution with a pH greater than six and is depends on the formation of cyclic 5-membered hydrogen -bonded (H---O or H---N) structures. A scheme for hydrogen abstraction of MEA can de seen in Figure 2-8. According to this figure there are proposed three alternatives for hydrogen absorbtion by free radicals. In the reaction(I)and (II) abstraction of a hydrogen happens from the β and α carobn respectively and in the reaction (III) from nitrogen. The degradation products in all three alternatives are ammonia (NH_3) , aldehyde or aldehyde radical. [12]

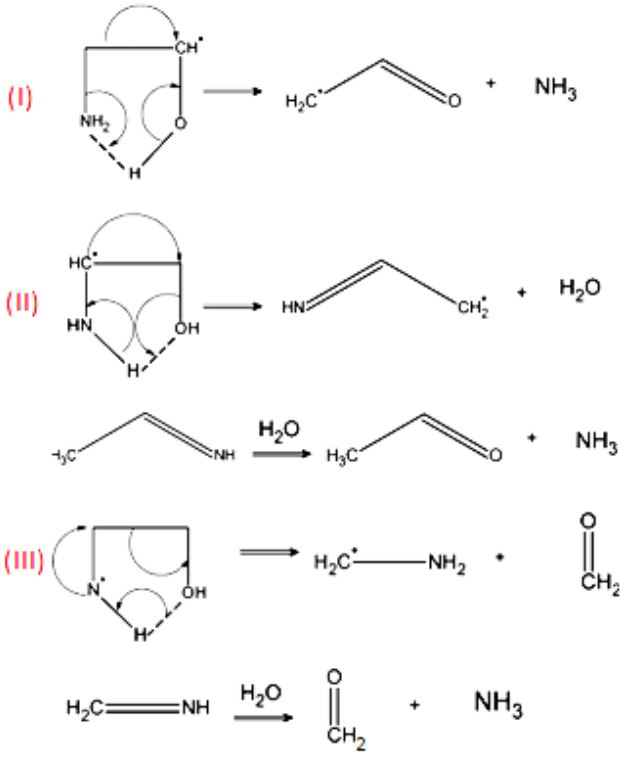

Figure 2-8: Hydrogen abstraction mechanism for oxidative degradation of MEA. [12]

2.3 Process description

The CO_2 capture technologies classified into several categories such as post combustion, pre combustion, oxy-fuel and chemical looping. In post combustion CO_2 is removed from flue gas after the combustion of fossil fuel. There are several methods (chemical and physical) for separating of CO_2 from the flue gas by post combustion, but the most common method is absorption of CO_2 by using aqueous amine (MEA in this study) .

The plant is mainly composed of an absorber, desorber (stripper) and the auxiliary equipment such as pumps, heat exchangers and heaters/coolers. Figure 2-9 shows a simplified flow chart of the process.

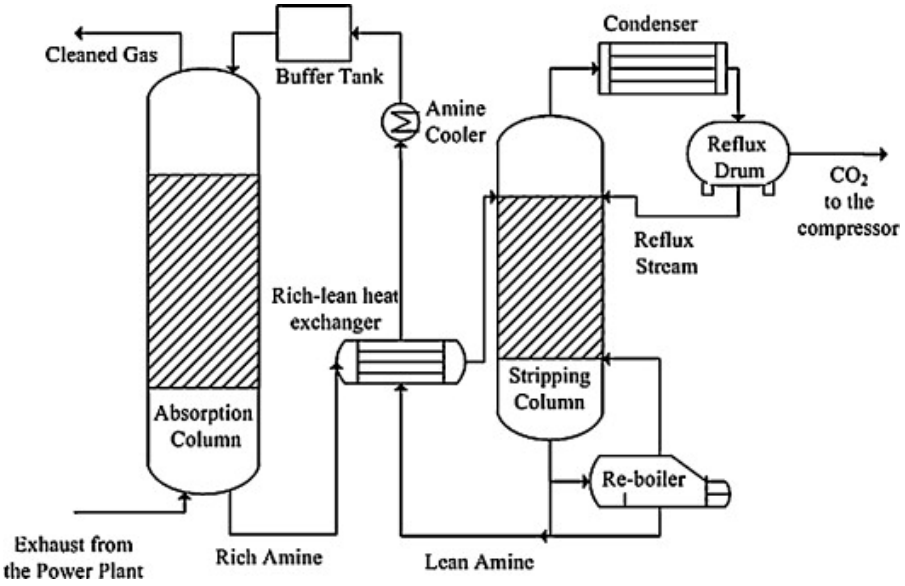

Figure 2-9: Flow sheet for CO_2 capture from flue gases using amine-based system.[13]

Flue gas containing CO_2 entering from the bottom of the absorber column, during the upward flow of flue gas the CO_2 contains in the flue gas reacts with the MEA solution which entering from top section of the column and produce CO_2 rich MEA solution. Cleaned gas leaving the top of the absorber and the rich MEA solution is sent through a counter-current heat exchanger (rich-lean heat exchanger), where it is pre-heated by the lean amine solution before being sent to the stripper column. The CO_2 rich amine solution downwards through the packing section where the CO_2 is stripped out from the MEA solution and leaves from the top section of the column, separation of CO_2 from MEA occurs by using the steam which is provided in the bottom of stripper column (re-boiler). The MEA solution leaving the bottom of the stripping column called lean MEA is then sent through the counter-current heat exchanger to be cooled before being recycled to the absorber column.

2.4 Quantitative chemical analysis

Since there is insecurity in all measurements, it is important to find out what accuracy actually is and how different errors have entered into measurements, due to this a study of errors is a first step in finding ways to reduce them. In the following section the quantification of errors will be explained.

2.4.1 Classification of errors

Errors which effect experimental results are classified in two main types i) Systematic errors and ii) Random errors. [14]

2.4.1.1 Random error

Random error is error which is always present in a measurement and impossible to prevent this error. The errors occur due to causes which the analyst has no control over it. If a large number of observations are taken and the results can be shown as a curve, an inspection of this curve shows a) more frequently for small errors than large ones; and b) the positive and negative errors have same possibility to occur. The distribution of x with random and none random error can be shown in Figure 2-10, as illustrate in this figure the random errors doesn't affect the average value, only adds variability to the data. [15]

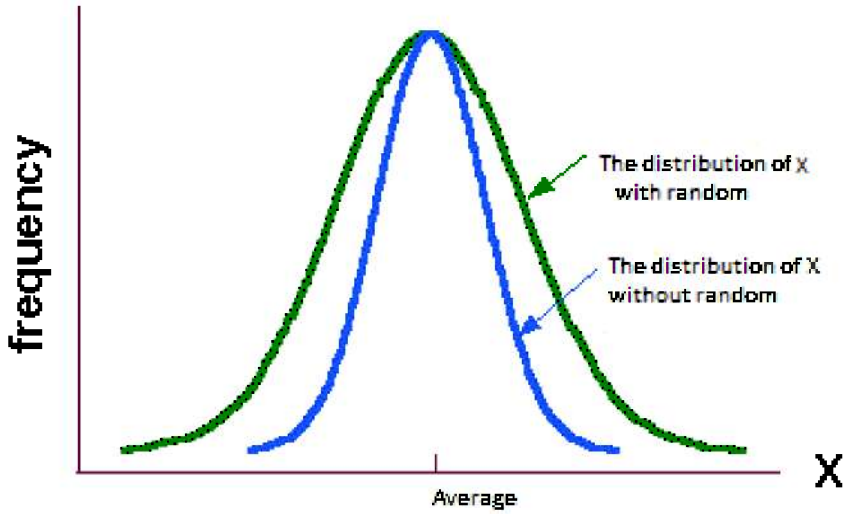

Figure 2-10: The distribution of x with random and none random error.[15]

2.4.1.2 Systematic error

Systematic error in experimental observation is sometimes considered to be bias in measurement due to tend to be consistently either positive or negative. These errors can be avoided or their magnitude can be determined. Instruments often have both systematic and random errors. The distribution of x with systematic and none systematic error can be shown in Figure 2-11, as illustrate in this figure the systematic errors does affect the average value. Both curves have random errors. [16]

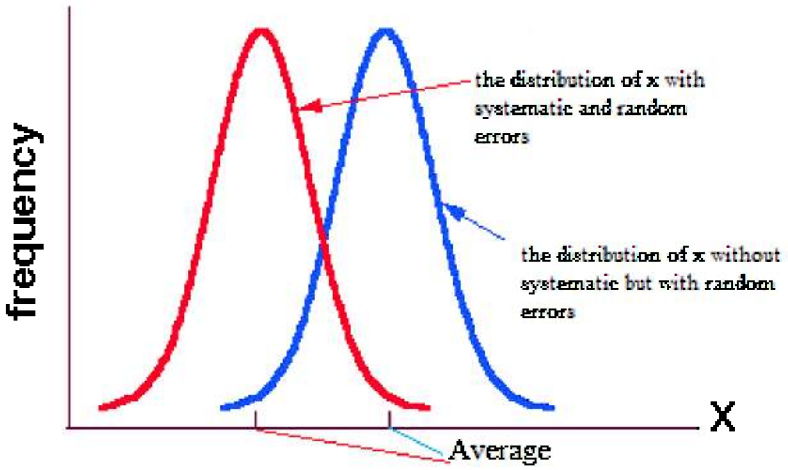

Figure 2-11: The distribution of x with systematic and none systematic error. [15]

Following are some of the reasons of systematic errors in results: [16]

- *Operational and personal errors:* these errors are not related to the procedure or method used however the analyst is responsible for these type errors.
- *Instrumental and reagent errors:* these errors occur due to use of uncalibrated or improperly instruments, such as weights, graduated glassware or faulty constriction of analytical scales.
- *Errors of the method:* These are errors which arise from improper sampling as well as from incompleteness of a reaction.
- *Additive and proportional errors:* The absolute value of additive error is independent of the amount of the constituent present in the determination while the absolute value of the proportional errors depends upon the amount of the constituent. One example for additive errors can be errors in the weight and the presence of this error is revealed by taking samples from different weights. The proportional error can occur from an impurity in a standard substance which influences the molarities of the standard solution.

2.4.2 Mean value

In chromatography data processing to reduce random errors a mean value can be used, where an experimental data is measured several times with the same sample. The mean value can be calculated by using Equation 2-3. [17]

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \ldots + x_n}{n} = \frac{\sum x_i}{n} \qquad \textit{Equation 2-4}$$

Where:

$\bar{x}$ = arithmetic mean value

x_i = experimental measured data
n = the number of individual measurements.

2.4.3 Standard deviation

Standard deviation is a statistical measurement that shows dispersion of the values in a population of observations. The more spread apart the data, the higher the deviation.

It is required to have a small deviation as possible. Standard deviation (s) can be shown by Equation 2-4.

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2} \qquad \textit{Equation 2-5}$$

The square of the standard deviation is called variance (σ).

Relative standard deviation (R.S.D) is a measure of precision (see equation 2-5) and often expressed in percent and known as coefficient of variance (C.V). Equation 2-6 shows coefficient of variance.[14]

$$RSD = \frac{s}{\bar{x}} \qquad \textit{Equation 2-6}$$

$$C.V = \frac{s}{\bar{x}} * 100 \qquad \textit{Equation 2-7}$$

2.4.4 Correlation coefficient and determination coefficient

In order to use instrumental methods it requires making calibration curve and to make a calibration curve two statistical tests should be applied a) to prove if the graph is linear, or in the form of a curve b)to evaluate the best straight line or curve through the data points.

The Pearson's correlation coefficient (r) that vary from -1 to +1 indicates the strength of the linear relationship between two variables X and Y. Figure 2-12 shows the correlation indicated by the specific r- value.

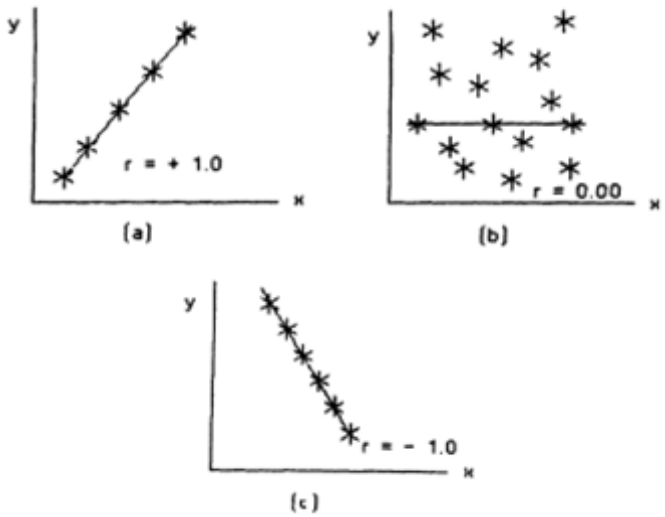

Figure 2-12: Example of various values of r. Each graph illustrates the correlation indicated by the specific r-value. [15]

As shown in Figure 2-12:

a) when r = 1 it is very strong positive linear relationship between X and Y, means a change in the X variable will predict a change in the same direction of Y variable. b) When r = 0 it is no linear relationship between X and Y i.e. Y does not tend to increase or decrease as X increases and c) when r = -1, it's a very strong negative linear relationship between X and Y, means that change in the X variable will predict a change in the opposite direction of Y variable.

Equation 2-7 shows the correlation coefficient (r).

$$r = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{\sqrt{n\sum {x_i}^2 - (\sum x_i)^2}\sqrt{n\sum {y_i}^2 - (\sum y_i)^2}} \quad \textit{Equation 2-8}$$

Where:

n =the number of data points.

Determination coefficient (R^2) is a measure of the proportion of variability explained by the fitted model. Equation 2-9 shows definition for determination coefficient.

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (yi - \overline{y_1})^2}{\sum_{i=1}^{n} (yi - \overline{y_1})^2} \quad \textit{Equation 2-9}$$

If R^2 =1, the fit is perfect.

2.4.5 Linear regression

As be shown in Figure 2-12 a high probability to have a linear relationship between Y and x can be by the value of the correlation coefficient (r), therefore it's important to estimate the best straight line through the data points. The straight line is calculated from least squares method. (See Equation 2-10).

$$y = ax + b \qquad \textit{Equation 2-10}$$

Where a, and b is calculated from equations 2-11 and equation 2-12:

$$a = \frac{n\sum x_1 y_1 - \sum x_2 \sum y_2}{n\sum {x_1}^2 - (x_1)^2} \qquad \textit{Equation 2-11}$$

$$b = \bar{y} - a\bar{x} \qquad \textit{Equation 2-12}$$

Where:

$\bar{x}$ = the mean of all x_1 values

$\bar{y}$ = the mean of all values of y_1

2.5 Calibration methods

The concentration of an unknown sample can be found by creating a calibration curve. There are four main methods to making a calibration curve include i) Area normalization ii) Internal standard iii) External standard and iv) Standard addition method. The following sub chapters will provide a brief explanation of those methods.

2.5.1 Area normalization

The main use of area normalization method is in the gas chromatography analyses of hydrocarbons, because in this method all sample compounds must have the same response, as well this method require detection of all sample compounds eluted in the analytical separator. The unknown peak has to be calculated from using Equation 2-13. [18]

$$\%X = \frac{100 * A_X}{A_X + A_Y + A_Z} = \frac{100 A_X}{\sum_{i=1}^{n} A_i} \qquad \text{Equation 2-13}$$

Where:

X= an unknown peak

Y and Z= two other peaks.

2.5.2 Internal standard

Internal standard method is a very accurate method. It is based in the preparation of several standard solutions containing a constant amount of internal standard. So it is calculated the ratio of peak hight and peak area for each analysis relative to internal-standard and the results is plotted in a graph as a function of internal standard concentration and peak area. Equation 2-14 is used in internal standard method to calculation of the composition.

$$\%X = \frac{A_x . f_x . W_{i.s}}{A_{i.s} . W_{i.s}} .100 \qquad \textit{Equation 2-14}$$

Where:

f_x = correction factor for component x.

A_x = peak area for component x.

$W_{i.s}$ = concentration of internal standard.

$A_{i.s}$ = peak area of internal standard.

2.5.3 External standard

The most common method to calibrations is the external standard method. In this method an external calibration curve is prepared, where response in standards is plotted as a function of concentration versus peak area. The concentration in unknown samples is determined by measuring the response in this samples and comparing to the calibration curve.

2.5.4 Standard addition

The standard addition method is particularly useful for analyzing complex samples that matrix effects are present [17]. This method is a combination of calibration between internal and external standard methods. The matrix effects can be detected by calculation of recovery rate in % (W), which is the ratio of the measured mean value ($\bar{x}$) under repeating conditions with the true value (x_R) of the analyte in the sample [18]. See equation 2-15.

$$\%W = \frac{\bar{x}}{x_R} * 100 \qquad \text{Equation 2-15}$$

3 The theory of chromatography

In this chapter the classification of chromatographic methods, the method used in this project and the ion chromatograph include the column, detector, mobile/stationary phase and functional groups will be described in detail and later the quality of chromatographic separation and the factors that assessing the quality is discussed.

3.1 Introduction to chromatography

Chromatography is a powerful separation technique whereby the components of a mixture may be separated by passing solution of these components (analyte) through a glass column packed bed of material (stationary phase) and transported by a mobile phase. Chromatography was invented and named by the Russian botanist Mikhail Tswett at beginning of the twentieth century [14].

3.2 Classification of chromatographic methods

A fundamental classification of chromatographic method is based on: the type of mobile and stationary phases and the kind of equilibrium regarded to the solutes transfer between phases. With respect to the classification, the chromatography methods can be categorized in three main classis including liquid chromatography, gas chromatography and supercritical-fluid chromatography which have mobile phase as liquid, gas and supercritical fluid respectively. Figure 3-1 shows an overview of this three groups chromatography and its type of equilibrium, stationary phase and specific method [14]. In this work it is focused on the liquid chromatography. More detailed description of this separation method is given in following sections.

General Classification	Specific Method	Stationary Phase	Type of Equilibrium
Liquid chromatography (LC) (mobile phase: liquid)	Liquid-liquid, or partition	Liquid adsorbed on a solid	Partition between immiscible liquids
	Liquid-bonded phase	Organic species bonded to a solid surface	Partition between liquid and bonded surface
	Liquid-solid, or adsorption	Solid	Adsorption
	Ion exchange Size exclusion	Ion-exchange resin Liquid in interstices of a polymeric solid	Ion exchange Partition/sieving
Gas chromatography (GC) (mobile phase: gas)	Gas-liquid	Liquid adsorbed on a solid	Partition between gas and liquid
	Gas-bonded phase	Organic species bonded to a solid surface	Partition between liquid and bonded surface
	Gas-solid	Solid	Adsorption
Supercritical-fluid chromatography (SFC) (mobile phase: supercritical fluid)		Organic species bonded to a solid surface	Partition between supercritical fluid and bonded surface

Figure 3-1: Classification of chromatographic methods.[14]

3.3 Liquid chromatography

A liquid chromatography (LC) is classified in five main types based on the mechanism of separation. These categories include 1) adsorption chromatography or liquid-solid 2) partition chromatography or liquid-liquid 3) ion-exchange chromatograph (IEC) 4) size-exclusion chromatography or High Performance Ion Chromatography Exclusion (HPICE) and 5) affinity chromatography. Figure 3-2 is shown these five main categories of liquid chromatography. In this work the ion-exchange chromatography has been chosen to quantify amine loss from the amine degraded samples. A detailed description of this separation method is given in the next subchapter. [14, 18]

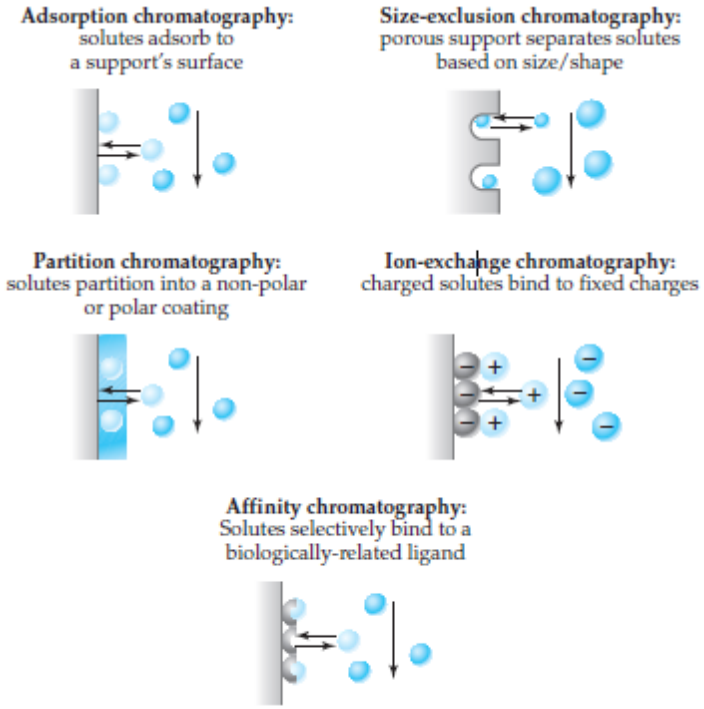

Figure 3-2: Five main categories of liquid chromatography.The various shaded circles represent different types of solutes that are passing through the chromatographic system.[19]

3.3.1 Ion exchange chromatography

Ion-exchange chromatography is an ideal method for analyzing and measuring concentrations of both organic and inorganic anions and cations by separating them based on interaction between ions in the solution and oppositely charges groups in the column resin. An ion-exchange chromatography system can be divided into instrumentation and chemistry components. The instrumentation components are the pump, injector, column, detector and data station, whereas the chemical components are the mobile phases and the stationary phases which in the next sub chapters will briefly discuss about each of these phases. Figure 3-3 shows a general design of a system for ion-exchange chromatography.

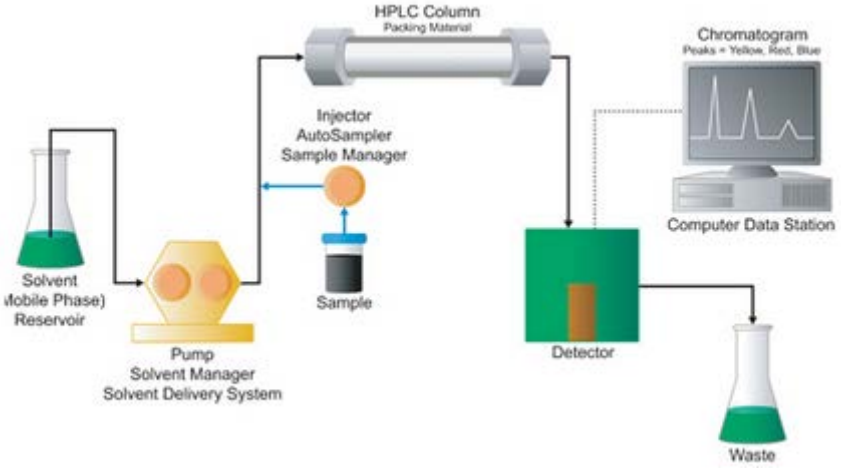

Figure 3-3: General design of a system for ion-exchange chromatography. [20]

The mobile phase is delivered to the chromatography system by the pump while the sample is injected into the system via injector and is transported to the column by the mobile phase. Typical injection volumes for the samples are between 5-100 µL. This mobile phase is then forced through a stationary phase, which is fixed in place in the column. The column is the most important part in the chromatography system because column is the part of a chromatography where the separation of the sample takes place. . The packing material used in the column influence the stability of the column .One of the factors which influence the quality of the analysis is choice of the stationary phase. The detector which is wired to the computer data station detects and quantifies the analytes by generate the chromatogram on its display .There are many kind detectors, which a conductivity detector is most commonly used detector in ion chromatography. Due to corrosive eluents used in the system, all parts which being susceptible to these liquids should be made of metal-free materials.[18]

3.3.2 Principle of ion chromatography in the column

Having a glance at the principle of ion chromatography in the column can be shown in Figure 3-4. The principle is executed in four main steps: 1) equilibration , involves setting up the starting conditions, so that the desired solute molecules are associated to opposite charge ions due to pH and ionic strength, 2) adsorption of sample substances, in which solute molecules moved appropriate charge and bind reversibly to the gel, 3) removing components from the column by changing the elution conditions, for instance increasing the ionic strength of the eluting buffer or change pH, 4) regeneration, implies removing of components not eluted from the column under previous experimental conditions and regeneration for new analyses [21].

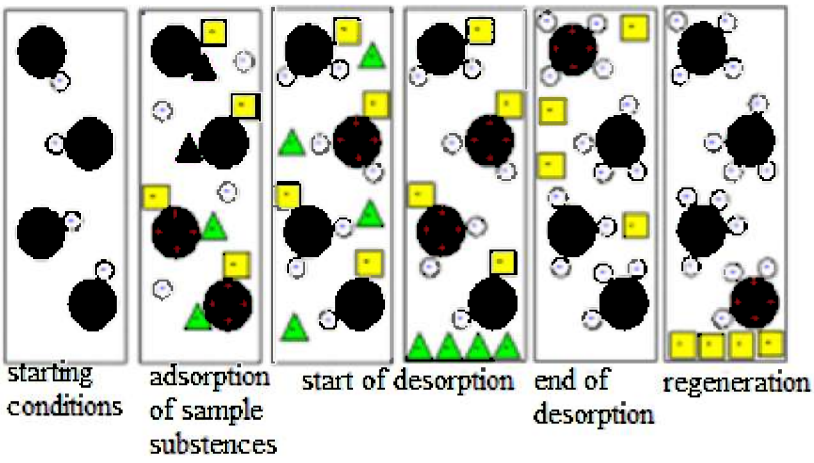

Figure 3-4: The Principle of ion chromatography in five steps.[22]

As illustrate in Figure 3-5 different components in the column are separate in various times due to differences in their migration speed, and a series of peaks rising from a baseline on a time axis, which each peak represents the detector response for a component. The migration speed is decided of the components equilibrium distribution, chemical and physical properties between mobile and stationary phase. With equal migration speed, does not separation between the components.

simultaneously with elution of components in the column a chromatogram obtained in computer display.

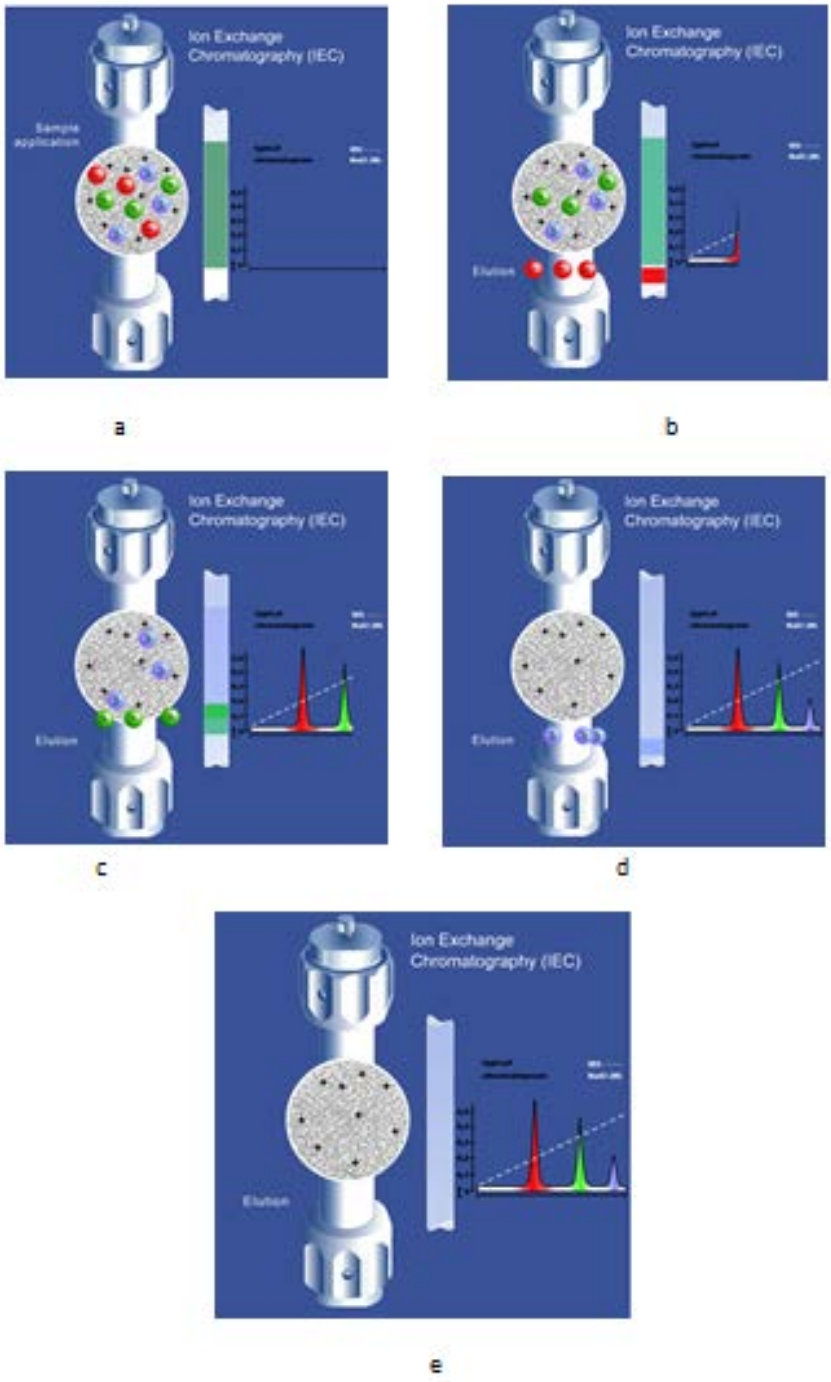

Figure 3-5: Principle of separation of different components in the colum. [23]

3.4 Detector signal

A detector signal is the output of detector associated with the response of detector to the analyte. The fundamental properties of detector signal are sensitivity, limit of detection, response time and noise characteristics [24].

Sensitivity defined as capability of detector to discriminate small differences in concentration or mass of the test analyte and in practical it determined by the slope of the calibration curve. The lowest concentration of analyte in a sample that can be detected is called limit of detection. For

many chromatographic detectors the relationship between response and analytes mass or concentration is linear for a wide range of analyte concentration. The noise arise by interaction of the detector by its environment, electric signal fluctuations and other factors such as the mobile phase, stationary phase, change in flow rate and ambient temperature.[17, 24]

There are three type of noise, Lang-term noise or low frequency noise (Figure 3-6 .c), short term noise or high frequency noise (Figure 3-6.b) and drift.

Noise usually has much higher frequency than actual chromatographic peaks. The signal to noise ratio (S/N) is en useful method to describe the quality of an analytical method or the performance of an instrument. In the general it is impossible to detect a signal when the signal to noise ratio is less than 2-3, i.e. the detection limit is the injected amount that results in a peak with a height at least two or three times as high as the baseline noise level.[17] (see Figure 3-6.a)

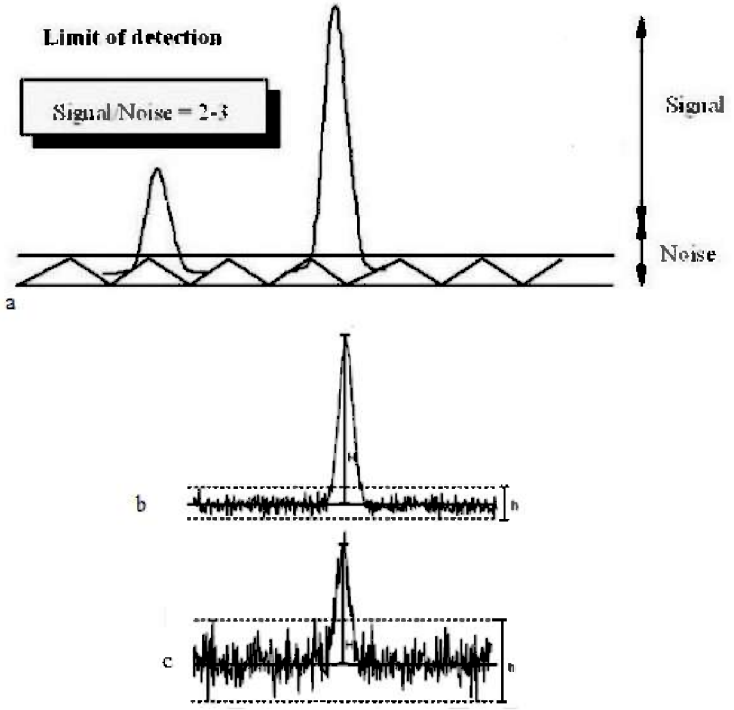

Figure 3-6: A sketch of long-term noise c) short term noise b) and S/N ratio.

3.5 Eluent (mobile phase)

The mobile phase is the most important parameter in the chromatography system. It carries the analytes through the stationary phase in the column. Common mobile phases used in chromatography are a combination of water with various organic solvents such as acetonitrile, methanol, etc. The elution mode for eluent can be isocratic or gradient. The easiest method is isocratic where the amount is equal through the analyses whereas gradient elution is more complex and requires more regular maintenance compared to isocratic elution. Gradient elution is used if the retention between the early and late elution ions is large. [25]

3.6 Stationary phase

There are two major ion-exchange chromatography models based on the types of stationary phases, i) anion-exchange chromatography and ii) cation-exchange chromatography .In cation-exchange chromatography the molecules that are positively charged are attracted to the negatively charged molecules in the stationary phase . Conversely, in anion-exchange chromatography, negatively charged molecules are attracted to positively charged molecules in the stationary phase (see Figure 3-7) [21]. Choice of stationary phase and chromatographic conditions determine the quality of analysis. Due to use of dilute acids as the eluent in the cation-exchange chromatography, the stability over the whole pH range (a condition provided by organic polymers) is not required. Therefore some supports materials such as Silica and polystyrene/divinylbenzene is used to increase chromatographic efficiency [26].

During this study, cation-exchange chromatography has been chosen to quantify amine loss in the oxidative degraded samples.

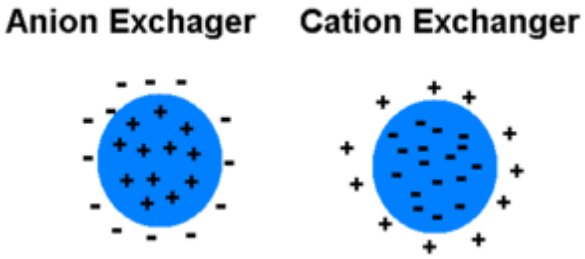

Figure 3-7: Ion exchanger types. [27]

3.7 Functional groups

The ion exchange functional groups can be further categorized as either strong or weak. The Strong ion exchange functional groups are charged ionized across a wide range of pH levels while the weak ion exchange functional groups are ionized within a narrower pH range. Table 3-1 shows the most common functional groups used on ion exchangers.[28]

Table 3-1: Functional groups for anion-exchangers and cation-exchangers.[28]

Anion exchangers	Type of exchanger	Functional group
Quaternary ammonium (Q)	strong	-O-CH_2-CHOH-CH_2-O-CH_2-CHOH-CH_2-$N^+(CH_3)_3$
Diethylaminoethyl (DEAE)	weak	-O-CH_2-CH_2-$N^+H(CH_2CH3)_2$
Quaternary aminoethyl (QAE)	weak	-O-CH_2-CH_2-$N^+(C_2H_5)_2$-CH_2-CHOH-CH_3
Cation exchangers	Type of exchanger	Functional group
Sulfopropyl (SP)	strong	-O-CH_2-CHOH-CH_2-O-CH_2-CH_2-$CH_2SO^-_3$
Methyl sulfonate (S)	strong	-O-CH_2-CHOH-CH_2-O-CH_2-CHOH-$CH_2SO^-_3$
Carboxymethyl (CM)	weak	O-CH_2-COO

3.8 Chromatogram

The output signals from the detector are registered in form of chromatogram. A typical chromatogram for to component mixture is shown in Figure 3-8. Different peaks on the chromatogram correspond to different components in the mixture.

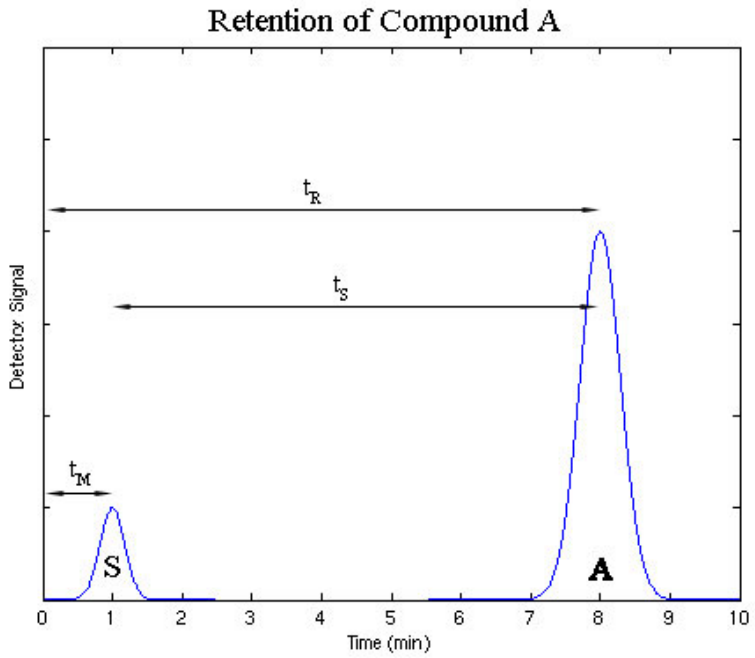

Figure 3-8: A typical chromatogram of two- component mixture.

3.9 Distribution coefficient

As shown in Equation 3-1 the distribution of an analyte (A) between the mobile phase and stationary phase can often be described quite simply, so that an analyte is in equilibrium between these two phases. [17]

$$A_{mobil} \Leftrightarrow A_{stationary} \quad \textit{Equation 3-2}$$

The distribution-coefficient (K_D) is the ratio of molar concentration of solute in the mobile phase and stationary phase (See Equation 3-3) and indicate difference in solubility of compounds in these two phases. A high value of K_D displays a high affinity between the solute and the stationary phase and values of K_D near to zero will be characteristic of system where the solute has not preference by stationary phase.[14]

$$K_D = \frac{C_s}{C_M} \quad \textit{Equation 3-4}$$

Where:

C_s = the molar concentrations of the solute in the stationary phase

C_M = the molar concentrations of the solute in the mobile phase

3.10 Retention time

The time between the injection of a sample and achieving to the detector is known as the retention time (t_R). The time in which unreacted components, after elution has started, use to reach detector is called dead time (t_M). Retention time for component A (see Figure 3-8) can be shown as Equation 3-5 where (t_S) is called the solute retention time in which the components do not travel along the column.[14, 18]

$$t_R = t_M + t_S \quad \textit{Equation 3-6}$$

Retention time can be influenced by many factors, some factors such as type and properties of the stationary phase, composition and properties of the mobile phase, the temperature in the column and the intermolecular forces between the component, mobile and stationary phase.[29]

3.10.1 The effect of the temperature and the flow rate

In some separations retention time can be control by the column temperature. The given equation by Van't Hoff (see Equation 3-7) shows the dependence of the distribution coefficient with temperature.[30]

$$\frac{d \ln K_D}{dT} = \frac{\Delta H}{RT^2} \quad \textit{Equation 3-8}$$

Where:

(K_D)= distribution coefficient

ΔH= enthalpy of the solution

If the stationary and mobile phase ratio (V_S/V_M) is independent of temperature so $K_D = k'$. Thus Equation 3-9 can be rewritten as Equation 3-10.

$$\frac{d \ln k'}{dT} = \frac{\Delta H}{RT^2} \quad \textit{Equation 3-11}$$

Where:

k' = capacity facto (see section 3.12.2)

Equation 3-12 shows that the retention time is inversely proportional to the square of the temperature.

3.10.2 Intermolecular forces (Coulomb's Law)

Intermolecular forces between the solute and the stationary phase which influence the retardation of the component are based on Coulomb's Law.

In Ion chromatography separation of components are based on the strong attraction between opposite charge ions and the exchange of ions between the analyte in the mobile and stationary phase. There are two main types of electrostatic interaction between molecules, i) Polar Van der Waal's retention forces arising from interaction between molecules having a surface charge which the consequence of dipole-dipole interactions and hydrogen bonding between molecules are of the forces, ii) Non-polar dispersion forces between neutral molecules or functional group such as London's forces. [29]

3.10.3 The relationship between the retention time and distribution constant

There are a relationship between the retention time and the distribution constant, the relationship can be expressed by Equation 3-13.

$$\bar{v} = u * \text{fraction of time solute spends in the mobile phase} \quad \textit{Equation 3-14}$$

Where:

$\bar{v}$ = migration rate

u= velocity of the mobile phase

The fraction of time solute spends in the mobile phase is the ratio between moles of solute in the mobile phase ($C_{m*}V_m$) and total moles of solute ($C_{s*}V_s$ +$C_{m*}V_m$). So Equation 3-15 can rewrites as Equation 3-7.

$$\bar{v} = u * \frac{C_m V_m}{C_m V_m + C_s V_s} \qquad \textit{Equation 3-16}$$

Where:

C_m = the solute in that phase

V_m= volume of mobile phase

C_s = the solute in the stationary phase

V_s, = volume of stationary phase

3.11 The quality of chromatographic separation

Normally, the quality of the chromatographic separations can be explained by factors as peak shape, peaks width and peak asymmetry. Following section will describe these factors.

3.11.1 The shape of chromatographic peaks

The peak shape in chromatography is a measurement of the quality of the separation. In a first approximation, a Gaussian curve (see Figure 3-9) is used to describe the shape and error of a chromatographic peak. An ideal separation occurs when the height of the peak is larger in compared to the width of the peak. The σ is standard deviation and describe the spread of molecules in a band.[18]

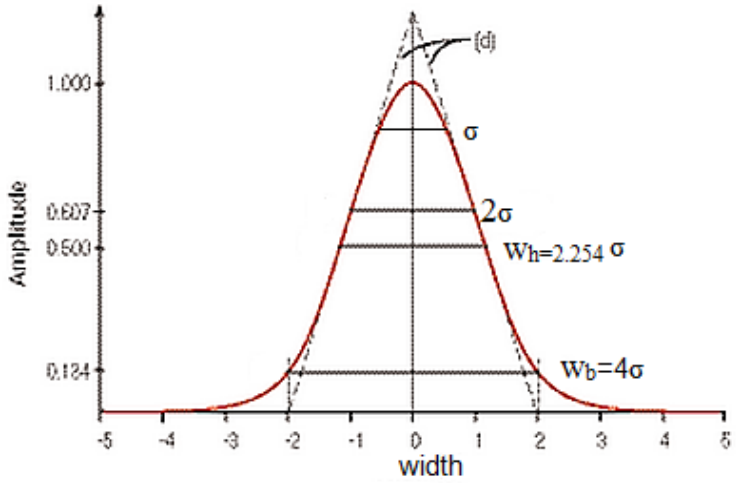

Figure 3-9: A Gaussian curve.

With too width peaks in a chromatogram arise problems with the separation. A sketch of good and bad peak shape is shown in Figure 3-10.

Figure 3-10: A sketch of good and bad peak shape.

3.11.2 Peak width

The peak width denotes the distribution of the molecules in the column, and it is a measure of the band broadening. The broadening is a fundamental disadvantage in the chromatography and caused by diffusion processes and flow processes. Some factors such as the sample injection, detector characteristics, system temperature and column retention processes influence the peak width. [18] As shown in the Figure 3-9 peak width (w_b) (given by 4σ) determined by the intersection points of the tangents drown to the peak above its point of inflection. The standard deviation (σ) describes the spread of molecules in a band. If peaks in a chromatogram are too wide, they won't separate and problems arise with the separation. A sketch of good and bad separation due to peaks widths is shown in Figure 3-11.

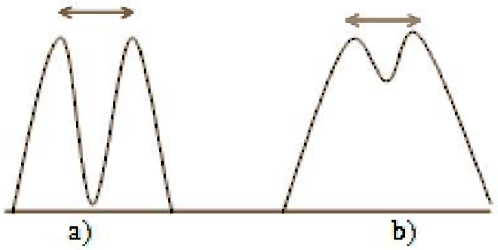

Figure 3-11: Shows quality of separation due to peak width. a) Peaks are fully separated because they are narrow. b) Peaks are not separated because they are wide.

It is required to get less band broadening as possible to get a better separation. Band broadening can be measured by the plate number (N) or the plate height (H). The greater N values the better column efficiency thus lesser band broadening occurred. Equation 3-8 shows the relationship between the standard deviation (σ) and the plate number, N.

$$\sigma^2 \alpha \frac{1}{N} \qquad \textit{Equation 3-17}$$

As shown in Equation 3-9 the plate number is a function of the length of the column (L) and the plate height (H).

$$N = \frac{L}{H} \qquad \textit{Equation 3-18}$$

The plate hight can be calculated from Equation 3-10.

$$H = \frac{1}{16} * \frac{(4\sigma)^2}{L} \qquad \textit{Equation 3-19}$$

Where $4\sigma=w_b$ (the peak width at base line). (See Figure 3-9).

By combination Equation 3-9 and Equation 3-10 the number of plates can be shown as Equation 3-11. [18]

$$N = \frac{L^2}{\sigma^2} \qquad \textit{Equation 3-20}$$

3.11.3 Peak asymmetry

Peak asymmetry (A_s) is one of the factors that can be used to measure the quality of a peak. An ideal peak of a chromatogram should occur as perfect Gaussian peak. The asymmetry of a peak is determined using Equation 3-21.

$$A_s = \frac{b}{a} \textit{ At 10 \% h} \qquad \textit{Equation 3-22}$$

Where (b) is the peak width after the peak center at 10% peak height and (a) is the peak width at baseline before the peak center (see Figure 3-12). If A_s –value is higher than 1, the asymmetry is called “tailing” which adsorption process are responsible for such effect, while with an A_s –value lower than 1, the asymmetry is called “leading” or “fronting” that the effect occurs when some of sample ions pass the peak center due to the stationary phase which does not have enough suitable adsorption sites. For practical applications an A_s -value between 0.9 and 1.2 is an acceptable value.[18] A sketch for tailing and fronting is shown in Figure 3-12 also.

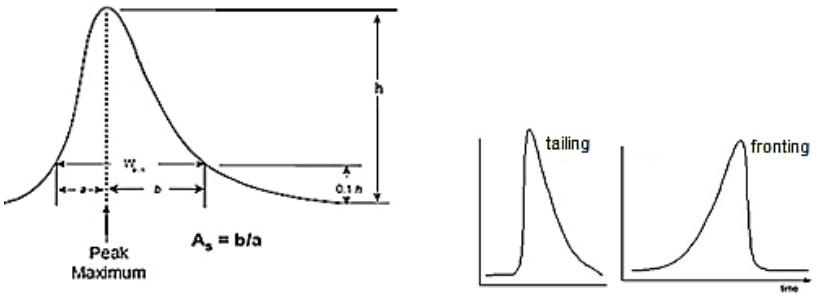

Figure 3-12: A sketch of peak asymmetry, tailing and fronting.[31]

3.12 Parameters for assessing the quality of a separation

In this section the parameters that can be used to assessing the quality of the separation is described. Of the parameters can mention resolution, retention factor, selectivity factor and column efficiency.

3.12.1 Column efficiency

The chromatographic column efficiency is measured by the plate height (H) and theoretical plate number (N). As shown in previous section the number of plates achieves by Equation 3-9. The higher the N value is the better separation efficiency of the column occurs, similarly as H value became smaller the efficiency increasing.

3.12.2 Capacity factor

Capacity factor also called retention factor (k') is an important factor to describe the relative velocity of a component in a column. The capacity factor is a measure of the time the analytes spends in the stationary phase versus the mobile phase. In a poor separation k' value is small, on the other hand, with a high k' value peak broadening, longer analysis times and decreasing in the sensitivity occurs. [18]

Equation 3-13 shows the retention factor (k') for a component A:

$$k'_A = \frac{(K_D)_A V_S}{V_m} \quad \textit{Equation 3-23}$$

Where:

$(K_D)_A$= the distribution constant for component A

V_s = volume of the stationary phase

V_m =volume of the mobile phase

3.12.3 Selectivity factor

The Selectivity factor (α) of two sample components is the ratio of their capacity factor or distribution factors. It is a measurement of how well these components are separated and is calculated according Equation 3-14.

$$\alpha = \frac{K_{D2}}{K_{D1}} = \frac{k'_2}{k'_1} = \frac{t_{R2} - t_M}{t_{R1} - t_M} \quad \textit{Equation 3-24}$$

Where k'_1 is the retention factor and K_{D1} is the distribution constants for the less strongly retained (more rapidly) and k'_2 is the retention factor and K_{D2} is the distribution constants for the more strongly retained sample components.[14]

If α = 1, there will be no separation between the two sample components because, there is no thermodynamic difference under given chromatographic condition. The larger value of selectivity factor the greater the separation. The mobile phase compositions influence the selectivity factor [18].

3.12.4 Resolution

Resolution (R_S) of two neighboring peaks is defined as:" *the quotient of the difference of two peak maxima(difference between the gross retention times) and the arithmetic mean of the respective peak widths, w_b, at the peak base [18]"*

resolution is a column ability to separate to analytes [17]. Figure 3-13 shows chromatograms for two mixture components A and B with resolution values of 0.75 (Figure 3-13.a), 1.0 (Figure 3-13.b) and 1.5 (Figure 3-13.c). As illustrate from this figure, a resolution of 1.5 gives a complete separation of the two components [32].

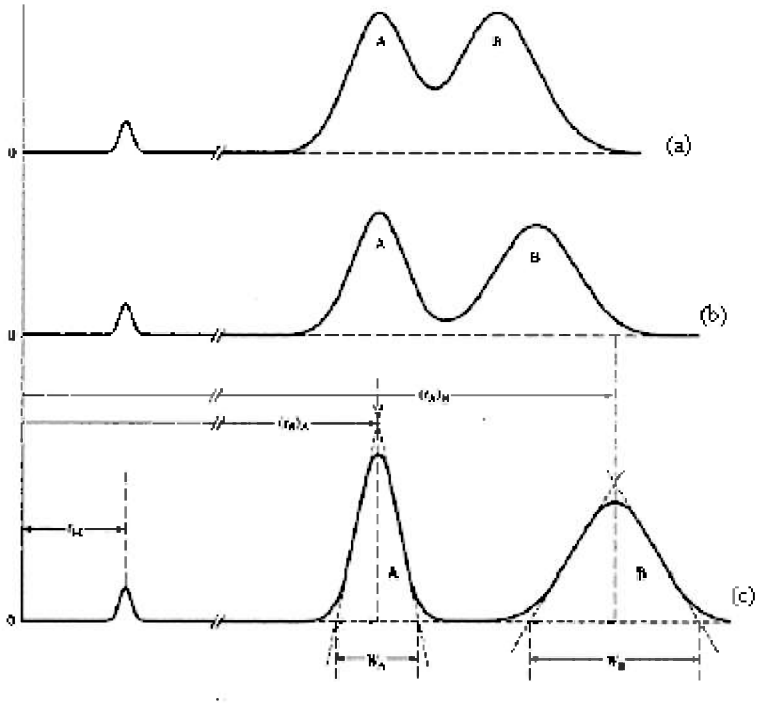

Figure 3-13: Separation of two peaks with resolution values of (a) 0.75, (b) 1.0 and (c) 1.5.[32]

The resolution can defined as Equation 3-15, where the terms $(t_R)_B$ and $(t_R)_A$ refer to the retention time and W_B and W_A to the width of each peaks at baseline.

$$R_S = \frac{2((t_R)_B - (t_R)_A)}{W_A + W_B} \quad \textit{Equation 3-25}$$

4 Equipment section

The cation-exchange chromatograph has been used for analysis of degraded samples from the CO_2-capture pilot plant. The first thing to do before the experiment is to familiarize with the equipment and get knowledge of different equipment parts and the software. This chapter describes the different parts of the cation-exchanger chromatograph apparatus used in the experiment, the procedures for startup the apparatus and preparing standard and oxidative degradation samples. Information of the chemicals used in this equipment, turning procedure of the cation chromatograph and preparing the mobile phase can be found in Appendix B, C and D respectively.

4.1 Cation exchanger chromatograph

The cation chromatograph used in this project was a Dionex DX _500 ion chromatograph analyser and the program used to experimental design was the MODDE 9 software program. A picture of the equipment is shown in Figure 4-1.

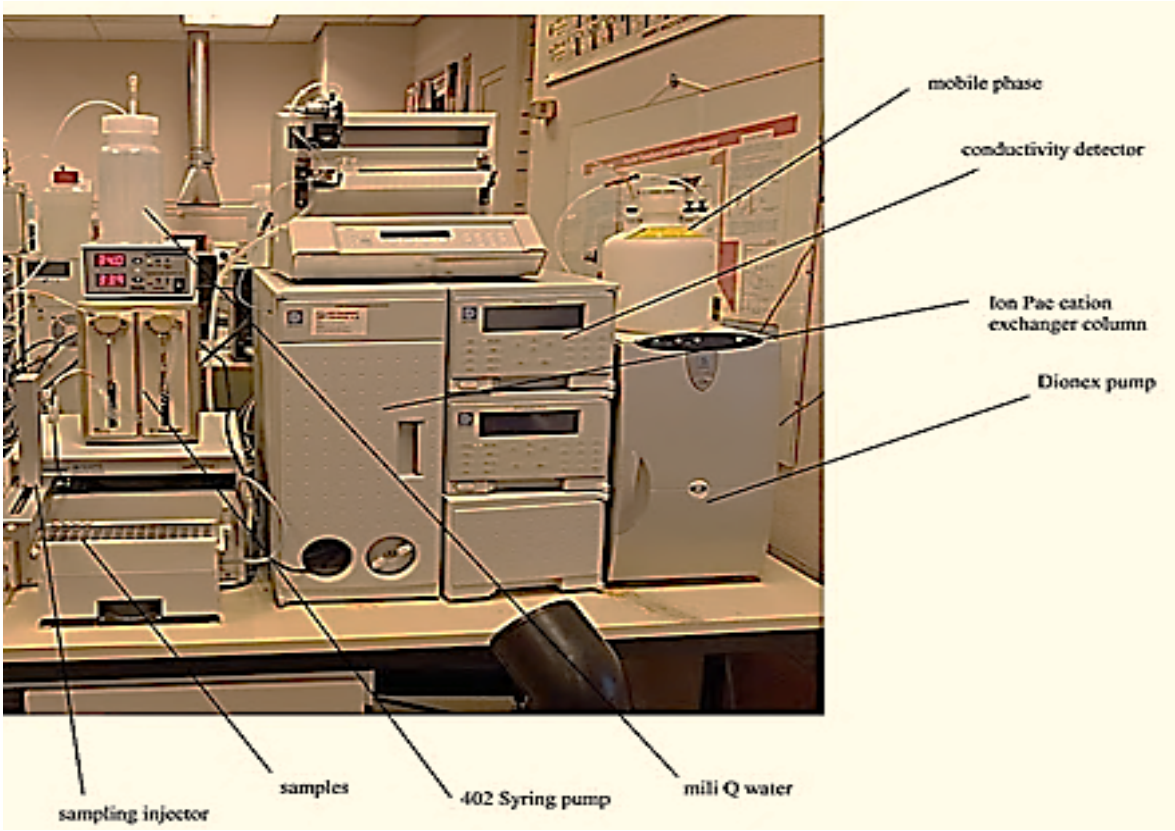

Figure 4-1: The cation chromatograph apparatus.

The equipment consists of the main parts:

- Dionex IonPac SCS1 (4x250 mm) cation-exchange column.
- Dionex ICS-3000 isocratic pump.

- Dionex CD20 conductivity detector.
- Gilson 402 syringe pump .
- Gilson 231XLsampling injector.

4.1.1 Dionex IonPac SCS 1 (250x4) cation exchange column

The installed column in the chromatographic system is an IonPac SCS 1(Silica Cation Separator) column which is designed for cation determination using non suppressed conductivity detection. This column is a unique hydrophilic, low capacity weak cation exchanger which especially suited for analysis of the common inorganic cations (sodium, potassium, magnesium, calcium and ammonium), alkanolamines and transition metals such as zinc and copper.

The substrate for the IonPac SCS 1 column is silica-based poly (butadiene-maleic acid) with a particle diameter of 4.5 µm which is coated with a unique carboxylic acid functionalized layer. Figure 4-2 shows structure of the IonPac SCS 1 packing particle.[33]

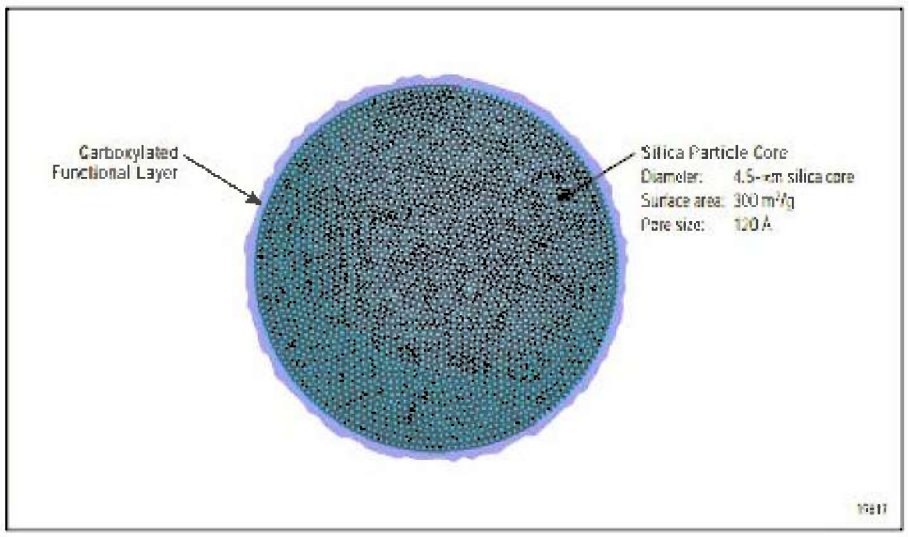

Figure 4-2: Structure of the IonPac SCS 1 Silica Cation Separator packing particle.[33]

Table 4-1 shows the structural and technical properties of the IonPac SCS 1 column used in the cation-chromatograph analyser. More specification about the column is in appendix E.

Table 4-1: The structural and technical properties of IonPac SCS 1 column.

Dimension (length *I.D) [mm]	250x4
Maximum Operating Pressure [psi]	4000
pH-range	2-7
Solvent compability [%]	100
Capacity [µequiv /column]	318
Bead Diameter [µm]	4.5(silica)
Flow rate [mL/min]	1
Ion Exchange Group	Grafted carboxylic acid
Functional Group Characteristics	Medium hydrophobic
Column Construction	PEEK with 10-32 threated ferrule style end fittings.

4.1.1.1 Troubleshooting guide for IonPac SCS 1 column

Some of the operating problems which may arise by using IonPac SCS 1 column is tabulated in Figure 4-3, in addition the cause of the problems and guide to solve it is shown in this figure.

Observation	Cause	Action
High Back Pressure	Unknown Component	Isolate Blockage
	Plugged Column Bed Supports	Replace Bed Supports
	Plugged System Hardware	Unplug, Replace
High Background Conductivity and/or High Noise		
Contamination	Bad Eluents	Remake Eluents
	Contaminated Column	Clean Column
	Cell	Check Cell Calibration
Poor Peak Resolution		
Poor Efficiency	Large System Void Volumes	Replumb System
	Sluggish Injection Valve	Service Valve
	Contaminated or Deformed Bed Support	Replace Bed Support
	Column Headspace	Replace Column
	Column Overloading	Reduce Sample Size
	Low sample pH	Reduce Sample Size Dilute Sample Use OnGuard II A
	Tubing and Cell	Clean and/or replace tubing
Fronting Peaks	Low Sample pH	Reduce Sample Size Dilute Sample Use OnGuard II A
	Column Overloading	Reduce Sample Size
	Contaminated or Deformed Bed Support	Replace Bed Support
	Column Headspace	Replace Column
Tailing Peaks		
	Column Overloading	Reduce Sample Size
	Column Contaminated	Clean Column
	Tubing and Cell	Clean and/or replace tubing
Short Retention Times	Flow Rate Too Fast	Recalibrate Pump
	Bad Eluent	Remake Eluent
	Column Contamination	Clean Column
Spurious Peaks	Column Contamination	Pretreat Samples, Clean column
	Sluggish Injection Valve	Service Valve
Poor Quantification of Divalents	Sample Loop Contamination	Flush or Replace
	Contaminated Cell	Clean Cell

Figure 4-3: The operating problems, cause of the problems and guide to solve this in IonPac SCS 1 column.[34]

4.1.2 Dionex ICS-3000 pump

The Dionex ICS-3000 pump designed for both standard bore and micro bore applications with flow rate 0.001 to 10.0 mL/min and operating pressures up to 35 MPa (5000 psi). There are two commercial models of the pump, the ICS-3000 Dual Pump (DP) and ICS-3000 Single Pump (SP). The SP contains one isocratic pump or one gradient pump while the DP contains two gradient pumps, two isocratic pumps, or one isocratic pump and one gradient pump. The isocratic pump delivers one eluent, while the gradient pump can deliver gradient mixtures up to four eluent components.[35]

In this research the single pump that contains one isocratic pump has been used. Figure 4-4 is shown the liquid flow path throught an isocratic pump.

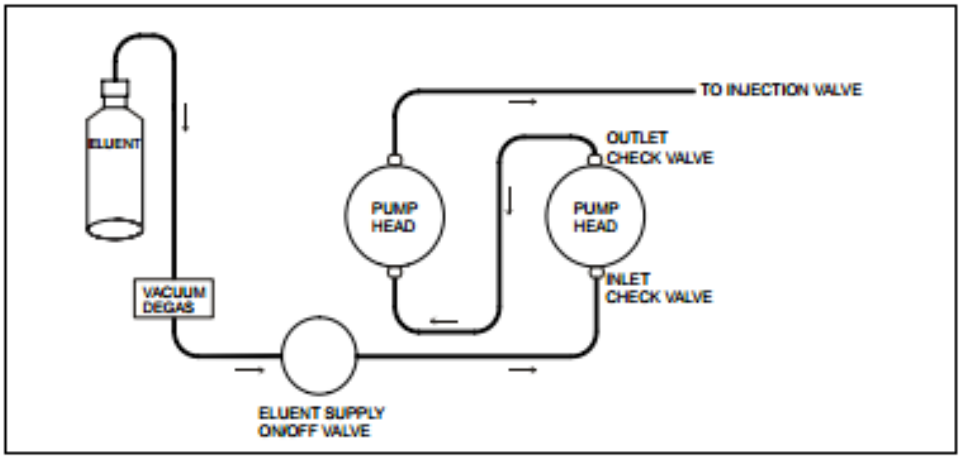

Figure 4-4: Isocratic Pump Flow Schematic.[35]

The pump can be controlled by chromeleon software on the computer or locally, on the front panel keypad. In the Figure 4-5 the main specifications of the ICS-3000 isocratic pump is tabulated.

More specification about the pump is in appendix E.

DP AND SP PUMP SPECIFICATIONS	
Available Configurations	SP Isocratic SP Gradient DP Isocratic/Gradient DP Gradient/Gradient
Applicability	Gradient and Isocratic separations with 1–9-mm columns
Construction	Chemically inert, metal-free PEEK pump heads and flow path, compatible with aqueous eluents of pH 0–14 and reversed-phase eluents.
Type	Serial dual-piston, constant stroke
Control Modes	Remote by Chromeleon software through USB; Stand-alone through standard Chromeleon Xpress control
Pressure Limit Alarms	Programmable upper and lower limits
Flow Rate Range	0.001–10 mL/min
Flow Rate Accuracy	±0.1% at 1 mL/min
Flow Precision	±0.1% at 1 mL/min
Pressure Range	50–5000 psi
Pressure Ripple	1% (typical)
Gradient Proportioning Accuracy	±0.5% at 2 mL/min
Gradient Proportioning Precision	±0.5% at 2 mL/min
Number of Solvents	Isocratic: one solvent Gradient: four solvents
Gradient Mixer Delay Volume	2-mm GM4 < 290 µL 3–9-mm GM3 < 500 µL
Vacuum Degassing	SP Isocratic: one channel, (optional) SP Gradient: four channels, built-in DP Isocratic/Gradient, built-in DP Gradient/Gradient, built-in
Wetted Parts	PEEK, sapphire, ruby, ceramics, UHMW polyethylene, PCTFE, PTFE
Leak Detection	Optical sensor, (no calibration required)
Computer Connection	Through USB device connector; with USB hub (three) connectors
I/O Interfaces *Inputs/Outputs*	Four programmable relays; motorized switching-valve port; analog output for system pressure Three digital inputs for Start, Stop, and Hold
Power Requirements	90–120 V, 200–240 V; 47–63 Hz
Operating Temperature Range	4–40 °C (40–104 °F)
Operating Humidity Range	5–95% relative, noncondensing
Dimensions (h × w × d)	41 × 22 × 56 cm (16 × 8.5 × 21.6 in.)
Weight	SP: 20.4 kg (45 lb); DP: 24.1 kg (53 lb)

Figure 4-5: The main specifications of the ICS-3000 isocratic pump.[36]

4.1.3 Dionex CD20 conductivity detector

The CD20 conductivity detector is a microprocessor-driven precision detector which is very sensitive, accurate, and universal instrument for detecting and quantifying ionic analytes in ion chromatography. The main specifications for the CD20 conductivity detector are summarized in the

Table 4-2. More specification about the column is in appendix E. in addition information for troubleshooting of the detector can be found in this appendix.

Table 4-2: Specification of CD20 conductivity detector.

Electrical	Main power	85 to 270 Vac. 47/63 Hz, 40 W max, 25 W typical. The CD20 power supply is auto-sensing and requires no voltage adjustment.
	Fuses	Two 3.15 amp fast-blow ICS127 fuses
	Analog output	User-selectable full-scale output of 10, 100, or 1000 mV
Environmental	Operating temperature	4 ºC to 40 ºC
	Operating humidity	5 to 95% relative humidity, non-condensing
Physical	Dimensions	22.5 cm W x 17.0 cm H x 42.0 cm D 6 cm clearance required behind the detector
	Weight	8.2 kg
Detector	Range	0.01 µS to 3000 µS, full-scale
	Temperature compensation	0.0 to 3.0% per ºC
	Cell drive	Variable 8 kHz square wave
	Local operation	Front panel controls and display status of all functions
	Remote operation	Control of four functions via TTL or Relay contacts
Conductivity cell	Cell body	PEEK
	Active volume	1.0 mL
	Maximum pressure	2.0 MPa
	Electrodes	316 stainless steel
	Over- voltage alarm	8.5 V
	Over- temperature alarm	40 ºC

4.1.4 Gilson 402 syringe pump

The 402 Syringe Pump is a low pressure syringe pump for transferring liquids. There are three types of the pump for a wide range of applications: i) single syringe and single valve, ii) dual syringe with Tee junction and iii) dual syringe and dual valve. The syringe pump used in this equipment is a dual syringe with Tee junction. The flow path materials inside the valve are ceramic and PEEK and inside the Tee junction is PEEK. Major parts of the pump can be autoclaved or cleaned.[37]

4.1.5 Gilson 231XLsampling injector

The auto-sample injector is designed to inject 1-100 μL sample amount, automatically into the ion chromatograph with an error less than 0.5 % volume, difference from injection to injection. The injection system can also be controlled manually.[38, 39]

4.2 Specifications

The standard samples and oxidative degradation samples are analyzed with same conditions and method. Table 4-3 shows the conditions for cation - exchanger chromatography in this experiment.

Table 4-3: Conditions for cation- exchanger chromatography.

Injection volume	20 μL
Temperature in chromatograph oven	30 ºC
Flow rate	1mL/min
Eluent	8 mM MSA and 7% v/v ACN
Analysis time	20 minutes

4.2.1 Mili-Q water

The contamination has high effect in the results, therefore to get the best results it is important to use water with high purity. Due to this mili-Q water is used in all the experiment. This water is high quality water with a resistivity of 18.2 MΩ.cm

4.2.2 Mobile phase

As mentioned in the section 3.5 choose of mobile phase is one of the most important parameter in the chromatography system. The main requirement for correct selection of mobile phase is that it can dissolve the analytes up to the concentration appropriate for detection. The eluents used in the SCS 1 column should be eluents in 2-7 pH range. The SCS 1 column is compatible with typical

organic solvents such as acetonitrile and acetone up to 100% concentration levels. alcohols should be avoided in this column, since form esters in the column and reduce the column capacity [33]. The thermo scientific studies [33] of the SCS 1 column shows to determination the common inorganic cations, ammonium, alkanolamines (including MEA, diethanol amine, and triethanol amine) and transition metals, require different eluent concentration and compositions (see Table 4-4), for instance to resolve potassium and diethanolamine in the mixture of alkanolamines in addition to 3 mM MSA, 10 % acetonitrile should be added to the eluent. Adding acetonitrile in the mobile phase increase the quality of separation and cause invention of more peaks in the analysis (see Figure 4-6).

Table 4-4: Some of the eluent used in the SCS 1 column for determination of different analytes.[33]

The analytes	**The eluent**
Common inorganic cations, Ammonium and Ethanolamine	3mM MSA
Trace Sodium in high Ethanolamine	3mM MSA
Trace Ammonium in high Sodium	3mM MS
Alkanolamines (including MEA, diethanol amine, and triethanol amine) and the common inorganic cations	10% acetonitrile to the 3 mM MSA
4.2Transition Metals and Common Inorganic Cations	4.0 mM tartaric acid and 2.0 mM oxalic acid
Alkanolamines, transition Metals, and the common ©inorganic cations in Simulated Feed Water	2.5 mM MSA eluent modified with 0.8 mM oxalic acid

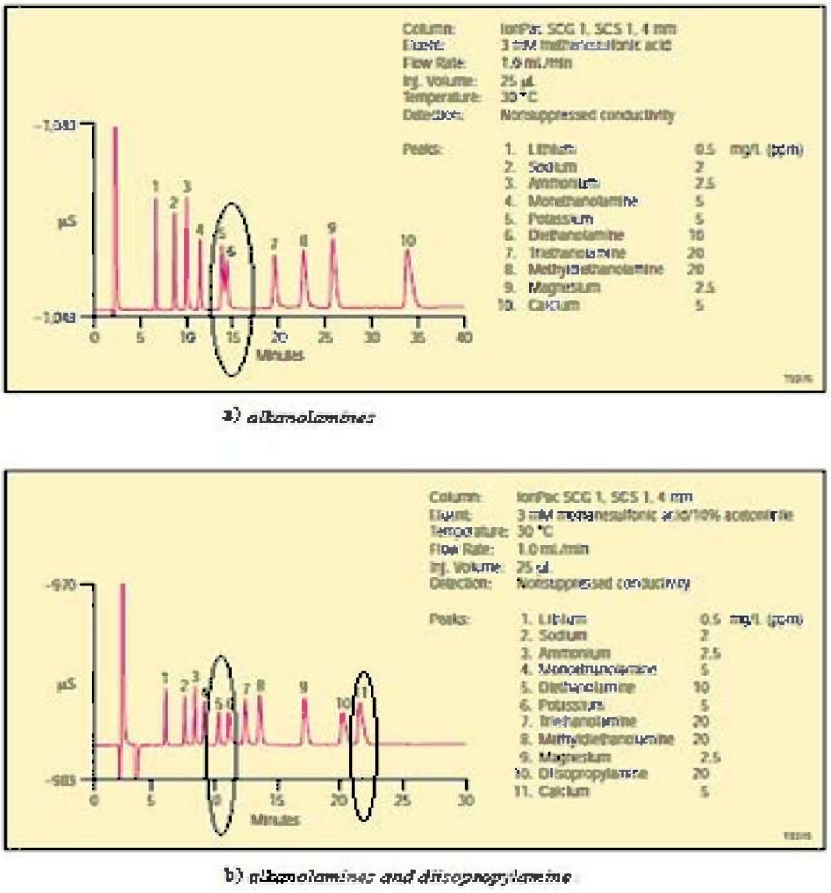

Figure 4-6: Determination of alkanolamines, using the IonPac SCS 1 using 3 mM MSA eluent a) and using 3 mM MSA with 10% acetonitrile b).[33]

The mobile phase used in this work was 8 mM MSA and 7% v/v ACN. Preparing the mobile phase can be found in Appendix D.

4.2.3 Startup of the cation chromatograph

Before starting the experiments, the mobile phase should be prepared manual (see Appendix D) and replaced in the mobile phase bottle. It is important to purge the pump to remove the air. Wait to the system is stable before begin to experiments. It is important to change the Milli-Q water each week to avoid the degradation of the water quality.

Detailed procedure for startup the cation chromatograph is described in Appendix C.

4.2.4 Standard preparation

The standard solution is prepared from MEA. Properties and manufacturer for MEA is shown in Table 4-5.

Table 4-5: Properties and manufacturer for MEA.

Name of chemical	Abbreviation	Purity (%)	M.W. (g/mol)	Type of chemical	Manufacturer
Monoethanolamine	MEA	99.5	61.08	Liquid	Merck

Volumetric procedure is used to prepare the standard solution. The concentration ranges fluctuate between 0.5 mM/l to 5 mM/l. Mili-Q water has been used to dilute MEA. It is important to clean the sample glasses with mili-Q water. See Appendix F-1 and F-2 for more detailed procedure description.

4.2.5 Dilution of oxidative degraded samples

The oxidative degradation samples of MEA are 23 samples from a CO_2-capture pilot plant with unknown MEA concentrations. The samples are in liquid form. A picture of the samples is shown in Figure 4-7.

Figure 4-7: The 23 samples from CO_2-capture pilot plant.

It is important before starting the preparations of the samples be careful for some points such as, clean and dry glasses with Mili-Q water, use a new disposable pipette for every oxidative degradation sample (original sample) and use Mili-Q water to dilution. In addition keep the samples in a dark and cold place to prevent more degradation from occurring. A gravimetric procedure is used to dilute the oxidative degradation samples, allowing a small amount of sample is weight and diluted with Milli-Q water in a ratio of 5000:1. See Appendix H for more detailed procedure description.

5 Results

The first part of this chapter will contain the work done to choose of the correct dilution factor for the oxidative degradation samples while the second part is the results from the calibration curve and calculation of the systematic errors of the calibration curve. Finally the results from analyzing of oxidative degradation samples will be shown.

All the sample analyses are performed with pump flow rate at 1 mL/min, column temperature of 30 ºC, injection volume at 20 µL and constant analyses time.

5.1 Choose of the correct dilution factor

As discussed in the section 3.11.3, asymmetry is one of the factors that can be used to explain the equality of peaks in the chromatogram. due to this before starting the analyses of samples it is important to optimal dilution ratio of the samples. Therefore some samples (number 1 to 10) was diluted and analyzed in the ratio 2000:1.

The focus is only on the MEA peak in all the samples. Figure 5-1 shows the MEA peak in the chromatogram for sample number 6 with dilution ratio 2000:1.

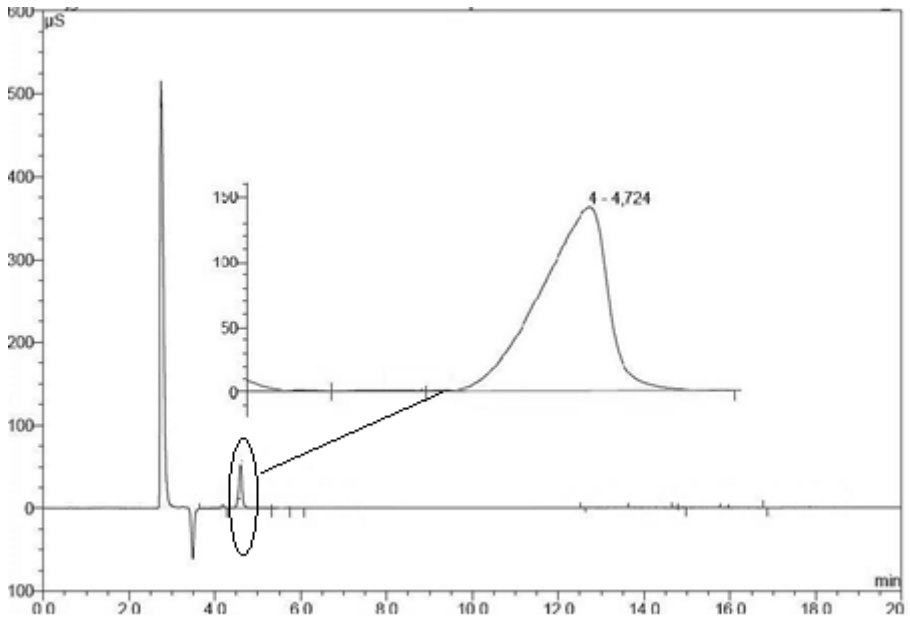

Figure 5-1: The MEA peak for sample number 6 with dilution ratio 2000:1.

As illustrate from above figure the peak has fronting with low asymmetry (0.74). The problem can be solved by increasing the dilution ratio (see Figure 4-3). Figure 5-2 shows with increasing the dilution factor to 5000:1 the asymmetry increased to 0.963 that is an acceptable value. See Appendix M for similar chromatograms of other samples.

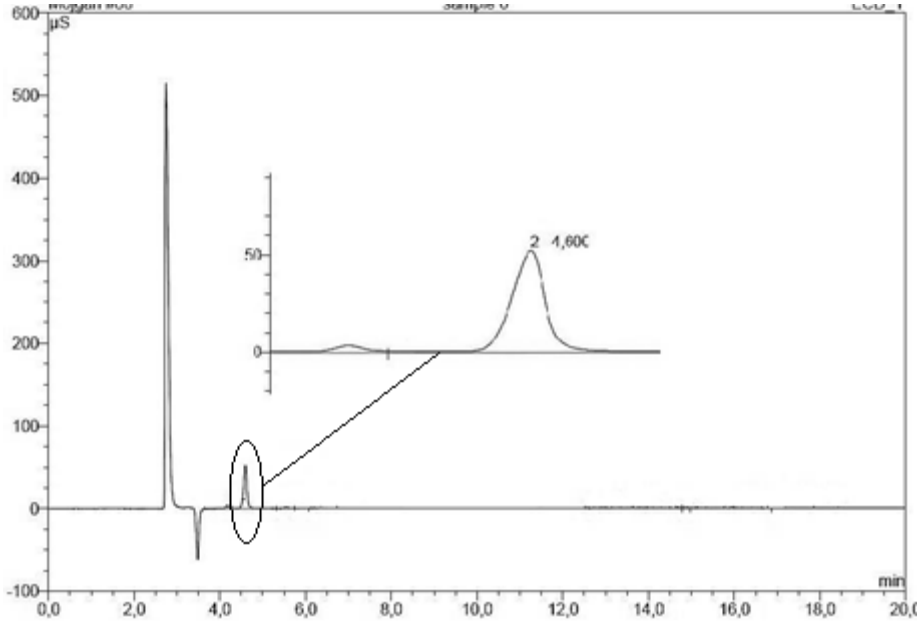

Figure 5-2: The MEA peak for sample number 6 with dilution ratio 5000:1.

Change in the dilution ratio influence the results of analyses, i.e. area of curves and retention time in addition to the asymmetry. The results from compering different dilution ratios (2000:1 and 5000:1) for sample number 6 are summarized in Table 5-1.

Table 5-1: From compering different dilution ratios (2000:1 and 5000:1) for sample number 6.

Dilution factor	Area (µS*min)	Peak height (µs)	Asymmetry	Retention time(min)
2000:1	15.4809	142.601	0.740	4.724
5000:1	5.0765	52.219	0.963	4,600

Figure 5-3 illustrate differences in the asymmetry for MEA peak for oxidative degradation samples (nr: 1 to 10) with 2000:1 and 5000:1 dilution ratios.

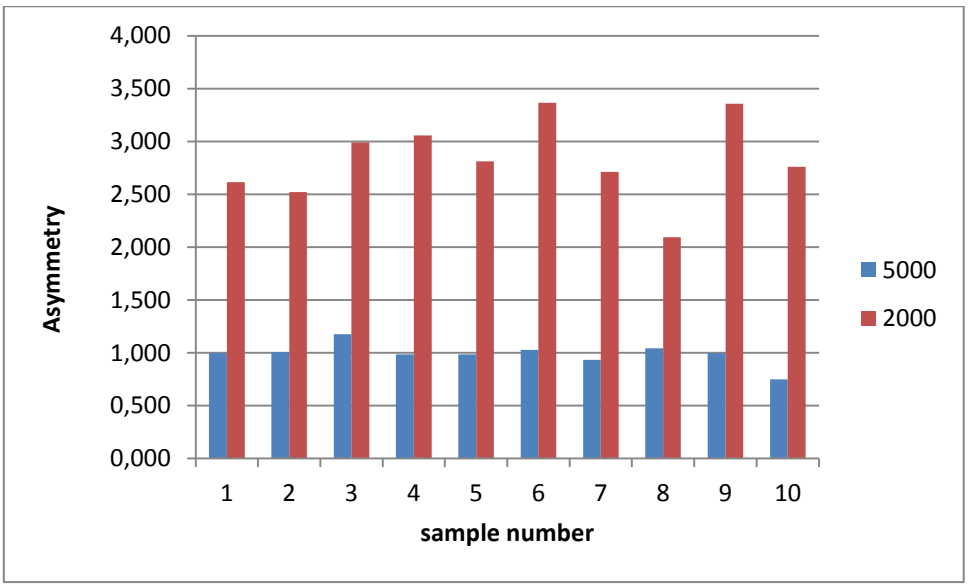

Figure 5-3: Asymmetry for MEA peak for oxidative degradation samples (1 to 10) with 2000:1 and 5000:1 dilution ratio.

The above graph shows the best asymmetry for a dilution factor equal to 5000:1.

5.2 Calibration curve

"*The calibration curve is constructed by measuring the instrumental signal for each standard and plotting this response against the concentration*".[16]

In order to determine actual concentrations in the samples, a series of standards must be analyzed to calibrate the response between peak area and actual concentration for each ion. The external standard method is used for making the calibration curve. The calibration curve is prepared from MEA and diluted with Mili Q water .Analyses of MEA are performed with concentration of 0.5, 1, 2, 3, 4, and 5 mM/l. Each of the concentrations has been analyzed four times and a sample of pure mili-Q water has been lying between every four parallel samples to get more responsible results. The chromatograms and calculations for the standards and calibration curve can be finding in Appendix K-1 and K-2.

Table 5-2 shows the results from the analyses. The mean values are calculated from Equation 2-4, the standard deviation from Equation 2-5, and the C.V from Equation 2-7.

.

Table 5-2: Mean value, standard deviation and coefficient of variation of MEA.

Concentration [mM/l]	Mean value of peak area [µS*min]	Standard deviation [%]	C.V[%]
0.5	3.153	±8.346	2.647
1	5.218	±10.723	2.055
2	10.011	±22.088	2.206
3	14.909	±34.187	2.293
4	19.626	±31.629	1.612
5	23.905	±24.809	1.038

Figure 5-4 shows the peak area versus concentration for each of the data points. The determination coefficient (R^2) is only 0.04 % from the perfect fit. This value is acceptable and the results can be used in further work. For all the data points in the calibration curve the standard deviation is plotted. As shown in Table 5-2 the highest value for standard deviation is ±34.187 % for 3 mM/l and the lowest value is ±8.346% for 0.5 mM/l. (see Appendix K-2.)The deviation can arise from the system which is very sensitive or from the sample preparation that some of these errors are calculated in the next section.

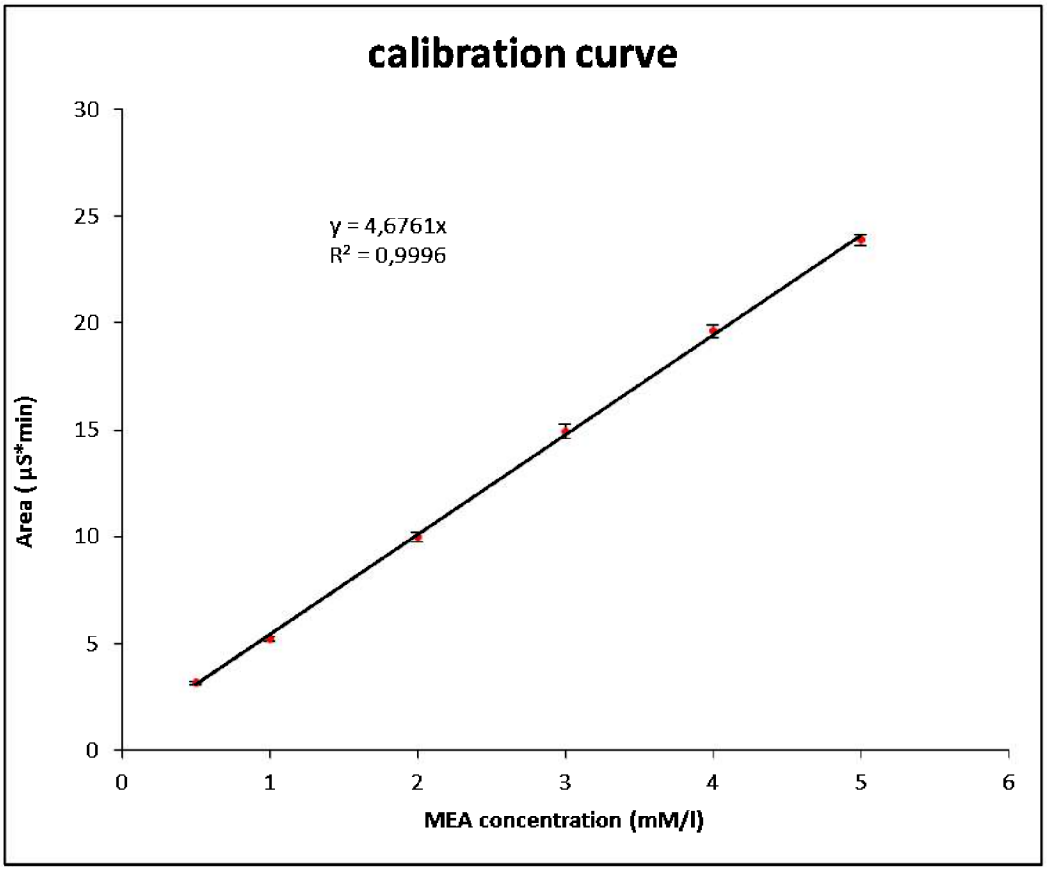

Figure 5-4: Calibration curve of MEA.

Figure 5-5 shows an example of chromatogram for MEA before degradation with 4mM/l concentration. See Appendix K-1 for similar chromatograms with different concentrations.

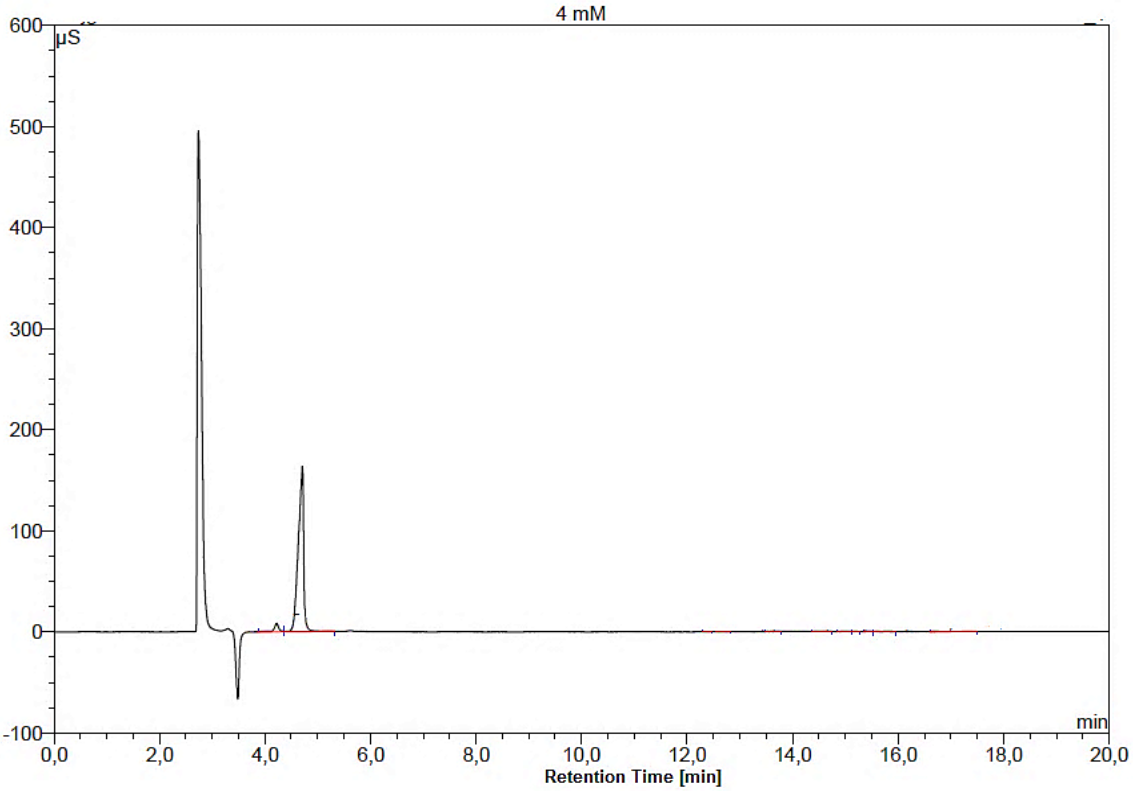

Figure 5-5: Example of chromatogram for MEA.

5.2.1 Systematic errors in calibration curve

On the basis of the theory in chapter 2 one kind of the errors which affect an experimental result is systematic errors and to have a reliable calibration curve it is necessary measure these errors. Table 5-3 shows the quantification of some of these systematic errors. Detailed calculation procedure has been shown in Appendix F-2.

Table 5-3: The quantification of some of systematic errors.

Concentration (mM/l)	**Equipment**	**Standard error (ml)**	**systematic error (mM/l)**	**Real concentration**
10 mM/l MEA	Flask (100ml)	0.100	0.022	10± 0.022
	Initial solution (100mM/l)	0.119		
	Pipette (10 ml)	0.015		
5.0 mM/l MEA	Flask (10ml)	0.100	0.056	5±0.056
	Initial solution (10mM/l)	0.022		
	Pipette (5ml)	0.022		
4.0 mM/l MEA	Flask (100ml)	0.100	0.043	4±0.043
	Initial solution (100mM/l)	0.119		
	2*Pipette (2 ml)	0.015		
3.0 mM/l MEA	Flask (100ml)	0.100	0.038	3±0.038
	Initial solution (100mM/l)	0.119		
	Pipette (2ml)	0.015		
	Pipette (1 ml)	0.01		
2.0 mM/l MEA	Flask (100ml)	0.100	0.015	2±0.015
	Initial solution (100mM/l)	0.119		
	Pipette (2ml)	0.015		
1.0 mM/l MEA	Flask (100ml)	0.100	0.010	1±0.010
	Initial solution (100mM/l)	0.119		
	Pipette (1ml)	0.010		
0.5 mM/l MEA	Flask (100ml)	0.100	0.003	0.5±0.003
	Initial solution (10mM/l)	0.022		
	Pipette (5ml)	0.022		
100 mM/l MEA	Initial solution (100mM/l)	0.100	0.119	100±0.119
	analiytical scal	0.004		

As expected the errors associated with the sample preparation due to operational and instrumental errors has been measured. These errors are small and acceptable.

Retention time for the standard samples during the four analyses with different concentrations is shown in Table 5-4 with the mean values and standard deviations. As shown in this table the standard deviation is small and the small change in retention time can arise from sensitivity of the system.

Table 5-4: Change in retention time for the standard samples.

Concentration [mM/l]	Sample 1 [min]	Sample 2 [min]	Sample 3 [min]	Sample 4 [min]	Mean value of retention time [min]	Standard deviation [%]
0.5	4.603	4.607	4.613	4.607	4.608	± 0.412
1	4.627	4.622	4.624	4.620	4.623	± 0.299
2	4.660	4.660	4.660	4.660	4.660	0
3	4.684	4.683	4.687	4.687	4.685	± 0.206
4	4.710	4.710	4.710	4.707	4.709	± 0.150
5	4.737	4.740	4.737	4.740	4.739	± 0.173

Figure 5-6 shows the retention time against the concentration for each of data points. Increase in the concentration cause increase in the retention time.

The mean value of retention time for different concentrations of the standard is used to identify the remaining MEA concentration in oxidative degradation samples.

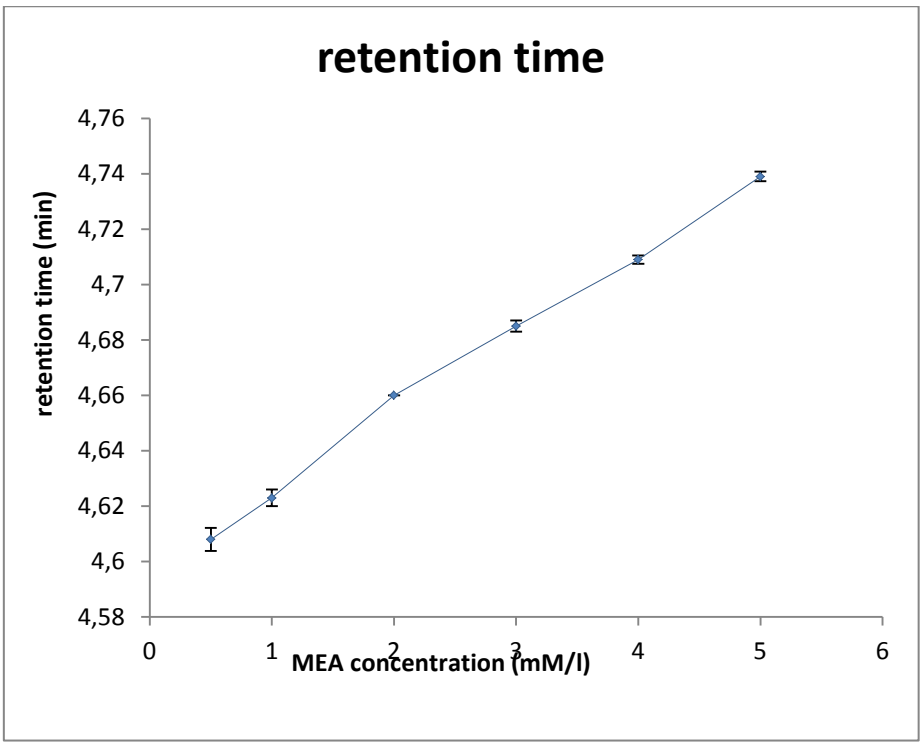

Figure 5-6: Change in retention time against concentration for each of the data point.

5.3 Oxidative degradation samples

As explained in previous chapter the oxidative degradation samples of MEA are 23 samples with unknown concentrations of remaining MEA. All oxidative degradation samples are prepared with the same procedure (gravimetrically) with dilution factor as 5000:1 and analyzed under the same conditions. The exact values can be found in Table 5-5. Appendix M, shows the sample chromatograms and the calculations to prepare the samples.

Each of the samples has been analyzed tree times and a mili-Q water sample has been lying between every tree parallel samples to get more responsible results. The concentration of MEA in the each sample is calculated from the calibration curve. Table 5-6 shows the results from the analyses. The mean values are calculated from the Equation 2-4. Figure 5-7 shows the results obtained for remaining of MEA in the samples as a graph.

Table 5-5: The exact dilution values of 23 degraded MEA samples.

Sample number	Amount of sample [g]	Total amount (sample+ mili-Q water) [g]	Exact dilution ratio
1	0.015	100.1157	4540:1
2	0.0193	100.1376	5187:1
3	0.0201	100.8390	5016:1
4	0.0196	100.1794	5110:1
5	0.0180	100.0889	5559:1
6	0.0196	100.1580	5109:1
7	0.0195	100.0481	5130:1
8	0.0203	100.1991	5033:1
9	0.0182	100.0482	5496:1
10	0.0204	102.5720	5027:1
11	0.0180	100.1260	5562:1
12	0.0186	99.1818	5331:1
13	0.0180	100.2975	5571:1
14	0.0183	100.2676	5478:1
15	0.0188	100.1226	5325:1
16	0.0184	100.1811	5444:1
17	0.0187	100.2062	5358:1
18	0.0178	100.1438	5625:1
19	0.0180	100.0240	5556:1
20	0.0204	100.0661	4904:1
21	0.0183	100.0771	5468:1
22	0.0184	100.1770	5443:1
23	0.0185	100.1906	5415:1

Table 5-6: MEA concentration in the 23 degraded samples.

Sample number	Mean value of peak area [µS*min]	Mean value of retention time [min]	Concentration [mM/l]	Average asymmetry
1	4.665	4.822	0.998	0.963
2	4.712	4.608	1.008	0.957
3	5.499	4.630	1.176	0.973
4	4.612	4.610	0.986	0.953
5	4.606	4.688	0.985	0.943
6	4.806	4.604	1.028	0.963
7	4.363	4.601	0.933	0.933
8	4.880	4.609	1.044	0.967
9	4.657	4.608	0.996	0.953
10	4.748	4.610	1.015	0.947
11	4.210	4.607	0.900	0.950
12	4.730	4.603	1.012	0.963
13	4.228	4.603	0.904	0.933
14	4.148	4.600	0.887	0.967
15	5.041	4.627	1.078	0.967
16	4.598	4.607	0.983	0.963
17	4.391	4607	0.939	0.967
18	4.682	4.610	1.001	0.973
19	4.632	4.607	0.991	0.973
20	5.170	4.610	1.106	0.967
21	5.262	4.610	1.125	0.943
22	4.945	4.603	1.058	0.980
23	3.897	4.600	0.833	0.970

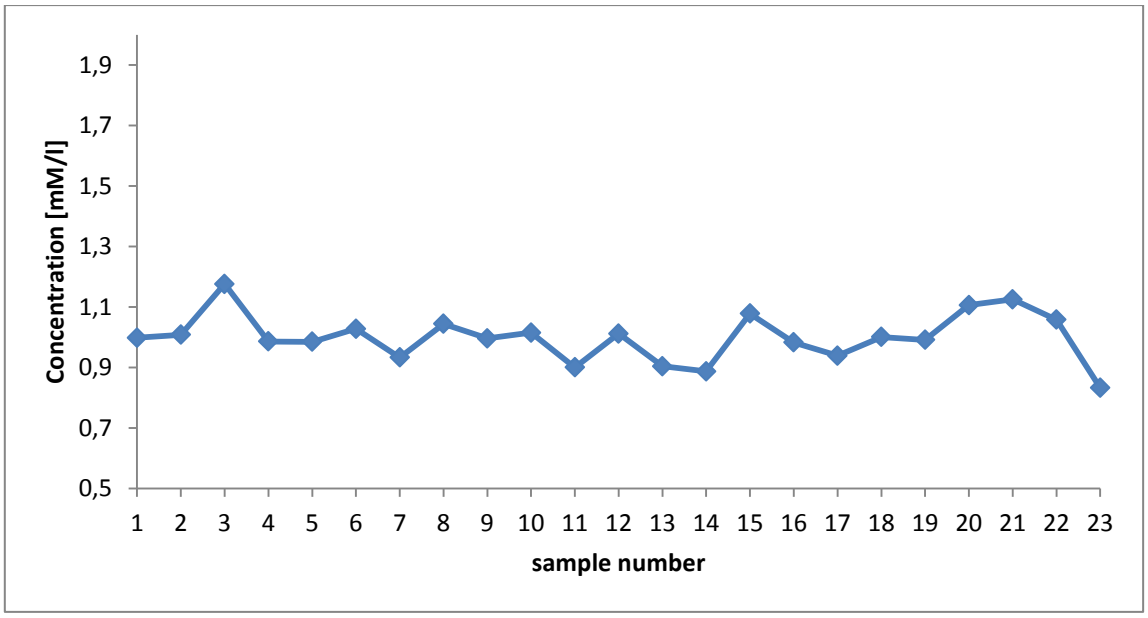

Figure 5-7: Results obtained for remaining of MEA in the samples.

6 Discussion

In this chapter the errors form calibration curve, the noise, the problems during the experiment and the affects in the restates, mobile phase, dilution of the samples and method applications will be discussed.

6.1 Calibration curve

One of the most important tasks in this project was unification of a calibration curve for MEA. A calibration curve was needed to identify the remaining MEA in the oxidative degradation samples. a volumetric procedure was used to prepare the standard samples from MEA before degradation, The concentration ranges fluctuate between 0.5 mM/l to 5 mM/l. the MEA diluted with mili Q water and mixed completely. The standard samples were analyzed four times to get a more responsible value and the mean value was used in the calibration curve plotting as a function of concentration. The errors that arise from the cation chromatography system and sample preparation can influence the results. Therefore a standard deviation was calculated for the mean value of peak area for each concentration. A line through every data point presenter a good analyses. With a determination coefficient equal to one (R^2=1) occur a perfect fit calibration curve. The determination coefficient of the calibration curve was 0.9996 that is an acceptable value for further work. A low determination coefficient means the standard deviation is high. Of the factors which can affect the result are sample preparation and system errors.

It is important to get a small standard deviation as possible. Low value of standard deviation shows that the value is close to the mean value. As shown in Table 5-2 the highest value for standard deviation in this work was ±34.187 % and the lowest ±8.346% for 3 mM/l and 0.5 mM/l MEA respectively. The high value for 3 mM/l can arise due to more steps in the preparation of this sample. Generally, the factors that affect the result are sample preparation and system error. The chromatograms for calibration curve (MEA chromatograms) show many noises. A detailed discussion about the noise is given in section 6.3.

6.2 Mobile phase

Selection of the correct mobile phase in the chromatography is very important due to many factors such as influence of pH of mobile phase in the retention time and asymmetry, in addition the ability of mobile phase to dissolving components to detection limit. As the work began (previous task) one of the aims was to analysis methylamine ((CH3) $NH3^+$) and dimethylamine ((CH3)2$NH2^+$) cations in the degraded samples from the pilot plant. Due to this reason according the researches from Wang Tielin [40], the optimal mobile phase (8 mM MSA and 7% ACN) was used to analyses the degraded samples. But due to limitation of time, problems with the apparatus and personally situation the experiments was only focused in the MEA in the sample analyses.

As discussed previously ,according studies by thermo scientific of the SCS 1 column adding ACN to the mobile phase cause increasing of the quality of separation and invention of more peaks in the analysis, due to resolving ability of components in the ACN [33],while non-influencing in the retention time and plate number [41]. High MSA concentration reduces pH of mobile phase and it followed by increasing in the acidity. Reduction of pH in the mobile phase cause increasing in the resolution factor[42]. Figure 6-1 shows an example for a chromatographic separation where resolution goes from an unacceptable value (1.4) to an acceptable value (3.0) when the mobile phase pH is decreased by only 0.1 units.

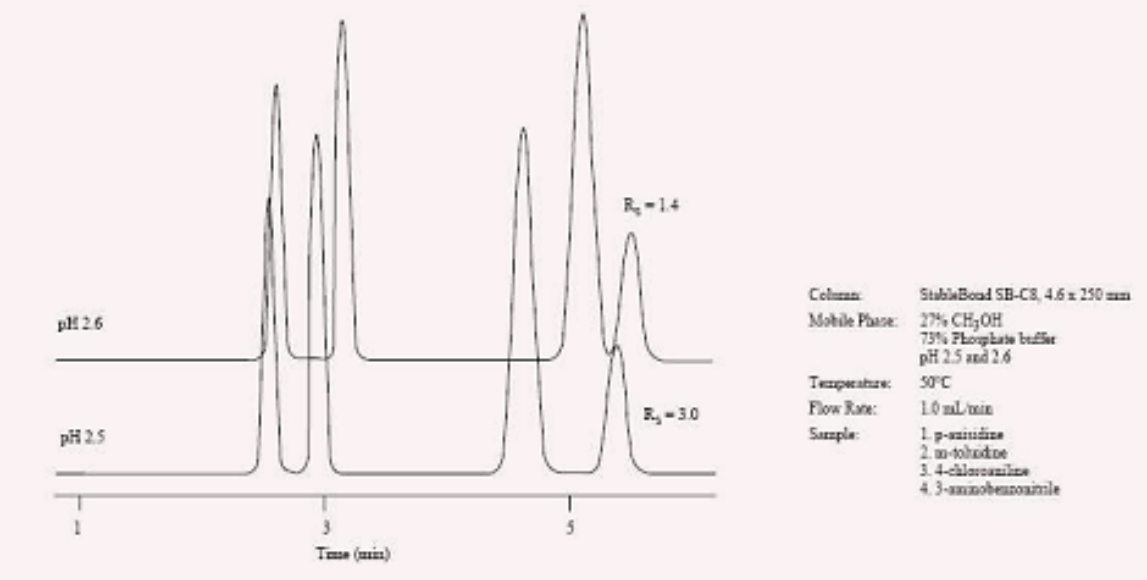

Figure 6-1: Increasing in resolution from 1.4 to 3.0 by decrease the mobile phase pH by 0.1 unit.[42]

6.3 Noise

The noise problems has seen in the all chromatograms (both calibration curve and the degraded samples) for this experiment since the system is very sensitive some noise occur in the method used for analyses..

Many factors influence development of baseline noise which some of the factors is impossible to delete from the system. Of the factors can mention the external environment, the pump with low quality (make long-term noise), the detector electronics (short-term noise), the column contamination, the mobile phase, stationary phase, change in flow rate, temperature effects, leak, other electronic equipment on same line, and air in mobile phase, detector cell or pump.[43-45]

Figure 6-2 and Figure 6-3 shows chromatograms for a water sample and standard MEA with 0.5 mM concentration respectively from this experiment.

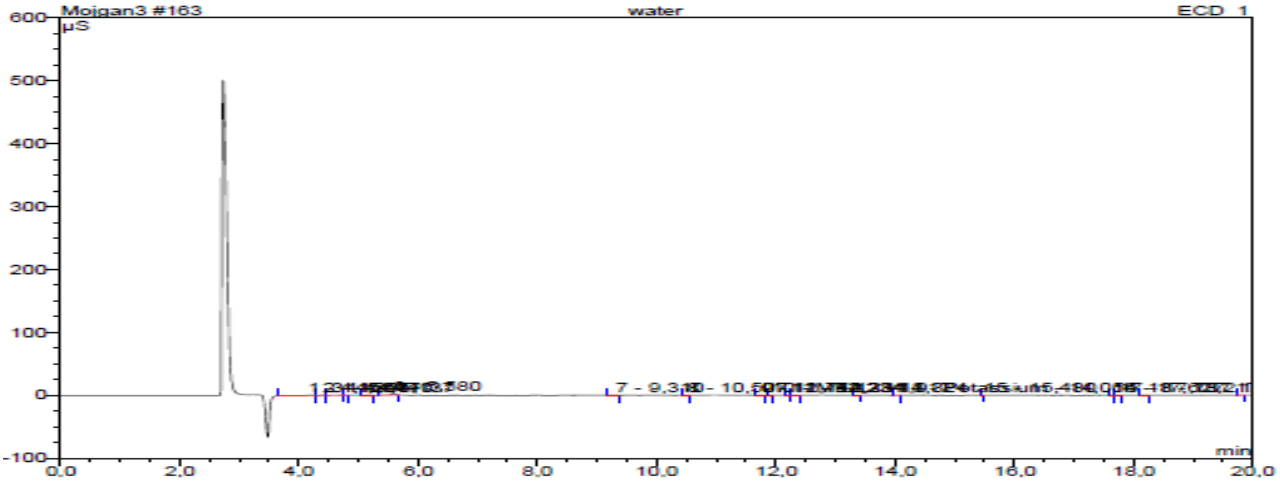

Figure 6-2: A water sample chromatogram with mobile phase 8 mM/l MSA, 7 % ACN.

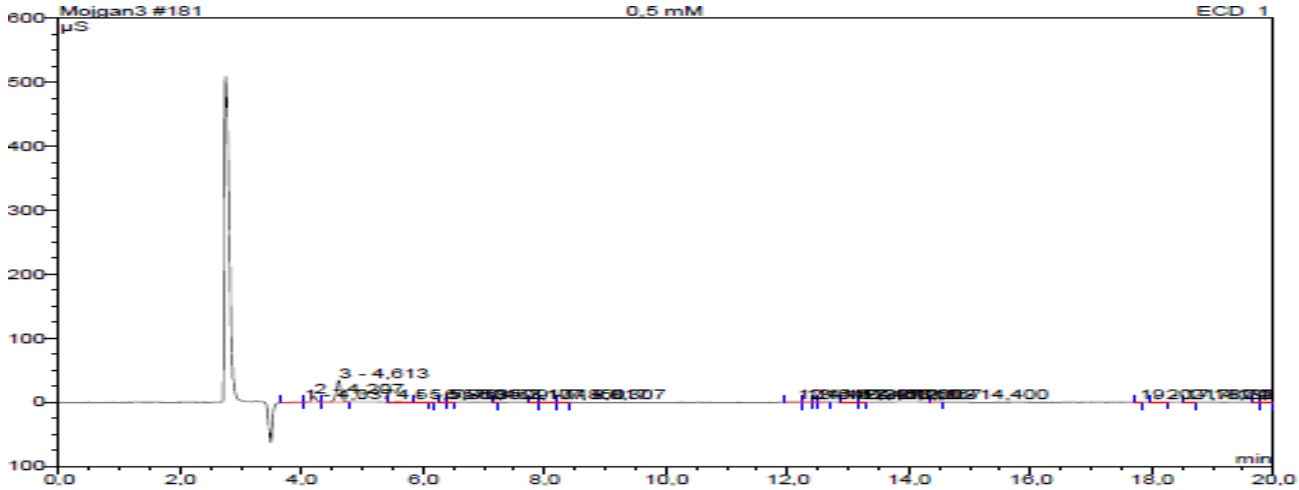

Figure 6-3: chromatogram for 0.5 mM MEA.

The temperature stabilization is important to have low noises [43], which during this experiment was difficult to stabilize the temperature of column.

The mobile phase impurities, not well mixing mobile phase and available air in the mobile phase (bubbles) are factors in the mobile phase which effecting noise in the detector. Additionally to this factors the high concentration of MSA in the mobile phase, contaminated in the mobile phase or not prepared from high quality chemicals in this experiment can be one reason to the noises [44]. L.Miguel [41] in his experiments have showed the effect of MSA concentration in the mobile phase to arising noises in the results. Figure 6-4 and Figure 6-5 shows two chromatograms from his research which mobile phase has 8 mM and 3 mM MSA concentration respectively, the chromatograms is for a same sample.

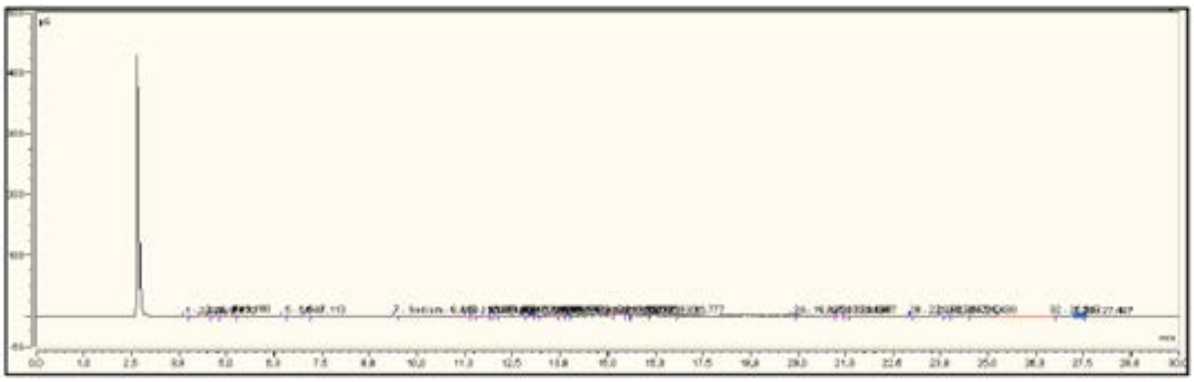

Figure 6-4: Influence of mobile phase in the noise of the chromatogram:8 mM/l MSA.[41]

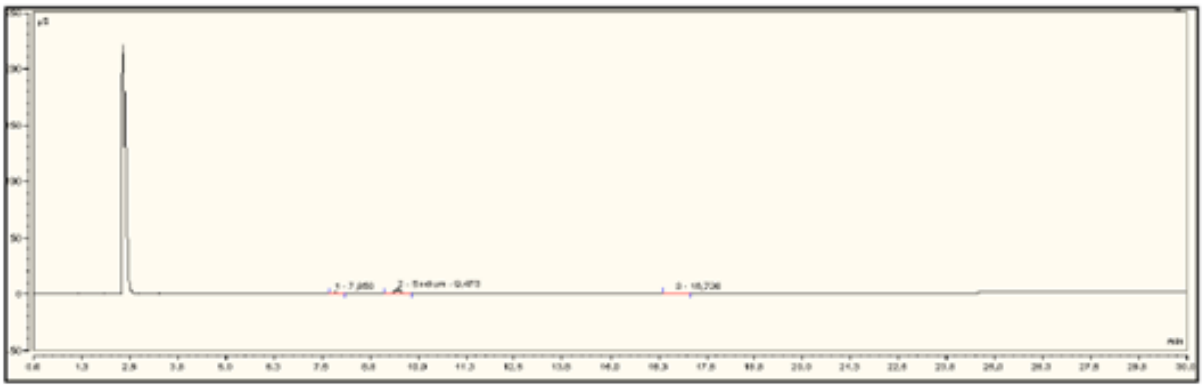

Figure 6-5: Influence of mobile phase in the noise of the chromatogram:3 mM/l MSA.[41]

Filtering the mobile phase through a 0.2 or 0.45 µm filter using a vacuum filtration apparatus eliminates dissolved gas is an recommendation to remove impurities in the mobile phase [44]. A well maintained pulse free pumping system can help to a smooth baselines [43].

6.4 Dilution

The dilution ratio (5000:1) was chosen for dilution of samples which give asymmetry more than 0.9 even though the asymmetry is furthest away from 1, but it is an acceptable value and was chosen due to detection limits for other components (recorder highest number of peaks).

6.5 Problems

During the laboratory work for this project occurred many problems such as, suddenly increasing in the temperature for column which should a fan be used to keep the temperature constant. The cation chromatograph system has leak and other electronic equipment is working in this lab on the same line. All this problems can affect the results. Additionally the apparatus was stopping during the analyses which can affect the results, due to for example changing in the temperature of samples or mobile phase.

The leakages have seen from both the Gilson 402 syringe pump and the column part, which cause incorrectly connections and noise problems respectively. [44, 45]

6.6 Method application

One requirement in this project was assessed a theoretically chromatographic procedure. There are many factors which can be changes or developed to increase the quality of the peaks and separations. As described in chap 3 the quality of the peaks can be assessed by the peak shape (asymmetry, width and height) and a god separation can arise by optimization in the resolution factor, selectivity factors and column efficiency.

Improving the column efficiency can be obtained by increase the number of plates and decrease the plate height and keep the temperature constant. A large number of plates can be achieved by ensuring short diffusion paths in the stationary phase pores, hence a stationary phase with small particle diameter tends to high performance chromatography [46]. Figure 6-6 shows this effect in two different columns. To give a total of 7000 theoretical plates in both columns, a 3µm material needs a column with 6 cm length (above chromatogram), while a 10µm material needs a column with length of 20 cm (below chromatogram).

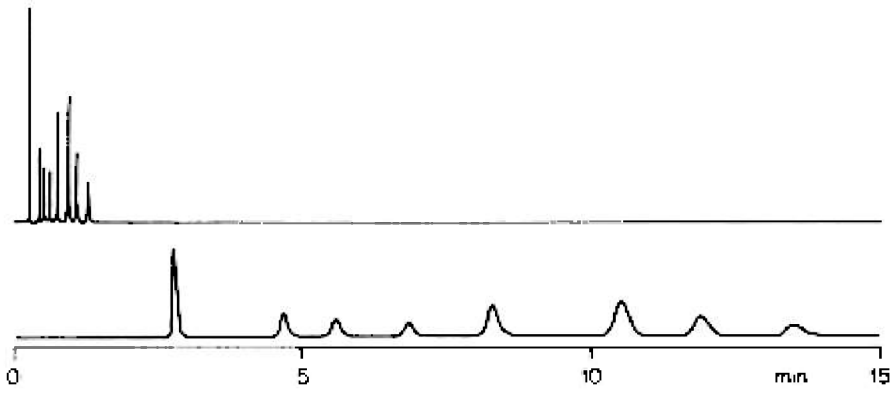

Figure 6-6: Above) 6cm x 4.6 mm i.d column with 3µm material. Below 20cm x 4.6 mm i.d column with 10µm material.[46]

Retention time can be influenced by the type of stationary phase (column type), composition and properties of mobile phase and column temperature.

Mobile phase's pH is an important variable to be manipulated in the optimization of the separation since the grade of adsorption is determined by this factor. Mobile phases which give the optimal charge have to be chosen.

Note that the SCS 1 column can use in a wide range of samples with 2-7 pH range and alcohols should be avoided in this column .Temperature affects the separations quality through effect on the structure of the protein. Although temperature does not affect the electrostatic interaction [47].

It is required to get a large value of selectivity factor, thus the mobile phase composition influence the selectivity factor. The broadening is a fundamental disadvantage in the chromatography and caused by diffusion processes and flow processes. Some factors such as the sample injector, detector characteristics, system temperature and column retention processes influence the peak width.

.

7 Conclusion

Due to emissions of greenhouse gases governments and authorities around the world are increasingly concerned about CO_2 capture as remedy to the reduce greenhouse gas emission issues. The most widely used CO_2 capture technology is the chemical absorption-stripping process which amines are the most commonly used solvents in this method. Degradation of amines during the CO_2 capturing process is considered as one of the growing concerns. Therefore it is important to get knowledge about the degradation products and minimize these. The base for this report was to analyses oxidative degradation samples from pilot plant with a cation exchange chromatograph and assessed a theoretically chromatographic procedure with respect to the sample analyzed. The silica based IonPac SCS 1 analytical column with ion exchanger grope (Grafted carboxylic acid) was used in this experiment. The eluent was 8 mM MSA with 7 % ACN. Pump flow rate was (1 mL/min) and column temperature 30 °C.

An important part to this work was to prepare calibration curves for MEA. The result shows highest value for standard deviation equal to ±34.187 % for m mM/l and the lowest value equal to ±8.346% for 0.5 mM/l MEA. Determination coefficient for calibration curve was 0.9996 with 0.04 % deviation from the perfect fit. To get the best results it is important, to choose the correct mobile phase, keep the temperature of column constant, prevent air in the system for instance prime the pump, make correct mobile phase and try to avoiding systematic errors.

8 Further work

Some suggestions for further work for analyzing the samples and work with cation chromatograph may be:

- Try another method, for instance increase or decrease the pump flow rate and column temperature, to see how that affects the result, and compare the results with previous results.
- Change composition and concentration of mobile phase.
- Use gravidisk method to prepare the standards and compare the results with previous results.
- Try to identify the unknown peaks from the oxidative degradation samples.
- Try to change the column and use columns with another stationary phase.
- Try to find the leakage from the system and fix it.

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Appendices

Appendix A: Task description

Appendix B: chemicals used in this equipment

Appendix C: turning procedure of the cation chromatograph

Appendix D: preparing the mobile phase

Appendix E: information's about SCS 1 column, pump, detector (on CD)

Appendix F-1: procedure of the standard sample preparation

Appendix F-2: calculations of preparation the standard samples with errors (on CD)

Appendix H: Procedure for preparing oxidative degradation samples

Appendix K-1: chromatograms of standards. (MEA)

Appendix K-2: calculations for the calibration curve (on CD)

Appendix M: results from samples and preparation calculations (on CD)

Appendix A:

Telemark University College
Faculty of Technology

FMH606 Master's Thesis

Title: Oxidative stability of primary amines - structure-property relationship

TUC supervisor: Klaus J Jens, Wang Tielin

External partner: Tel-Tek, Statoil

Task description:

The task is to analyse by cation chromatography samples of degraded MEA carbon capture solvent originating from a pilot plant. A calibration curve is to be established for a known procedure. The chromatographic procedure is to be theoretically assessed with respect to the samples analysed. A short introduction is to be given to the area of carbon capture solvent degradation.

Task background:

Carbon dioxide removal from flue gas streams is important to reduce its greenhouse effect. Aqueous amines are often proposed to capture CO_2 from low partial pressure sources, but their use in the presence of oxygen is more limited due to oxygen caused amine degradation, which is the main distinct difference and challenge as compared to traditional acid gas capture.

This task description has been adjusted Feb 2013 due to the personal situation- and in agreement with the student. A final version of the document is prepared today.

Student category:

PT or EET students

Practical arrangements:

Suitable equipment to analyze amine solvent degradation is available in the CO_2 lab.

Signatures: Mojgan Zarsav Klaus J Jens 4.10.2013

Student (date and signature): Supervisor (date and signature):

Adress: Kjølnes ring 56, NO-3918 Porsgrunn, Norway. **Phone:** 35 57 50 00. **Fax:** 35 55 75 47.

Appendix B:

Chemicals used in this experiment:

Name of chemicals	Abbreviation	Purity (%)	M.W. (g/mol)	Type of chemical	Manufacturer
Monoethanolamine	MEA	99.5	61.08	liquid	Merck
Methanesulfonic acid	MSA	99	96.11	liquid	Merck
Acetonitrile	ACN	99.8	41.05	liquid	Sigma-Aldrich

Appendix C:

Turning of the cation chromatograph:

- Open nitrogen valve from the nitrogen bottle.
- Open the nitrogen valve in the equipment (2 bar)
- Switch on the column heat exchanger (temperature=30)
- Run chromatogram management system program and select cation , with press "Ctrl+tab"
- Open the waste value of the pump
- Select "Manual/purge" in the software and wait 5 minutes until pump is off.
- Close the waste value of the pump and press "on" in the software until pressure is increase to 2000 bar.
- Wait to the system is stable (conductivity be close to zero) before begin to experiments.
- Make new experiments with select "File/New" and make name, position and running method for prepare samples in the auto sampler. Press "Ctrl+A" to add more chromatograms.
- To start experiments select "Bach/start/Ready check/Ok/start"
- When the experiment is finished, switch off the pump in the chromatogram software, switch off the column heat exchange, close the nitrogen valve.
- It is important to change the Milli-Q water, used to clean the needle each week to avoid the degradation of the water quality.

Appendix D:

Preparing 2000 mL mobile phase: (8 mM MSA, ACN 7.0 % (v/v))

- First make 2000 mL MSA solution with concentration of 8mM/l :
- from following equation
- Mass of MSA =(volume*concentration*molweight)/purity of MSA
- Add to a 2000 mL flask and fill with mili-Q water and shake .
- Take 1860 mL of the 8 mM MSA solution and put into another 2000 mL flask.
- Take 140 mL ACN and add into the flask with 1860 mL MSA and shake.

Appendix F-1:

Procedure for preparing standard sample

(For making the calibration curves and for check unknown peaks)

Milli-Q water has been used to dilute MEA. The concentration ranges fluctuate between 0.5 mM/l to 5 mM/l. The needed pipettes for preparing the samples are 10, 5, 2 and 1 mM pipettes.

- Meke a general sample with a concentration of **100 mM/l** . The components are weighed in an analytical scale.
- **10 mM/l sample**: Blend the pipette (10 ml) with the general solution (100 mM/l) . Take 10 ml of initial solution (100 mM/l) and put it into the flask (100 ml). Fill and flush with milli-Q water and shake.
- **Sample 5 mM/l**: Blend the pipette (5 ml) with the 10 mM/l solutiom. Take 5 ml of the solution and put it into the flask (10ml). Fill and flush with milli-Q water and shake.
- **Sample 4 mM/l:** Blend the pipette (2 ml) with the general solution (100 mM/l) two times. Take 2 ml of initial solution to times and put it into the flask (100 ml). Fill and flush with milli-Q water and shake.
- **Sample 3 mM/l**: Blend the pipette (2 ml and 1 ml) with the general solution two times. Take3 ml of initial solution (100 mM/l) and put it into the flask (100 ml). Fill and flush with milli-Q water and shake.
- **Sample 2 mM/l**: Blend the pipette (2 ml) with the general solution two times. Take 2 ml of initial solution (100 mM/l) and put it into the flask (100 ml). Fill and flush with milli-Q water and shake.
- **Sample 1 mM/l**: Blend the pipette (1 ml) with the general solution two times. Take 1 ml of initial solution (100 mM/l) and put it into the flask (100 ml). Fill and flush with milli-Q water and shake.
- **Sample 0.5 mM/l:** Blend the pipette (5 ml) with the 10 mM/l solution two times. Take 5 ml of initial sample (10 mM/l) and put it into the flask (100 ml). Fill and flush with milli-Q water and shake. In the appendix F.2 (excel) the calculations has been showed.

Prepare the sample to be analyzed with the IC. Take an amount of every solution into small sample glass and Place the sample glass in the sample injection place in cation chromatograph.

Appendix H:

Procedure for preparing oxidative degradation samples

The needed equipment for preparing the samples are Weight, disposable pipette, 100 ml Volumetric flask for preparing the degradation samples and Mili Q water.

Clean all flaks with Mili Q water and dry it.

Mark all the flasks with correct sample number.

Use a new disposable pipette for every new sample.

Weight up an amount of the degradation sample and write down the amount of the sample.

Dilute the sample with Mili- Q water and write down total amount of the total solution.

Mix the solution with turn it up and down.

Take an amount of every solution into small sample glass and place the sample glass in the sample injection place in cation chromatograph.