SEPARATION OF WASTE AMINE

by

MOHAMAD HILMY BIN BORHAN

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHAMAD HILMY BIN BORHAN

ABSTRACT

The objectives of this research project are to:-

1-Demonstrate the separation of mixture of waste amines through 2 types of membrane systems. RO and UF
2-Investigate the effect of pressures different, on the separation of waste amines.
3-Compare the finding of the research with the other literatures.

Amine is widely used as an absorption medium for H_2S and CO_2. In industry this gas also called as acid gas. They react with amines to form compounds which may be broken down by flashing and heating. This reversible reaction may represented as

$$\mathrm{MDEA} + H_2O + CO_2 <\!=\!=\!=\!> \mathrm{MDEAH}^+ + HCO_3^-$$

This project will highlight the use of membrane technology in the separation of waste amine and their contents. Nowadays amine does not recycle back, so this report will study on how the amine can be reused as it can give so many advantages in the industry.

These are the list of the advantages of amine. Amine that extracted from plant is called alkaloids. The number of unknown alkaloids exceeds 5000. They are a special interest because most are characterized by a high level of biological activity. Some examples include cocaine, coniine and morphine. Amine also used in as medicine. An azo dye called Prontosil is use to treat a serious, potentially fatal staphylococcal infection. More discussion in Chapter 2: Literature Review And Theory.

This project involves a research and experiment. Research has to be done to know about the properties of chemical used which are waste amine. It's content of MEA and DEA. The equipment used to analyze the sample is a Gas Chromatography. The separation of waste amine and their mixture is done by Reverse Osmosis and Ultrafiltration membrane.

This report will concentrate on the theory of RO and UF membrane. The research about the separation of waste amine and their content using it is still devoid. The RO membrane used in this system with salt rejection of 98%-99%; and UF membrane with molecular weight cut-off of 10,000. [Wayne T.Bates and Rocco Cuozzo, Integrated Membrane System]. The waste amine would be separated to the highest level possible so that the amount of amine can be reused increases. Analyzing process will be done to the feed and permeate sample. So their percentage could be determined. And also how it can help the industry in recirculated the waste amine.

From the data that recorded from the experiment, a few graphs were plotted. For RO membrane, three graphs were plotted using different pressure, 8.5 bar, 20 bar and 50 bar. 50 bar give higher permeate concentration. This is because RO membrane is imperfect barriers to dissolved salts in feedwater. There is always some salt passage through the membrane. When higher pressure is applied, this salt passage is increasingly overcome as water is pushed through the membrane at a faster rate that salt can be transported. [FilmTec Corporation, Factors Affecting RO Membrane Performance]

For UF membrane, the applied pressure is 2.8 bar, 3.43 bar and 4 bar. An increasing in pressure also increasing the permeate concentration. UF will give higher permeate concentration than RO. This is because RO has a particle size cut-off less than 0.001µm. UF is 0.01 to 0.1µm.[Ahmad Afdzal B Md Isa, et.al., Treatment Of Amine Contaminated Effluent Water via Membrane Application]. UF has bigger pores sizes that allow more molecules to pass through.

Both UF and RO, their feed and permeate sample were analyzed using Gas Chromatography (GC). For RO membrane at 50 bar give highest salt rejection for Monoethanolamine (MEA), 93%. Diethanolamine (DEA) is 100% rejected because the size is bigger with molecular weight 105.14 g/mole. MEA molecular weight is 61.08 g/mole. [Safety MSDS for Monoethanolamine and Diethanolamine]. For UF membrane at each applied pressure, there is no salt rejection because the concentration at permeate is higher than the feed.

ACKNOWLEDGEMENT

In the name of Allah, The Most Merciful.

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ABBREVIATIONS AND NOMENCLATURES

ABBREVIATIONS

UTP	University Teknologi PETRONAS
RO	Reverse Osmosis
UF	Ultrafiltration
MEA	Monoethanolamine (Primary amine)
DEA	Diethanolamine (Secondary amine)
MDEA	Methyldiethanolamine (Tertiary amine)
GC	Gas Chromatography

NOMENCLATURE

CO_2	Carbon Dioxide
H_2S	Hydrogen Sulfide
^0C	Degree Celsius
C_p	Permeate concentration
C_b	Feed concentration
J	Permeate flow rate
R_m	Membrane Resistance
ΔP	Trans membrane Pressure
ppm	part per million
L	Liter
Min	Minute

CHAPTER 1: INTRODUCTION

1.1 Background of Study

Amine had been widely used for CO_2 removal in gas treating system. As to reduce the possibility of carbon dioxide solids forming in the downstream low temperature operations, reduce the potential for corrosion in downstream operations and ensure compliance with hydrocarbon product delivery specifications. MDEA are among the favourite amines used because of the low energy requirement and it's simple design operation.[GPP, Operation and maintenance Manual]. H_2S and CO_2 are known as the main sources of corrosion to the pipelines. When mixed with moisture, impurities in natural gas, especially H_2S and CO_2, form a corrosive mixture that destroys equipment and pipelines. H_2S may cause hydrogen embrittlement in certain metal so a distinctive metallurgy is required to guard against H_2S corrosion. Hydrogen embrittlement occurs whenever a particular metal is exposed to an aqueous environment containing H_2S. The sulfide ion promotes adsorption of hydrogen produced by the corrosion reaction on the metal surface. Over the years, slowly there will be crack initiated at the metal surface. Under a higher load applied, it may results in fracture when the remaining ligament in the metal is insufficient to sustain the overloading. The example of this phenomenon is indicated in the Figure below: -

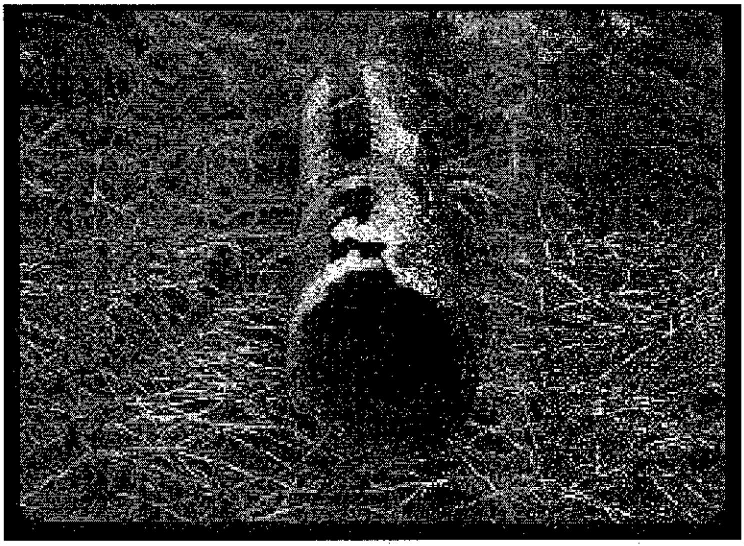


Figure 1.1: Metal fatigue, including hydrogen embrittlement or Sulfide stress cracking

In this research to separate the waste amine and their content of MEA and DEA, the equipment use is the Hybrid Reverse Osmosis Pilot System. This equipment consists of three filters. Reverse osmosis, Ultrafiltration and Flat Sheet filter. In this experiment only Reverse Osmosis and Ultrafiltration been use. The waste amine will flow through the filters and it's permeate (product) be analyzed using Gas Chromatography. The composition that has been removed will be checked, whether the amine content is reduced or remains the same. Membrane technology has gained a huge importance in the last 30 years, competing with long established technologies for water desalination, food processing, and emerging as unique solution in medical applications such as artificial kidney. Membranes are also now playing a special role in the field of alternative energy, as one of the fundamental parts of a fuel cell. In this sense, membrane technology has a potential contribution towards green chemistry.

1.2. Problem Statement

1.2.1. Problem identification

CO_2 removal using amines is well understood because of it has been widely used for acid gas removal. However it is expensive and hard to get. Cost for fresh Amine is RM 2760/drum.[Shahrizal B Hambalee, Amine Rejuvenation,]. One way to reduce the cost of amine is by recovered and recirculated back into the process stream. Amine carry over is a commonly discussed problem in gas plant utilizing amine as a medium to obliterate acid gases from the incoming gas stream. Amine carry over will potentially end up in the effluent water thus, if improperly discharge will pollute the environment. As known, mixture of amine with water is tenacious and well mixed mixture, hence to separate them is an arduous and a formidable challenge.[Ahmad Afdzal B Md Isa, et.al., Treatment Of Amine Contaminated Effluent Water via Membrane Application]. Realizing the effectiveness and crucial need of it, few methods has been developed to optimize the recovery of the amine. This research will investigate the factors contribute to the separation of amines and also the suitable methods in order to optimize the recovery of amine.

1.2.2. Significant of the project

This project is very useful and has significant effects especially to the recovery and gas production industries. RO and UF membrane have been tested via pilot system. From the study, concluded that the application of membrane can achieve the objective and then apply it for commercial and industrial development. Basically, this project will helps in contributing to the researches in optimizing the usage and recovery of amines. Besides for amine recovery, the result from this project also can be used and referred for studies of membrane separation technology and application.

1.3. Objectives and Scope of Study

1.3.1. The relevancy of the Project

This project is relevance in the industry. Amines such as MEA, DEA and MDEA are commonly used to eradicate acid gases from the incoming gas stream in liquefied natural gas (LNG) production. Nowadays industries need to recycle back the amines that have been used. That helps to reduce the cost of chemical, operating and maintenance. The study of using membrane to separate waste amine compound and its content is still new and unprecedented. This is due to the tenacious nature of the mixture. This make this intricate separation process is a formidable challenge and its result is a must see result by most of the affected plants around the world. This research project will focus on the possibility of utilizing membrane process to separate waste amine with their content (MEA and DEA).

1.3.2. Feasibility of the Project within the Scope and Time Frame.

18 weeks were given to complete this project. However there is a time constraint to finish the project perfectly. The method to operate the equipment Hybrid RO pilot system is given by the supervisor. But own research have to be done to find the suitable method for analyzing the permeate. Every week meeting was conducted with the supervisor. Discussion was done, advising and how to improve the project. This project is divided into three main parts. Firstly experimental has to be done by using Hybrid RO Pilot System in order to get the feed and permeate sample. The second part is analyzed all the sample using Gas Chromatography in order to determined the concentration of each sample. Finally all data is compiling into one full report.

CHAPTER 2: LITERATURE REVIEW AND THEORY

2.1 Amine

Amines are organic compounds containing nitrogen as the key atom in the amine functional group. Amines have structures resembling ammonia, where one or more hydrogen atoms are replaced by alkyl groups or other groups where the nitrogen is bonded to a carbon atom in the group (groups symbolized by **R** below). If only one the hydrogens in ammonia is replaced by a carbon based group, then it is a primary amine. If two of the hydrogens are replaced by two carbon based groups, then it is a secondary amine. If all three hydrogens are replaced with three carbon based groups, then it is a tertiary amine.

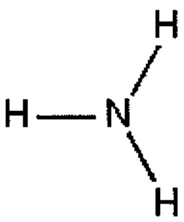
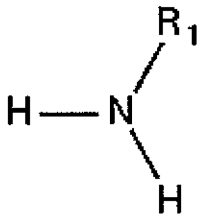
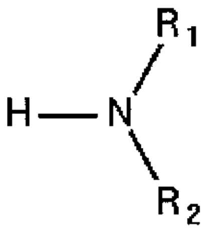
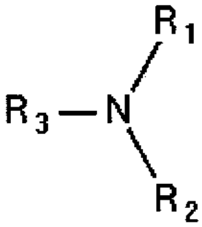
Ammonia	**Primary Amine**	**Secondary Amine**	**Tertiary Amine**
			

Figure 2.1: Types of Amine

Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine are feasible for refinary applications. Amine reactivity ranking start with primary, then secondary and tertiary. [MSDS HyperGlossary Amine].Reactivity is determined by amine molecular weights.The hydrocarbon groups are larger than a hydrogen atom. This extra bulk reduces the ability of an incoming reactant molecule to interact with the nitrogen atom.

In addition to the primary, secondary and tertiary amines, a fourth type of amine compound is known, namely the fully alkylated ammonium derivative $(R_4N)^+X^-$ where the $(R_4N)^+$ carries a positive charge like the cation $(NH_4)^+$ in the ammonium salts. X^- is an anion such as chloride, sulphate or hydroxyl ion. Such substances are called quaternary ammonium compounds. The salts of amines are similarly constituted e.g.

$(RNH_3)^+ X^-$, $(RR'NH_2)^+ X^-$ and $(RR'R''NH)^+ X^-$. It is this last type of salt, which is important in the absorption of TEA and DMEA.[Simdean Envirotec Foundry Amine Removal]. Because quaternary ammonium salts are ionic species, they are good electrolytes. Such salts are often used in detergents and other cleaning agents

2.1.1. Primary amine

MEA [Monoethanolamine] and DGA [2-(2-aminoethoxy) ethanol] are primary amines, with molecular weight range from 60-80. MEA with one ethanol group attached to the basic nitrogen atom is the strongest amine. It reacts quickly with both hydrogen sulfide and carbon dioxide, forming strong but thermally regenerative chemical bonds. MEA is effective at removing virtually all hydrogen sulfide and carbon dioxide, but requires a large quantity of heat to regenerate, i.e.: break the chemical bonds formed. MEA is used when the specification requires maximum hydrogen sulfide and carbon dioxide removal, particularly at low pressure. MEA reacts with carbonyl sulfide and carbon disulfide, forming non-regenerative degradation products.

*Refer to table 2.1.1 in the appendices for the properties of Monoethanolamine

2.1.2. Secondary amine

DEA [Diethanolamine] and DIPA [Diisopropanolamine] are secondary amines with two ethanol groups or two isopropanol groups, respectively attached to the nitrogen atom. Their molecular weight ranged from 100 to 120. The additional alcohol groups draw more of the free electron character away from the nitrogen atom, which makes secondary amines somewhat weaker bases. Secondary amines are suited for gas steams with less stringent product specifications. DEA is used when the specification allows for some carbon dioxide to be left in the treated gas. DEA does not form non-regenerative degradation products with carbonyl sulfide, which makes it a suitable choice for treating refinery gases. Secondary amines are less corrosive, require less heat to regenerate and can be used in treat gas streams containing carbonyl sulfide and carbon disulfide. However, secondary amines are not effective at deep carbon dioxide removal.

*Refer to table 2.1.2. in the appendices for the properties of Diethanolamine

2.1.3. Tertiary amine

MDEA [Methyl-diethanolamine] is a tertiary amine with molecular weight from 110 to 150. MDEA has two ethanol groups attached to the nitrogen atom, along with a methyl group. MDEA is a weak base that reacts much faster with hydrogen sulfide than with carbon dioxide, making it particularly selective under the proper design conditions. MDEA is used selectively on higher-pressure gas steams (20.6 Barg and above) for deep hydrogen sulfide removal with only moderate carbon dioxide removal. MDEA can also be used non-selectively for bulk removal of carbon dioxide from gas streams, but bulk removal requires the aid of absorption enhancing additives. Tertiary amines are less inherently corrosive and can be used in higher concentrations, but tertiary amines are not a good choice when the raw gas pressure is low or the specification calls for deep carbon dioxide removal. However, tertiary amines, particularly MDEA, are well suited for selective absorption on high-pressure gas streams.

2.2. Advantages of Amines

2.2.1.Amines as Natural Products

The ease with which amines are extracted into aqueous acid, combined with their regeneration on treatment with base, makes it simple matter to separate amines from other plant materials, and nitrogen-containing natural products were among the earliest organic compounds to be studied. Their basic properties led amines obtained from plants to be called alkaloids. The number of unknown alkaloids exceeds 5000. They are of special interest because most are characterized by a high level of biological activity. Some examples include cocaine, coniine and morphine.

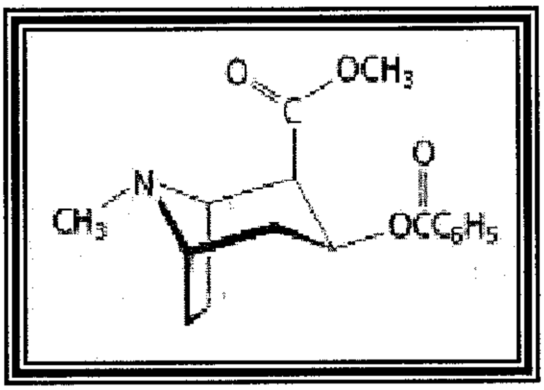


Figure 2.2.1(a): Cocain-A central nervous system stimulant obtained from the leaves of the coca plant.

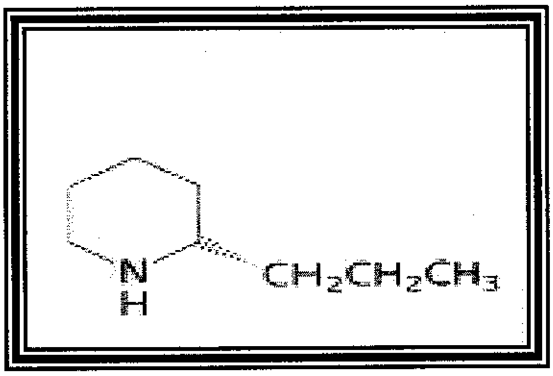


Figure 2.2.1(b): Coniine-Present along with other alkaloids in the hemlock extract used to poison Socrates.

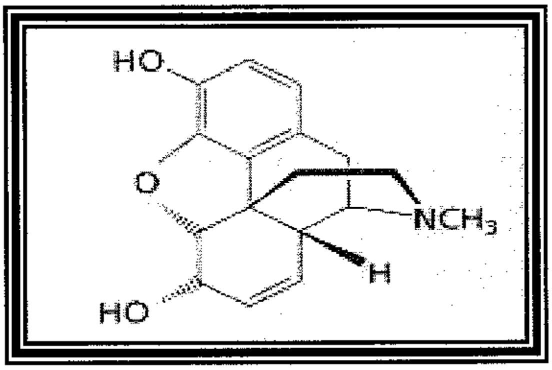


Figure 2.2.1(c): Morphine-An opium alkaloid. Although it is an excellent analgesic, its use is restricted because of the potential for addiction. Heroin is the diacetate ester of morphine.

Many alkaloids, such as nicotine and quinine, contain two or more nitrogen atoms. Several naturally occurring amines mediate the transmission of nerve impulses and are referred to as neurotransmitters. Two examples are epinephrine and serotonin. (Strictly speaking, these compounds are not classified as alkaloids, because they are not isolated from plants.)

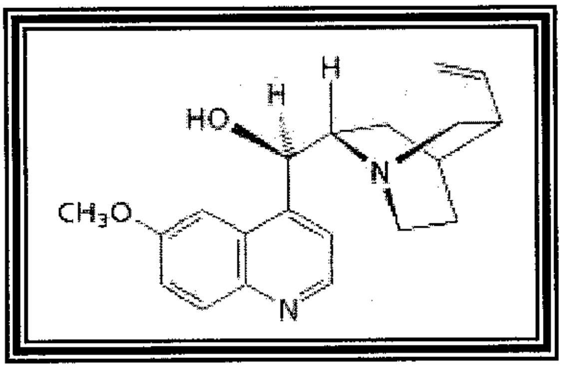


Figure 2.2.1(d): Quinine-Alkaloid of cinchona bark used to treat malaria

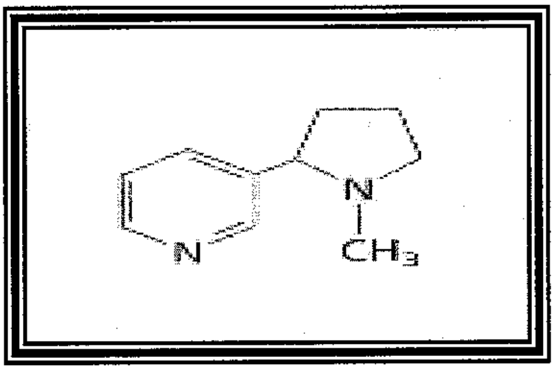


Figure 2.2.1(e): Nicotine-An alkaloid present in tobacco. A very toxic compound sometimes used as an Insecticide.

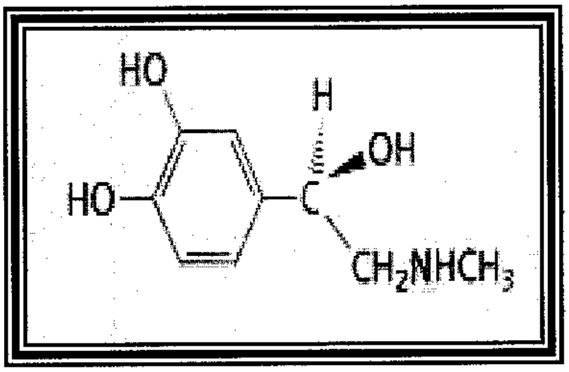


Figure 2.2.1(f): Epinephrine-Also called adrenaline. A hormone secreted by the adrenal gland that prepares the organism for "flight or fight."

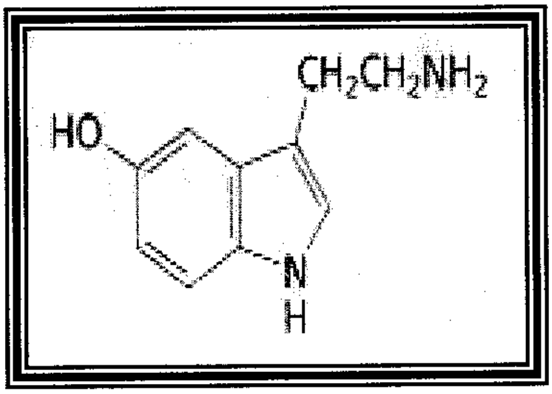


Figure 2.2.1(g): Serotonin-A hormone synthesized in the pineal gland. Certain mental disorders are believed to be related to serotonin levels in the brain.

Bioactive amines are also widespread in animals. A variety of structures and properties have been found in substances isolated from frogs, for example. One, called epibatidine, is a naturally occurring painkiller isolated from the skin of an Ecuadoran frog. Another family of frog produces a toxic mixture of several stereoisomeric amines, called dendrobines, on their skin that protects them from attack.

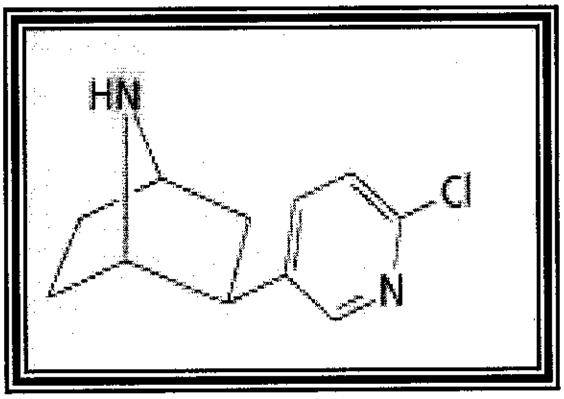


Figure 2.2.1 (h): Epibatidine-Once used as a arrow poison, it is hundreds of time more powerful than morphine in relieving pain. It is too toxic to be used as a drug.

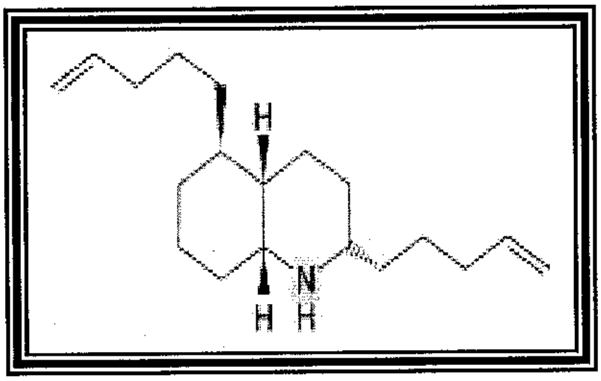


Figure 2.2.1 (i): Dendrobine-Isolated from frogs of the dendrobatidae family. Related compounds have been isolated from certain ants.

Among the important amine derivatives found in the body are a group of compounds known as polyamines, which contain two to four nitrogen atoms separated by several methylene units. These compounds are present in almost all mammalian cells, where they are believed to be involved in cell differentiation and poliferation. Because each nitrogen of polyamine is protonated at physiological pH 7.4, putrescine, spermidine, and spermine exits as cations with a charge of +2, +3 and +4, respectively, in body fluids. Structural studies suggest that these polyammonium ions affect the conformation of biological macromolecules by electrostatic binding to specific ionic sites. The negatively charge phosphate groups of DNA, for example. [J.D Seader / Ernest J.Henley, Separation Process Principle]

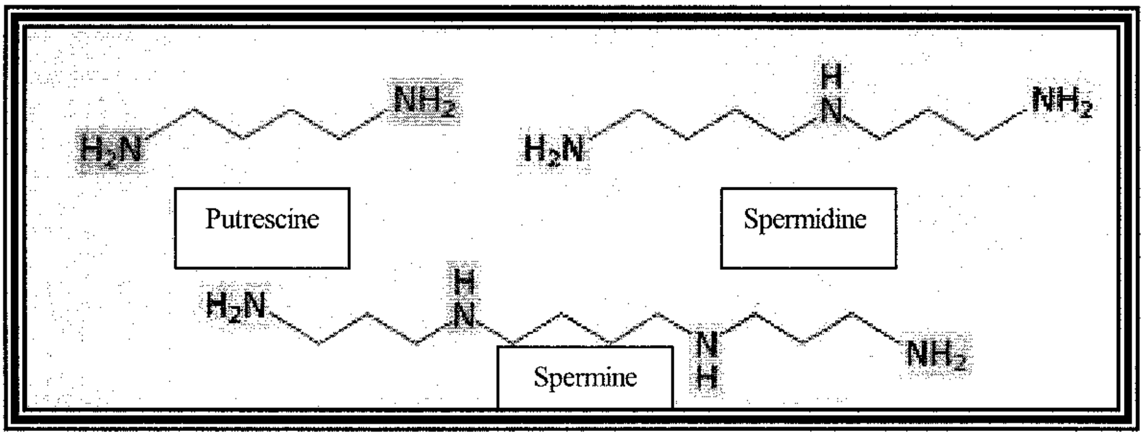


Figure 2.2.1 (j): Putrescine, Spermidine and Spermine

2.2.2 Amines in medication: From Dyes to Sulfa Drugs

The medicine cabinet was virtually bare of antibacterial agents until, sulfa drugs burst on the scene in the 1930s. Before sulfa drugs become available, bacterial infection might transform a small cut or puncture wound to a life-threatening events. It was known that many bacteria absorbed dyes, and staining was a standard method for making bacteria more visible under the microscope. Might there not be some dye that is both absorbed by bacteria and toxic to them? A German scientist, I.G Farben undertook a program to test antibacterial properties. He used in vitro testing and then proceeds with in vivo testing. In vitro testing of antibiotics is carried out using bacterial cultures in test tubes or Petri dishes. Drugs that are found to be active in vitro progress to the stage of in vivo testing. In vivo testing is carried out in a living organisms whether laboratory animal or human volunteer. I.G Farben found that some dyes did posses antibacterial properties, both in vitro and in vivo. Others were active in vitro but were converted to inactive substances in vivo and therefore of no use as drugs. Unexpectedly, an azo dye called Prontosil was inactive in vitro but active in vivo. In 1932, a member of the I.G Farben research group, Gerhard Domagk, used prontosil to treat his own daughter suffering from a serious, potentially fatal staphylococcal infection. Her infection was cured and her recovery was rapid and complete.

In spite of the rationale on which the testing of dyestuffs as antibiotics rested, subsequent research revealed that the antibacterial properties of Prontosil had nothing at all to do with its being a dye. In the body, Prontosil undergoes a reductive cleavage of its azo linkage to form sulfanilamide, which is the substance actually responsible for the observed biological activity. This is why Prontosil is active in vivo, not in vitro. Bacteria require p-aminobenzoic acid in order to biosynthesize folic acid, a growth factor. Structurally, sulfanilamide resembles p-aminobenzoic acid is mistaken for it by the bacteria. Folic acid biosynthesis is inhibited and bacterial growth is slowed sufficiently to allow the body's natural defenses to affect a cure. Because animals do not biosynthesize folic acid but obtain it in their food, sulfanilamide halts the growth of bacteria without harm to the host. Identification of the mechanism by which Prontosil combats bacterial infections was an early triumph of pharmacology, a branch of science at the interface of physiology and biochemistry that studies the mechanism of drug action. By recognizing that sulfanilamide was the active agent, the task of preparing structurally modified analogs with potentially superior properties was considerably simplified. Instead of preparing Prontosil analogs, chemistry synthesized sulfanilamide analogs. They did this with a vengeance. About 5000 compounds related to sulfanilamide were prepared during the period 1935-1946. Two of the most widely used sulfa drugs are sulfathiazole and sulfadiazine.

We tend to take the efficacy of modern drugs for granted. One comparison with the not-too distant past might put this view into better perspective. Once sulfa drugs were introduced in the United States, the number of pneumonia deaths alone decreased by an estimated 25,000 per year. The sulfa drugs are used less now then they were in the mid-twentieth century. Not only are more effective, less toxic antibiotics available, such as the penicilins and tetracyclines, but many bacteria that were once susceptible to sulfa drugs have become resistant.[J.D Seader / Ernest J.Henley, Separation Process Principle]

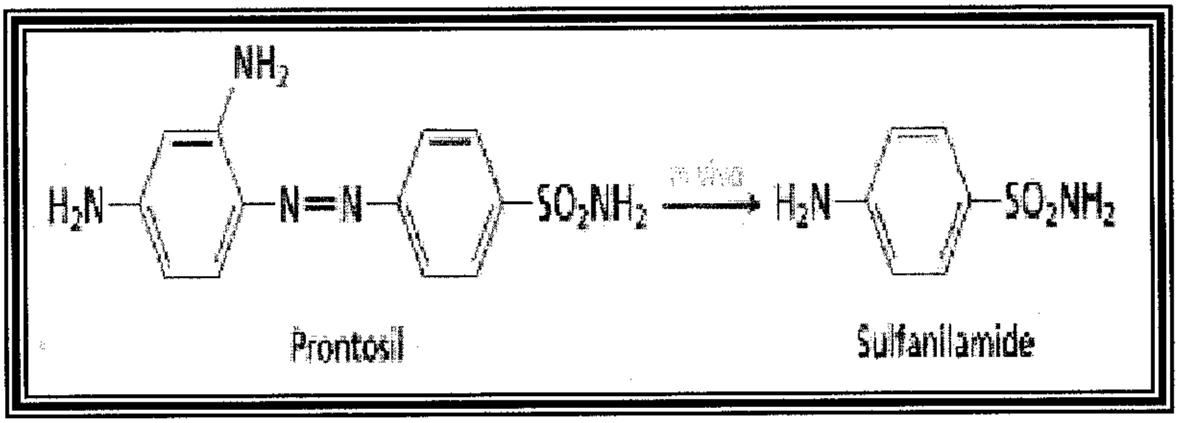


Figure 2.2.2(a): Prontosil undergoes a reductive cleavage of its azo linkage to form sulfanilamide

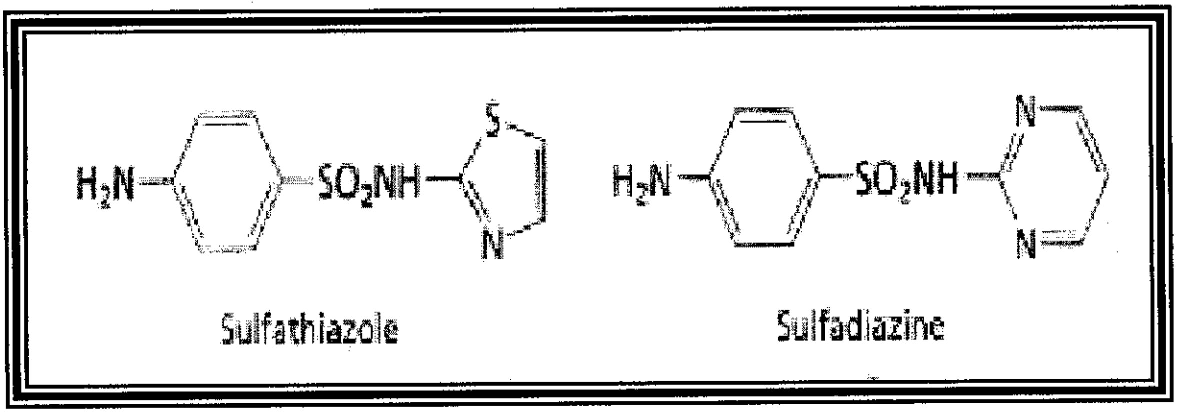


Figure 2.2.2(b): Two of the most widely used sulfa drugs are sulfathiazole and sulfadiazine.

2.3. Amine separation methods

Researches have been conducted on various methods and possibilities of separation as an innovative approach to amine separation that optimizes costs, space, safety, production, and control.

Amine purification technique, which has been the most successful so far, is distillation. However, the tendency of amines to degrade and their close boiling point with some degradation compounds preclude separation by conventional atmospheric or vacuum distillation. [A novel process for Diethanolamine Recovery from Partially Degrade Solutions, 1999]. Canadian Chemical Reclaiming Ltd. (CCRL) has developed a process to reclaim degraded amine solutions which consists of two basic steps: caustic pretreatment followed by vacuum distillation in a flash separator.

The process can be enhanced by replacing its single stage flash separator with a distillation column containing several theoretical stages. Additional stages should lead to overhead and underflow products that are richer and leaner in amine, respectively. The problems associated with multistage distillation can be overcome by introducing a suitable inert, high boiling carrier liquid. This liquid is blended with the contaminated amine feed and sent to the distillation column.

In crystallization method, the high heat requirements, numerous disadvantages of solid transport over fluid transport, as well as the difficulties in obtaining a high purity separation economically discounted this as a possible method of separation. Thus, research indicated that conventional distillation would be the most plausible means of separation of ethanolamines. [MLA Process Works, Inc., 2000]

Due to the high boiling point of ethanolamines, liquid-liquid extraction was considered as an option in order to avoid high temperatures and heat costs. The extraction is begun by dissolving the mixture in a suitable organic solvent, which has low solubility in water like diethyl ether. However the solubility characteristics of the different ethanolamines are too similar to make this a feasible and advantageous process.) [MLA Process Works, Inc., 2000].

(Another method of separating amines is using High-Performance Liquid Chromatography (HPLC). It is a form of liquid chromatography to separate compounds that are dissolved in solution. Compounds are separated by injecting a plug of the sample mixture onto the column. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase.)

The presence of analytes in the column effluent is recorded by detecting a change in refractive index, UV-VIS absorption at a set wavelength, fluorescence after excitation with a suitable wavelength, or electrochemical response. Mass spectrometers can also be interfaced with liquid chromatography to provide structural information and help identify the separated analytes.

Researches also had been done on the separation of amines through a membrane.
A process for removing and recovering one or more undissociated aromatic amines dissolved in aqueous fluid, the process comprising the steps of transferring the amines from the aqueous fluid to an acidic stripping solution, wherein transfers of the solution occurs across a membrane: wherein the membrane is a non porous, selectively permeable membrane [Livingston; Andrew Guy (London, GB) in 2000].

In general, the higher the concentration of total aromatic amine in the acidic stripping solution at a given pH, the higher will be the concentration of undissociated aromatic amine. This undissociated aromatic amine will act to reduce the driving force for mass transfer of undissociated aromatic amine from the aqueous fluid to the acidic stripping solution. This effect will be relatively greater for the aqueous fluid in the section of membrane near the point of exit of the aqueous fluid from the membrane

For separation of amines from their mixtures, as the properties of amine are quite close to each other, it is difficult to separate each component. For this, the mixture of amines along the quarternary ammonium salt is distilled with potassium hydroxide. The quartenary salt, being non-volatile is left behind while the mixture of amines distils over. This mixture is then separated by any of the following methods: fractional distillation or Hoffsmann's method. In Hoffsmann's method, the mixture of amines is treated with ethyl oxalate when several reactions take place. Secondary and tertiary amines do not give this test. Therefore this reaction has been used to distinguish primary amines from 2^0 and 3^0 amines. [Robert C.Atkins / Francis A.Carey, Organic Chemistry].

An old proven method for acid gas removal is Benfield process, which has been introduced to the industries over 30 years ago. Benfield process is a thermally generated cyclical solvent process that uses an activated, inhibited hot potassium carbonate solution to remove CO_2, H_2S and other acid gas components. The Benfield solution has a wide market in industries but it requires long time for passivation. Although the usage of amine is highly corrosive and very hard to get, it is more preferable because the effectiveness in CO_2 removal. Below is the pros and cons of Benfield and amines in acid gas removal.

Table 2.3: Comparison of amine and Benfield solution

Solvent	Advantages	Disadvantages
Benfield solution	- less harmful to the environment - easy to get (wide market) - minimal losses of hydrocarbon and synthesis gas due to low solubility in benfield solution - prevent hydrocarbon condensation due to high operating temperature	- corrosive - promote crystallization - require long time passivation for start-up - need regen for shut-down
amines	- better CO_2 removal - easy for start-up and shut down	- highly corrosive - low CO_2 loading can cause

	- no passivation or regen needed - less energy utilisation	amine to absorb hydrocarbon

The use of bio-treater utilizing bacteria as a treatment media is one of the selected solutions for amine separation. However, the extent use of the process is somewhat limited and cannot be utilized in the case of very high contaminants in the amine. [Ahmad Afdzal B Md Isa, et.al., Treatment of Amine Contaminated Effluent Water via Membrane Application]

2.4. Membrane Process

Membrane is a type of separation process utilizes a permeable thin pliable layer acting as boundary, lining or partition to separate impurities from streams. The streams can be either gas or liquid. In membrane process, the application of shear-enhanced filtration is a technique used to separate the impurities i.e. suspended or dissolved material or waste material according to molecular weight and size. Application of pressure within the system, cause the membrane to act like a sieve. As its function is tantamount to a sieve, membrane construction must engulf thousands of pores within its surface area. Particle smaller than the size of the pore will pass through likewise, particle larger than pore size will be rejected as concentrate.

Membrane are rated for suitability as an application filter based on the criteria such as pore size and morphology, hydrophilicity, chlorine resistance, chemical resistance, pH range tolerance, temperature and pressure tolerance, permeability, stability of the pore structure, clean ability, fouling resistance and quality of the membrane. Today, apart from other separation industries, membrane process is widely used in water purification industry or waste water treatment plants to obviate suspended and dissolved solids, heavy metals and other kind of impurities from the water stream.[Ahmad Afdzal B Md Isa, et.al., Treatment Of Amine Contaminated Effluent Water via Membrane Application]

2.4.1. Darcy's Equation

The basic approach to the characterization of a membrane is using a simple form of Darcy's equation

$$J = \frac{\Delta P}{R_m} \quad \text{..Equation 1}$$

ΔP is a trans-membrane pressure (TMP), which can be calculated as

$$\Delta P = P_{feed} - P_{permeate} \quad \text{.............................. Equation 2}$$

Darcy's equation applies well when only water is flowing in the system and can be used to find the resistance of the membrane to water flow.[Romipure^{TM} Pure Water Ultrafilters, Reverse Osmosis (RO) Pilot System].

2.4.2. Retention

The efficiency of a separation process is determined by the selectivity of the membrane. The retention coefficient, R_{obs}, is

$$R_{obs} = 1 - \frac{C_p}{C_b} \text{ ....Equation 3}$$

$R_{obs} = 0$, when the concentration of a solute is same in the bulk and permeate. So the membrane has been no separation to this solute. $R_{obs} = 1$, when the concentration of solute in the permeate is 0. Its means that the membrane has a 100% rejection to this solute. The better rejection of the membrane to the solute is when the R_{obs} is higher. [Romipure^{TM} Pure Water Ultrafilters, Reverse Osmosis (RO) Pilot System].

2.4.3. Membrane Classes

As far as membrane world is concerned, there are four main clusters of membrane available in the market today. The classes of membrane are determined by the pore cut-off size and molecular weight cut off point.[Ahmad Afdzal B Md Isa, et.al., Treatment Of Amine Contaminated Effluent Water via Membrane Application].

Table 2.4.3: Membrane classes

Membrane Type	**Particle Size Cut-Off (μm)**	**Molecular Weight Cut-Off (D)**
Reverse Osmosis	< 0.001	< 100
Nanofiltration	0.001 – 0.01	100 - 1000
Ultrafiltration	0.01 – 0.1	1000 – 500,000
Macrofiltration	> 0.1	> 500,000

2.5. Reverse Osmosis

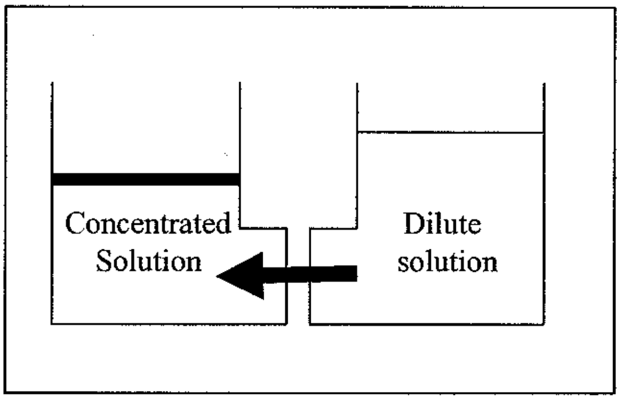


Figure 2.5(a): Osmosis

Water diffuses through a semipermeable membrane toward region of higher concentration to equalize solution strength. At equilibrium, the height difference between the concentrated and dilute sides corresponds to the osmotic pressure differential between the two sides.

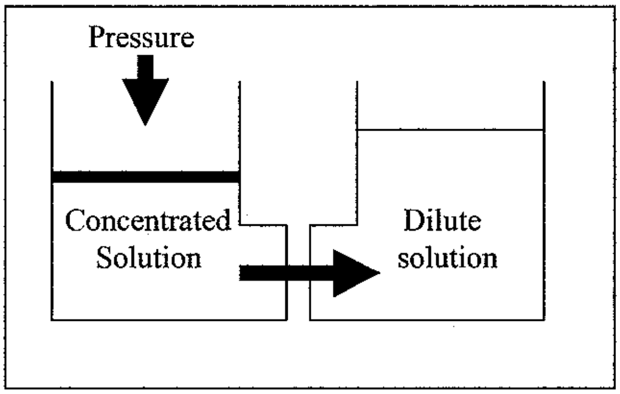


Figure 2.5(b): Reverse Osmosis

Applied pressure in excess of osmotic pressure reverses water flow direction. Hence, the term "Reverse Osmosis" [FilmTec Corporation, Reverse Osmosis]

Osmosis is the phenomenon of water flow through a semi permeable membrane that blocks the transport of salts or other solutes. When two water (or other solvent) volumes are separated by a semi permeable membrane, water will flow from the side of low solute concentration to the solute concentration side. However, the flow may be stopped or even reversed by applying external pressure on the side of higher concentration. In such a case the phenomenon is called reverse osmosis (RO).

RO membrane filtration is a pressure-driven process that is used to separate relatively pure water from solution containing salts, dissolved organic molecules, and colloids. In order to allow water to pass through the membrane from the concentrated solution to the dilute solution, the applied pressure should be higher than the osmotic pressure. The pressures used in RO range is usually from 20 to 100 bars, which are much higher than those used in other membrane processes, such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF).

On the other hand, ultrafiltration is a low pressure-driven mechanical filtration process that uses semi-permeable membranes to preferentially separate different fluids or ions. Generally, UF process is capable of concentrating bacteria, proteins, dyes, and constituents that have a larger molecular weight of greater than 10,000 daltons, while sugars and salts can pass through the membrane. Besides the operating pressure, another important difference between RO and UF processes lies in the size of membranes pores. RO membrane is capable of rejecting contaminants or particles with diameters as small as 0.0001μm, whereas UF membrane can only reject contaminants no smaller than 0.01μm.

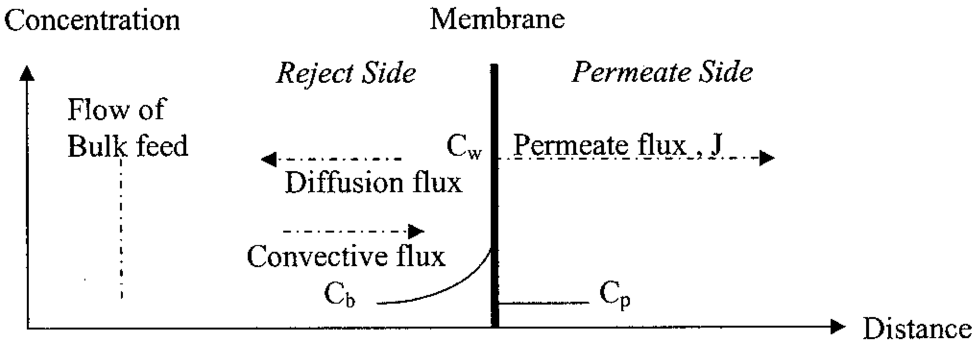


Figure 2.5(c): Concentrations and flows around the membrane.

Both during RO and UF processes, bulk solutions are forced towards the membranes by applied pressure. As water passes through, the retained solute always builds up at the membrane surface and causes an opposing diffusional flow of the solute from the membrane surface back into the bulk material. As the concentration of solute becomes greater at the membrane, the opposing effect of diffusion becomes greater and eventually limiting. This phenomenon is defined as concentration polarization (CP). [Romipure^{TM} Pure Water Ultrafilters, Reverse Osmosis]. There are three methods to reduce the concentration polarization effects. Reduce the pressure, reduce concentration at the membrane surface and reduce solids in feed.

2.5.1. Factors Affecting RO Membrane performance

The factors that affect the performance of RO membranes including pressure, temperature, feedwater salt concentration, permeate recovery, and system pH.

(1) Pressure

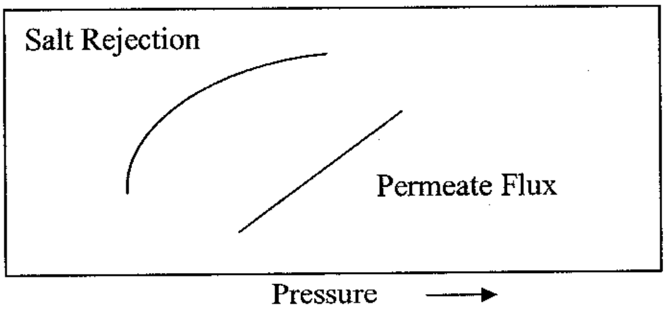


Figure 2.5.1(a): Effect of feed water pressure on flux and salt rejection.

Feedwater pressure affect both the water flux and salt rejection of RO membranes. Reverse Osmosis technology involves application of pressure to the feedwater stream to overcome the natural osmotic pressure. Pressure in excess of the osmotic pressure is applied to the concentrated solution and the flow of water is reversed. A portion of the feedwater (concentrated solution) is forced through the membrane to emerge as purified product water of the dilute solution side.

As shown in Graph above, water flux across the membrane increases in direct relationship to increases in feedwater pressure. Increased feedwater pressure also results in increased salt rejection but, the relationship is less direct than for water flux. Because RO membrane are imperfect barriers to dissolved salts in feedwater, there is always some salt passage through the membrane. As feedwater pressure increased, this salt passage is increasingly overcome as water is pushed through the membrane at a faster rate than salt can be transported. However there is an upper limit to the amount of salt that can be excluded via increasing feedwater pressure. As in the salt rejection curve indicates, above a certain pressure level, salt rejection no longer increases and some salt flow remains coupled with water flowing through the membrane.[FilmTec Corporation, Factors Affecting RO Membrane Performance]

(2) Temperature

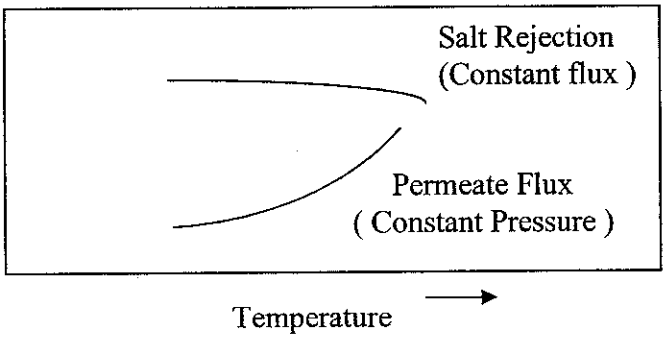


Figure 2.5.1(b): Effect of feed water temperature on flux and salt rejection.

As graph above, membrane productivity is very sensitive to changes in feedwater temperature. As water temperature increases, water flux increases almost linearly, due primarily to the higher diffusion rate of water through the membrane. Increased feedwater temperature also results in lower salt rejection or higher salt passage. This is due to a higher diffusion rate for salt through the membrane. The ability of a membrane to tolerate elevated temperatures increases operating latitude and is also important during cleaning operations because it permits use of stronger, faster cleaning processes. This is illustrated by the comparison of the pH and temperature ranges of FILMTEC FT30 thin-film composite membrane and a cellulose acetate (CA) membrane in Figure 2.5.1(d). [FilmTec Corporation, Factors Affecting RO Membrane Performance]

(3) Feedwater salt concentration

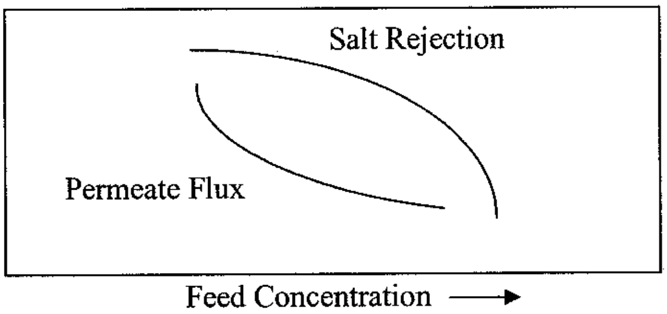


Figure 2.5.1(c): Effect of increasing salt concentration on flux and salt rejection.

Osmotic pressure is a function of the type and concentration of salts or organics contained In feedwater. As salt concentration increases, so does osmotic pressure. The amount of feedwater driving pressure necessary to reverse the natural direction of osmotic flow is, therefore, largely determined by the level of salts in the feedwater. Graph above demonstrates that, if feed pressure remains constant, higher salt concentration results in lower membrane water flux. The increasing osmotic pressure offsets the feedwater driving pressure. Increasing in salt passage through the membrane (decrease in rejection) as the water flux declines.[FilmTec Corporation, Factors Affecting RO Membrane Performance]

(4) Permeate recovery

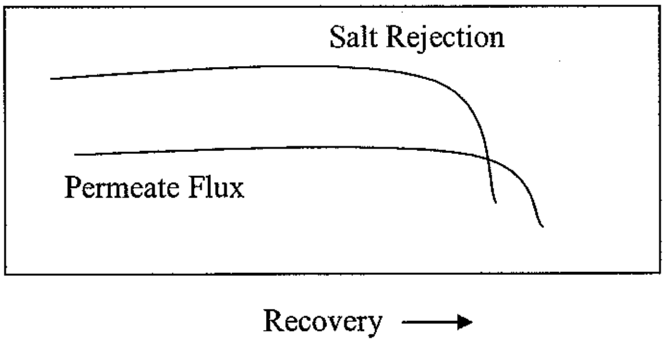


Figure 2.5.1(d): Effect of increasing recovery on flux and salt rejection.

Reverse Osmosis occurs when the natural osmotic flow between a dilute solution and a concentrated solution is reversed through application of feedwater pressure. If percentage of recovery is increased (and feedwater pressure remains constant), the salts in the residual feed become more concentrated and the natural osmotic pressure will increase until it is as high as the applied feed pressure. This can negate the driving effect of feed pressure, slowing or halting the reverse osmosis process and causing permeate flux and salt rejection to decrease and even stop.

The maximum percent recovery possible in any RO system usually depends not on a limiting osmotic pressure, but on the concentration of salts present in the feedwater and their tendency to precipitate on the membrane surface as mineral scale. The most commonly sparingly soluble salts are calcium carbonate (limestone), calcium sulfate (gypsum), and silica. Chemical treatment of feedwater can be used to inhibit mineral scaling. [FilmTec Corporation, Factors Affecting RO Membrane Performance]

(5) pH

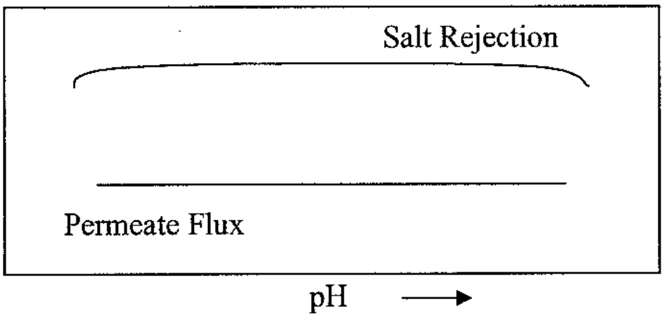


Figure2.5.1 (e): Effect of feed water pH on water flux and salt rejection.

The pH tolerance of various types of RO membranes can very widely. Thin-film composite membranes such as FILMTEC FT30 membrane are typically stable over a broader pH range than cellulose acetate (CA) membranes and, therefore offer greater operating latitude (Please refer Figure 2.5.1(f)). Membrane salt rejection performance depends on pH. Water flux may also be affected. Graph above shows that water flux and salt rejection for FILMTEC FT30 membranes are essentially stable over a broad pH range. As illustrated in Figure 2.5.1(f), the stability of FT30 membrane over a broad pH range permits stronger, faster, and more effective cleaning procedures to be used compared to CA membranes. [FilmTec Corporation, Factors Affecting RO Membrane Performance].

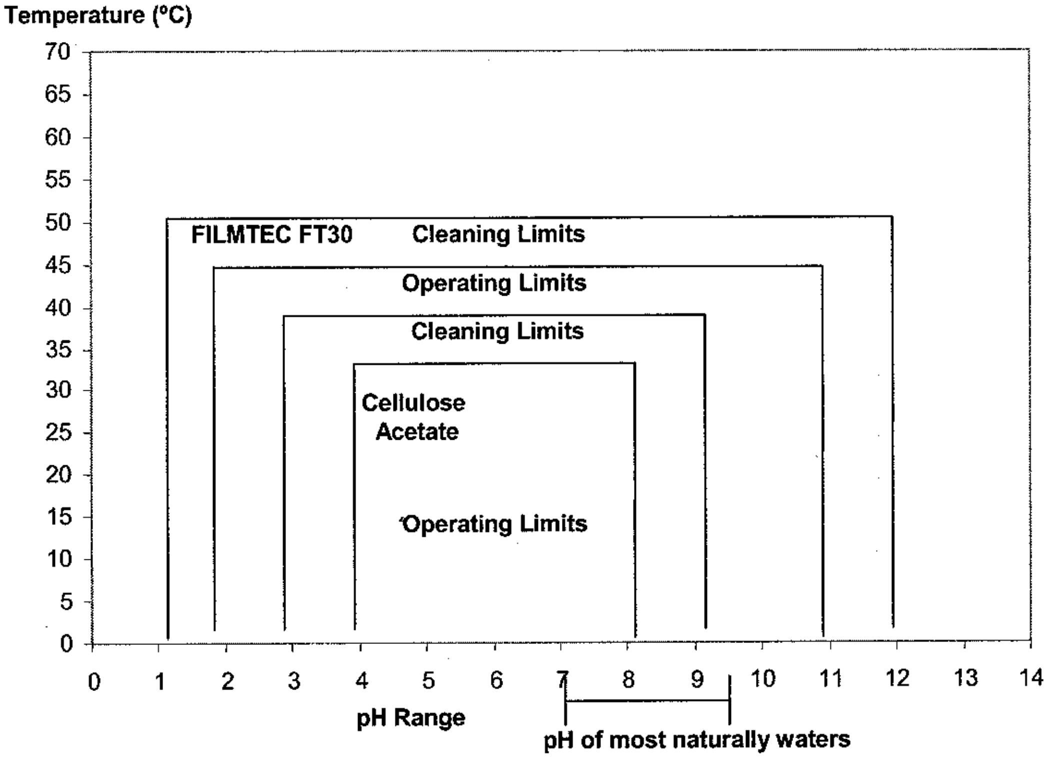


Figure 2.5.1(f): Comparison of operating and cleaning parameters for FT30 Thin-Film Composite Membrane and a CA Membrane

2.5.2. Transport in Membrane

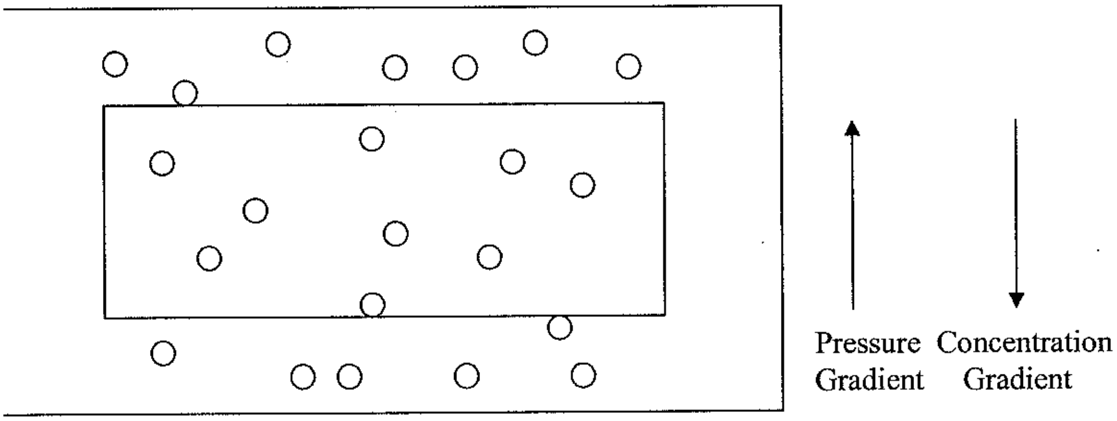


Figure 2.5.2 : Transport in Reverse Osmosis

In reverse osmosis a pressure gradient is use to push solvent through a membrane which is not permeable to the solute. This pressure must be greater than the osmotic pressure.

2.5.3. What is salt rejection?

Reverse osmosis membranes are designed to remove dissolved salts from water. While water passes readily through the RO membrane, dissolved salt passage through very slowly. Under natural conditions of osmosis, water will diffuse through a semipermeable membrane toward a region of higher salt concentration in order to equalize solution strength on both sides of the membrane. In order to overcome and reverse this osmotic tendency, pressure is applied to the feedwater, thereby producing a purified permeate stream.

Salt rejection is a measure of how well a membrane element rejects the passage of dissolved ions. Although an RO element may be called up upon to reject many different ions, sodium chloride (NaCl) is used as a measurement standard. With few exception of RO membranes reject divalent ions better than monovalent ions such as sodium and chloride. Therefore if a membrane exhibits excellent rejection of NaCl , the membrane can be expected to perform even better in rejecting the passage of such divalent ions as iron, calcium, magnesium and sulfate. Thus NaCl (salt) rejection has been universally accepted as the standard for measuring a membrane element's ionic rejection performance.

It is important to remember that, while we are focusing here on rejection of ionic contaminants, membranes are also called upon to remove, or at least tolerate, other impurities in feedwaters, including organics, silica and gases. The evaluation of RO elements should also include analysis of their ability to remove or tolerate these non-ionic contaminants.[FilmTec Corporation, Salt Rejection]

2.6. Ultrafiltration Membrane (UF)

The time has arrived for users of RO membranes to re-evaluate the cost and operating benefits of UF membrane as RO pretreatment. This is particular true when confronted with having to process a high fouling feed water sources such as surface water, waste water, or open–intake seawater. UF membranes have large advantages to use in front of RO system as a pretreatment, rather than the conventional design pretreatment.[Wayne T.Bates, Rocco Cuozzo, Integrated Membrane System].The advantages are :-

(1) UF filtrate quality is better. The colloidal fouling load to the RO is reduced with significantly lower SDI(Slit Density Index) and turbidity.

(2) Filtrate quality remains much more constant since it is an absolute membrane barrier. This is true even for those surface or waste water sources afflicted by rapidly fluctuating quality.

(3) RO cleaning frequencies due to colloidal fouling is reduces.

(4) Require less time and be easier to operate than some conventional filtration processes, particularly those prone system upsets.

(5) UF concentrated waste streams are easier to dispose of relative to chemically-enhanced conventional pretreatment processes.

(6) Operating costs are competitive.

(7) Future expandability is easier to design in.

2.6.1. Yesterday's perspective

The interest in using UF as pretreatment to RO for processing high fouling feed waters (e.g. surface waters and waster waters) dates back to the 1980s.[Wayne T.Bates, Rocco Cuozzo, Integrated Membrane System].The UF design was generally dismissed as a commercial alternative to conventional pretreatment for a number of reasons. The primary reasons were:

(1)Capital Costs

The UF capital costs were too high for treatment of surface waters. A UF sub-system had a capital cost that was close to 100% of the capital cost of the RO system. Capital costs for conventional pretreatment systems (e.g. clarifiers, gravity filters, lime-softeners, multimedia filters, carbon filters) were 20% to 50% of the capital cost of the RO system. [Wayne T.Bates, Rocco Cuozzo, Integrated Membrane System]

(2)Operating Costs

UF operating cost savings versus conventional pretreatment was difficult to substantiate and guaranty without the benefits of empirical data collection from a pilot plant.

(3)Pilot Plant Required

Small system and industrial users not bound by government regulations tend to refrain from the use of pilot plants for a number reason (e.g. cost and time limitation).

(4)Performances Guaranties

Historically, the Original Equipment Manufacturer (OEM) has borne the responsibility of the total system performance warranty when a bid is issued. Without the benefits of pilot plant data to substantiate the merits of UF system in a competitive bid situation, the default pretreatment system was comprised of conventional pretreatment components.

(5)Aversion to Unproven Technology

UF was essentially new technology. Concerns included the risk of buying a system that was considered a serial number one, where there were only a few UF membrane suppliers to choose from, or where the UF membrane design was proprietary in nature and would limit future replacements or service to only one firm.

2.6.2. Today's Perspective

The use of UF as water filtration process has exploded over the last couple of years in the municipal market place. There are several hundreds of UF systems in operation for municipal drinking water systems throughout the world, with capacities that are evenly distributed exceeding 200mgd (million gallons per day) total. In the United States, UF technology has been readily accepted to achieve portable drinking water quality in terms of controlling pathogenic microorganisms and potentially carcinogenic Disinfection By-Products (DBP). These microbiological and DBP guideline were generated by federal government actions by establishing present and future regulations as set in the Surface Water treatment Rules (SWTR), the Enhanced Surface Water Treatment Rules (ESWTR), and the Disinfectant/Disinfection By-Products Rule (D/DBPR).[Wayne T.Bates, Rocco Cuozzo, Integrated Membrane System]. The benefits resulting from the expended use of UF, both commercially and technically are numerous. There are: -

(1)Polymer chemists have developed improved UF membranes in both capillary and spiral-wound configurations.

(2)UF membrane manufacturers and OEM have developed improved operational techniques that reduce the rate of fouling and chemical cleaning frequency to acceptable intervals.

(3)There are at least eight major suppliers of UF membranes and system.

(4)The large volume of actual UF membranes sales have reduced the unit cost of these membranes to make UF system costs competitive with conventional pretreatment.

(5)The requirements of the municipal market place have allowed for extensive on-site pilot testing to be conducted under well-defined test conditions and under the supervision of competent engineering firms and/ or consultants. Extensive evaluation of the pilot data has enhanced the ability of membrane suppliers to better projects expected operating parameters for varying feed water condition, cleaning frequencies and filtrate quality.

2.6.3. UF membrane characteristics

UF membranes designed for use as pretreatment to RO have nominal molecular weight cutoffs of 20,000 to 750,000 Dalton (0.002 to 0.05 microns). Typical operational transmembrane pressure, (TMP) range from 3-30 psi. TMP is defined as the pressure required to force water through the membrane and is the feed pressure less the filtrate pressure. Filtrate is the industry name for the UF product water. TMP requirement will be higher for tighter membranes with smaller pore sizes, with higher flux rates, colder water temperature, and when fouling occurs.

UF membrane can be developed from inorganic material (e.g. ceramic) or from organic polymers. Common polymeric membrane materials include polyolefin, polyether sulfone, polysulfone, polypropylene and cellulosic. Most membranes materials typically have a wide pH tolerance range to accommodate for low and high pH cleaning chemicals. Most membranes also have a free chlorine tolerance that allows for continuous sanitization. UF membrane can come in many configurations such as spiral wound, flat sheet, hollow fiber, tubular and plate-and-frame. The prevalent configurations for pretreatment to RO are hollow fiber and spiral wound based on the combined attributes of capital cost, energy efficiency, fouling resistance and the ability to restore flux by a combination of flushing and chemical cleaning. [Wayne T.Bates, Rocco Cuozzo, Integrated Membrane System]. UF membrane operated in two different services mode: -

(1)Dead-end flow

Also known as direct-flow is similar to that of a cartridge filter where is only a feed flow and filtrate flow (no concentrate flow). Allow for optimal recovery of feed water in the 95 to 98% range, but is limited to feed streams of low suspended solids (e.g. < 10 NTU turbidity).

(2)Cross-flow

Used for feed waters with higher suspended solids (e.g. 10 to 100 NTU turbidity). This mode results in 90 to 95% recovery of the feed water.

In some cases, fed water recovery for UF systems can be improved up to 99% by collecting and processing further the concentrated fed water and/ or the water used for periodic backwashes. This secondary processing step can be accomplish by using conventional solid-settling systems or by the use of another UF system. A major reason for the re-emergence of UF technology has been improvements in the control of fouling during the service operation and by improved foulant removal techniques. The basic premise to remember is that UF system is specifically designed to effectively remove foulants and to be cleaned. RO system are designed to remove salts, not foulants, and not specifically designed to be fouled and cleaned frequently.

UF membranes are operated in a flux range of 36-110 gfd (gallons per square foot per day). Lower fluxes are used for feed waters with high suspended solids and fouling potential (e.g. tertiary waste waters). And higher fluxes for with lower suspended solids loading (e.g. 70gfd for surface water sources).

2.6.4. Transport in Membrane

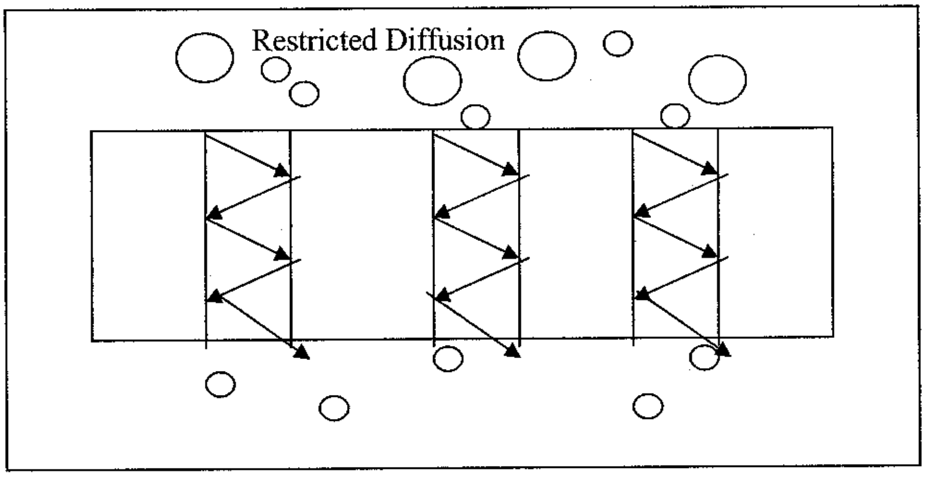


Figure2.6.4: Transport in Ultrafiltration

The small pore size will allow for separation of smaller components, for example separating a small molecule from solvent.

2.7. Membrane Modules

2.7.1.Tubular

Tubular membranes are typically 0.5 to 5.0 cm in diameter and up to 6m in length. The thin, dense layer is on either the inside or the outside surface of the tube. The porous supporting part of the tube is fiberglass, perforated metal, or other suitable porous material.

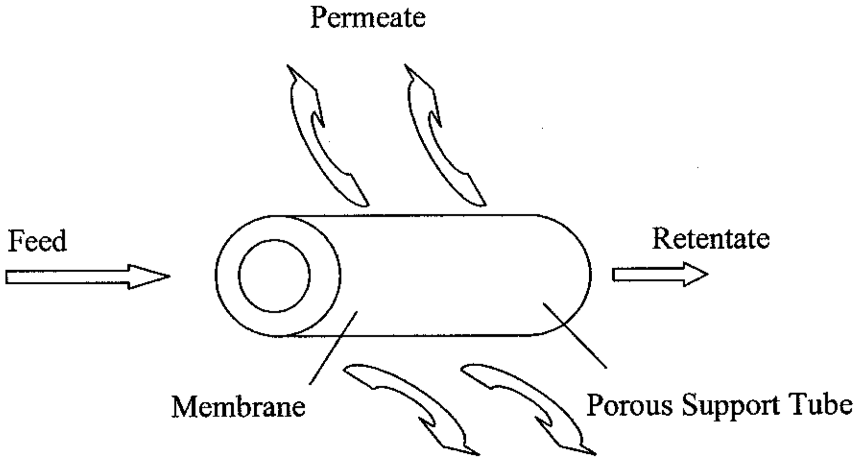


Figure 2.7.1: Tubular Module

These modules are now generally limited to ultrafiltration applications, for which the benefit of resistance to membrane fouling outweight the high cost. Tubular membranes contains as many as 5-7 smaller tubes, each 0.5-1.0 cm in diameter, nested inside a single larger tube. In a typical tubular membrane system, a large number of tubes are manifold in series. The permeate is removed from each tube and sent to a permeate collection header.[J.D Seader / Ernest J.Henley, Separation Process Principle]

2.7.2. Hollow Fibre

Very small diameter hollow fibers, first reported by Mahon in the 1960s, are typically 42 μm internal diameter by 85 μm outer diameter by 1.2m long with a 0.1 to 1.0 μm thick dense skin. Hollow fibers shown in figure above provide a large membrane surface area per unit volume.

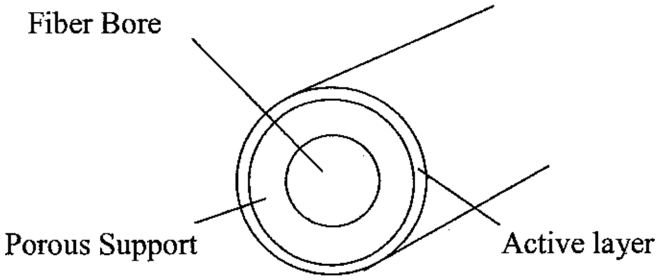


Figure2.7.2: Hollow Fiber Module

Hollow fibre modules are characteristically 4-8 inch in diameter and 3-5 feet long. Hollow fibre units are almost always run with the feed stream on the outside of the fibre. Water passes through the membrane into the inside or "lumen" of the fibre. A number of hollow fibres are collected together and "potted" in an epoxy resin at both ends and installed into an outer shell. Hollow fibre membrane modules are formed in 2 basic geometries: (A) shell side feed design (B) bore side feed design.

The design of a hollow fiber permeator can package a tremendous amount of membrane area into a small volume. However this fibers act almost like a string filter. This design requires a high level of feedwater pretreatment to minimize the fouling potential of the feedwater. And when they are fouled, they are very difficult to regenerate by cleaning methods. Each hollow fiber unit requires installation of one feedwater inlet, one concentrate outlet, and one permeate outlet. [J.D Seader / Ernest J.Henley, Separation Process Principle]

2.7.3. Spiral Wound

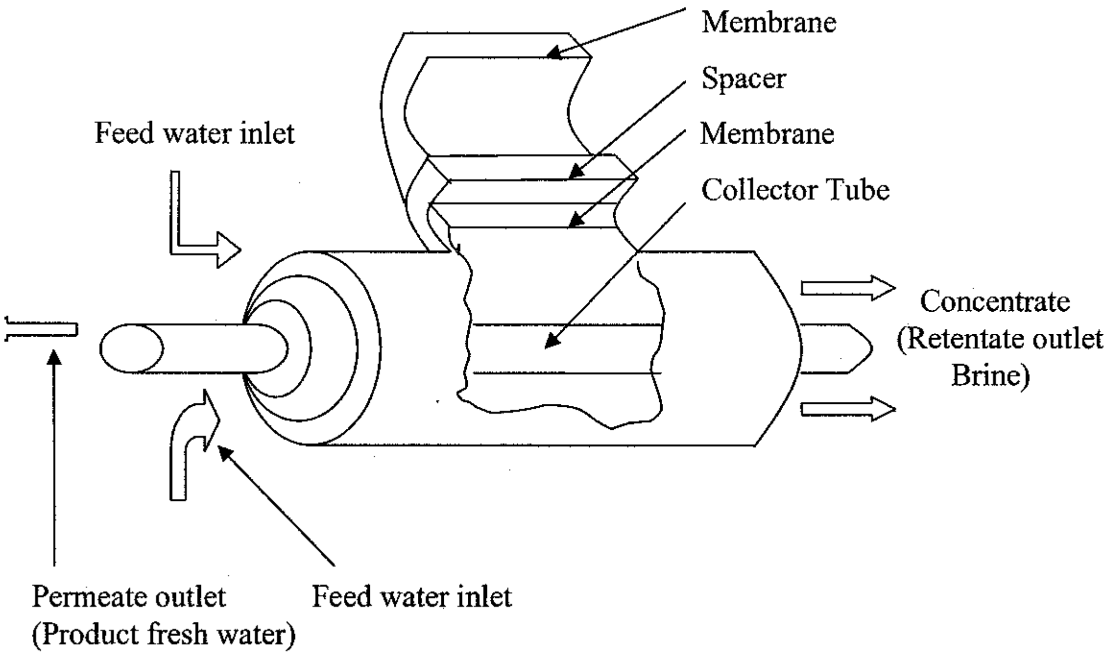


Figure 2.7.3: Spiral Wound Module

Industrial scale modules contain several membrane envelopes, each with an area of 1-2m^2, wrapped around the central collection pipe. Multi envelop designs minimize the pressure drop encountered by the permeate traveling toward the central pipe. The standard industrial spiral wound module is 8 inch in diameter and 40 inch long. 4-6 spiral wound membrane modules are normally connected in series inside a single pressure vessel. A typical 8 inch diameter tube containing 6 modules has 100-200m^2 of membrane area.

Contains 2 layers of membrane glued back-to-back onto a permeate collector fabric (permeate channel spacer). This membrane envelope is wrapped around a perforated tube into which the permeate empties from the permeate channel spacer. A plastic netting is wound into the device, and maintains the feed-stream channel spacing. It also promotes mixing of the feedstream to minimize concentration polarization.

Spiral wound units can be linked together into series of two or seven elements within a single pressure vessel. Thus, up to seven times the flow of product water can be handled with only a single set of plumbing connections for feed, concentrate and permeate to a pressure vessel. [J.D Seader / Ernest J.Henley, Separation Process Principle]

2.7.4. Flat Sheets

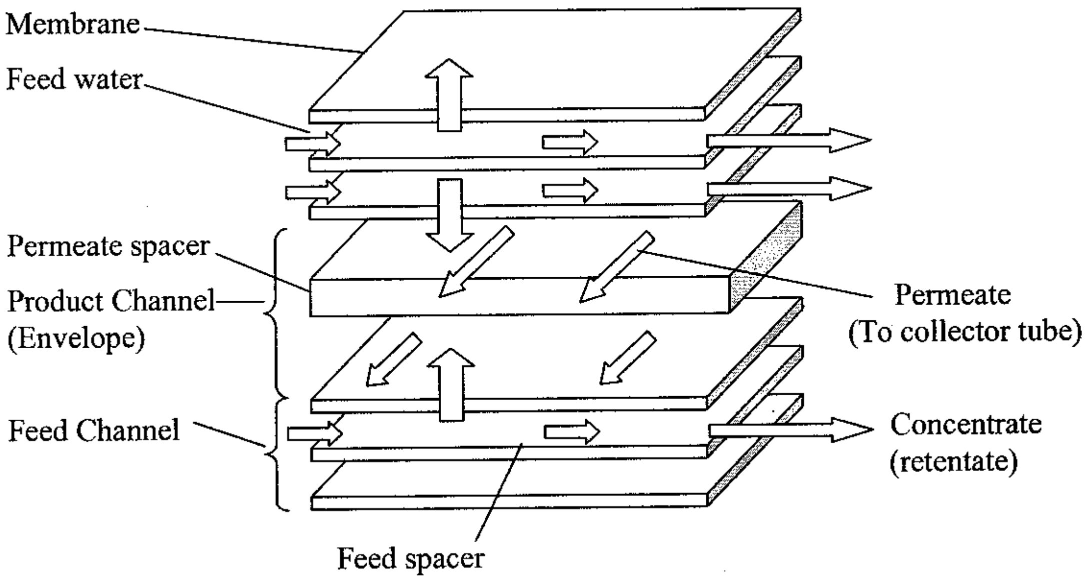


Figure 2.7.4: Flat Sheets Module

Flat sheets have typical dimensions of 1 m by 1m by 200μm thick, with a dense skin or thin, dense layer 500 to 5,000 Å in thickness. The plate and frame modules were one of the earliest types of membrane system, but because of their relatively high cost they have been largely replaced in most applications by spiral wound modules and hollow fibre modules. Plate and frame modules are now used only in electrodialysis and pervaporation systems and in a limited number of reverse osmosis and ultrafiltration applications with highly fouling conditions. [J.D Seader / Ernest J.Henley, Separation Process Principle]

2.8. Membrane material

Proper membrane material selection is critical in achieving desired products. Membrane media is the determining component of a diffuser and controls the operating and long term performance capabilities of the diffuser allowing operation at a reasonable headloss and release of fine, discrete gas bubbles. Below is the table describes membrane material and its characteristics.

Table 2.8(a): Diffuser Membrane Material [Environmental Dynamics Inc. of Columbia]

Type	**Best application**	**Temperature range**	**Attacked by**
Ethylene Propylene Diene Monomer (EPDM)	Typical municipal / industrial waters	Up to 350 ^{0}F	hydocarbons
polyurethane	Industrial wastes	-30 ^{0}F to 175 ^{0}F	Acids, ketones
Nitrile	Oily or greasy water	-40 ^{0}F to 250 ^{0}F	Polar solvents (acetone)
Hydrin	Applications without specific chemical requirement	-50 ^{0}F to 225 ^{0}F	Ketones, esters, aldehydes
Silicone	High temperature or specific chemical requirements	-150 ^{0}F to 450 ^{0}F	
Neoprene	Petrochemical applications	-50 ^{0}F to 250 ^{0}F	Oxidizing agents, esters, ketones
Viton	In Petrochemical	-50 ^{0}F to 250 ^{0}F	

Almost all industrial membrane processes are made from natural or synthetic polymers (macromolecules). Natural polymers include wool, rubber and cellulose. synthetic polymers are produced by polymerization of a monomer. [J.D Seader / Ernest J.Henley, Separation Process Principle]

Cellulose triacetate

Cellulose triacetate is the reaction product of cellulose and acetic anhydride. Cellulose is the most readily available organic raw material in the world. The repeat unit of cellulose is identical to that shown for cellulose triacetate in the table, accept that the acetyl, Ac (CH_3CO) groups are replaced by H. Typically the number of repeat unit in cellulose is 1,000 to 1,500, whereas that in cellulose triacetate is around 300. Partially acetylated products are cellulose acetate and cellulose diacetate, with blends of two or three of the acetates being common. The triacetate is highly crystalline, of uniformly high quality, and hydrophobic.

Polyisoprene (natural rubber)

Polyisoprene (natural rubber) is obtained from at least 200 different plants, with many of the rubber-producing countries being located in the Far East. Compared to the other polymes in the table, polyisoprene has a very low glass-transition temperature. Natural rubber has a degree of polymerization of from about 3,000 to 40,000 and is hard and rigid when cold but soft, easily deformed and sticky when hot. Depending on the temperature, it's slowly crystallizes. To increase the strength, elasticity and stability of rubber, a process that introduces cross-links, but still allows unrestricted local motion of the polymer chain.

Aromatic polyamide

Aromatic polyamides (also called aramids) are high melting crystalline polymers that have better long term thermal stability and higher resistance to solvents than do aliphatic polyamides, such as nylon. Some aromatic polyamides are easily fabricated into fibers, films and sheets. The polyamide structure shown in the table is that of Kevlar, a trade name of DuPont.

Polycarbonates

Polycarbonates, which are characterized by the presence of the –OCOO- group in the chain, are mainly amorphous in structure. The polycarbonate shown in the table is an aromatic form, but aliphatic forms also exist. Polycarbonate differs from most other amorphous polymers in that they posses ductility and toughness below T_g. Because polycarbonates are thermoplastic, they can extruded into various shapes, including films and sheets.

Polyamides

Polyamides are characterized by the presence of aromatic rings and heterocyclic rings containing nitrogen and attached oxygen. The structure shown in the table is only one of a number available. Polyamides are tough, amorphous polymers with high resistance to heat and excellent wear resistance. They can be fabricated into a wide variety of forms, including fibers, sheets and films.

Polystyrene

Polystyrene is a linear, amorphous, highly pure polymer of about 1,000 units of the structure shown in the table. Above a relatively low T_g, which depends on molecular weight, polystyrene becomes a viscous liquid that is easily fabricated by extrusion or injection molding. Like many other polymer, polystyrene can be annealed (heated and then cooled slowly) to convert it to a crystalline polymer with a melting point of 240°C. Styrene monomer can be copolymerized with a number of other organic monomers, including acrylonitrile and butadiene to form ABS copolymers.

Polysulfones

Polysulfones are relatively new synthetic polymers, first introduced in 1966. The structure in the table is just one of many, all of which contain the SO_2 group, which gives the polymer high strength. Polysulfones are easily spun into hollow fibers.

Polytetrafluoroethylene

Polytetrafluoroethylene is a straight chain, highly crystalline polymer with a very high degree of polymerization of the order of 100,000, which gives it considerably strength. It possesses exceptional thermal stability and can be formed into sheets, films and tubing.

In reverse osmosis, cellulose acetate (CA) was the first high performance RO membrane material discovered. The membranes are easy to make, mechanically though and resistant to degradation by chlorine and other oxidants. However, the flux and rejection of CA membrane have now been surpassed by interfacial composite membranes.

Table 2.8(b): Comparison of RO Membranes [FilmTec Corporation, Reverse Osmosis].

Membrane Type	Composite Polyamide (PA)	Cellulose Acetate (CA)
Membrane polymer	polyamide	Cellulose acetate
Surface charge	negative	neutral
NaCl rejection	99 to 99.7 %	95 to 98 %
Organic rejection	similar	lower
Test Pressure	225 psi	420 psi
Specific flux (gfd per 100psi)	13	5 to 6
pH range	3 to 10	4 to 6
Temperature limit	113 ^{0}F (45 ^{0}C)	104 ^{0}F (40 ^{0}C)
Chlorine tolerance	1000 ppm-hr	26 280 ppm-hr
Hydrophilicity	62^0 angle	50^0 angle

2.9. Analyzer: Gas Chromatography

A gas chromatographic method has been developed to analyze amine solutions for acid gases, hydrocarbons, water and amine content. Good separations and sharp peaks were obtained for most components with Tenax-GC and Poropak Q columns when combined with temperature programming. The GC method has numerous advantages over the titration methods. These include approximate 10 minute analysis time, better reproducibility, the capability for on-line sampling and less interference. [Gary D.Robbins, Jerry A.Bullin, Analysis of Amine Solutions by Gas Chromatography]:

2.9.1. Development of the GC method

(1)Ethanolamines are very reactive compounds.

The polar hydroxyl and amine groups have a strong adsorption affinity for silaceous column supports. The success of a stationary liquid support was improbable due to the strong physicochemical interactions and slow diffusion of the amines through the liquids. However a short column with Tenax-GC packing can be used to analyze MEA, DEA, TEA and their impurities. A sharp distinct peaks with good separation were obtained.

(2)Formation of thermal degradation products at high column temperatures in the GC.

The degradation of amines is probably more a function of time than of temperature. In a GC, the time spent on the columns is very short so degradation is insignificant.

(3)Amine boiling point range

Problem with analyzing the components in amine solutions was their tremendous range of boiling points from -80°C for CO_2 to 250°C for MDEA. Thus an isothermal column oven could not be used and a rapid temperature program was needed for a short elution time. A high injection port temperature would be required to vaporize the sample. Furthermore, a flame ionization detector would not be satisfactory since H_2O and CO_2 are not combustible.

2.9.2. Column Configuration

The Tenax-GC column alone was incapable of producing a separation between the light components (H_2S, CO_2, H_2O, C_1, C_2, etc). To separate the light components, a simple column switching device with two columns in series was constructed. The first column containing Tenax-GC was designed to give good separation between the amine and light components. The second column containing Poropak Q was designed to separate the light components. Poropak Q is an ethylvinylbenzene-divinylbenzene copolymer that is cross-linked and can withstand temperatures to at least 250°C before polymer degradation occurs. [Gary D.Robbins, Jerry A.Bullin, Analysis of Amine Solutions by Gas Chromatography]:

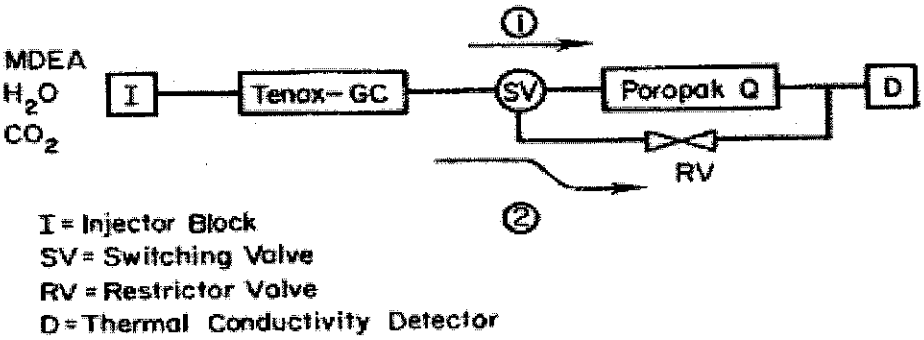


Figure 2.9.2: GC column configuration.

Optimum GC Operating Conditions:

- Injector/detector temperature – 270°C
- Initial column temperature – 120°C
- Final column temperature – 240°C
- Rate of temperature program – 20°C/min
- Detector current – 60 mA
- Carrier gas flowrate – 40 ml/minute
- GC attenuation – 1
- Integrator attenuation – 4

CHAPTER 3: AMINE IN INDUSTRY

3.1. Amine Rejuvenation

This chapter is about how amine is controls in the plant. It is specifically for the amine used in the gas processing plant. Even until today, there are no plants in Malaysia which recycle their amine and reused it back in the acid gas absorption process. Also no effort had been done to separate the content of the waste amine (primary, secondary, tertiary, H_2S, CO_2) in order to reuse it back. However there is one plant which filter backs the amine, to reduce the hydrocarbon level and then is use again to absorb acid gas. This chapter is about how to reduce the hydrocarbon, oil and grease, and foam in the waste amine.

In industry why amine needs to be recirculated: -

(1)Current plant amine strength is at lower side that lead to decision to look possibility of retreating the contaminated amine.

(2)Price of fresh amine is quite expensive

(3)Contaminated amines which contain high hydrocarbon content lead to high foaming.

(4)Waste water treatment plant is not capable of handling and treating amine.

(5)High disposal cost to Kualiti Alam.

The objective and target of the industry is to rejuvenate 100% contaminated amine to the acceptable limit for the make up to Acid Gas Removal Unit System (AGRU).

Oil and Grease (hydrocarbon) < 20mg/liter (ppm)
Foam Height < 300ml
Amine Strength < 15%

3.1.1. How to reduce carbon?

Theoretically the hydrocarbon can be removed from amine by treating using carbon filter. BASF (Amine supplier) proposed to use carbon filter for hydrocarbon separation.

Pilot Study at laboratory

Setup pilot unit at Laboratory scale to represent the amine filtering unit. The result showed that O&G (hydrocarbon) is reduced significantly by treating with carbon filter & filter paper.

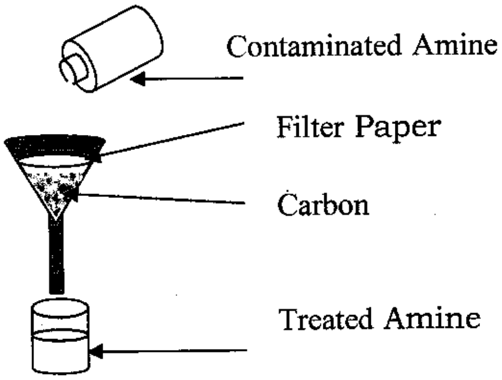


Figure 3.1.1: Amine Filtering

Table 3.1.1: Amine Filtering

	Amine content (%)	Oil & Grease (mg/L)	Foam Height (ml)
Before Treating	20	251.5	Over range
After Treating (5 X)	20	190	400

3.1.2. Setup Offline Amine Rejuvenation Unit

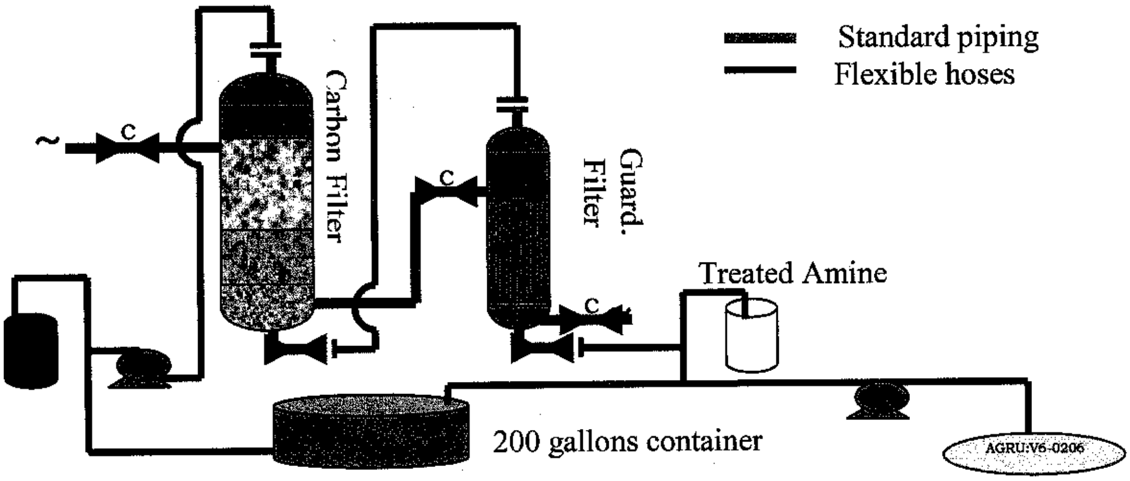


Figure3.1.2 (a): Amine Rejuvenation Unit

Amine rejuvenation unit is set up to recycle the waste amine. The purpose is to reduce the content of the hydrocarbon, oil and grease, and foam in the amine. This unit consists of three steps.

Step A: Amine Selection

(1)Labeled the pallet number
(2)Lab test for each pallet (concentration, O&G, foam height)
(3)Selection for rejuvenation based on contaminants level.

Step B: Treating Method

(1)Set up equipment
(2)Pumped 4 pallets (16 drums) of contaminated amine into carbon filter.
(3)Let the amine passing through guard filter by opening the inlet valve.
(4)Received partially treated amine in water tank.

Step C: Amine circulation pump

(1)After receiving treated amine up to 1/3 polytank volume, pump is started to circulate amine back to carbon filter.
(2)Done visual check for colour changes for treated amine.
(3)Let the amine circulated for 2 days and did a lab sampling for oil and grease and foam height.

Result

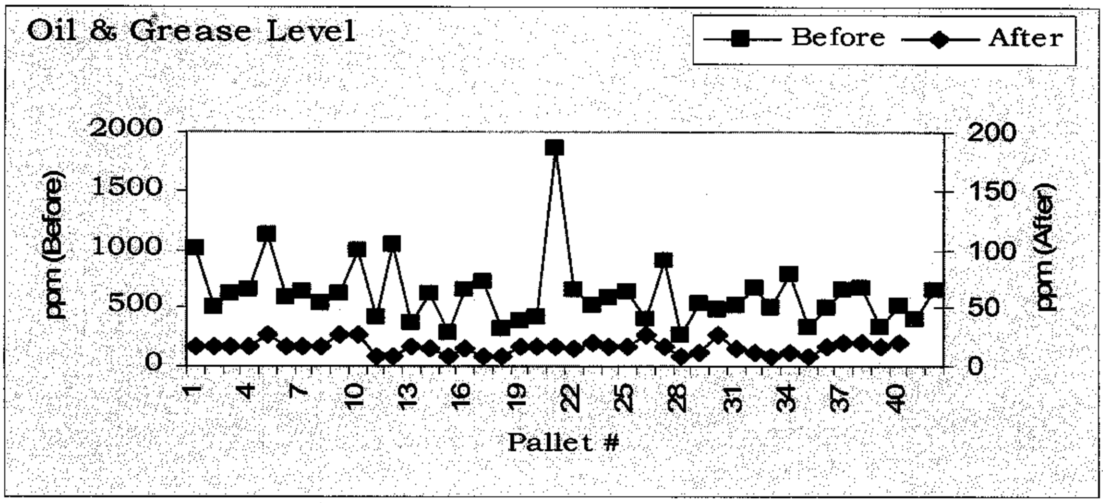


Figure 3.1.2(b): Oil And Grease Level

Table 3.1.2(a): Oil And Grease Level

Pallet	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
O & G Before	1002	496	615	656	1124	590	641	534	630	998	425	1044	369	620	292	656	721	313	389	414	1
O & G After	16.2	16.9	16.9	16.2	26.4	16.9	16.2	16.2	26.4	26.4	9.2	9.2	16.9	14.3	9.2	14.3	9.2	9.2	16.9	16.9	1
Pallet	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	
O & G Before	653	521	587	637	405	914	272	533	488	515	674	503	783	339	498	658	667	329	528	405	
O & G After	14.3	20	16.9	16.9	26.4	16.9	9.2	11.2	26.4	14.3	11.2	9.2	11.2	9.2	16.9	20	20	16.9	20		

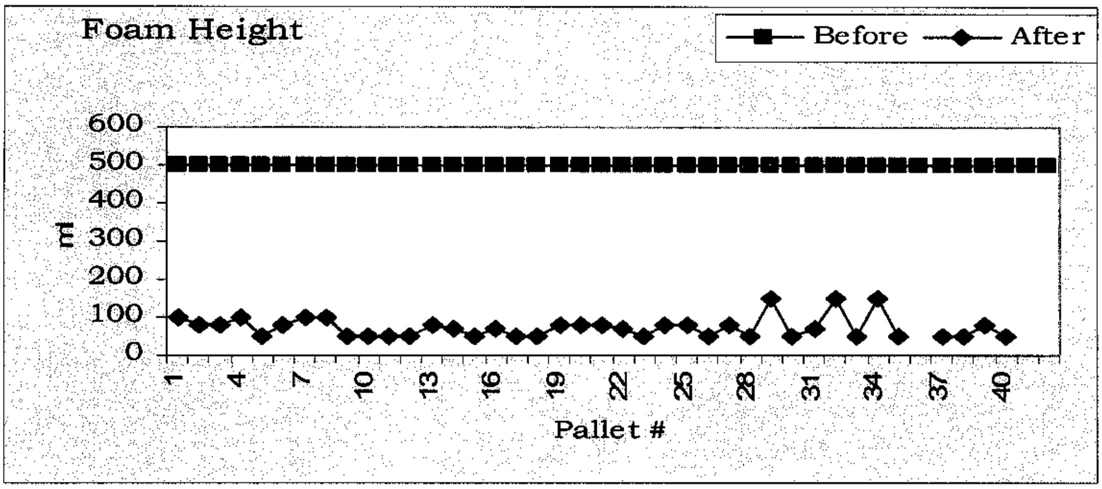


Figure 3.1.2(c): Foam Height

Table 3.1.2(b): Foam Height

Pallet	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
FH Before	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500
FH After	100	80	80	100	50	80	100	100	50	50	50	50	80	70	50	70	50	50	80	80	80
Pallet	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42
FH Before	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500
FH After	70	50	80	80	50	80	50	150	50	70	150	50	150	50		50	50	80	50		

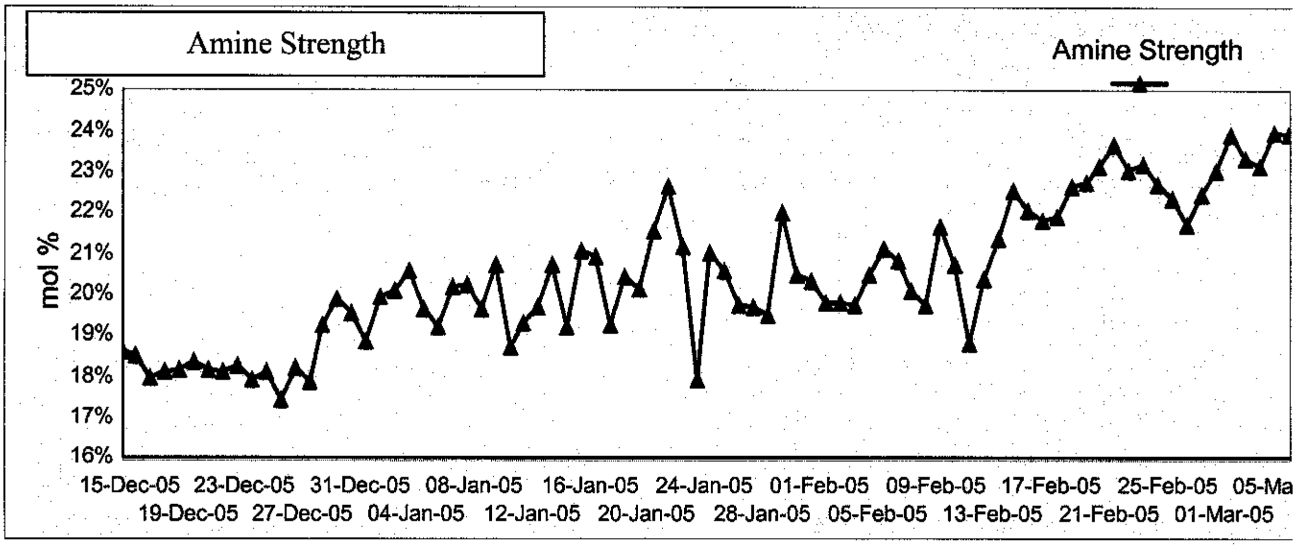


Figure 3.1.2(d): Actual Plant Amine Strength After Make-Up

3rd Week of Dec-04, Amine strength was only at 18 %. 2nd Week of Mar 05, Amine strength was increased up to 23.9 % which increment of at 5.9 **%.** Increment 2.9 **%** is calculated from amine rejuvenation project.

Table 3.1.2(c): Target

Objective	Target (Apr-05)	Result (13-Mar)	Remark
Completion of Rejuvenation Process	100 % 256 drum	86 % 220 drum	28 drum has been put on hold due to high Hg content. Only remaining 8 drums to be completed by Apr-05.
Achieve the Amine Quality Acceptable Limit	O&G:<20 ppm Fm Ht:<300ml Strength >15%	All treated Amine meet the spec.	Rejuvenation process is efficient enough to achieve the acceptable limit.
Cost of Schedule Waste Disposal to Kualiti Alam	RM 0	RM 0	Nil

3.1.3. Increased Of Plant Production

Increased of 2.9 mol % of Amine strength resulting of average 7 ton/hr of Feed Gas Load which create the added value to Petronas.7 ton/hr x RM 390/ton = RM 2,730 /hr (RM65, 520/day)

Overall Saving
=Total Cost Saving – Total Cost Incurred
=(Disposal cost + Value of recovered amine) – (Guard filter replacement+ Technicians)
= RM 384,240.00 - RM 28,035.00
= RM 356,205.00

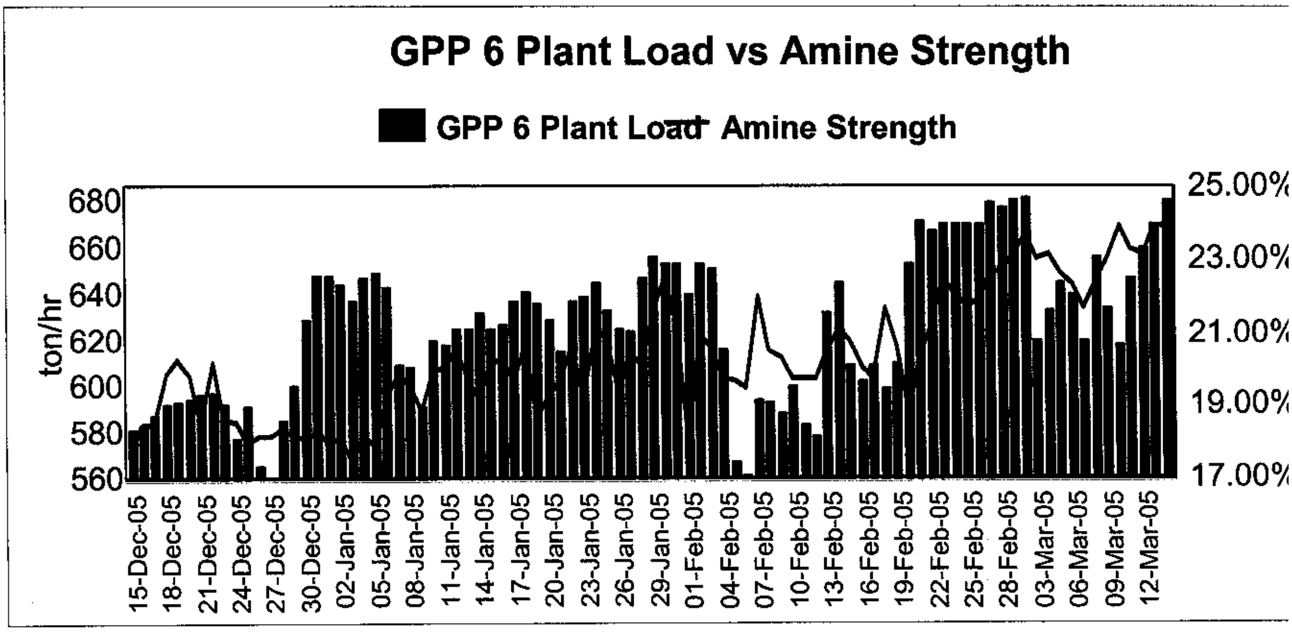


Figure 3.1.3: Plant Load Vs Amine Strength

Conclusion

Contaminated amine which can be effectively rejuvenated by utilizing the standby Carbon filter and Guard filter. The advantage of this amine rejuvenation technique is amine can be re-circulated effectively to meet the specification. Also support the HSE Policy by minimize the generation of waste.[Shahrizal B Hambalee, Amine Rejuvenation]

Way forward

(1)To establish a standard procedure for amine rejuvenation process for future treatment.

(2)To share the technique with other OPU's

(3)To increase the carbon filter change out frequency from every 3 years to acceptable period (6 months)

3.2. Applications of membrane

3.2.1. Reverse Osmosis

-Desalination of brackish water

-Treatment of wastewater to remove a wide variety of impurities

-Treatment of surface and ground water

-Concentration of foodstuffs

-Removal of alcohol from beer and wine

3.2.2. Dialysis

-Separation of nickel sulfate from sulfuric acid

-Hemodialysis (removal of waste metabolites, excess body water, and restoration of electrolyte balance in blood)

3.2.3. Electrodialysis

-Production of table salt from seawater

-Concentration of brines from Reverse Osmosis

-Treatment of waste waters from electroplating

-Demineralization of cheese whey

-Production of ultrapure water for the semiconductor industry

3.2.4. Microfiltration

-Sterilization of drugs

-Clarification and biological stabilization of beverages

-Purification of antibiotics

-Separation of mammalian cells from a liquid

3.2.5. Ultrafiltration

-Preconcentration of milk before making cheese

-Clarification of fruit juice

-Recovery of vaccines and antibiotics from fermentation broth

-Color removal from Kraft black liquor in paper making

3.2.6. Prevaporation

-Dehydration of ethanol-water azeotrope

-Removal of water from organic solvents

-Removal of organics from water

3.2.7. Gas permeation

-Separation of $C0_2$ or H_2 from Methane and other Hydrocarbons

-adjustment of the H_2/CO ratio in the synthesis gas

-Separation of air into Nitrogen - and Oxygen - enriched streams

-Recovery of Helium

-Recovery of Methane from Biogas

3.2.8. Liquid membranes

-Recovery of zinc from wastewater in the viscose fiber industry

-Recovery of nickel from electroplating solutions

CHAPTER 4: METHODOLOGY

4.1. Technical Specification of Hybrid Reverse Osmosis Pilot System

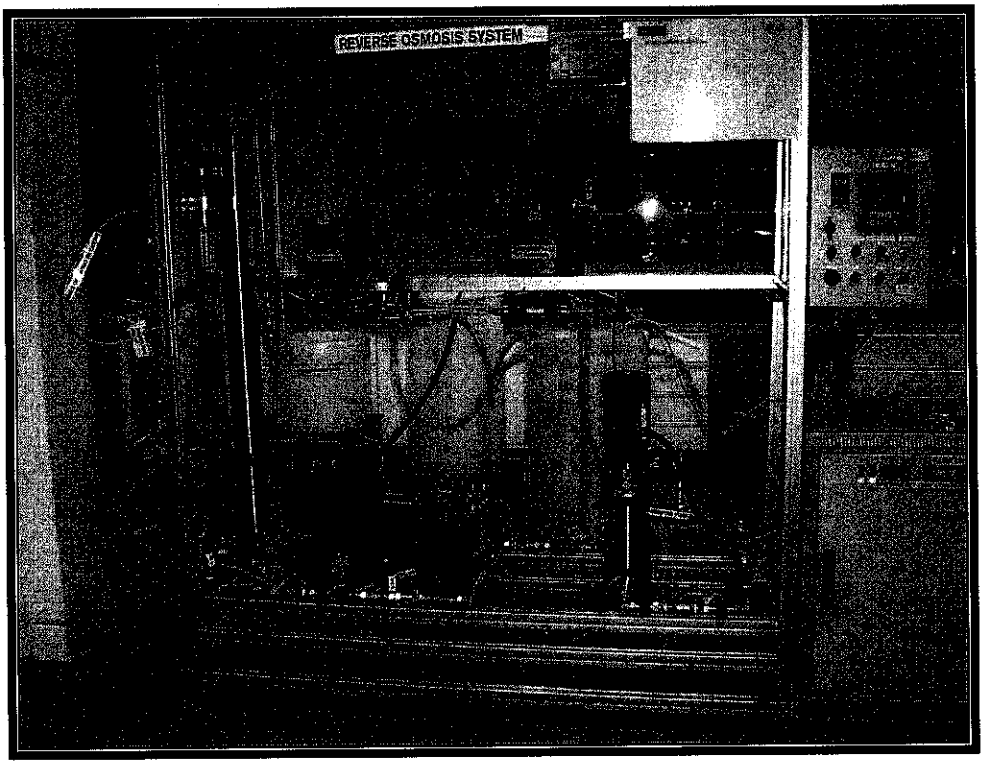


Figure 4.1(a): Hybrid Reverse Osmosis Pilot System

Table 4.1(a): Technical Specification of Hybrid Reverse Osmosis Pilot System

Pump

No	Description	Brand	Type	Range/Capacity
1	High Pressure Pump	Speck	NP 16/18-130	5.0KW
2	Booster Pump	Grundfos	CRN 1-13	0.75KW

Instrumentation

No	Description	Brand	Type	Range/Capacity
1	Flowmeter 1	Bademeter	Primo	0.32-106 L/Min

2	Flowmeter 2	Badermeter	Primo	0.57-190 L/Min
3	Pressure Indicator 1	Wika	ECO-1	0-10 bar
4	Pressure Indicator 2	Wika	ECO-1	0-160 bar
5	TDS meter 1	Hanno	HI 983329	0-999ppm
6	TDS meter 2	Hanno	HI-710	0-32,000ppm
7	Water Circulator	Eibo	Eibo Clx	NIL

Tank

No	Description	Brand	Type	Range/Capacity
1	Permeate Tank	NIL	NIL	20L
2	Concentrate Tank	NIL	NIL	50L
3	Feed Tank	NIL	NIL	100L

Membrane

No	Description	Brand	Type	Range/Capacity
1	Spiral Wound RO	Hydranautics	SWC1-4040	Max 1000psi
2	Hollow Fiber UF	Koch	ROMICON HF53	Max 100psi

Table 4.1(b): Chemicals used for the project

No	Chemicals
1	Waste amine mixture consist of MEA and DEA

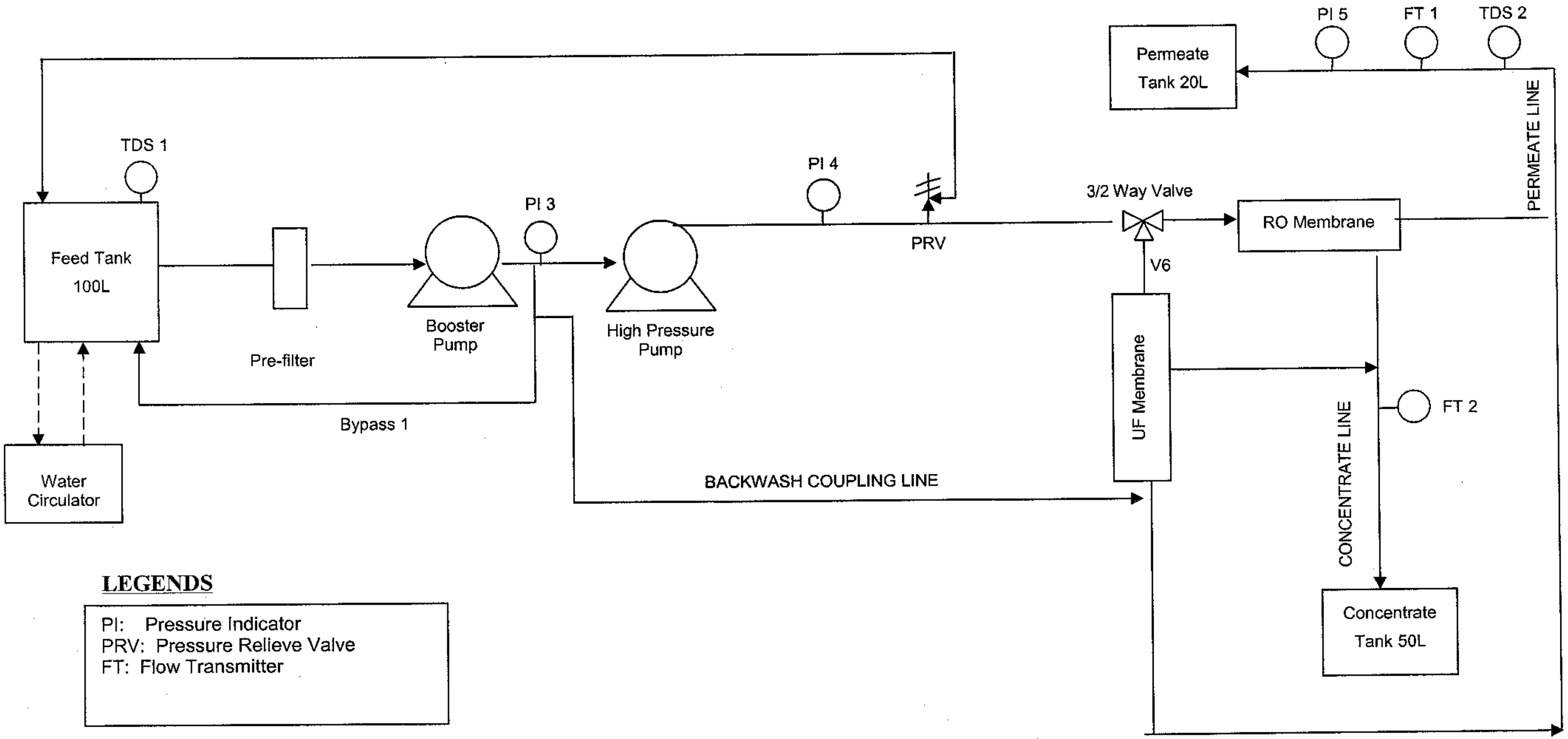


Figure 4.1(b): Schematic Diagram Hybrid Reverse Osmosis Pilot System

4.2. UF Method

4.2.1. Preparation of waste amine in the feed tank

(1)Waste amine is filled into the feed tank until the required concentration is achieved. It is displayed in TDS 1.

(2)Concentration probe is placed in the feed tank.

(3)V4 is closed and V1,V2,V3 is set opened.

(4)Booster Pump is on. It will activate the pump to mix well the waste amine in the feed tank.

(5)Waste amine is recycled back into the feed tank for about 10 min.

4.2.2. Experimental Procedure

(1)3/2 way valve,V6 is set to UF membrane path.

(2)Valve V1, V2, V4, V5 and V7 is set opened while V3 is closed.

(3)Only Booster Pump is on to start the UF experiment.

(4)Control Valve, NV1 and NV2 are regulated to obtain the desired pressure. Wait about 5 min to achieve a steady state.

(5)Permeate pressure, permeate flowrate, concentrate out pressure, TDS1 and TDS2 reading is recorded.

(6)Sample of feed and permeate is collected. Their colors are compared.

(7)The system is switch off by pressing the 'Booster Pump Off' button.

4.2.3. Cleaning the feed tank.

(1) Same step used in 4.3. RO Method

4.2.4. UF Membrane Backwash

(1)Full filled the feed tank with tap water.

(2)3/2 way valve,V6 is set to UF membrane path.

(3)Valve NV2, V3, V4 and V7 is closed while DV4 is opened.

(4)Backwash coupling tubing is plugged into 'Backwash Inlet'.

4.3. RO Method

4.3.1. Preparation of waste amine in the feed tank

(1)Similar step used as in 4.2. UF Method

4.3.2. Experimental Procedure

(1)3/2 way valve,V6 is set to RO membrane path.

(2)Valve V1, V2, V4 and V5 is set opened while V3 is closed.

(3)Booster Pump is on to start the RO experiment. Wait 1 min for the pump flow to stabilize.

(4)Then the High Pressure Pump is on.

(5)Control Valve, NV1 and NV2 are regulated to obtain the desired pressure. Wait about 5 min to achieve a steady state.

(6)Permeate pressure, permeate flowrate, concentrate out pressure, TDS1 and TDS2 reading is recorded.

(7)Sample of feed and permeate is collected. Their colors are compared.

(8)The system is switch off by pressing the 'Booster Pump Off' button.

4.3.3. Cleaning the feed tank.

(1)All the waste amine in the feed tank is drained into its original tank.

(2)Then 1/2 of the feed tank is supply with the tap water.

(3)Valve V1, V2, and V3 is set opened while V4 is closed.

(4)Booster Pump is on for 10 min to clean off the remaining waste amine in the feed tank.

4.3.4. RO Membrane Cleaning

Repeat step (1) to (4) in 4.3.2.Experimental Procedure, using the tap water only.

4.4. Analyzer (Gas Chromatography)

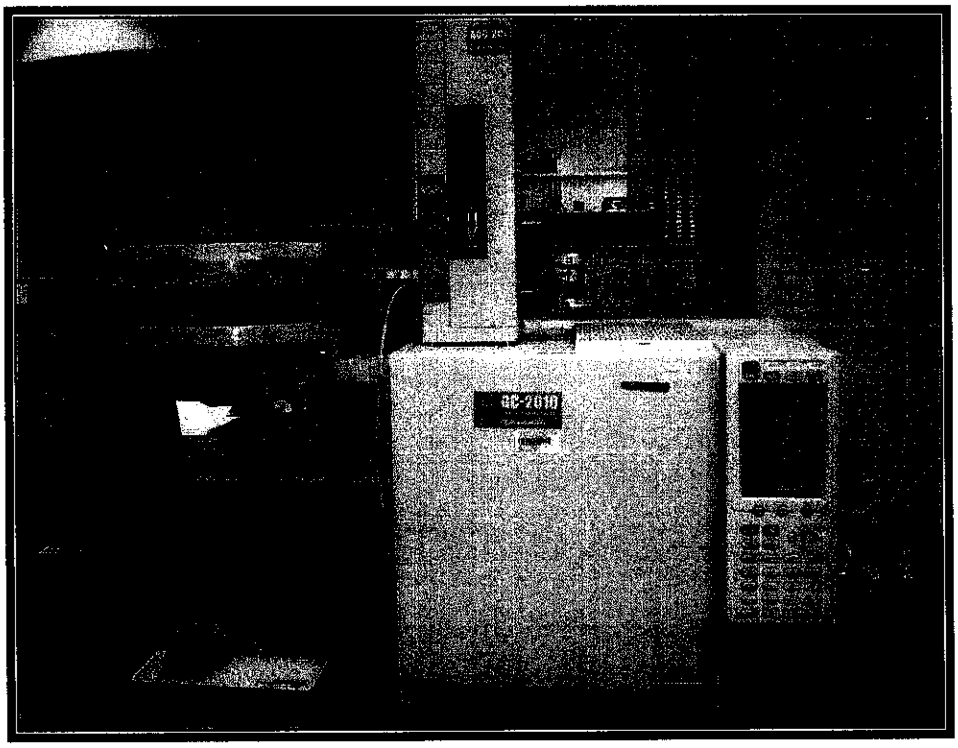


Figure 4.4(a): Gas Chromatography

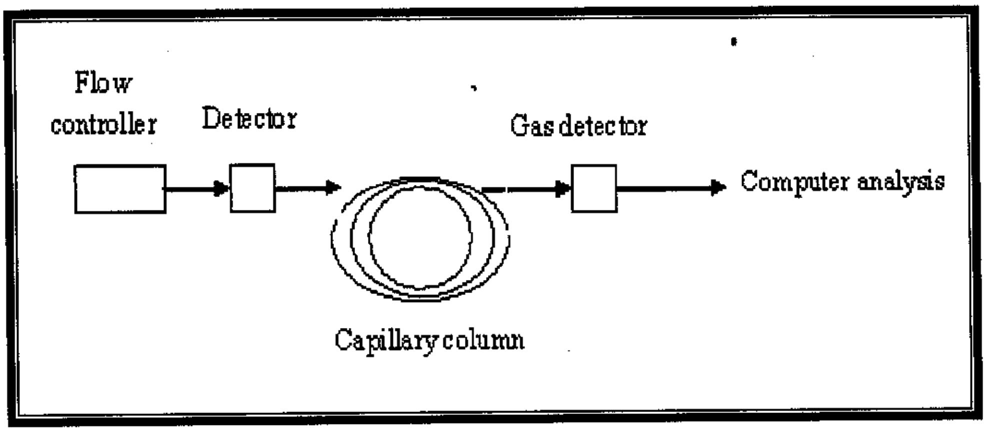


Figure 4.4(b): Gas Chromatography Flow Diagram

In the GCMS, the sample is injected and heated while flowing in the capillary column and turned into gas. The gases formed are detected at the end of the column by a sensor and transfer the data to the connected computer.

4.4.1. To Determine The Concentration of Amines In The Sample.

(1)Standard solutions were prepared using pure MEA, DEA and MDEA with concentration of 200, 300, 1000, 2000, 4000, 6000 and 8000ppm. This is to plot a standard concentration curve as a reference for the samples.

(2)Filled the standard solutions and the samples into the labeled sample bottle.

(3)After the GC is ready, the samples bottles are arranged in the auto sampler and start the analyzer.

(4)The samples will be automatically injected into the analyzing column one by one. 10 minutes is taken for each sample to be analyzed.

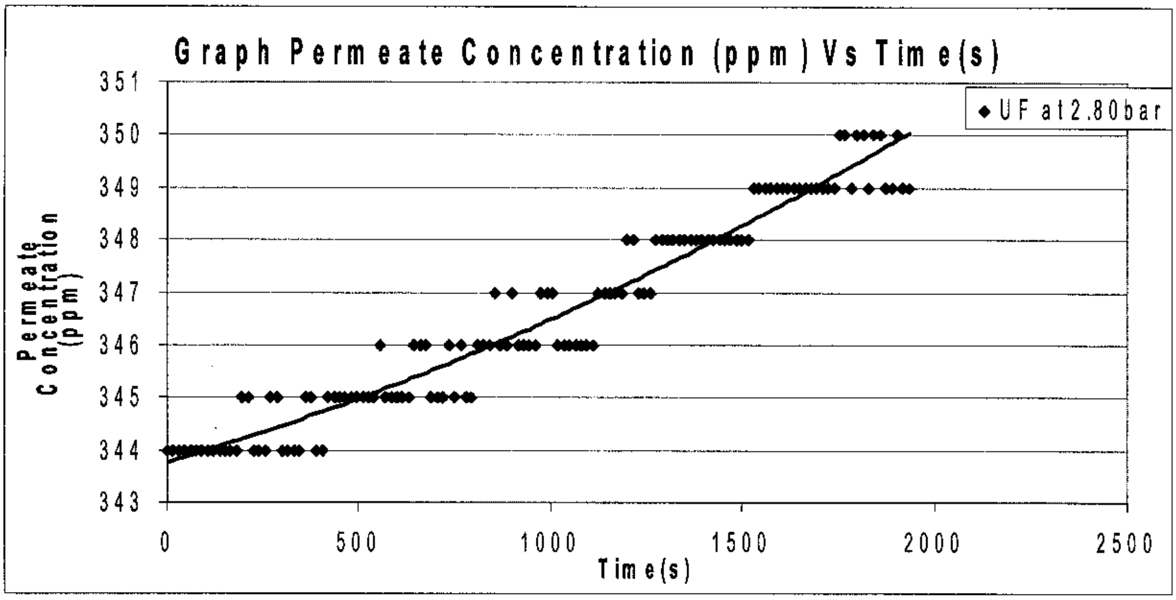
(5)The result shown is in term of peak graphs where area under the peak represents the concentration of the component.

Table 4.4.1: Method of Analysis

Injection volume	1.0 μL
Temperature	280 ^{0}C
Carrier gas	N2 / Air
Pressure	99.9 kPa
Total flow	18.3 mL/min
Column type	BPX-5
Column length	30.0 m
I. Diameter	0.25 mm

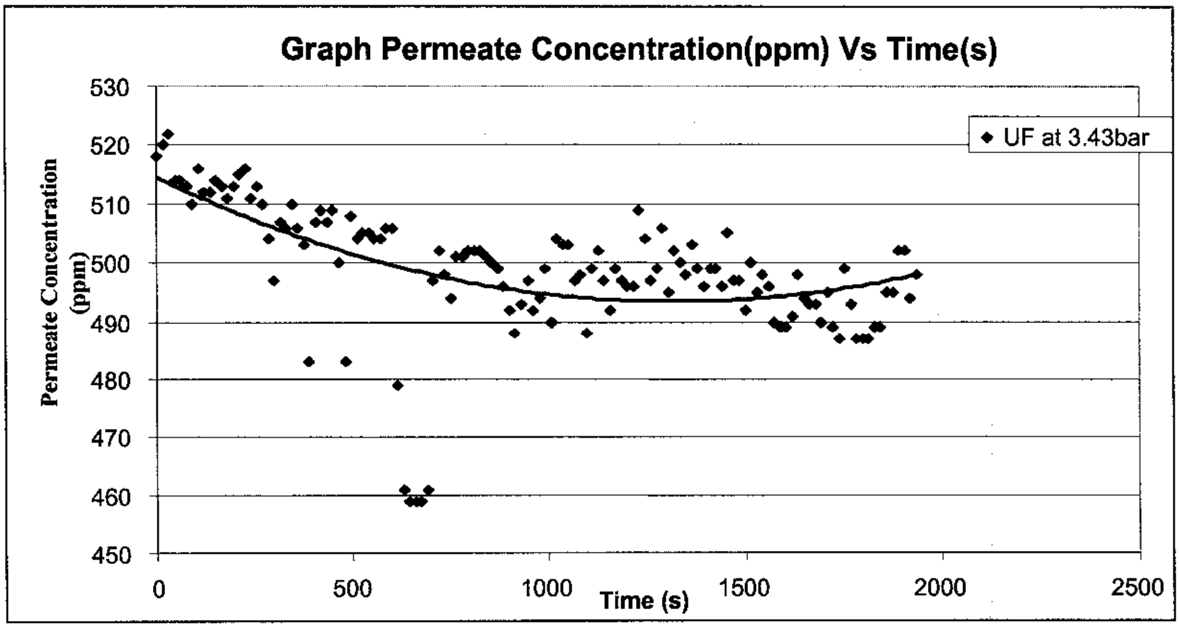
CHAPTER 5: RESULTS AND DISCUSSION

5.1. Ultrafiltration Membrane



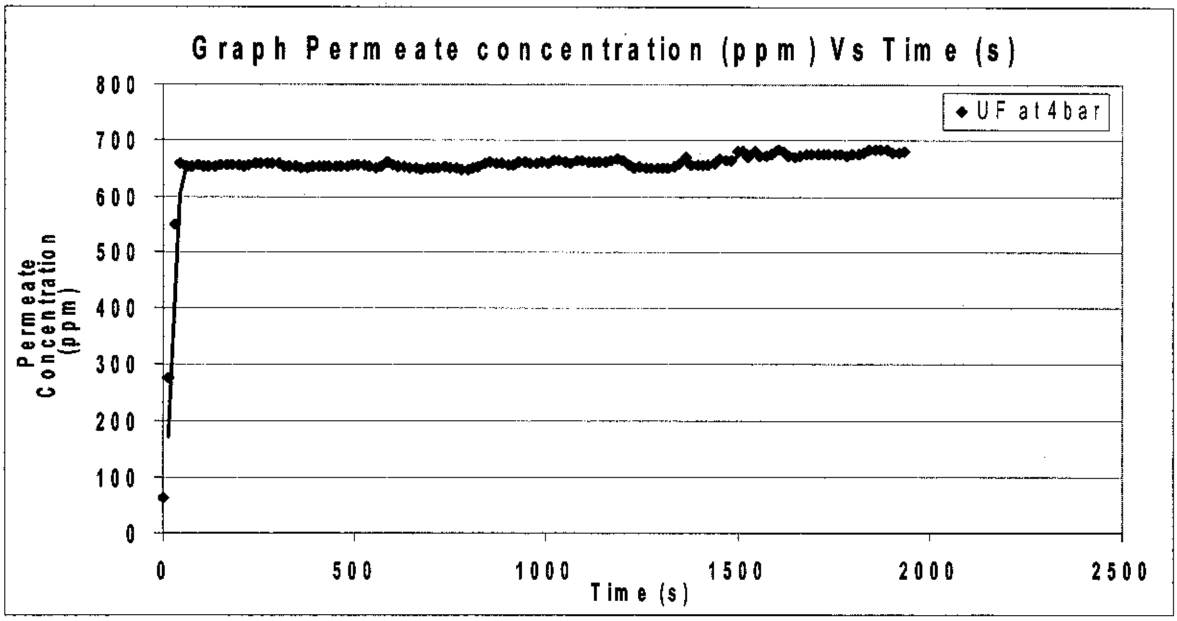
Increasing in permeate concentration = 6ppm

Figure 5.1(a): Unknown Concentration (MEA and DEA)



Decreasing in permeate concentration = 20ppm
Increasing in permeate concentration = 3ppm

Figure 5.1(b): Unknown Concentration (MEA and DEA)



Increasing in permeate concentration = 30ppm

Figure 5.1(c): Unknown Concentration (MEA and DEA)

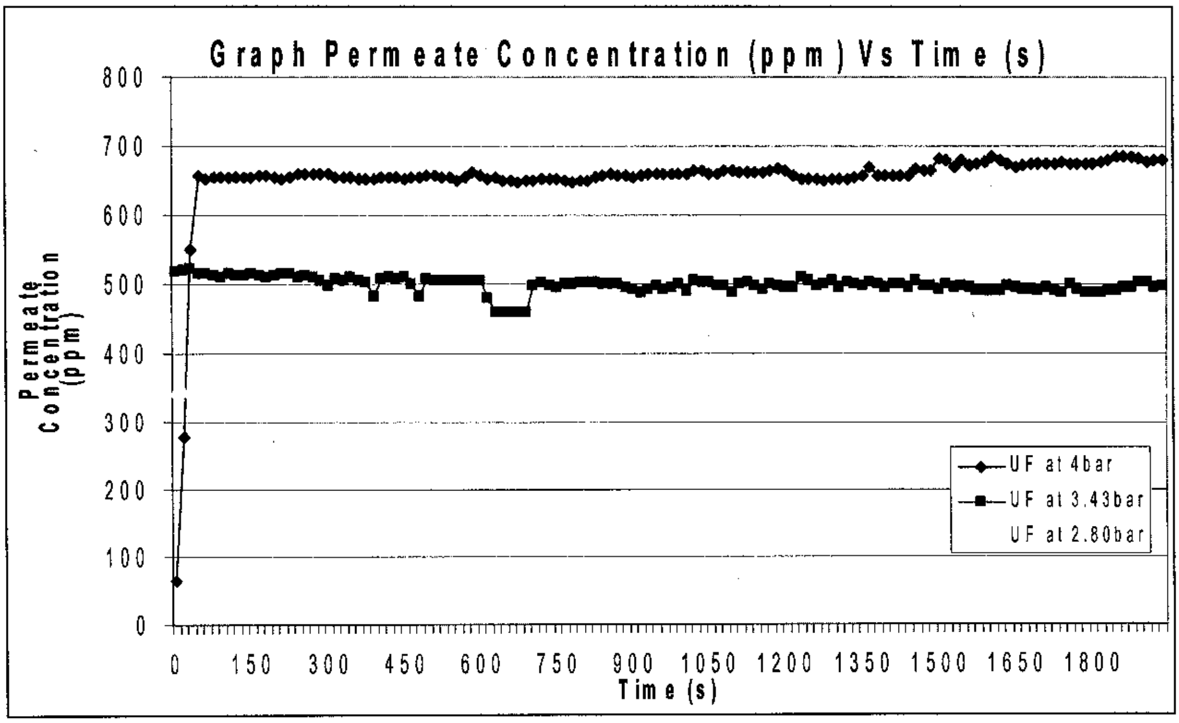


Figure 5.1(d): Combination of varies pressure

The waste amine that had been used is from the industry. The permeate consist of unknown concentration (MEA and DEA) that passes through the membrane. Theoretically, after a certain time, the concentration of the unknown that separated from the waste amine will increase. Their molecules were push through the membrane and give a higher concentration. Permeate concentration is increasing when higher pressure is applied. This pressure will overcome the osmotic pressure and then increase the unknown concentration that passes the membrane. When the concentration that passes the membrane is increasing, it's proves that they were separated from the waste amine. Increasing in permeate concentration is higher in UF than RO because the dissolve of amine in water can passes the membrane due to the bigger pore size. Particle Size Cut-Off for Ultrafiltration is 0.01 – 0.1 μm while for Reverse Osmosis is lesser than 0.001 μm.

For Figure 5.1(a), pressure applied is 2.80 bar and feed concentration, C_b is 360 ppm. After half an hour the unknown concentration, C_p that passes through the membrane is 350 ppm. The initial C_p recorded is 344. This shows that UF membrane had increasing the unknown concentration that passes the membrane for about 6ppm. The permeate pressure is 0.8 bar. Transmembrane Pressure, ΔP is 2 bar. The graph line is found to be almost linear.

For Figure 5.1(b), pressure applied is 3.43 bar and feed concentration, C_b is 448 ppm. After half an hour the unknown concentration, C_p that passes through the membrane is 498 ppm. The initial C_p recorded is 495.This shows that UF membrane had increasing the unknown concentration for about 3 ppm. The permeate pressure is 1.16 bar. Transmembrane Pressure, ΔP is 2.27bar. At t=0 until t=1250s the unknown concentration is decreasing. It start to increasing when t=1250s.This because the reading is still not reach it steady state. Theoretically the increasing in unknown concentration will be higher than 2.80 bar. This result will be more accurate if the time for the experiment was elongated.

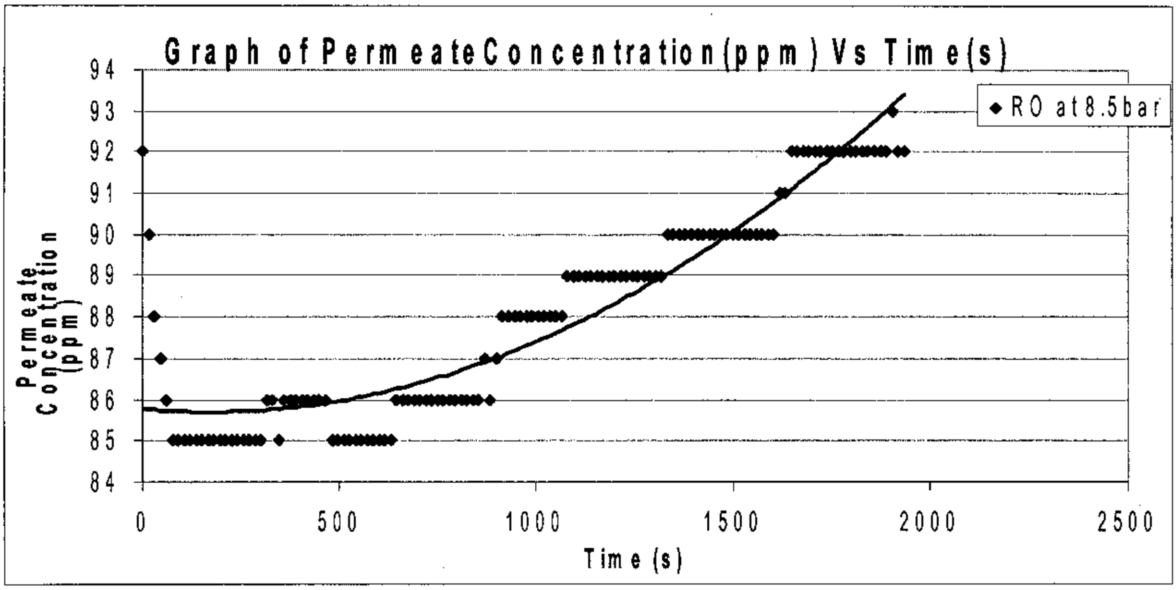
For Figure 5.1(c), pressure applied is 4bar and feed concentration, C_b is 680 ppm. After half an hour the unknown concentration, C_p that passes through the membrane is 681ppm. The initial C_p recorded is 650. This shows that UF membrane had increasing the unknown concentration for about 31ppm. The permeate pressure is 1.40 bar. Transmembrane Pressure, ΔP is 2.6 bar. From the graph, the initial unknown concentration increase rapidly at t=0 until t=50s. This is the time for the value to reach it steady state.

Table 5.1: UF at 25°C

Feed	**Permeate**		**Transmembrane Pressure ΔP** = P_{feed} - $P_{permeate}$	**Increasing permeate Concentration (ppm)**
Pressure (P_{feed})	**Pressure** ($P_{permeate}$)	**TDS2** (**C_p, ppm**)		
2.80 bar	**0.80**	**350**	**2.00 bar**	**6**
3.43 bar	**1.16**	**498**	**2.27 bar**	**3**
4..00 bar	**1.40**	**681**	**2.60 bar**	**31**

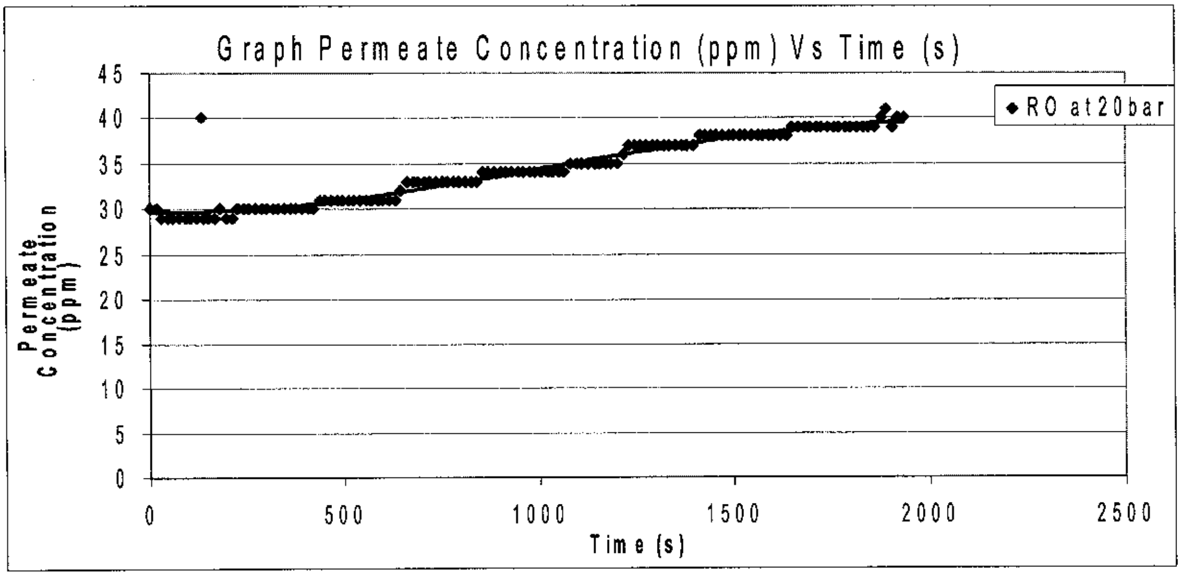
From all the results shows that a higher pressure will give a higher permeate concentration. It can be concluded that pressure of 4 bar is better than 2.80 and 3.43 bar. UF membrane can be more effective for the separation of waste amine if a higher pressure is applied. However UF membrane can't reduce amine concentration more effective than RO membrane because the size of the pore is bigger. Particle Size Cut-Off for Ultrafiltration is 0.01 – 0.1 μm while for Reverse Osmosis is lesser than 0.001 μm.

5.2. Reverse Osmosis Membrane



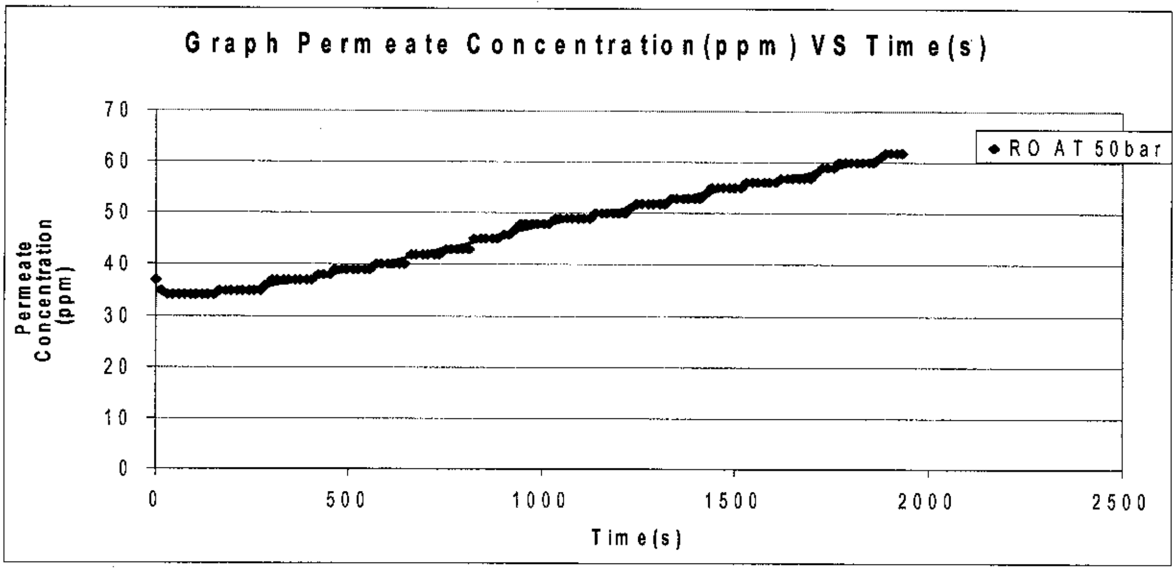
Increasing in permeate concentration = 8ppm

Figure 5.2 (a): Unknown Concentration (MEA and DEA)



Increasing in permeate concentration = 12ppm

Figure 5.2 (b): Unknown Concentration (MEA and DEA)



Increasing in permeate concentration = 28ppm

Figure 5.2 (c): Unknown Concentration (MEA and DEA)

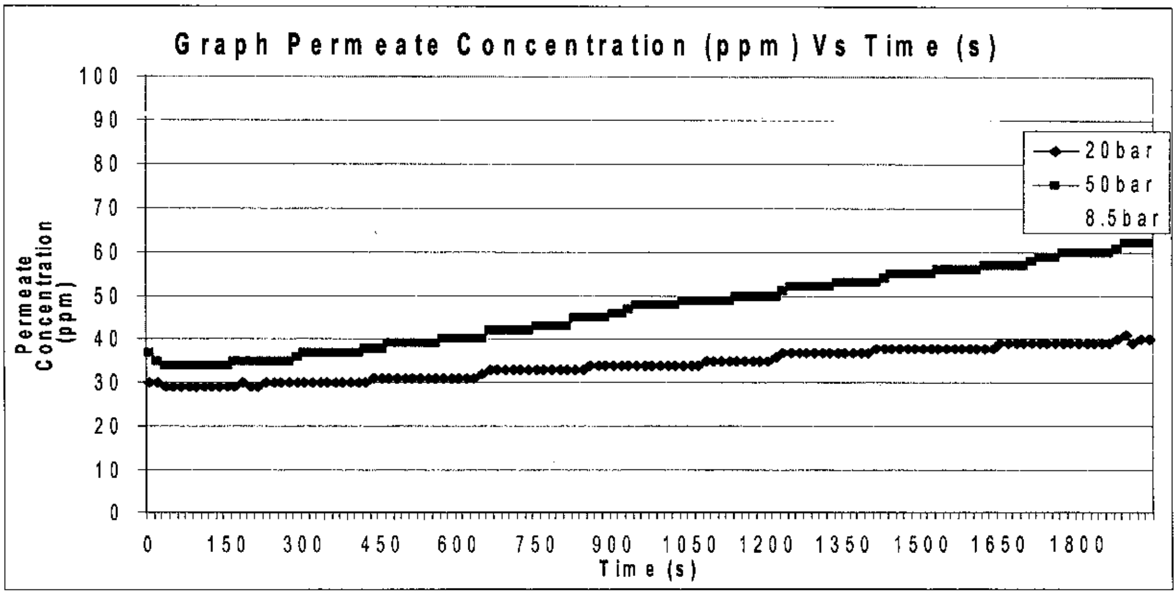


Figure 5.2 (d): Combination of varies pressure

For RO membrane it's also show that higher pressure applied will increase the unknown concentration that exit through the membrane.

For Figure 5.2 (a), pressure applied is 8.5 bar and feed concentration, C_b is 680 ppm. After half an hour the unknown concentration, C_p that passes through the membrane is 93 ppm. The initial C_p recorded is 85 ppm. This shows that RO membrane had increasing the unknown concentration for about 8 ppm. The permeate pressure is 0.03 bar. Transmembrane Pressure, ΔP is 8.47 bar. From the graph, the initial unknown concentration decrease rapidly at t=0 until t=100s. This is the time for the value to reach it steady state.

For Figure 5.2 (b), pressure applied is 20 bar and feed concentration, C_b is 438 ppm. After half an hour the unknown concentration, C_p that passes through the membrane is 41 ppm. The initial C_p recorded is 29 ppm. This shows that RO membrane had increasing the unknown concentration for about 12 ppm. The permeate pressure is 0.12 bar. Transmembrane Pressure, ΔP is 19.88 bar.

For Figure 5.2 (c), pressure applied is 50 bar and feed concentration, C_b is 570 ppm. After half an hour the unknown concentration, C_p that passes through the membrane is 62 ppm. The initial C_p recorded is 35 ppm. This shows that RO membrane had increasing the unknown concentration for about 27 ppm. The permeate pressure is 0.78 bar. Transmembrane Pressure, ΔP is 49.22 bar.

Table 5.2: RO at 25°C

Feed	**Permeate**		**Transmembrane Pressure, ΔP =** $P_{feed} - P_{permeate}$	**Increasing permeate Concentration (ppm)**
Pressure (P_{feed})	**Pressure** ($P_{permeate}$)	**TDS2** (C_p,ppm)		
8.5 bar	**0.03 bar**	**92**	**8.47 bar**	**8**
20 bar	**0.12 bar**	**40**	**19.88 bar**	**12**
50 bar	**0.78 bar**	**62**	**49.22 bar**	**27**

From all the results shows that a higher pressure will give a higher permeate concentration. It can be concluded that pressure of 50bar is better than 20 and 8.5 bar. RO membrane can be more effectively for the separation of waste amine if a higher pressure is applied. RO membrane is more effectively than the UF membrane due to the pore size which is smaller, and will selectively left the bigger molecular size.

When using RO, the feed pressure is fluctuated in a very big range. This is due to the running of both the Booster pump and High pressure pump. The High pressure pump vibrates strongly and keeps the feed pressure values fluctuated. It effect the value of the permeate concentration recorded. However UF membrane did not experience a big fluctuated feed pressure.

After a long period of time, when the entire unknown is separated from the waste amine, the concentration in the residual feed will become more concentrated. Osmotic pressure will increase until it same as the applied pressure. This will cause the permeate concentration and salt rejection to decrease.

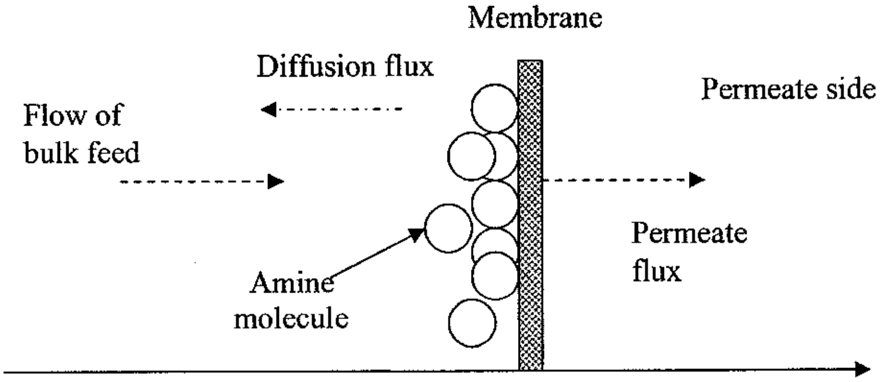


Figure 5.2(e): Concentration Polarization

The retained amine will build up at the membrane surface and cause a diffusional flow from the membrane to the bulk. This phenomenon is known as the Concentration polarization. The higher concentration of amine at the membrane will increase diffusional flow and finally limiting the amount of solute that passes the membrane. This concentrated amine will form a gel layer which becomes a secondary barrier at the membrane.

5.3. Analyzer: Gas Chromatography

5.3.1. RO

Table 5.3.1(a): 50 bar

Concentration(ppm)		
	MEA	DEA
Feed	2568.471	2392.190
Sample 45	237.118	-
Sample 87	198.386	-
Sample 130	162.112	-

Rejection (%)	
MEA	DEA
[(Feed – Permeate) / Feed] **X** 100% = 93.7%	[(Feed – Permeate) / Feed] **X** 100% = 100%

From the analyzing done using GC, DEA is rejected 100% after passes the RO membrane. The concentration detected in the feed sample is 2392.190ppm. But no concentration is found in the permeate sample. So none DEA molecule can passes the membrane. However for MEA, the rejection is 93.7%. From theory RO membrane used have salt rejection from 98% to 99%. [Wayne T.Bates and Rocco Cuozzo, Integrated Membrane System]. The value from the experiment is lower because some error happened. There are concentration polarization that happened at higher pressure. Also human error while handling and operating the equipment and during taking the reading.

The concentration of the sample decreasing from feed to the last sample, sample 130. This show RO membrane is effective for the separation of waste amine mixture of MEA and DEA. From the result, the best salt rejection and separation is when using the suitable applied pressure. High pressure will give higher salt rejection. DEA cannot passes RO membrane due to the size, which is bigger than MEA. DEA is left in the feed side while MEA passes the membrane to the permeate side.

Table 5.3.1(b): 20 bar

Concentration(ppm)		
	MEA	DEA
Feed	4922.028	947.319
Sample 45	966.365	-
Sample 87	480.293	-
Sample 130	460.214	-

Rejection (%)	
MEA	DEA
[(Feed – Permeate) / Feed] **X** 100% = 90.6%	[(Feed – Permeate) / Feed] **X** 100% = 100%

For pressure 20 bar, DEA is also rejected 100% after passes the RO membrane. The concentration detected in the feed sample is 947.319 ppm. But no concentration is found in the permeate sample. So none DEA molecule can passes the membrane. However for MEA, the rejection is 90.6% and is lower compare with pressure 50 bar. This show that applied pressure is proportional to salt rejection.

Table 5.3.1(c): 8.5 bar

Concentration(ppm)		
	MEA	DEA
Feed	4392.293	-
Sample 45	1313.130	-
Sample 87	1094.164	-
Sample 130	1067.886	-

Rejection (%)	
MEA	DEA
[(Feed – Permeate) / Feed] **X** 100% = 75.7%	No separation occur

For pressure 8.5 bar, DEA is not detected in the feed and permeate sample. Supposedly there is DEA in the feed because the same mixture of waste amine is use for every experiment. But due to some error it is not detected by GC. Theoretically there will be a value for the feed sample. But the permeate sample will not consist of any DEA molecule like 20 and 50 bar. This is due to the bigger size of DEA than the pores of the RO membrane. For MEA, the rejection is 75.7% and is lower compare with pressure 50 bar and 20 bar. This is supposedly to happen. Salt rejection will increase when using higher pressure, we can simply it,

50 bar > 20 bar > 8.5 bar

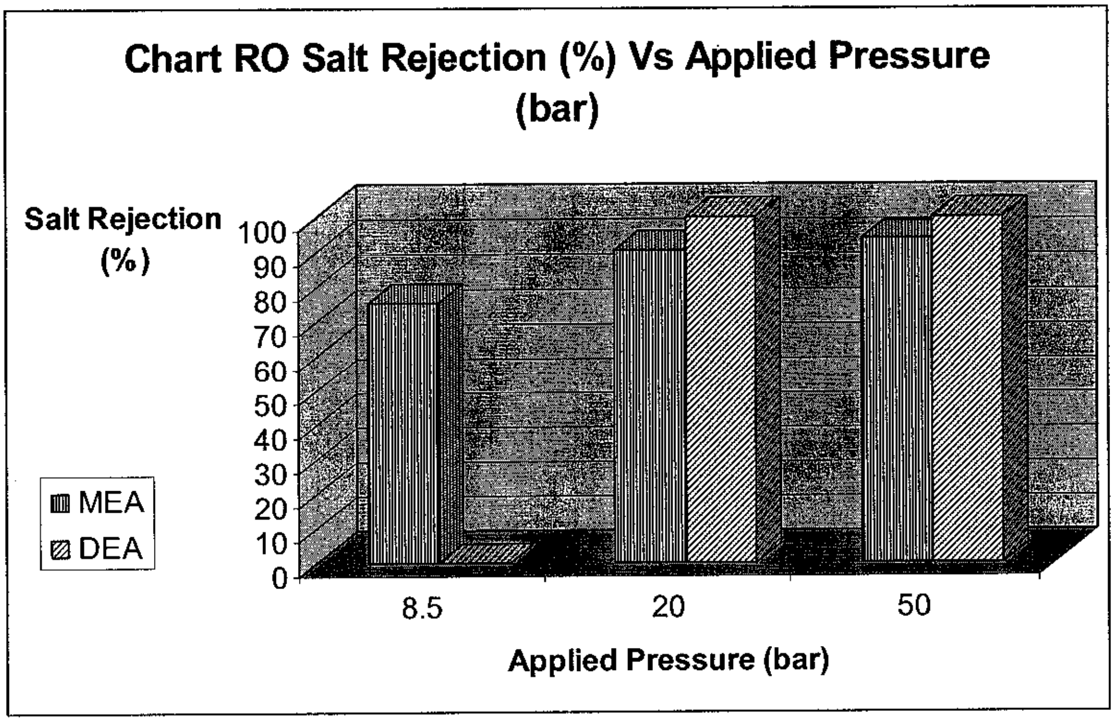


Figure 5.3.1: RO Salt Rejection (%) Vs Applied Pressure (bar)

In figure 5.3.1.show that salt rejection best applied at pressure equal to 50 bar. Found that DEA rejection is 100% while MEA rejection is 93.7%. Followed by pressure at 20 bar, DEA rejection also 100% while MEA is 90.6%. At 8.5 bar, No DEA concentration is detected thus no salt rejection can be calculated. However MEA rejection is 75.7%. DEA cannot pass the membrane due to the bigger molecular size compare to MEA.

5.3.2. UF

Table 5.3.2(a): 4 bar

	Concentration(ppm)	
	MEA	DEA
Feed	-	11.362
Sample 45	13.056	22.947
Sample 87	14.088	25.651
Sample 130	-	28.128

Rejection (%)	
MEA	DEA
unknown	No rejection because permeate is bigger than feed concentration

After the entire sample is analyzed, found that pressure 4 bar, 3.43 bar and 2.8 bar give the same results. There is no salt rejection by using UF membrane. For DEA, feed concentration is 11.362 ppm while sample 130 is 28.128 ppm. So it is considered that no salt rejection. Error occurs in MEA sample where feed and sample 130 are not detected by GC. However sample 45 and sample 87 show an increasing trend in concentration.

Table 5.3.2(b): 3.43 bar

Concentration(ppm)		
	MEA	DEA
Feed	-	919.807
Sample 45	48.725	959.269
Sample 87	38.352	993.552
Sample 130	24.464	965.359

Rejection (%)	
MEA	DEA
unknown	No rejection because permeate is bigger than feed concentration

At 3.43 bar, DEA also show no salt rejection due to the concentration of sample 130 is higher than feed sample. Salt rejection for MEA could not be determined because GC cannot detect the feed concentration.

Table 5.3.2(c): 2.8 bar

Concentration(ppm)		
	MEA	DEA
Feed	1922.975	1303.386
Sample 45	27.860	1043.196
Sample 87	2009.468	1498.889
Sample 130	1999.922	1480.259

Rejection (%)	
MEA	DEA
No rejection because permeate is bigger than feed concentration	No rejection because permeate is bigger than feed concentration

Both MEA and DEA give no salt rejection due to the permeate concentration is bigger than feed concentration.

5.4. Comparison of findings

The results obtained in this study reveal that the separation of waste amine is feasible by using membrane system, especially RO. Salt rejection of RO membrane is up to 98% to 99%. [Wayne T.Bates and Rocco Cuozzo, Integrated Membrane System]. For UF, rejection of small molecular weight organic salt is not very suitable due to larger pore size of the membrane. Particle Size Cut-Off for Ultrafiltration is 0.01 – 0.1 μm while for Reverse Osmosis is lesser than 0.001 μm.

Although the results from this project is not equal quantitatively to the theory due to some factors that affecting the performance, the findings still comply with the theory that between the two membrane systems, RO yield the highest salt rejection. From economic perspective, RO membrane is more expensive, but produces higher separation efficiency. In this case, the process selection is dependent on the application and product quality requirement.

Compare to the crystallization method where high heat requirement and cost is needed, the membrane process seems more advantageous. Membrane separation is also easier and lower in operating cost compared to the complex distillation method. However, there are some factors in membrane process that should be considered for commercial waste amine separation. Temperature, process recovery and pH limitations may become disadvantage factors. Most membrane in the market is provided with pH tolerance between 3 to10, while the pH of pure amine liquid is about 10 or 11. Higher pH outside the range will only resulting in faster membrane degradation. Furthermore, if the mixture solution is too viscous or has high amine concentration, the driving force for mass transport will be reduced and therefore the filtration rate will also be affected.

Problems associated with the use of RO membrane include potential membrane degradation by chemical action, membrane fouling by particles or precipitation, drops in water flux over time due to mechanical changes (compaction effects) in the membrane and membrane-solute interactions. Membrane polymer-solute interaction consists of sorption of the hydrophobic domain, specific interactions with polymer hydrophilic sites and electrostatic interactions with membrane charged groups. This membrane-solute interaction is a major factor contributing to flux drop.

Organics containing positive charges such as amine groups is expected to have stronger interactions with negatively charged polyamide membrane. [Martin Orue, Amino Acid and Peptide Solution: Mechanism of Separation, 1998]. Although many models are able to account for flux drop by manipulating empirical parameters, amine caused the highest water flux decreases, in addition to the hydrogen bonding effects.

Further study has to be done by using Bio-treater utilizing bacteria. This could be an interesting topic to do a research. However this techniques suitable for separation of amine that in low concentration. Not very fit for very high contaminants in the amine. [Ahmad Afdzal B Md Isa, et.al., Treatment of Amine Contaminated Effluent Water via Membrane Application]

Therefore, for industrial applications and long term benefits in waste amine separation, the modification of transport and membrane system had to be studied further in order to achieve optimum recovery.

5.5. Error analysis

Changes in operating parameters will have a normal effect on membrane performance. These influences can either result in an apparent reduction of permeate flow or quality that normally affect the membrane performance.

i. Loss of Flow:

The actual permeate flow could be decreased if the feedwater temperature is decreased without changes in the feed pump pressure. As the feedwater circulate through the pumps and equipment, heat is absorbs and the temperature increased. But the feedwater temperature decreased again when it reaches the water circulator where the feedwater is cooled down. This process is repeated without changes in pump pressure. So, the actual permeate flow may be decreased. Fouling at the membrane surface and increase in conductivity is another factor to loss of flow. Since this increases the osmotic pressure that has to be overcome to permeate water through the membrane.

ii. Loss of Water Quality

During the process, an increase in permeate concentration as ppm or conductivity results in lower water quality. The changes in operating parameters that mainly cause this phenomena is sudden increased in feedwater temperature or decrease in permeate flow, which reduces the water flux and results in less permeate water to dilute the salts that have passed through the membrane. Fouling and damage to the membrane surface, such as exposure to chlorine also allows more salts to pass.

iii. Inaccurate readings

The software connected to the equipment is used to record all the parameters during the experiment. However, some of the parameters detected can only be recorded with 1 decimal place. For example, if the real value is 0.02, the monitor will only display 0.0.

So, student has to record the data manually and this promotes to higher human error. The feed analyzer is also suspected malfunction or inaccurate. This is because some of the readings obtained do not comply with the values obtained from other analyzers, which have higher accuracy. Proper and regular maintenance on this equipment should be considered.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATION

6.1. Conclusions

The separation of amines from water can be conducted through the membrane systems like Reverse Osmosis (RO) and UF membrane. However UF membrane may not be suitable for amine rejection because the pore size is larger than salt dimension. RO membrane is capable of rejecting salt and particle as small as 0.001µm whereas UF membrane can only reject contaminants from 0.01µm to 0.1µm. The membrane resistance in RO is much higher than in UF because the RO membrane has much smaller pore size and compact construction.

Between RO and UF membrane, RO gives more reliable results and the most suitable method for the separation of waste amine, which consist of MEA and DEA. From the experiment, RO membrane at 50 bar give the best salt rejection. DEA molecule is rejected 100% while MEA molecule 93.7%. RO at 20 bar, DEA molecule rejected also 100% while MEA rejected is 90.6%. At 8.5 bar, MEA rejected is 75.7%. None DEA molecule is detected by GC in the sample.

From the experiment also concluded that UF membrane is not suitable for the separation. There is no salt rejection. Permeate concentration is found to be higher than the feed concentration. The factors affecting membrane performance are feedwater pressure, concentration, temperature, pH, concentration polarization and the membrane recovery. [FilmTec Corporation, Factors Affecting RO Membrane Performance]

In RO, salt rejection increases with increasing feedwater pressure until a certain limit. The best pressure applied for the best salt rejection is not too high or too low. From figure 2.3.1(a), as feedwater pressure increased, this salt passage is increasing as the mixture is pushed through the membrane at a faster rate than salt can be transported. However there is an upper limit to the amount of salt that can be excluded via increasing feedwater pressure. Above a certain pressure level, salt rejection no longer increases and some salt flow remains coupled with water flowing through the membrane.

Using Bio-treater utilizing as amine separation method is also an interesting subjects. However, the extent use of the process is somewhat limited and cannot be utilized in the case of very high contaminants in the amine. [Ahmad Afdzal B Md Isa, et al, Treatment of Amine Contaminated Effluent Water via Membrane Application].

The most successful separation so far is distillation. However, amines tendency to degrade and have close boiling point with some degradation compounds. [A novel process for Diethanolamine Recovery from Partially Degrade Solutions, 1999].

Crystallization also can be use as amine separation method. However In crystallization method requires a high heat. Also numerous disadvantages of solid transport over fluid transport, as well as the difficulties in obtaining a high purity separation. [MLA Process Works, Inc., 2000].

In liquid-liquid extraction method, due to the high boiling point of ethanolamines, liquid-liquid extraction was considered as an option in order to avoid high temperatures and heat costs. The extraction is begun by dissolving the mixture in a suitable organic solvent, which has low solubility in water like diethyl ether. However the solubility characteristics of the different ethanolamines are too similar to make this a feasible and advantageous process. [MLA Process Works, Inc., 2000].

Overall, the separation of waste amine using membrane system could be implemented but with several modification of transport and parameters that had to be studied further in order to achieve optimum results in the application. This RO membrane is feasible to use in industry because the waste amine that had been used can be recirculate easily based on the best pressure applied, temperature, feedwater salt concentration, permeate recovery, and system pH. No misspend or waste of money but more advantages and benefits. Also the feasibility in operating the RO membrane. Even fresh Amine is expensive and hard to get, cost around RM 2760/drum. [Shahrizal B Hambalee, Amine Rejuvenation] Although the RO membrane quite expensive to get but it is very efficient in recycle the waste amine. Maintenances have to be done on the filter change out in order to get a quality permeate.

Whatever method of separation that been used and chose by the company, the main objectives and the most important things are to optimize the costs, space, safety, production, and control of the products. More Research in comparing this method of separation will give a very big benefit. Industry can choose the best method based on their background company. What they need and how they want to satisfy in spent their money.

6.2. Recommendations

Overall, the separation of waste amine using membrane system could be implemented but with several modification of parameters that had to be studied further in order to achieve optimum results in the application. While the results of this initial stage of research were encouraging, expansion of the research program should be carried out. Few improvements are also recommended for this project for better observation and evaluations.

1.Install feed heater to the equipment

Currently, the RO Pilot system used to conduct the experiments has no temperature regulator or heater that can increase the feedwater temperature. The water regulator is used only to maintain the feedwater temperature at 25^{0}C. As discussed in the theory, feedwater temperature is also a contributing factor for membrane separation. Theoretically, an increased in operating temperature will resulting in lower salt rejection. By varying the temperature, comparisons could be made and larger scope of studies could be done. Therefore, installing a new heater to the equipment is highly recommended. [FilmTec Corporation, Reverse Osmosis]

2. Effect of pH

For future research, factor of pH should also be investigated because it is one of the important factors for molecule permeation through the membrane. At higher pH of the solution, where the molecules are mostly ionized, higher salt rejection will be obtained. So for this purpose, accurate pH indicators are also required to monitor the pH of the solution. [FilmTec Corporation, Reverse Osmosis]

3. Comparison of different membranes

Membrane material also contributes to separation performance. Different materials will require different parameter controls and thus show different results for the separation. For example, the membrane polymer-solute interactions are different in different type of polymer and solute. Expansion studies on this matter should be conducted in the future. Therefore, comparison could be made on justifying the most suitable membrane material for waste amine separation through membrane systems.

4. Integrated Membrane System.

From the studies in this report show that with the right combination of RO and UF membrane, significant amount of amine can be separated. This is referred as in integrated membrane system, where the system designed with UF membrane system in front of RO treatment. This is because UF system is specifically designed to effectively remove foulants and to be cleaned but not very efficient to remove salt. RO systems are designed to remove salt, not foulants and are not specifically designed to be fouled and cleaned frequently. UF is use as pretreatment to RO. [Wayne T.Bates, Rocco Cuozzo, Integrated Membrane System]

CHAPTER 7: REFERENCES

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CHAPTER 8: APPENDICES

Sample Calculation: -

Transmembrane Pressure, $\Delta P = P_{feed} - P_{permeate}$

$= 8.50\text{bar} - 0.03\text{bar}$

$= 8.47\text{bar}$

Salt Rejection (%) = [(Feed – Permeate) / Feed] X 100%

= [(4922.028 – 460.214) / 4922.028] X 100%

= = 90.6%

Prepare standard solution of DEA:-

Given that density, p = 1092g/l

MW = 105.14g/moles

$M_1V_1 = M_2V_2$ …….Need to find the value of V_1 in order to make dilution.

Where,

M_1 = Pure DEA Molar Concentration

V_1 = Volume needed to dilute

M_2 = Desired Molar Concentration

V_2 = Volume of Volumetric flask

Mass = pV

= 1092 g/l X 1l

= 1092 g

Moles = Mass / MW

= 1092 / 105.14

= 10.386moles

Moles = M_1V

10.386 = M_1 1l

So

M_1 = 10.386 Moles / l

= 10.386 Moles / l **X** 105.14g / Moles

= 1091 g / l

= 1091 **X** 10^3 mg / l

=1091 **X** 10^3 ppm

Therefore,

$M_1V_1 = M_2V_2$

[1091 **X** 10^3 mg / l] **X** V_1 = (200ppm)(100ml)

V_1 = 0.018ml

In order to get 200 ppm, V_1 = 0.018ml is dilute in 100ml volumetric flask with distilled water.

Table 2.1.1: Properties of Monoethanolamine

Nomenclature	Monoethanolamine	
Synonyms	2-Aminoethanol; 2-Hydroxyethylamine	
Molecular formula	C_2H_7NO	
CAS No.	[141-43-5]	
Chemical Structure	$H_2N — CH_2 — CH_2 — OH$	
Molecular Weight	61.08	
Physical Properties	Appearance	Clear hygroscopic liquid
	Colour	25 max
	Solubility in water	Soluble
	Freezing point, °C	10.3
	Boiling point, °C	172
	Boiling range, °C	165 – 176
	Flash point (PMCC), °C	93
	Auto ignition(Temp, °C)	420
	LEL (Vol%)	5
	UEL (Vol%)	17
	SG @ 20/20 °C	1.015 – 1.020
Packing	200 kgs HMHDPE drums, also supplied in road tankers.	
Transport Classification	IMDG Class	8
	U.N No	2491
	Packing Group	III
	Hazard Label	Corrosive

Table 2.1.2: Properties of Diethanolamine

Nomenclature	Diethanolamine	
Synonyms	2,2'-iminobisethanol, 2,2'-iminodiethanol, diethylolamine	
Molecular formula	$(HOCH_2CH_2)_2 NH$	
CAS No.	111 – 42 - 2	
Physical Properties	Appearance	Solid or viscous liquid with an amine odour
	Melting point, °C	28
	Boiling point, °C	268
	Vapour Density	3.6 (Air = 1)
	Density (g cm^{-3})	1.09
	Flash point, °C	169 (closed up)
Stability	Stable. Incompatible with CO2, strong acids, strong oxidizing agents. Deliquescent	
Toxicology	Harmful if swallowed or inhaled. Severe skin, eye and respiratory irritant.	

Sample Information

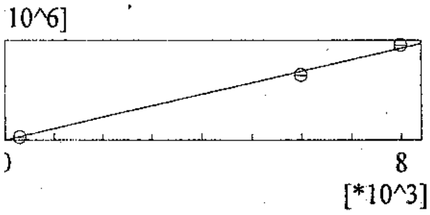
alysis Date & Time : 10/3/2005 3:41:04 PM
er Name : Admin
al# : 1
nple Name : 50,feed
nple ID :
nple Type : Unknown
ection Volume : 1
ılti Injection# : 1
lution Factor : 1.000
TD Amount : [1]=1.000
nple Amount : 1.000
vel# : 1
ta Name : C:\GCsolution\Data\FYP\july2005\awg 001.gcd
seline Data Name :
thod Name : C:\GCsolution\Data\FYP\july2005\amine.gcm
port Name :
tch File Name : C:\GCsolution\Data\FYP\july2005\awg 031005.gcb

Calibration Curve - Analytical Line 1 - Channel 1

)#:1 Name:MEA

x)=211.245*x+0.0
=0.9975936 R^2=0.995193
eanRF:194.3487 RFSD:26.50892 RFRSD:13.63988
urveType:Linear
roThrough:Weight on Origin
eightedRegression:None

xternal Standard

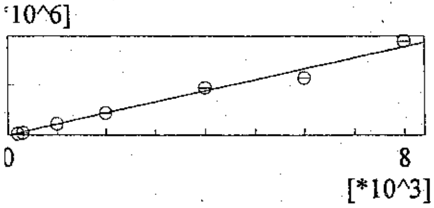


No.	Conc.	Area
2	300.000	49708
7	6000.000	1196151
8	8000.000	1743962

)#:2 Name:DEA

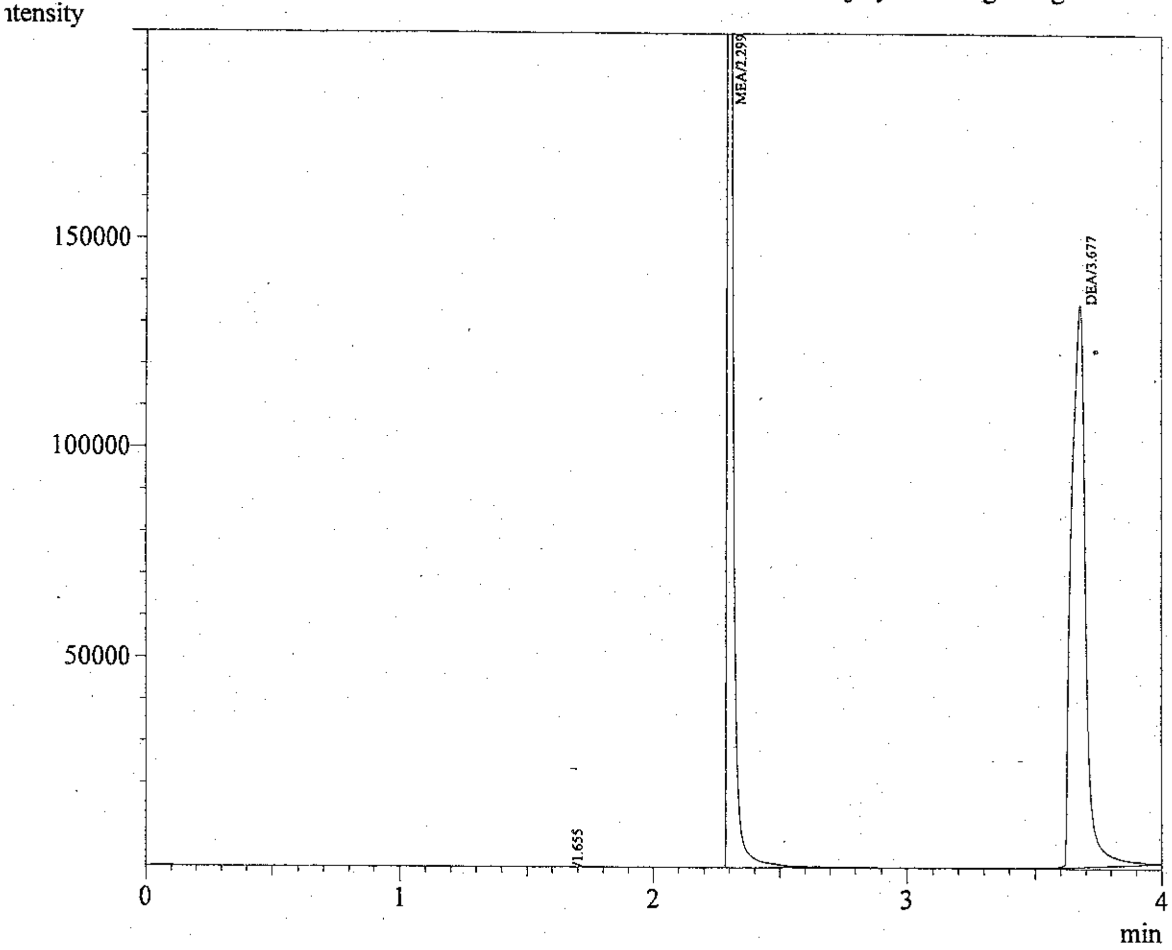
x)=220.093*x+0.0
=0.9911153 R^2=0.9823095
leanRF:192.4193 RFSD:47.65597 RFRSD:24.76674
urveType:Linear
eroThrough:Weight on Origin
/eightedRegression:None

xternal Standard



No.	Conc.	Area
1	200.000	24217
2	300.000	39517
4	1000.000	218321
5	2000.000	434524
6	4000.000	940713
7	6000.000	1136282
8	8000.000	1871907

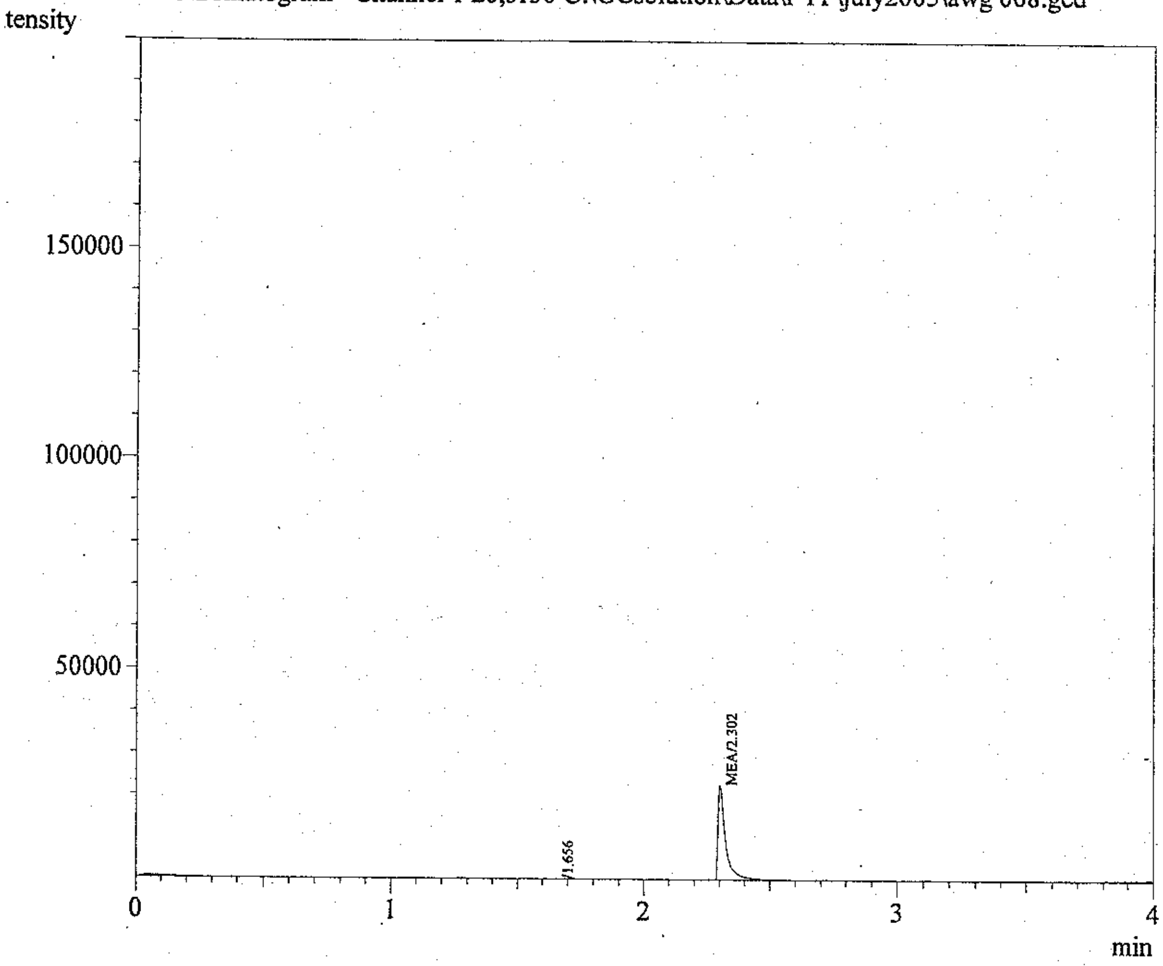
Chromatogram - Channel 1 20,feed C:\GCsolution\Data\FYP\july2005\awg 005.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.655	1788	618	0.000			
2	2.299	542577	397859	2568.471	ppm		MEA
3	3.677	526504	134415	2392.190	ppm		DEA
Total		1070869	532892				

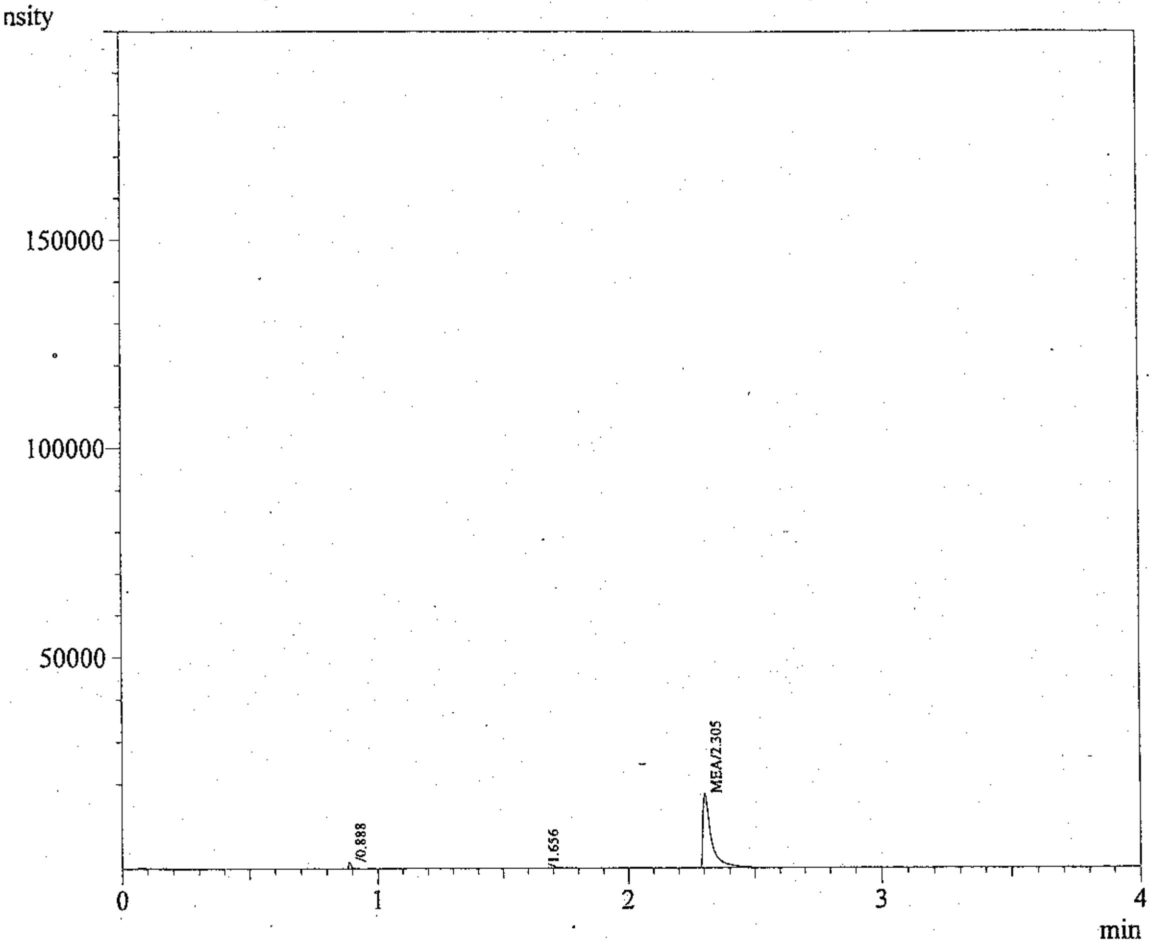
Chromatogram - Channel 1 20,s130 C:\GCsolution\Data\FYP\july2005\awg 008.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.656	1260	530	0.000			
2	2.302	50090	23054	237.118	ppm		MEA
Total		51350	23584				

Chromatogram - Channel 1 20,s85 C:\GCsolution\Data\FYP\july2005\awg 007.gcd

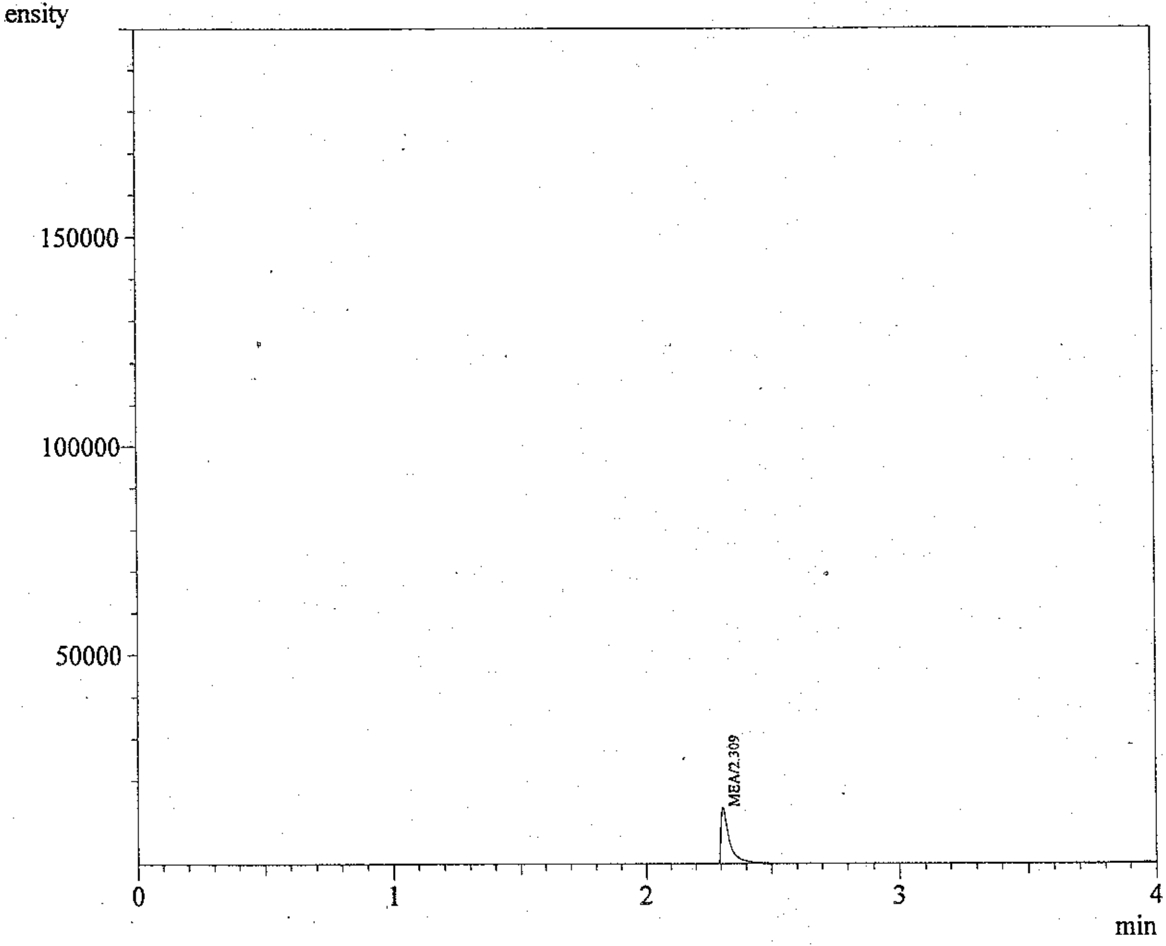


Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	0.888	2463	2446	0.000			
2	1.656	1216	529	0.000			
3	2.305	41908	17776	198.386	ppm		MEA
Total		45587	20750				

✓

Chromatogram - Channel 1 20,s44 C:\GCsolution\Data\FYP\july2005\awg 006.gcd

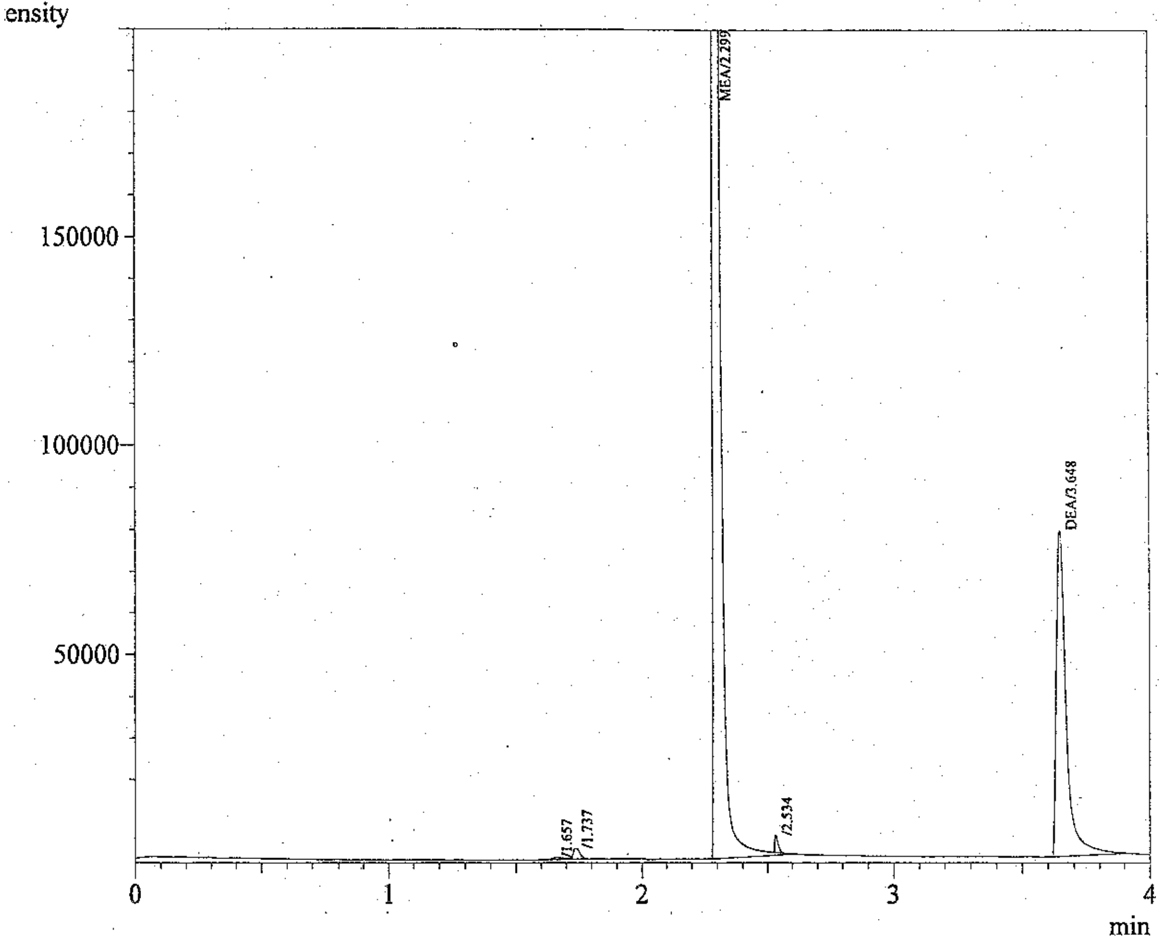


Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.309	34245	13876	162.112	ppm		MEA
Total		34245	13876				

✓

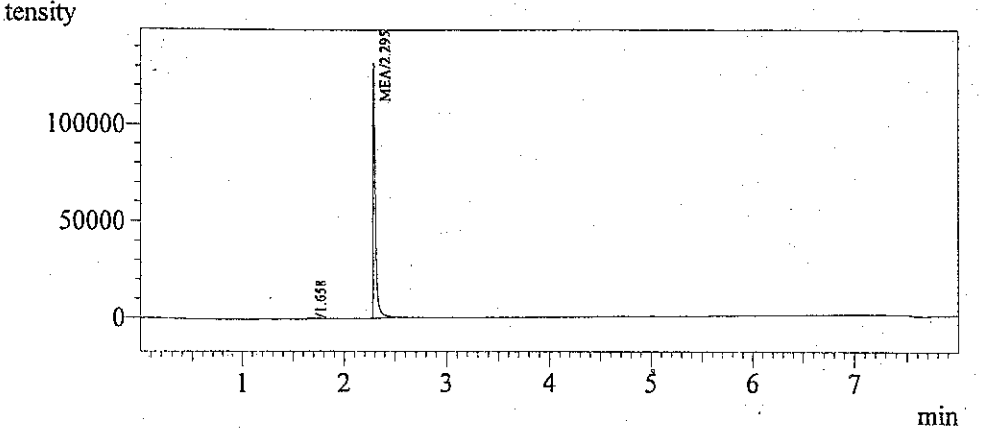
Chromatogram - Channel 1 50,feed C:\GCsolution\Data\FYP\july2005\awg 001.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.657	1834	508	0.000			
2	1.737	4569	2605	0.000		V	
3	2.299	1039754	757360	4922.028	ppm	S	MEA
4	2.534	3946	4142	0.000		T	
5	3.648	208498	77841	947.319	ppm		DEA
Total		1258602	842456				

Chromatogram - Channel 1 50,s45 C:\GCsolution\Data\FYP\july2005\awg 002.gcd

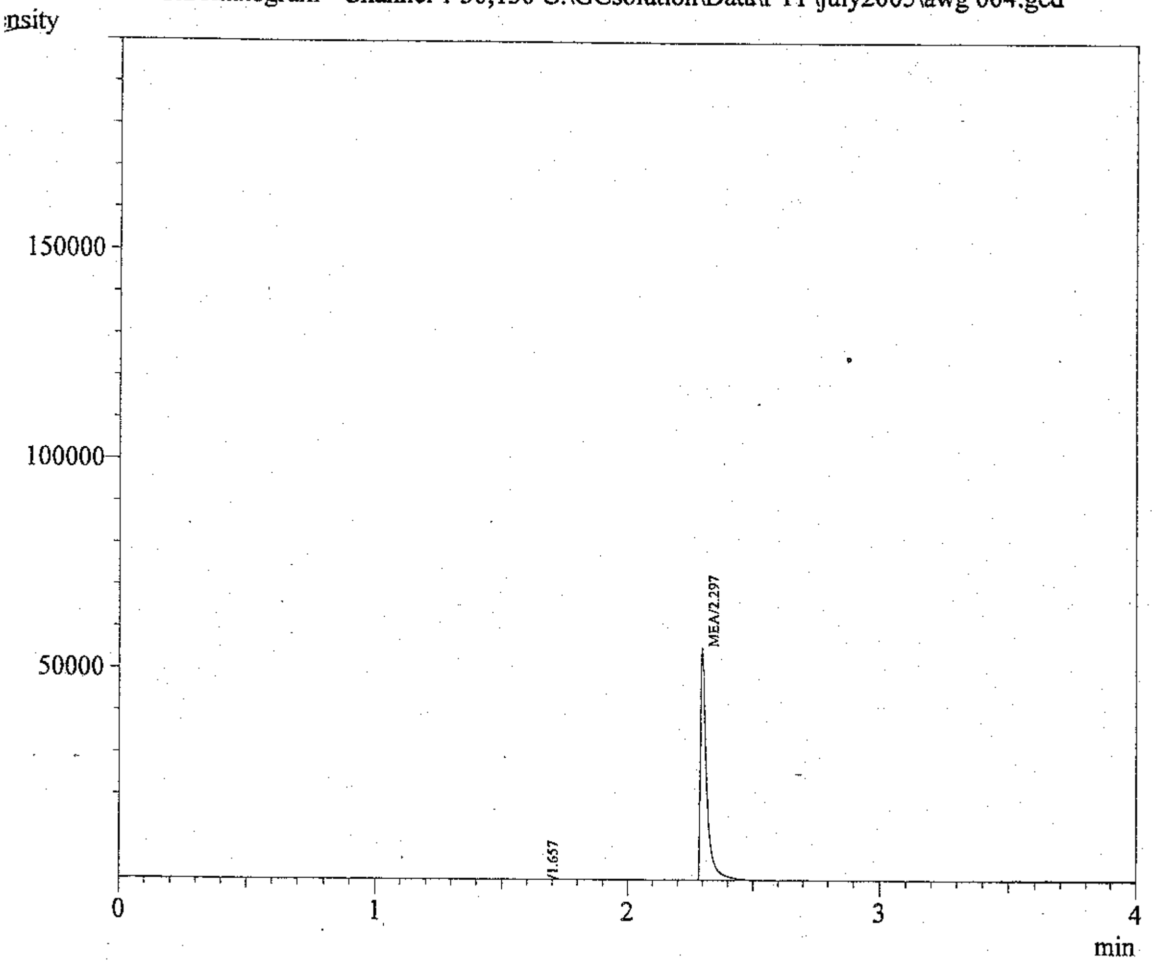


Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.658	2589	607	0.000			
2	2.295	204140	131318	966.365	ppm		MEA
Total		206728	131926				

✓

Chromatogram - Channel 1 50,130 C:\GCsolution\Data\FYP\july2005\awg 004.gcd

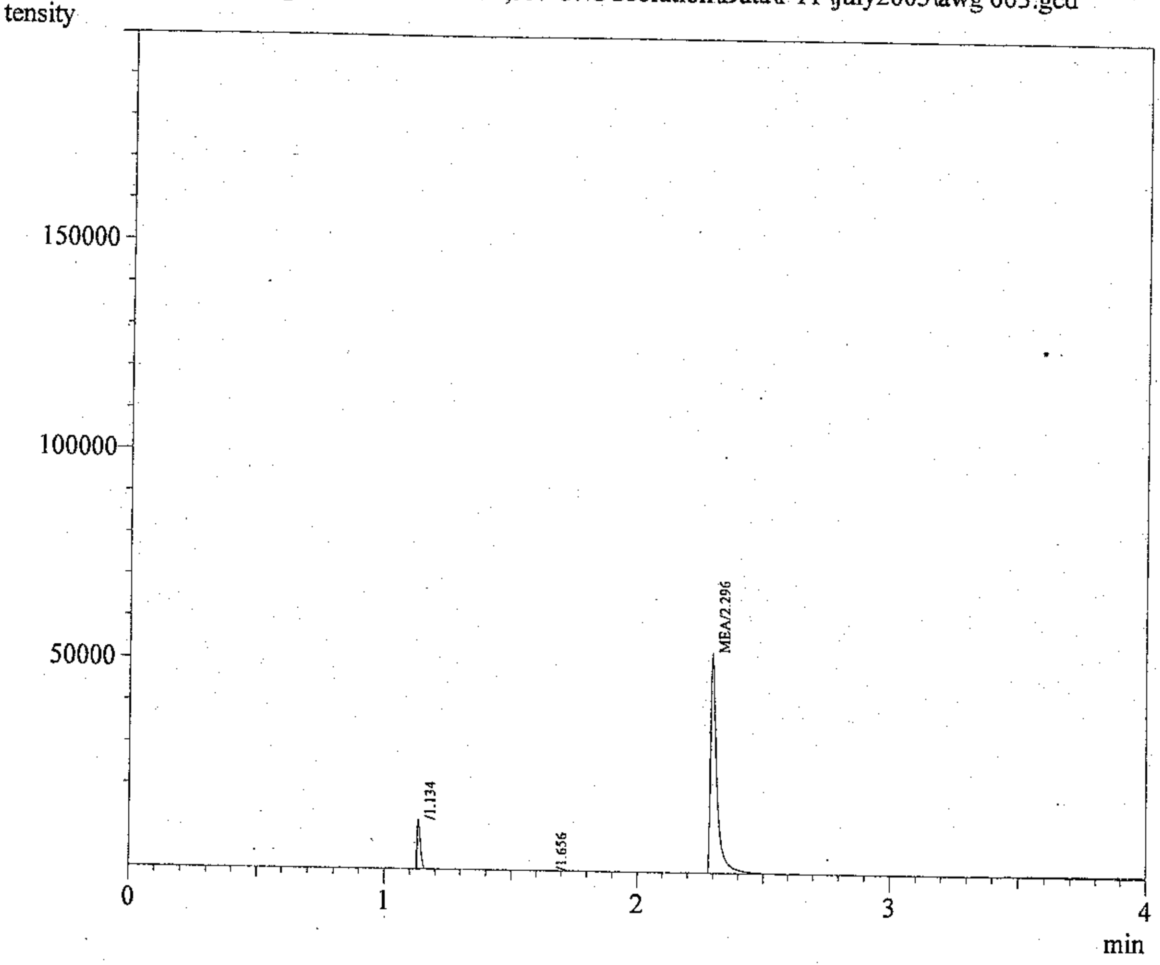


Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.657	1670	586	0.000			
2	2.297	101460	55196	480.293	ppm		MEA
Total		103130	55783				

✓

Chromatogram - Channel 1 50,s87 C:\GCsolution\Data\FYP\july2005\awg 003.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.134	12208	12486	0.000			
2	1.656	2313	553	0.000			
3	2.296	97218	53039	460.214	ppm		MEA
Total		111738	66078				

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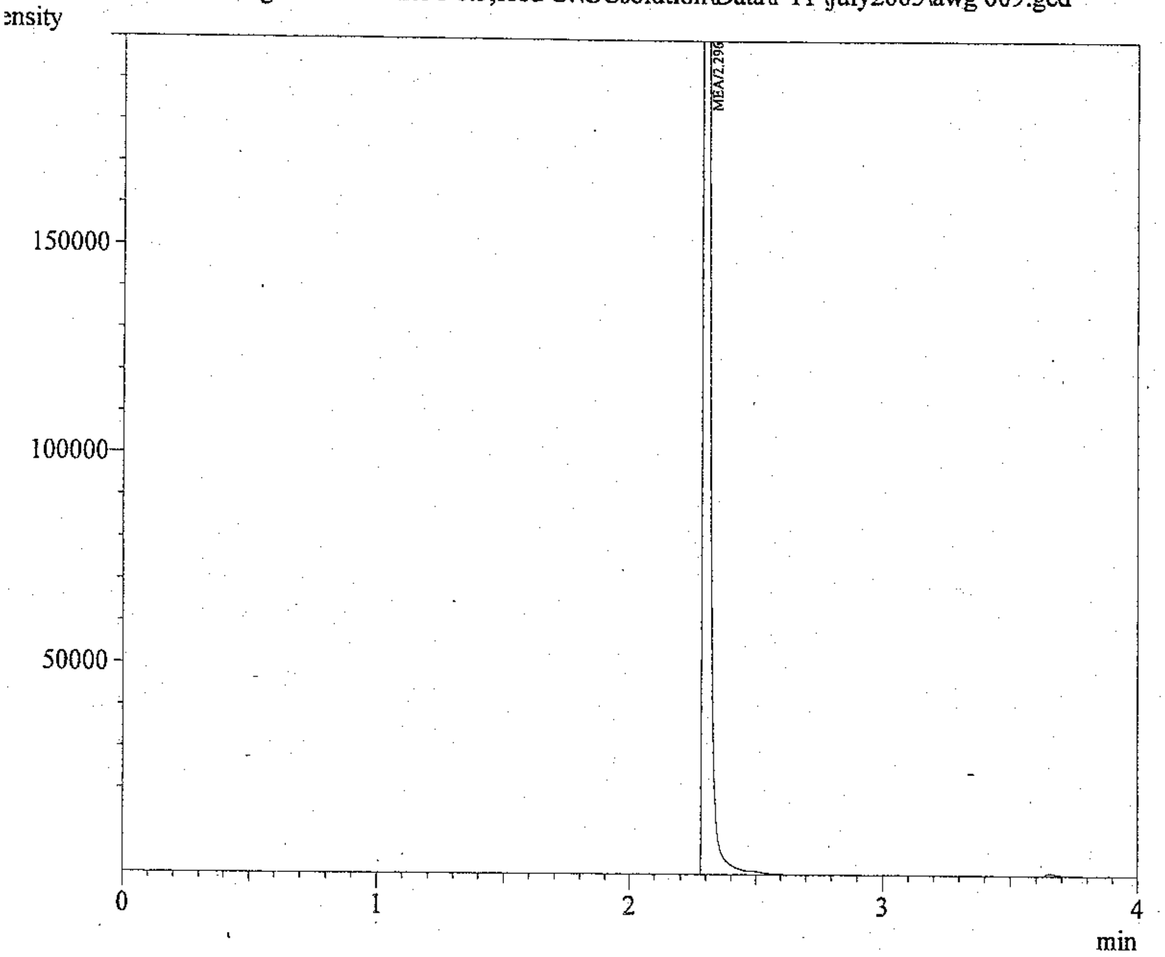
Chromatogram - Channel 1 8.5,feed C:\GCsolution\Data\FYP\july2005\awg 009.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.296	927850	683085	4392.293	ppm	S	MEA
2	6.790	24083	24626	0.000			
Total		951933	707710				

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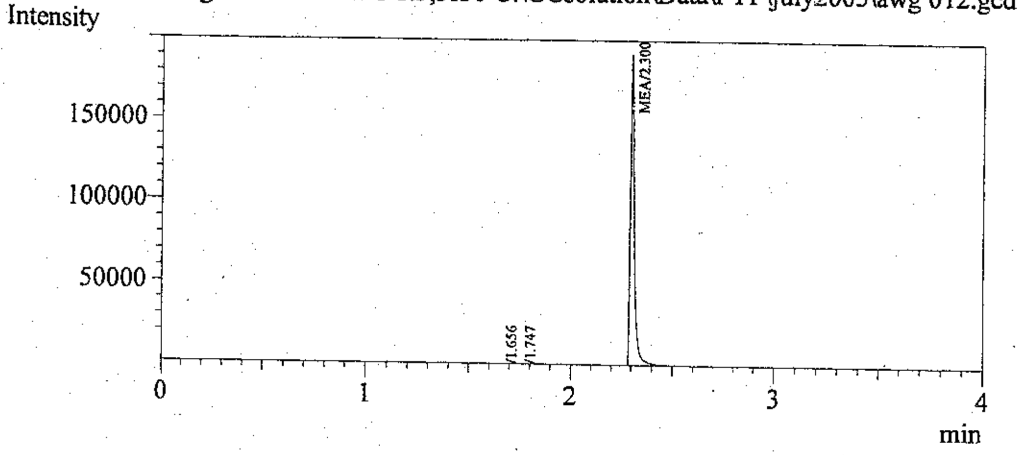
Chromatogram - Channel 1 8.5,s130 C:\GCsolution\Data\FYP\july2005\awg 012.gcd

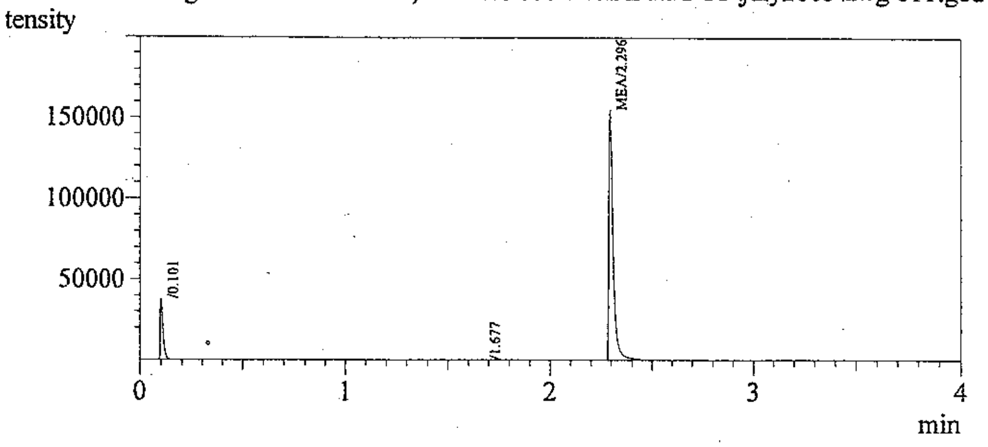


Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.656	1673	582	0.000			
2	1.747	1556	992	0.000		V	
3	2.300	277392	191444	1313.130	ppm		MEA
Total		280620	193018				

Fisher

Chromatogram - Channel 1 8.5,s88 C:\GCsolution\Data\FYP\july2005\awg 011.gcd

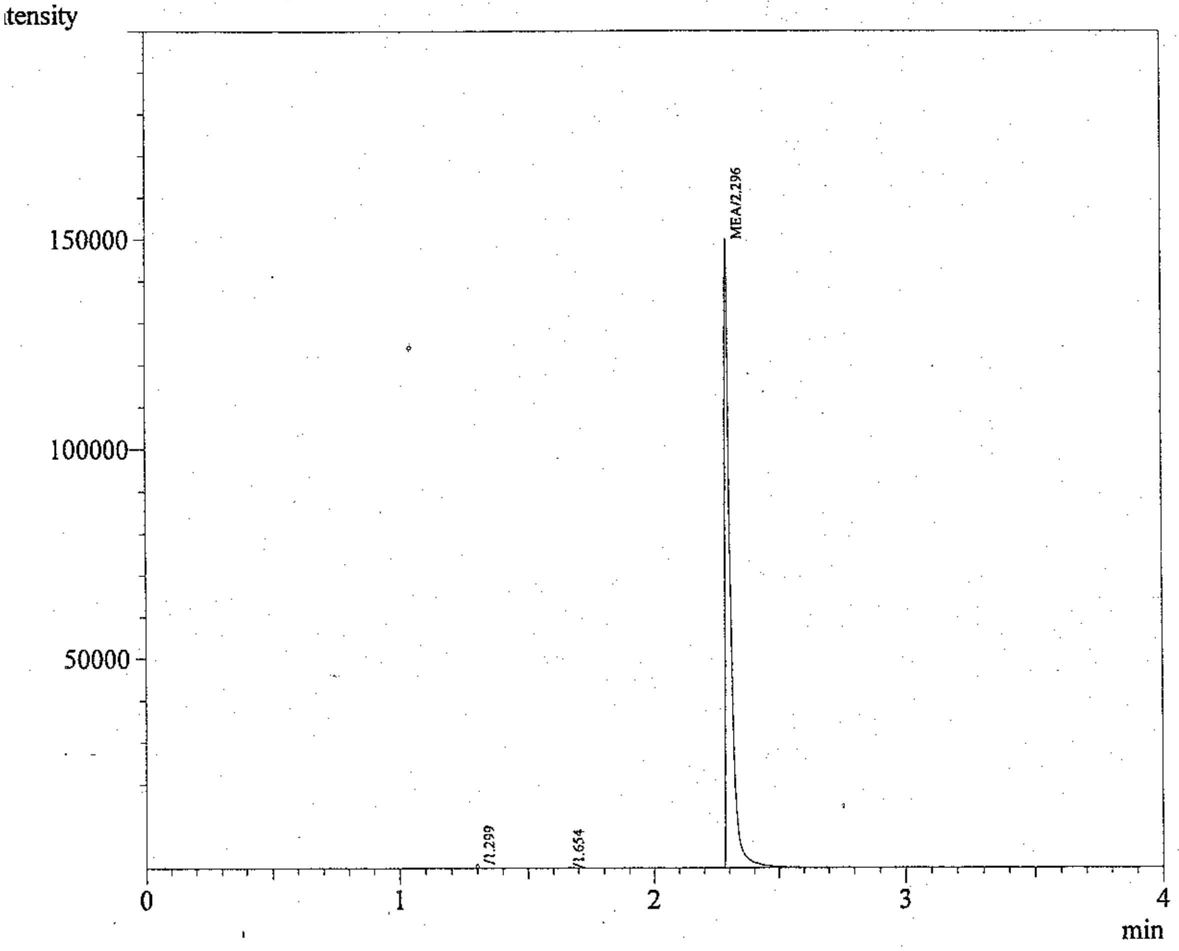


Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	0.101	37669	36609	0.000			
2	1.677	1900	536	0.000			
3	2.296	231137	154709	1094.164	ppm		MEA
Total		270706	191854				

✓

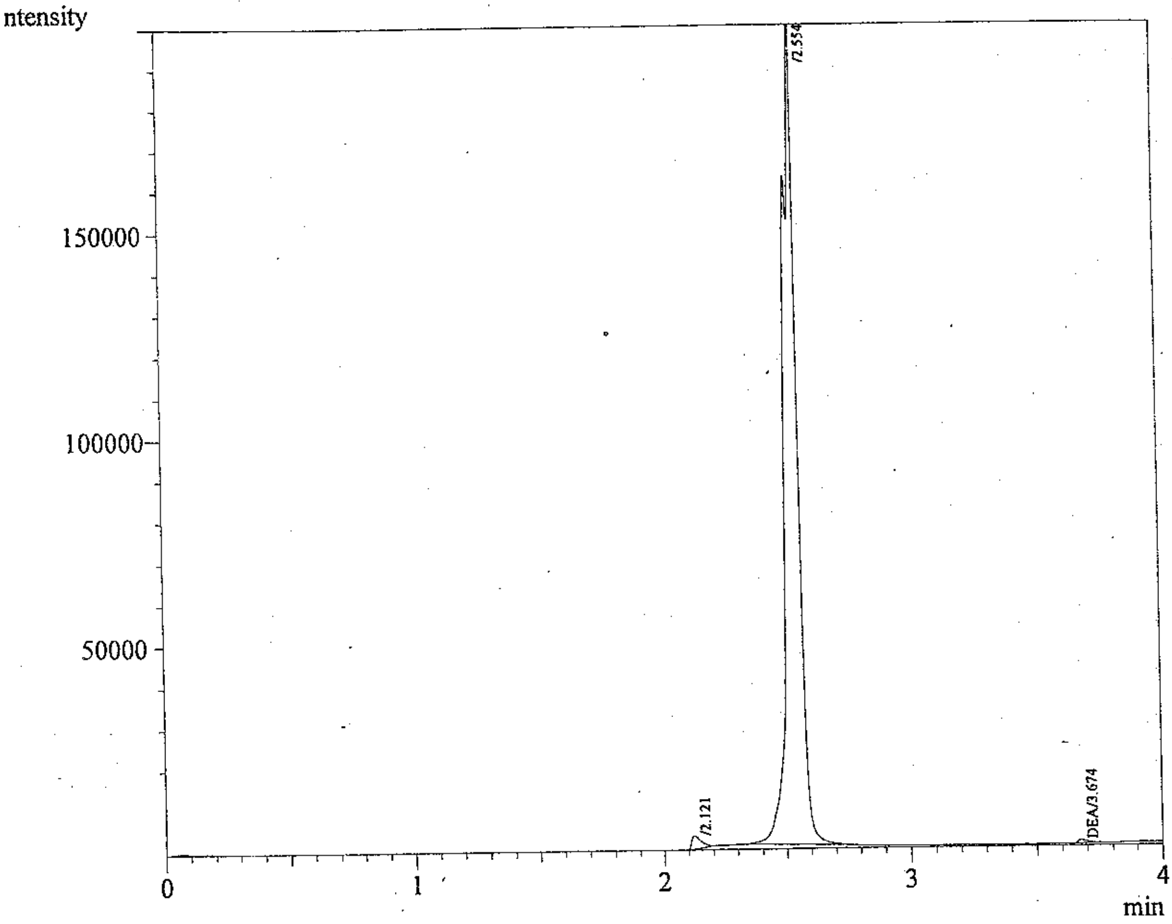
Chromatogram - Channel 1 8.5,s35 C:\GCsolution\Data\FYP\july2005\awg 010.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	1.299	2020	2001	0.000			
2	1.654	1964	560	0.000			
3	2.296	225586	149488	1067.886	ppm		MEA
Total		229569	152049				

Chromatogram - Channel 1 4,feed C:\GCsolution\Data\FYP\july2005\awg 023.gcd

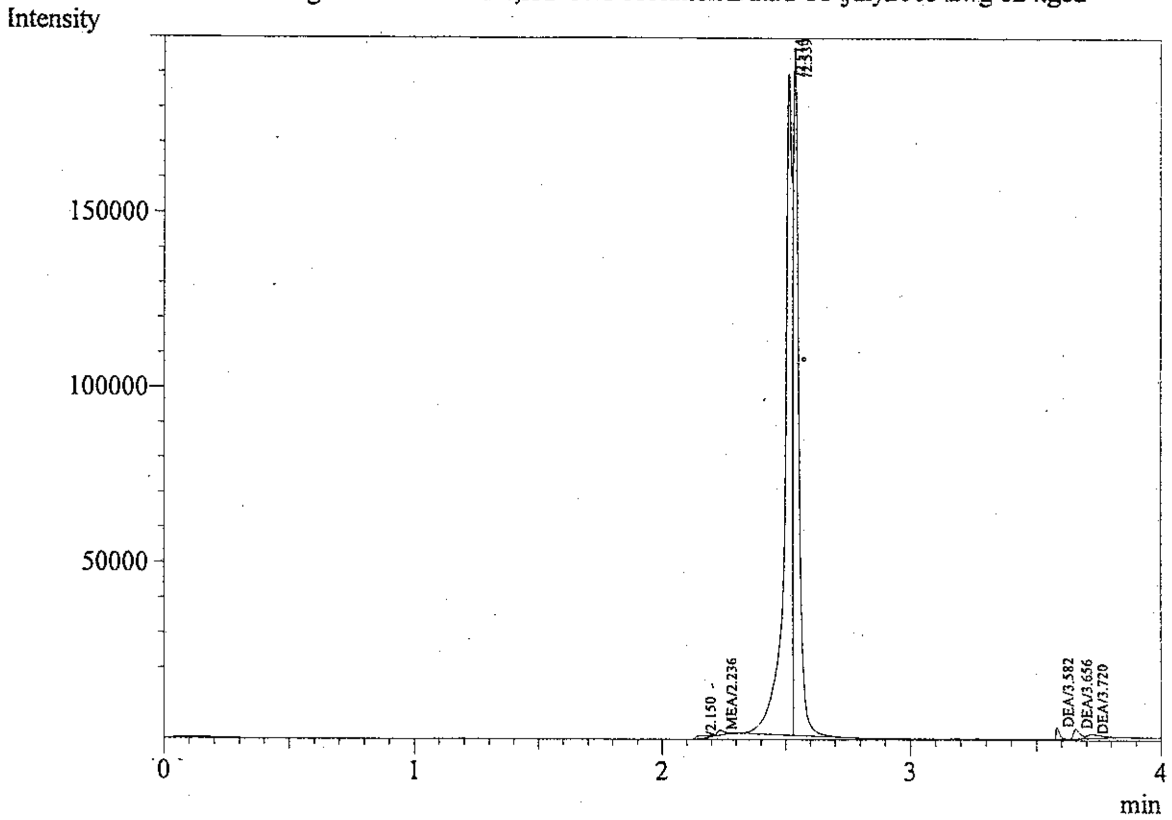


Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.121	9051	3365	0.000			
2	2.554	712868	202495	0.000			
3	3.674	2560	921	11.632	ppm		DEA
4	7.857	10639	10861	0.000			
Total		735118	217643				

[illegible]
Sample [illegible]

Chromatogram - Channel 1 4,s32 C:\GCsolution\Data\FYP\july2005\awg 024.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.150	3091	915	0.000			
2	2.236	2758	1423	13.056	ppm	V	MEA
3	2.514	404695	186668	0.000			
4	2.539	301447	195167	0.000		V	
5	3.582	3171	3258	14.407	ppm		DEA
6	3.656	5051	2679	22.947	ppm		DEA
7	3.720	4863	1164	22.095	ppm	V	DEA
Total		725074	391274				

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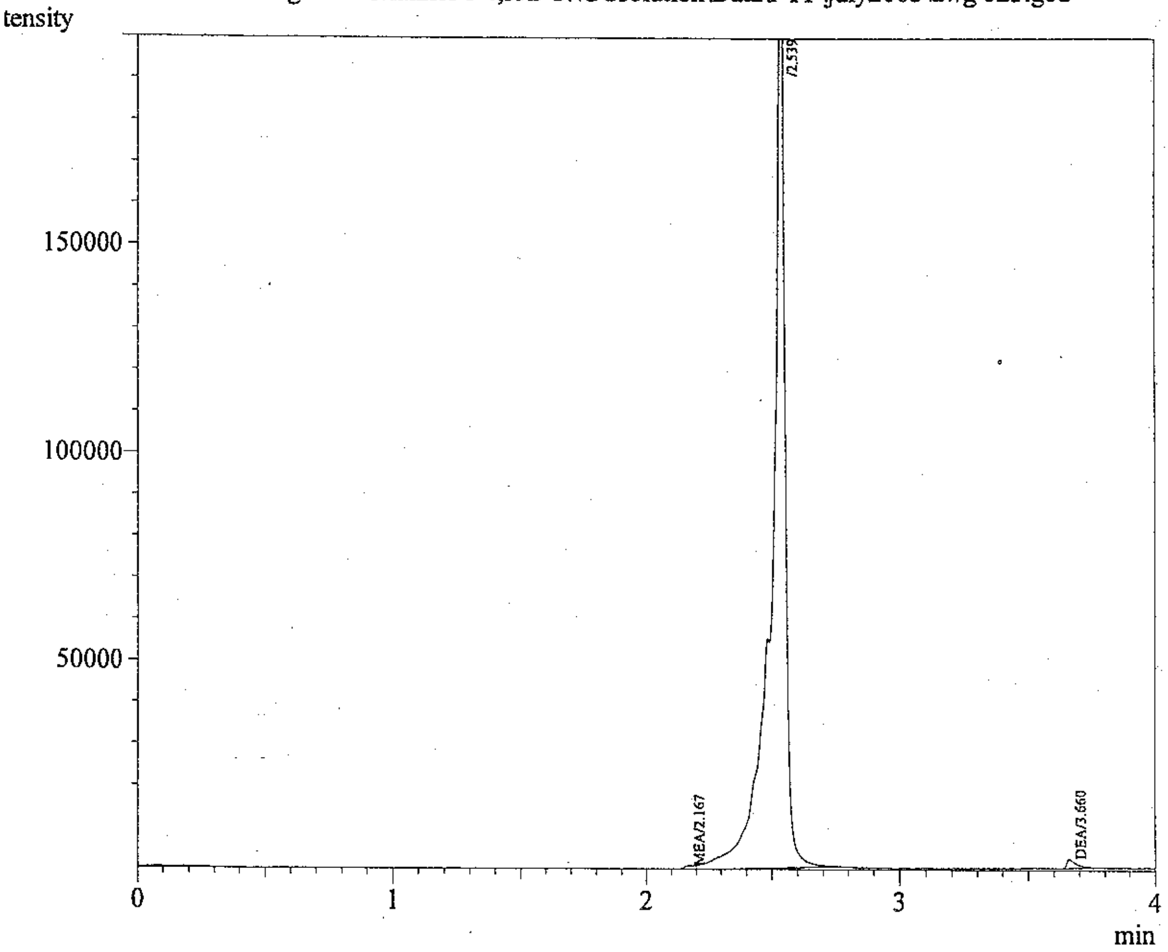
[illegible]

UTP-Kir

Chromatogram - Channel 1 4,s52 C:\GCsolution\Data\FYP\july2005\awg 025.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.167	2976	964	14.088	ppm		MEA
2	2.539	806956	252343	0.000		V	
3	3.660	5646	2122	25.651	ppm		DEA
4	4.106	1429	1494	0.000			
Total		817006	256922				

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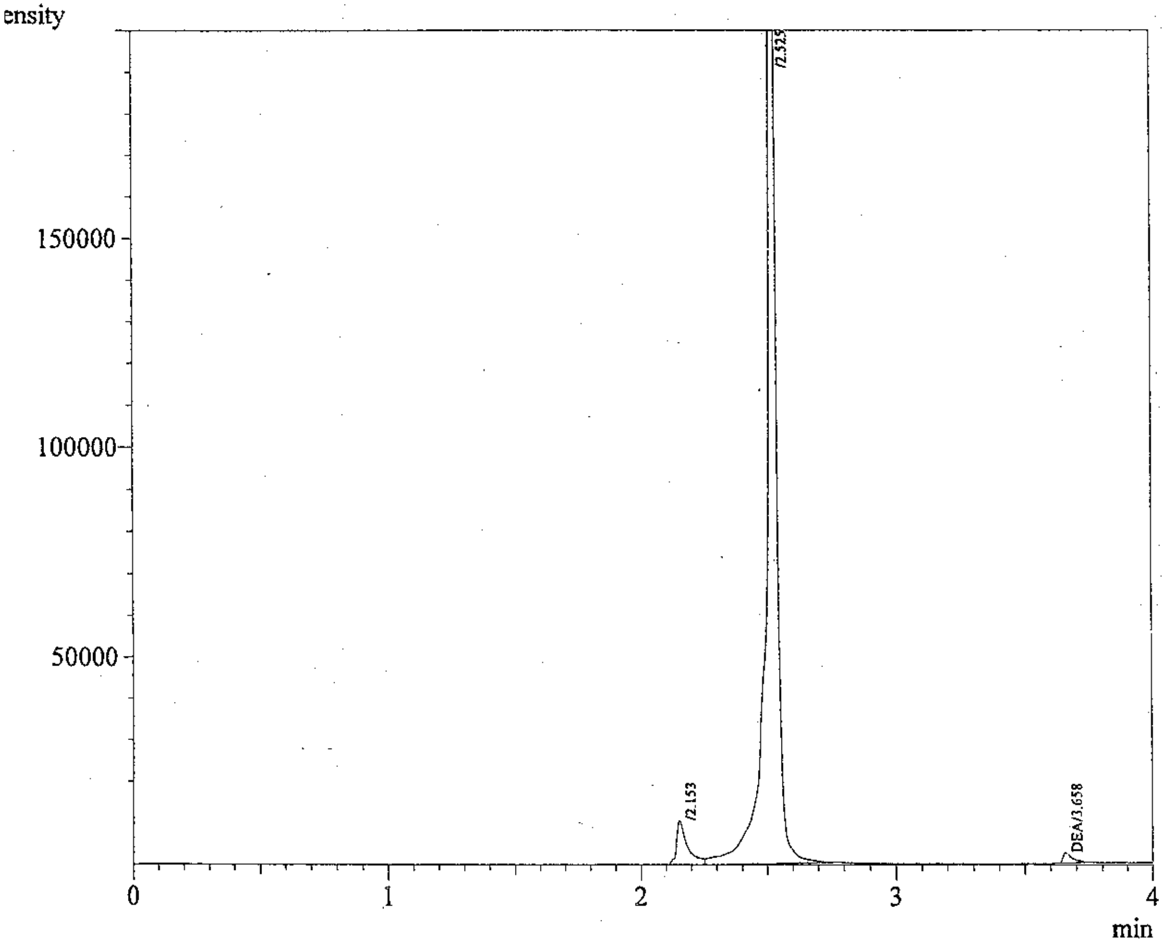
Chromatogram - Channel 1 4,s130 C:\GCsolution\Data\FYP\july2005\awg 028.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.153	34413	10951	0.000			
2	2.525	775096	373836	0.000		V	
3	3.658	6191	2475	28.128	ppm		DEA
Total		815700	387262				

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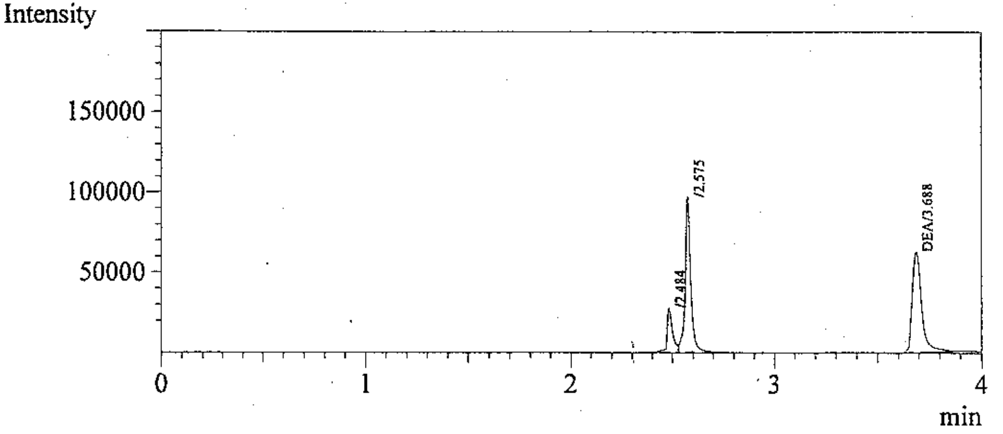
Chromatogram - Channel 1 3.43,feed C:\GCsolution\Data\FYP\july2005\awg 017.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.484	54304	27404	0.000			
2	2.575	183862	96501	0.000		V	
3	3.688	202443	62373	919.807	ppm		DEA
4	5.073	8495	3744	0.000			
5	5.198	2041	1001	0.000		V	
Total		451145	191022				

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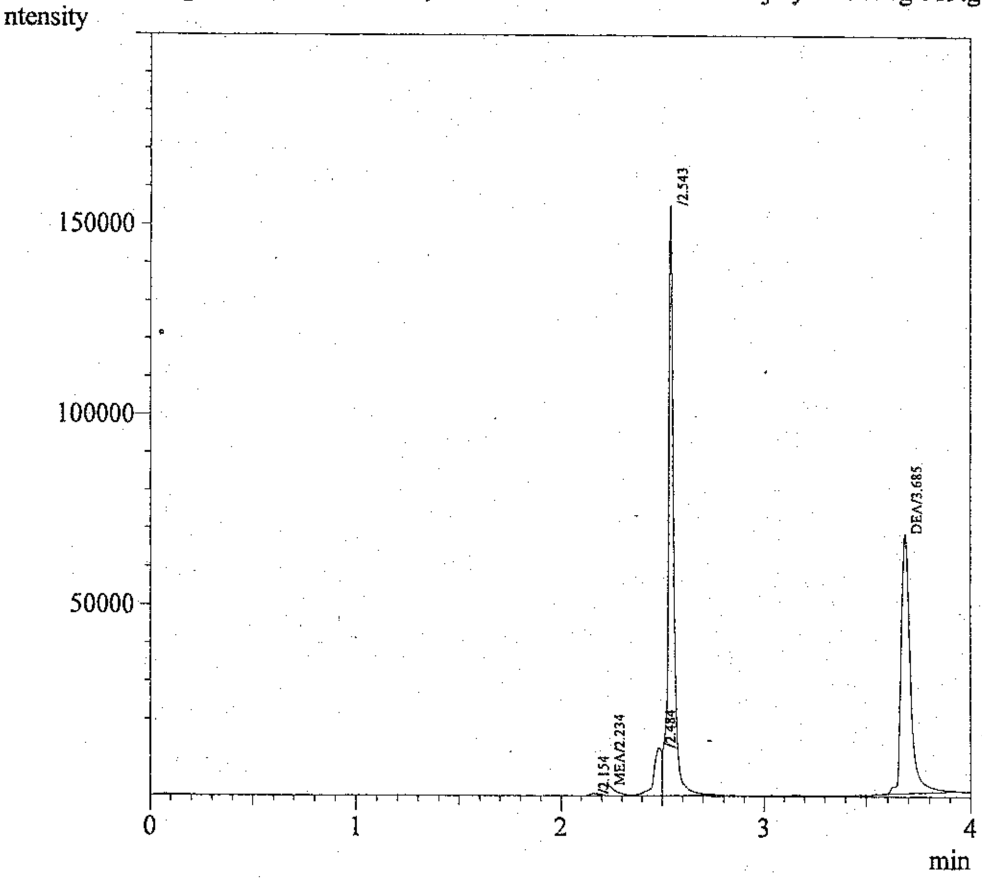
Chromatogram - Channel 1 3.43,t405 C:\GCsolution\Data\FYP\july2005\awg 019.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.154	3299	852	0.000			
2	2.234	10293	2909	48.725	ppm	V	MEA
3	2.484	35528	12679	0.000		V	
4	2.543	281619	153883	0.000		V	
5	3.685	211128	67825	959.269	ppm		DEA
6	5.070	7418	3414	0.000			
Total		549286	241562				

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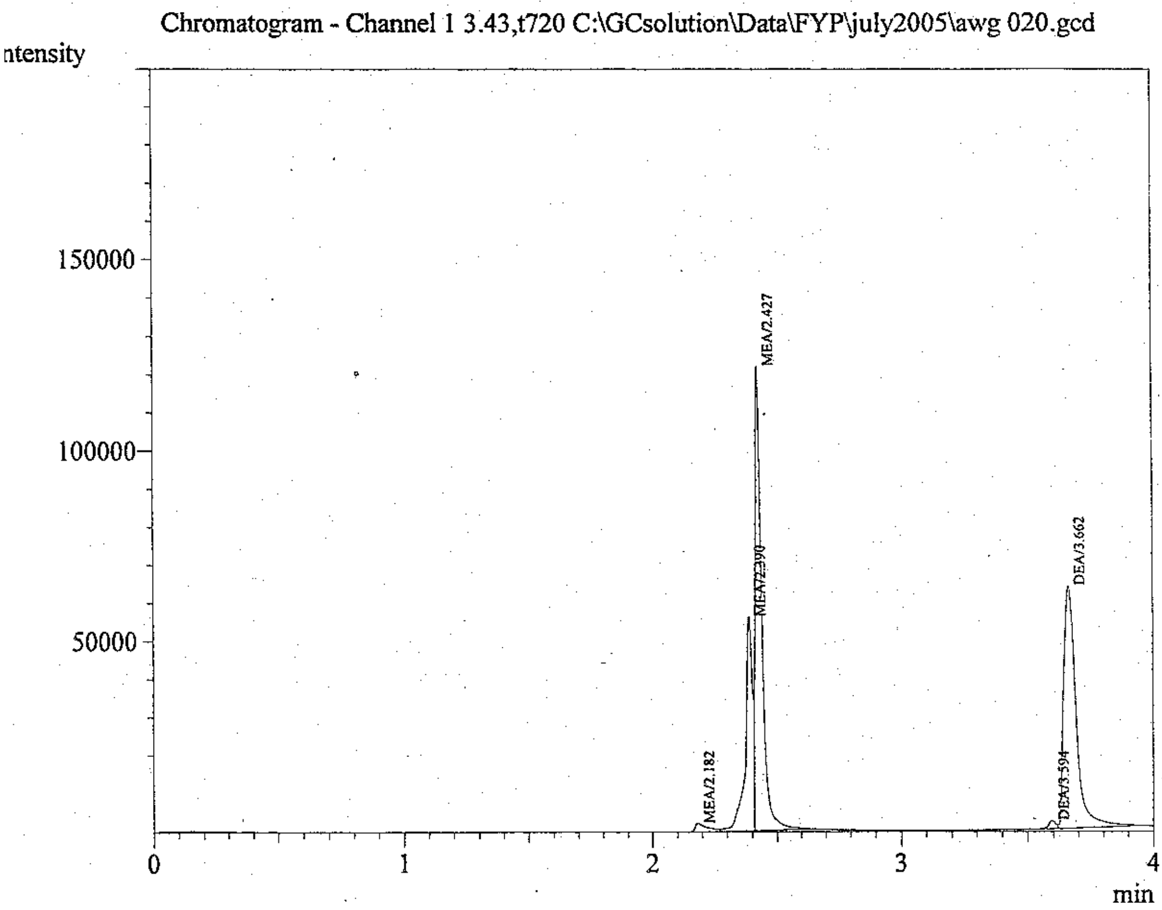

Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.182	8102	2286	38.352	ppm		MEA
2	2.390	116634	55591	552.128	ppm	V	MEA
3	2.427	215554	120206	1020.398	ppm	V	MEA
4	3.594	4044	2220	18.376	ppm		DEA
5	3.662	218674	63601	993.552	ppm	V	DEA
6	5.069	8815	4013	0.000			
7	5.195	1215	568	0.000		V	
Total		573038	248485				

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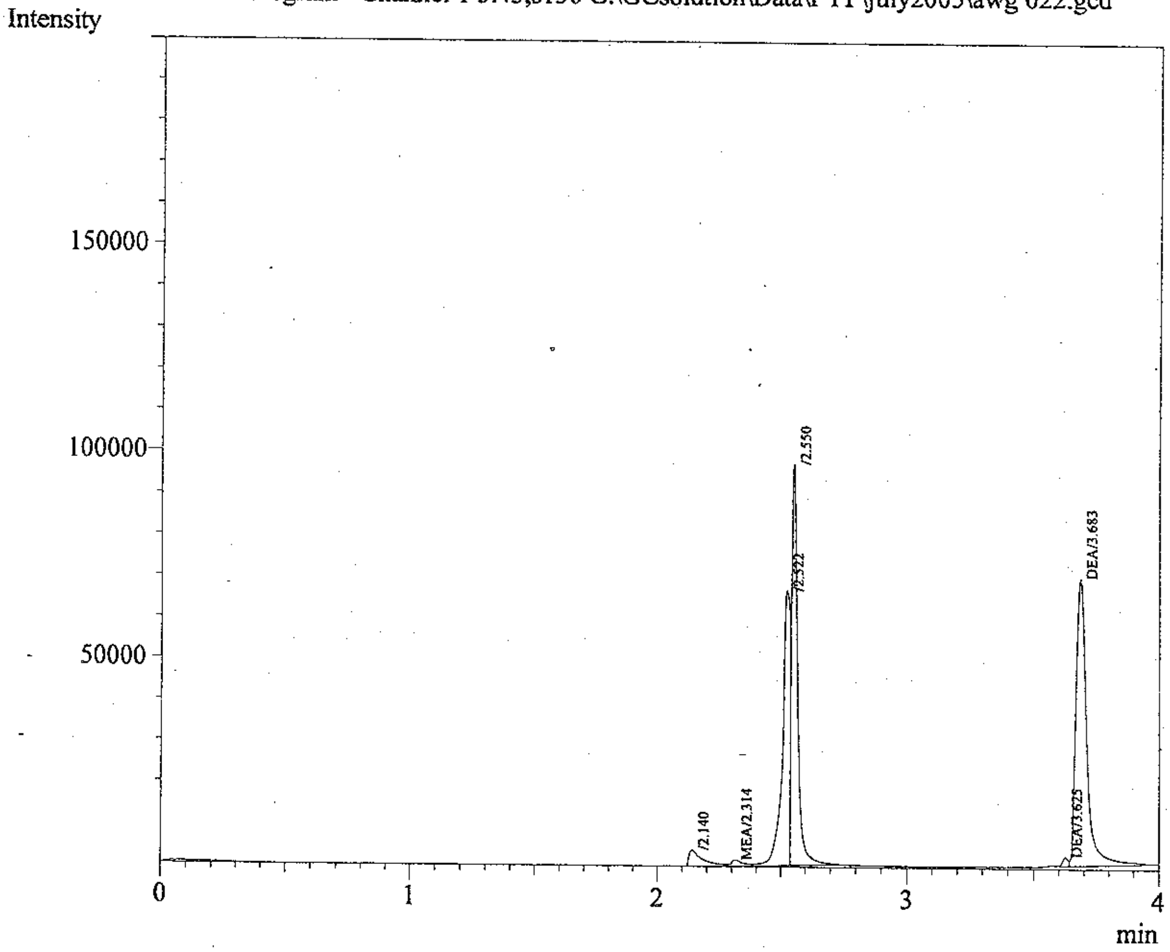
Chromatogram - Channel 1 3.43,s130 C:\GCsolution\Data\FYP\july2005\awg 022.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.140	15061	4025	0.000			
2	2.314	5168	1472	24.464	ppm	V	MEA
3	2.522	144197	66337	0.000		V	
4	2.550	164824	96557	0.000		V	
5	3.625	3265	2206	14.835	ppm	V	DEA
6	3.683	212469	69456	965.359	ppm	V	DEA
7	5.069	7655	3593	0.000			
8	7.155	5036	720	0.000			
Total		557675	244366				

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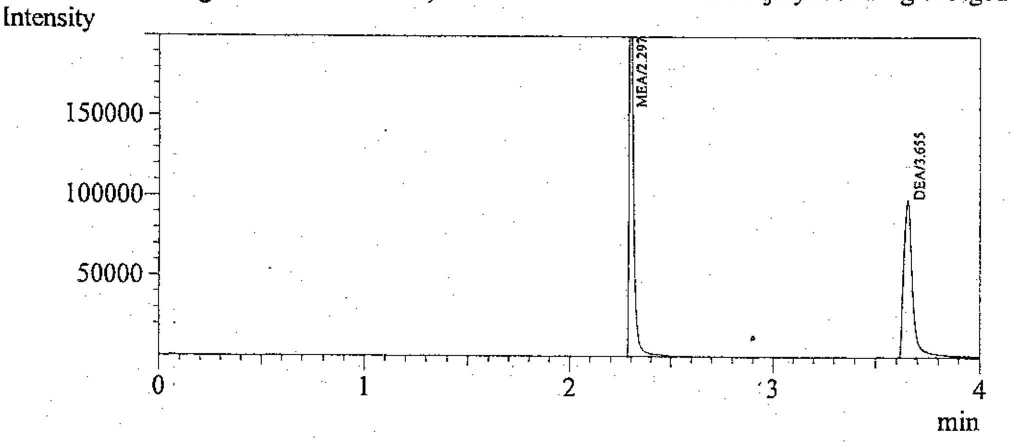
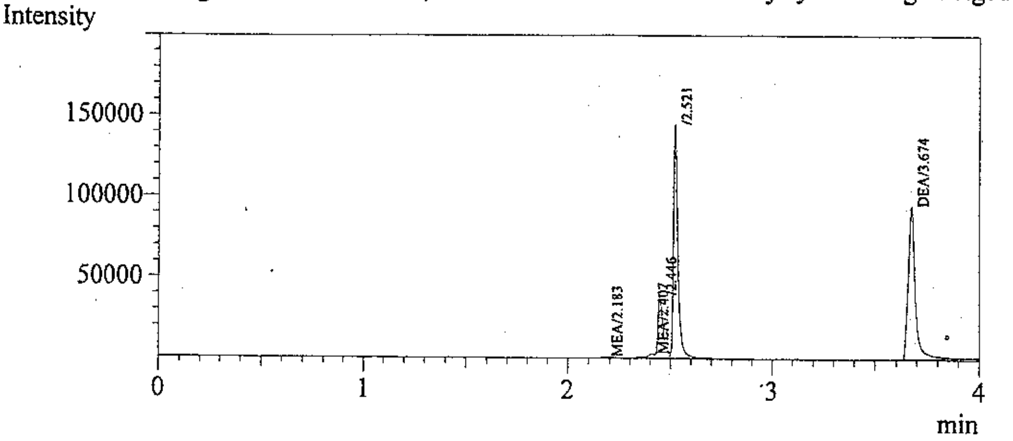
Chromatogram - Channel 1 2.8,feed C:\GCsolution\Data\FYP\july2005\awg 013.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.297	406219	287441	1922.975	ppm	S	MEA
2	3.655	286866	98090	1303.386	ppm		DEA
Total		693085	385532				

Chromatogram - Channel 1 2.8,s130 C:\GCsolution\Data\FYP\july2005\awg 016.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.183	3309	971	15.663	ppm		MEA
2	2.407	5885	2410	27.860	ppm		MEA
3	2.446	68811	38915	0.000		V	
4	2.521	222505	141393	0.000		V	
5	3.674	229600	93518	1043.196	ppm		DEA
Total		530110	277207				

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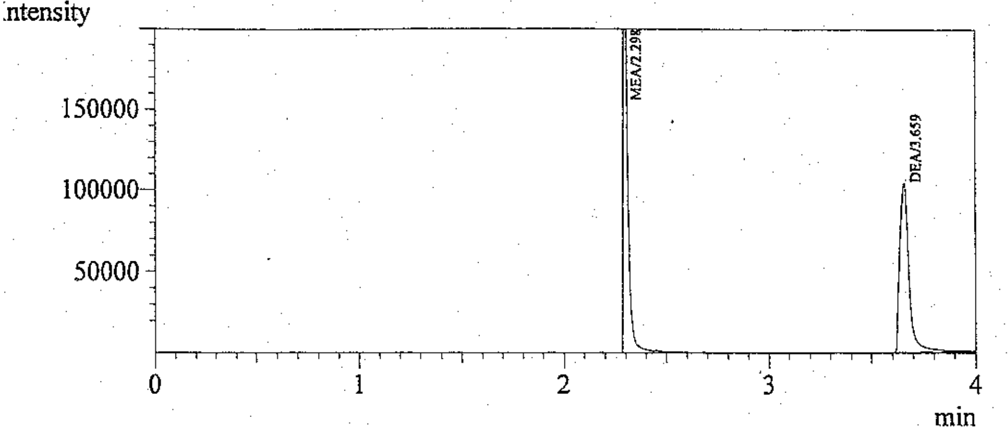
Chromatogram - Channel 1 2.8,s42 C:\GCsolution\Data\FYP\july2005\awg 014.gcd



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.298	424490	302935	2009.468	ppm	S	MEA
2	3.659	329895	103930	1498.889	ppm		DEA
Total		754385	406865				

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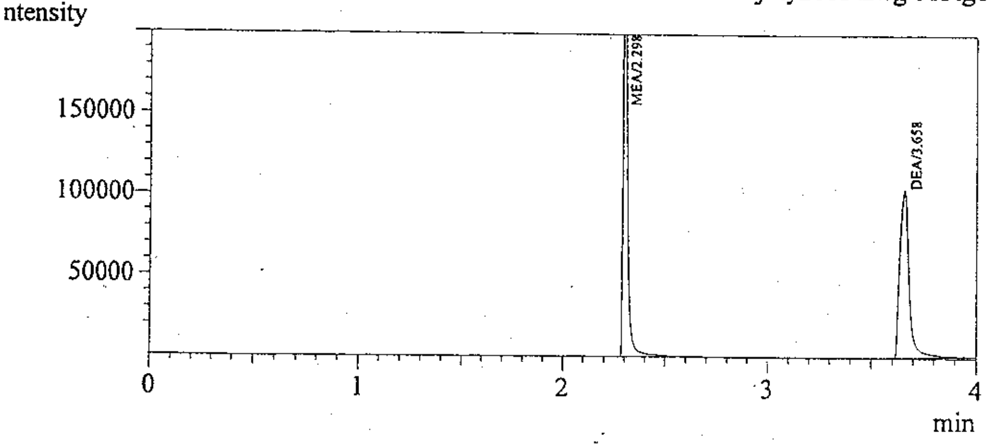
S130



Chromatogram - Channel 1 2.8,s83 C:\GCsolution\Data\FYP\july2005\awg 015.gcd

Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	2.298	422474	302263	1999.922	ppm	S	MEA
2	3.658	325795	103900	1480.259	ppm	V	DEA
3	5.783	2305	2229	0.000			
Total		750574	408393				