ASPECTS OF DEGRADATION OF MONOETHANOLAMINE SOLUTIONS DURING CO_2 ABSORPTION

THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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2011

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SUMMARY OF THESIS

The most common technique for carbon dioxide removal from gaseous streams is amine scrubbing, a proven technology in the oil and gas industries. The use of this route in coal fired power plants is not fully understood and the likelihood of solvent degradation is high. Decreased absorption efficiency, undesirable by-products, the environmental impact of their disposal and increased process costs are the main consequences.

In this study, two experimental rigs were designed and commissioned to explore the effects of gas composition and temperature on monoethanolamine degradation. Analytical procedures to detect and quantify its major thermal and oxidative degradation products were also developed.

It became apparent early on that solvent degradation, under actual plant conditions, is a slow phenomenon, thus, it was decided to focus on thermal degradation. The present study uniquely enabled the absorption/desorption behaviour of thermally degraded solvents to be evaluated. The major thermal degradation products were quantified.

After 14 full absorption/stripping cycles at the presence of 16% oxygen and 15% carbon dioxide, significant concentrations of nitrites and nitrates were detected in the samples. Thermal degradation at 160 ^{o}C for 8 weeks reduced monoethanolamine concentration by almost 95%, as evidenced by the chemical analysis, but the remaining solvent retained 22% of its capacity to remove carbon dioxide. Therefore, although not fully quantified, the requirement for monoethanolamine make-up may not be quite as serious as initially believed. There is some evidence to support that the rate of thermal degradation was enhanced as carbon dioxide loading increased and a 20% higher MEA loss was determined in the samples with the rich initial molar loading. A range of degradation products were quantified that correspond to those cited in the literature. 1-(2-hydroxyethyl)-2-imidazolidinone was indicated as the most stable MEA degradation product in the degraded samples at concentrations of up to 17% v/v.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my supervisors, Prof. Tony Griffiths and in particular Prof. Keith Williams, for their continuous support and guidance at all levels throughout this period of study. Thank you.

I would also like to thank the British Coal Utilisation Research Association (BCURA) for the funding provided and express my appreciation to my industrial supervisor, Dr. Michael Whitehouse, for his constructive input to this project.

I would like to thank Jeff Rowlands and Ravi Mitha, as well as Julian Steer and Martin Griffiths, for all the help and assistance they provided me with in the CLEER laboratories throughout this study.

I would like to acknowledge the support and understanding I received from my dear friends Reza Ahmadian, Glykeria Eliopoulou, Jennifer Geroni, Doria Tichit and Patricia Xavier.

I would like to thank my fiancé Spyros for his dearest love, his caring advice and for accompanying me through this venture.

Finally, I express my deep gratitude to my father Ioannis and my "fighter" mother Amerissa for encouraging and supporting me by all available means to achieve my goals.

I would like to dedicate this thesis to my uncle Sotiris.

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NOMENCLATURE

AMP	2-Amino-2-methyl-1-propanol
CE-DAD	Capillary Electrophoresis – Diode Array Detection
DCM	Dichloromethane
DEA	Diethanolamine
DGA	Diglycolamine
DIPA	Di-isopropylamine
ESA	Electric Swing Adsorption
FGD	Flue Gas Desulphurisation
FT-ICR/MS	Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
FT-IR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography Mass Spectrometry
GHG	Greenhouse Gases
HEEDA	N-(2-hydroxyethyl)-ethylenediamine
HEF	Hydroxyethyl-formamide
HEI	1-(2-Hydroxyethyl)-imidazole
HEIA	1-(2-hydroxyethyl)-2-imidazolidone
HPLC	High Performance Liquid Chromatography
HPLC-RID	High Performance Liquid Chromatography – Refractive Index Detection
IC	Ion Chromatography
IC-MS	Ion Chromatography Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission spectrometry
IDL	Instrument Detection Limits
IPCC	Intergovernmental Panel on Climate Change

LC-MS	Liquid Chromatography Mass Spectrometry
LVHRMS	Low Voltage High Resolution Mass Spectrometry
MDEA	Methyldiethanolamine
MDL	Method Detection Limits
MEA	Monoethanolamine
microGC	Micro Gas Chromatography
MTBE	Methyl Tertiary Butyl Ether
NMR	Nuclear Magnetic Resonance
PSA	Pressure Swing Adsorption
PZ	Piperazine
RSD	Relative Standard Deviation
TC	Total Carbon analyser
TEA	Triethanolamine
TETA	Triethylenetertamine
TOC	Total Organic Carbon analyser
TSA	Temperature Swing Adsorption
VLE	Vapour Liquid Equilibrium
VOC	Volatile Organic Compounds

CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

Carbon dioxide is one of the greenhouse gases that contribute to climate change. According to Chakravarti et al. (2001) about 60% of the CO_2 is emitted by utility or industrial power systems based on fossil fuel combustion in the USA. Currently, a few options are being considered to reduce CO_2 emissions produced by the combustion of fossil fuels. According to Herzog et al. (2009) these include post-combustion, pre-combustion, oxyfuel and chemical looping combustion, as well as a number of CO_2 separation methods such as absorption, adsorption, membranes and cryogenics separation, as potential CO_2 capture methods to currently uder research as potential methods to be used on large scale electricity production.

Amine scrubbing has been an established technology for acid gas removal in the chemical and oil industries, thus, it is considered that can be more easily implemented on large scale at existing power plants for CO_2 removal (Mangalapally et al., 2009). It is based on the reversible chemical reaction of the acid gas with amine family solvents. An important characteristic of the amine absorption process is the proper choice of solvent; the main characteristics of an appropriate solvent are the high CO_2 loading capacity and low heat of reaction with CO_2 according to Hermann, 2005. Aqueous solutions of 30 % w/v monoethanolamine are considered to be the reference solvents for such processes though as claimed by Moser et al. 2011.

Rochelle (2009) mention that hundreds of plants are used at the moment to remove CO_2 from natural gas, hydrogen and other gases with low oxygen, mainly using monoethanolamine. According to Rochelle (2009) only pilot scale plants operating to remove CO_2 from coal combustion, testing different solvents concerning their kinetics and thermodynamic properties as well as solvent degradation issues with MEA being considered the base case solvent for comparison. Four coal-fired power plants, with power outputs up to 30 MW, separate CO_2 from the flue gas using 20% w/v MEA (Rochelle 2009) and just one (ABB Lummus / Kerr-McGee) operating with 15-20% MEA to remove up to 400 ton CO_2/day from flue gas from coal fired power plant (Knudsen and Jensen, 2009). More than twenty pilot plants are using 30% w/v MEA to remove up to 330 ton CO_2/day (Rochelle 2009). Finally, according to Knudsen and Jensen (2009) a large number of plants also use the Mitsubishi proprietary, sterically hindered amine, KS-1 to remove up to 450 ton CO_2/day.

During the absorption-stripping process, considerable solvent losses occur. Amine solvents are very volatile and as a result are likely to evaporate from the liquid into the gas phase. MEA volatility, apart from the increase in the process costs because of the solvent make up and the need for additional water washes, it also has a significant environmental impact as MEA could move into the atmosphere and react producing environmentally hazardous compounds (Nguyen et al., 2011).

Moreover, the irreversible reactions which may occur during the process, that result in products from MEA that can not be recovered, are called degradation. Degradation causes MEA depletion from the system. Firstly, due to the presence of at least 5% of O_2 in the flue gas, MEA oxidation is caused in the absorber (Sexton and Rochelle, 2008). Oxidative degradation results in the formation of heat-stable salts and other by-products that decrease the system's efficiency. Secondly, thermal degradation at the presence of CO_2 which occurs in temperature encountered in the cross exchanger, stripper and the thermal reclaiming unit and causes the formation of large polymeric compounds (Davies, 2008). Finally, the presence of SO and SO_2 as well as NO_x can also cause the formation of heat stable corrosive salts (Blakstad 2010) that can not be reclaimed. Finally, fly ash can cause degradation and foaming resulting in plugging of the process equipment. According to Brakstad et al. (2010) MEA degradation has been studied to some extent, although there still exist a number of unidentified degradation products from this amine and some of the degradation pathways are to a large extent stil uncertain.

According to Strazisar (2003) about 2.2 kg of MEA/ton CO_2 captured need replacement due to solvent degradation. Apart from solvent losses, degradation products are believed to be responsible for equipment corrosion, foaming, fouling and an increase in the solvent's viscosity. Moreover, as the level of degradation products increases, the amine content of the solution decreases due to degradation and the solution losses its capacity to absorb acid gases as Abdi (1997) claim. Apart from solvent make up needed to maintain the system's efficiency, additional equipment is needed in order to remove the by-products generated during the procedure and these degradation products are disposed as hazardous chemical wastes Islam et al. (2011). Therefore, there is an impact on the process economics and the environmental impact of the disposal of the liquid and solid wastes recovered. The aforementioned conclusions illustrate the need for further research and understanding on the MEA degradation and the degradation products generated.

According to Brakstad et al. (2010) conclusive identification, by means of chemical analysis, of degradation products can be technically challenging. Therefore, the identification and quantification of the degradation products generated within the system, the chemistry of degradation and the degradation patways are the first research areas that need to be addressed. Methods for the accurate chemical analysis need to be developed for both to be able to assess the degradation products generated within a system but also for different amine screening and comparison to assess which solvent is less sensitive for a certain process. Accurate identification of degradation products would also help in developing methods to successfully reclaim them or to find appropriate inhibitors to avoid solvent losses due to degradation.

Moreover, the effect of the process parameters on solvent degradation needs to be assessed in order to control degradation and as a result reduce energy consumption and costs. The effect of degradation on the system's operation in terms of its CO_2 uptake capacity also needs to be assessed. Finally, understanding how oxidative and thermal degradation occurs may help in developing new absorber and especially stripper configurations, as Davis (2009) claim that stripping is the largest economic factor in the capture of $CO_{2.}$ Note here that thermal degradation occurs at stripper temperature conditions.

1.2 THESIS AIMS - KEY QUESTION

The key question that this thesis mainly aims to address is how thermal degradation affects the operational lifetime of the MEA solvent, which is the most common currently used solvent, in terms of its CO_2 uptake capacity deterioration and the generation of undesirable thermal degradation products.

As an attempt to answer this question the following objectives were set:

- design, build and commission a system capable of applying repeated cycles of absorption/stripping allowing the controlled contact of CO_2-laden gases with different amine solvents at conditions as close as possible to those expected in practice.
- determine the key parameters that affect the operational lifetime of the MEA solvent
- develop methods and procedures to be able to investigate the solvents' CO_2 uptake capability both during absorption and stripping
- develop methods and procedures to be able to detect, identify and quantify the range of MEA major degradation products that could contaminate the solvent and affect its operation
- design an experimental procedure facilitating the generation of thermally degraded samples within a reasonable timescale

1.3 THESIS OVERVIEW

After introducing the thesis in Chapter 1, Chapter 2 presents a review of the literature. It presents the background and state of the art of the technology related to the work presented in the following chapters. More specifically it describes the amine scrubbing industrial procedure and the amine solvents used in general, focusing mainly on MEA. The process chemistry for MEA as well as the disadvantages of it when used in real conditions are presented. Finally, both oxidative and thermal degradation are discussed paying specific attention to the thermal degradation, which is the main focus of the present research work.

Chapter 3 describes the experimental procedures developed and used in order to assess the effects of thermal degradation on the MEA solvent's operational lifetime in terms of both CO_2 uptake capacity and degradation products generated. The designing, commissioning and development work of the MEA absorption/stripping rig and the thermal degradation rig are discussed. The analytical equipment along with the method development, detection limits and calibration curves produced for the analysis of the MEA major degradation products are described. Last but not least, any other equipment and the results processing procedures are also presented.

In Chapter 4 the results produced in the present research study as well as comments and discussion on them are presented. More specifically, some initial efforts performed to produce MEA degraded samples in the absorption/stripping system and their analysis for degradation products are presented. The results of the CO_2 solubility experiments, performed during the commissioning of the thermal degradation rig, are also discussed. Finally, the effects of thermal degradation on the solvent's CO_2 uptake capacity, as assessed from the 6 thermally degraded MEA samples with "lean" and "rich" initial molar loadings (0.19 and 0.37 moles of CO_2/mole of MEA, respectively), are detailed.

Chapter 5 details the conclusions and future recommendations compiling from the present research study.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

The following chapter presents a literature review on the subject of post combustion carbon capture using amine scrubbing. More specifically, the industrial procedure and the technical issues that still need to be addressed, before it is used in large scale to remove CO_2 from flue gases of coal fired power plants, are briefly presented. The different amine solvents available and researched at the moment as potential solvents in an amine scrubber are discussed, taking a more focused approach on monoethanolamine (MEA). The MEA solvent management and the key issues that still need to be addressed are presented, focusing on the solvent degradation and more specifically on thermal degradation and its impact on the plant operation.

2.2 AMINE SCRUBBING

Amine scrubbing has been an established technology over the past several decades for removal of acid gases (such as CO_2 and H_2S) from gaseous streams in the chemical and oil industries. It is based on the reversible chemical reaction of the acid gas with organic solvents such as amines. Its application to the CO_2 removal from the flue gases produced by the combustion of fossil fuels and/or biomass has attracted much attention over the past few years. This technology generally requires very large equipment because of the large amounts of gases that need to be treated and due to the small CO_2 partial pressures in the flue gas. There are certain key concerns such as the potentially large amount of energy to regenerate the amines, corrosion of the equipment and degradation of the amine with time.

2.2.1 Industrial procedure

In a typical amine scrubbing system, shown in Figure 2.1, the flue gas is cooled down before it enters the absorber. In the absorber CO_2 comes into contact with the amine and, at temperatures of 40-60^{o}C, gets chemically bound by it. After the absorption stage, the CO_2 rich solvent is pumped up to the top of the stripper through a heat exchanger. In the stripper vessel the regeneration takes place at temperatures of up to 120-130 ^{o}C and at pressures close to atmospheric. Heat is supplied to the reboiler to maintain the temperature conditions in the stripper, which is usually supplied in the form of steam. After the regeneration process the amine is pumped back to the absorber through a heat exchanger and a cooler to get down to the absorber temperatures. The steam is recovered in a condenser and the CO_2 gas leaves the stripper. Additional equipment and processes may be needed in order to maintain the solvent quality, such as filters, carbon beds and thermally operated reclaimers.

The absorber columns used in amine scrubbing systems are packed or tray columns that promote good gas-liquid contact between the CO_2 containing flue gas and the solvent. Like the absorber, the stripper is a packed or a tray column, the CO_2 rich solvent enters at the top of the stripper and flows down countercurrent with the steam (stripping gas). Reclaimer is the unit used for the separation or reclaiming of the usable amine from its degradation products, these systems are used either to remove the contaminants from the solvent or to remove the solvent with or from the contaminant. The waste includes water, amines, amine degradation products, corrosion products and other chemicals.

Movagharnejad and Akbari (2011) present the typical conditions under which an amine scrubbing system operates as obtained by an amine scrubbing system used to remove CO_2 from the flue gas produced by a cement factory. Note here that these values differ from plant to plant as the flue gas, process design and conditions are different in different plants (see Section 2.2.2). According to this study, the inlet gas enters from the bottom of the absorber at flow rates of about 1.2e+06 kg/h and contains about 15% CO_2 its temperature is 50^oC and it is under pressure of 150 kPa. The lean aqueous MEA solvent, with concentration of about 29% wt, enters from the top of the absorber at a temperature of 50^oC and pressure of 150 kPa, its flow rate is about 6e+06 kg/h, with a remaining CO_2 content of about 4%. After the end of the absorption the CO_2 rich solvent (with CO_2 more than 50% of the maximum MEA loading) is heated at 90^oC and enters from the top of the stripper, heat is provided by the reboiler in the form of steam and is about 1.8e+009 kJ/h. About 80% CO_2 then leaves the stripper for the condenser and the lean MEA at about 120^oC leaves from the bottom of the stripper to return to the absorber via a heat exchanger.

According to Rochelle (2009), hundreds of plants remove CO_2 from natural gas, hydrogen and other gases with low oxygen. Four coal-fired power plants, with power outputs up to 30 MW, separate CO_2 from the flue gas using 20% w/v MEA and more than twenty using 30% w/v MEA. Furthermore, more than 10 plants use the Mitsubishi proprietary, sterically hindered amine, KS-1.

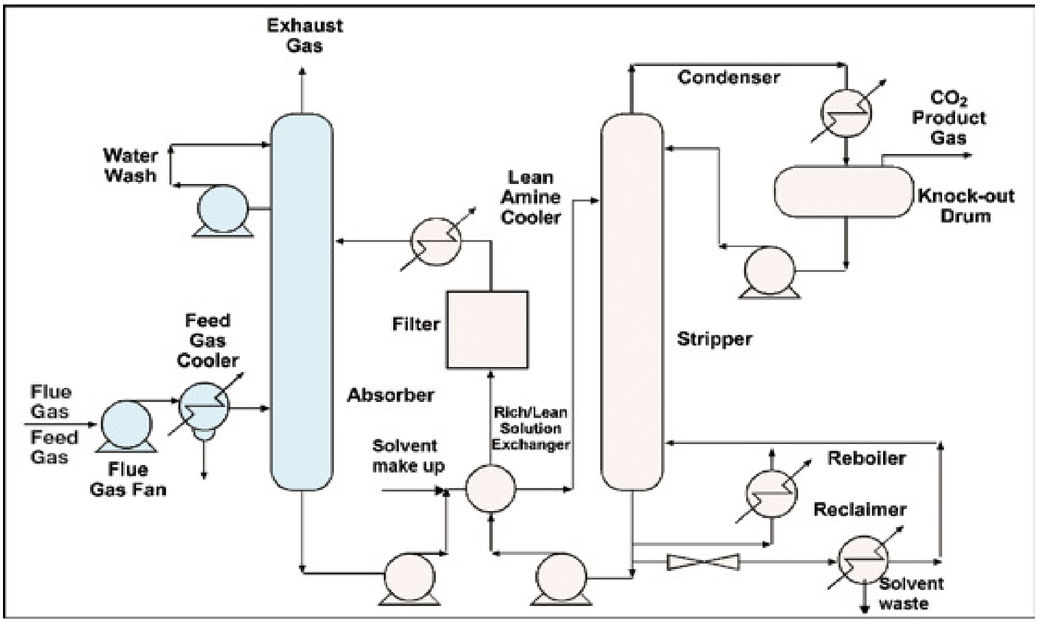


Figure 2.1 Amine scrubbing plant schematic (Davidson 2007)

2.2.2 Design, technical and economic operation

The key issues concerning the design and the technical and economic operation of an amine scrubbing system for a coal fired power plant include the selection of the appropriate solvent and its management for a specific system, the system's design characteristics and most importantly the energy requirements. According to Rochelle (2009), "The minimum work requirement to separate CO_2 from coal-fired flue gas and compress CO_2 to 150 bar is 0.11 megawatt-hours per metric ton of CO_2. Process and solvent improvements should reduce the energy consumption to 0.2 megawatt-hour per ton of CO_2".

- Solvent selection and management

Since coal flue gases contain CO_2 at very low partial pressures and concentrations of about 15 % vol,(Chakravarti et al. 2001), aqueous amines are considered the most suitable absorption solvents as they are active enough (fast reaction rates) to recover dilute CO_2 from atmospheric pressure flue gas, as stated by Chapel et al. (1999). An important characteristic of the absorption process is the proper choice of solvent for the given process duty. The high CO_2 loading capacity and low heat of reaction with CO_2 (lower energy requirements for stripping) are important characteristics of the solvent chosen for atmospheric flue gas CO_2 recovery (Hermann 2005). Last but not least, the solvent concentration is another key issue as low concentrations limit the amount of CO_2 that can be absorbed whereas high concentrations have been associated with corrosion problems encountered in existing plants' equipment (DuPart et al. 1993). Solvent volatility issues are also of great concern and can be addressed by adding water wash sections in parts of the equipment in order to avoid any amine vapours to be carried away by the pure CO_2 gas (McLees 2006). Furthermore, the flue gas contains O_2 and other impurities such as SO_2, NO_x, fly ash etc, therefore, the solvent chosen needs to have low by-product formation and low decomposition rates, to maintain solvent performance, limit the amount of waste materials produced and reduce the reclaiming needs.

- Equipment design

The flue gas flow rate determines the size of the absorber and the stripper, which contributes to the overall costs. The desired degree of CO_2 removal is also a key issue. For higher CO_2 recovery a taller absorption column is needed, higher energy penalties, therefore, increased costs. In practice, typical CO_2 recoveries are between 80% and 90% (Mariz, 1998). Last but not least, the solvent flow rate is a fixed parameter for each system and determines the size of most equipment apart from the absorber. It also has to do with the required CO_2 concentrations (loadings, moles of CO_2 / mole of solvent) within the lean and the rich solutions.

- Energy requirement

The energy consumption of the process is the sum of the thermal energy needed to regenerate the solvents and the electrical energy required to operate the pumps and the flue gas blower or fan. Abu-Zahra (2007) mentions that the thermal energy requirement of the absorption/stripping process is calculated to be around 4 GJ/ton CO_2. According to Davis (2009) the steam needed for regeneration is approximately one third of the steam generated from the plant and this is translated in an 8-13% efficiency losses and it is the largest economic factor in the capture of CO_2. Energy is also required to compress the CO_2 recovered to the final pressure required for transport and storage. Cooling is also needed to bring the flue gas before the absorber and the solvent, after the end of stripping, down to temperatures required for efficient absorption of CO_2. Moreover, the gas product from the stripper also requires cooling to recover steam from the stripping process.

2.3 AMINE SCRUBBING SOLVENTS

Alkaloamines are the most commonly used solvents for the reversible acid gas removal from gaseous streams. They fall under three categories, primary, secondary and tertiary, according to the number of organic groups attached to the nitrogen atom. Sterically hindered amines, which are also discussed, are a special subcategory of primary and secondary amines.

2.3.1 Primary Amines

Primary amines (Figure 2.2) have an alkanol chain, R^1, and two hydrogen atoms bonded to the nitrogen atom. They include MEA and diglycolamine (DGA).

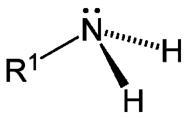


Figure 2.2 Primary amine

Although they require high heat for regeneration and foaming and corrosivity problems are faced during their use, they have good reaction kinetics and work well with low CO_2 concentrations and low pressures.

2.3.2 Secondary Amines

Secondary amines (Figure 2.3) have two alkanol chains, R^1 and R^2, and one hydrogen atom bonded to the nitrogen atom. They include diethanolamine (DEA) and di-isopropylamine (DIPA).

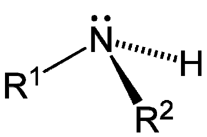


Figure 2.3 Secondary amine

They require less heat in the regeneration step than the primary amines. However, they have all the other problems of the primary amines.

2.3.3 Tertiary Amines

Tertiary amines (Figure 2.4) have three alkanol chains, R^1, R^2 and R^3 (without any hydrogen atoms) bonded to the nitrogen atom. They include triethanolamine (TEA) and methyldiethanolamine (MDEA).

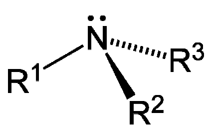


Figure 2.4 Tertiary amine

They require lower heat for CO_2 capture. They also have lower tendency to form degradation products, they are more easily regenerated and have lower corrosion rates. Their main drawback is their reaction rate which is slow, the weak bond they form with CO_2, their tendency to foam at high concentrations and their cost.

2.3.4 Sterically hindered amines

Sterically hindered amines are chemical compounds containing an amine group surrounded by a crowded steric environment. In other words, they belong to a special class of primary/secondary amines in which the amino group is bonded with bulky groups of carbons (or is attached to a tertiary carbon atom) that shield the amine group from reacting with CO_2. The formed carbamate is less stable, so they combine the high reaction rates of the primary/secondary amines with the higher absorption capacity and the lower heat of regeneration of the tertiary amines. One of the most common sterically hindered amines is 2-amino-2-methyl-1-propanol or AMP (a primary amine and more specifically the sterically hindered form of MEA).

2.3.5 Research on amine solvents

From the mid 30’s, numerous studies have been performed on the kinetic and thermodynamic properties of different solvents (mostly amines) that could be used in an amine scrubbing plant. Both experimental and modelling work has been performed aiming to compare different solvents, their CO_2 absorption and desorption rates, vapour liquid equilibrium (VLE) studies, equilibrium constants,

CO_2 solubilities into aqueous amine solutions, the optimum solvent concentrations and operating temperatures, the heats of absorption and desorption for each solvent, packing materials and design for absorbers and strippers, etc. The purpose of this literature review was to choose the optimum solvent, process and design configurations in order to build the gas-absorption stripping rig to perform studies on the solvent's absorption-stripping capacity on CO_2 uptake. A visit to the laboratories of the Department of Chemical Engineering in Texas University at Austin, just to see the systems and conditions used by other researchers in the same field, no experimental work was performed during that visit. This travel along with the literature review performed helped in gaining useful experience before building the gas absorption-stripping rig.

Table 2.1 and Table 2.2 present examples of the research performed on the kinetics and thermodynamics of different amines and blends of amines, respectively. In Table 2.1 a summary of the available research on the different solvents and their performance is presented, many solvents have been studied to assess how effective their potential use could be. From the mid thirties until 2010 in most of the studies MEA is one of the most commonly researched solvents and it is usually used to compare with different solvents.

Table 2.2 presents an example of the available studies performed on amine blends, as it can be seen a more focused interest on blends of amines started since the mid 90s and again MEA is one of the solvents researched in most studies. For example, if a small amount of a primary amine (such as MEA) is added to a solution of a tertiary amine can enhance the rate of absorption without affecting the stripping characteristics (as primary amines have high absorption rates but more energy is needed to release the CO_2 when compared to tertiary amines) as suggested by Liao and Li (2002).

Table 2.1 Sample of available research literature on kinetics and thermodynamics for different amine solvents

Solvent	Title	Authors	Year
DEA, TEA and Tetramine	Absorption of Carbon Dioxide by Amines Di- and Triethanolamine and Tetramine	Hirst L. L. and I. I. Pinkel	1936
MEA	Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times	J. K. A. Clarke	1964
3-(methylsulfonic)propylamine	3-(methylsulfonic)propylamine as a regenerative CO_2 absorbent	Gustafson P. R. and R. R. Miller	1969
AMP	Sterically Hindered Amines for CO_2 Removal from Gases	Santori G. and G. W. Savage	1983
MEA, DEA, DGA and MDEA	A Model of Vapor-Liquid Equilibria for Acid Gas-Alkaloamine-Water Systems	Augsten D. M. PhD thesis University of Texas	1989
AMP	Kinetics of the Reaction of Carbon Dioxide with 2-amino-2-methyl-1-propanol solutions	Xu S. et al.	1996
MEA, AMP, Alkazid M. (*N*-methylalanine)	An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds	R. J. Hook	1997
MEA	Performance Modelling of a Carbon Dioxide Removal System for Power Plants	Desideri U. and A. Paolucci	1999
PZ	Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility	Bishnoi R. and G Rochelle	2000
MDEA	Kinetics of absorption of carbon dioxide into solutions of *N*-methyldiethanolamine + water	Ko J. J. and M. H. Li	2000
MEA and AMP	Study of CO_2 Absorption and Desorption in a Packed Column	Yeh J. T. and H. W. Pennline	2001
MEA and PZ	Energy Performance of Stripper Configurations for CO_2 Capture by Aqueous Amines	Oyenekan B. A. and G. Rochelle	2006
Diglycolamine (DGA)	Absorption of CO_2 in Aqueous Diglycolamine	Al-Juaid M. and G. Rochelle	2006
MEA, AMP, MDEA, N,N-diethylethanolamine, 1-(2-aminoethyl)aminoethanol, N-methyl-1,3-propanediamine, diethylenetriamine and PZ	Comparative Study of the Heats of Absorption of Post-combustion CO_2 absorbents	Kim I. and H. F. Svendsen	2010

Table 2.2 Sample of available research literature on kinetics and thermodynamics for different blends of solvents

Blends of Solvents	Title	Authors	Year
Blends MEA and MDEA	Absorption of Carbon Dioxide into Aqueous Blends of Monoethanolamine and N-Methyldiethanolamine	Hagewiesche D. P. et al.	1995
MDEA, DEA, MEA and their blends	Thermodynamic Model for Acid Gas Loaded Aqueous Alkaloamine Solutions	Posey M. L. PhD Thesis University of Texas	1996
DGA and MDEA and their blends	Mass Transfer, Kinetics and Rate-based Modelling of Reactive Absorption	Pacheco M. A. PhD thesis University of Texas	1998
Blends piperazine (PZ) and MDEA	Absorption of Carbon Dioxide in Aqueous Piperazine/Methyldiethanolamine	Bishnoi R. and G Rochelle	2002
Blends of MEA and MDEA	Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + N-methyldiethanolamine	Liao C. H. and M. H. Li	2002
Blends of PZ and MDEA	Thermodynamics of Piperazine/Methyldiethanolamine/Water/Carbon Dioxide	Bishnoi S and G. Rochelle	2002
Blends K_2CO_3 and PZ	Kinetics of Carbon Dioxide Absorption into Aqueous Potassium Carbonate and Piperazine	Cullinane J. T. and G. Rochelle	2006
MEA, DEA, MDEA and AMP and their blends	Kinetics of carbon dioxide absorption and desorption in aqueous alkanolamine solutions using a novel hemispherical contactor—I. Experimental apparatus and mathematical modelling	Jamal A. et al.	2006
Blends of MEA and MDEA	Kinetics of the Absorption of CO_2 into Mixed Aqueous Loaded Solutions of Monoethanolamine and Methyldiethanolamine	Ramachandran N. et al.	2006
Blends 2-amino-2methyl-1-propanol (AMP) and MEA	Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine	Mandal B. P. and S. S. Bandyopadhyay	2006
Blends of MDEA and TETA	A New Aqueous Solvent Based on a Blend of N-MethylDiEthanolAmine and TriEthyleneTetrAmine for CO_2 Recovery in Post-Combustion: Kinetics Study	Amann J. M. G. and C. Bouallou	2009
Blends of MEA and AMP	Reaction rate of CO_2 in aqueous MEA-AMP solution: Experiment and modelling	Sakwattanapong R. et al.	2009

Sterically hindered amines, according to Santori and Savage (1983), offer advantages in absorption capacity, absorption rate, selectivity and degradation resistance when compared with conventional amines. The most commonly researched sterically hindered amine, at the moment, is AMP which is a primary amine. AMP has the same high loading capacity with MDEA (1 mole of CO_2/mole of amine) but it has a higher reaction rate constant with CO_2 (Xu et al. 1995). Yeh and Pennline (2001) suggest that comparing MEA with AMP, the absorption rate of CO_2 to AMP was less than to MEA but its thermal regeneration was much easier. In terms of blends of AMP with other solvents, it was observed that if a small amount of MEA is added to AMP could result in a significant enhancement of the CO_2 absorption rates as suggested by Xiao J. et al. (2000).

Much interest has been observed recently in the use of piperazine (PZ) as a solvent or in blends with other amines. PZ is believed to demonstrate much higher rate of reaction with CO_2 when compared with conventional alkaloamines as stated by Bishnoi and Rochelle (2000) and Dugas and Rochelle (2009). PZ and MDEA blends, have demonstrated high rate of reaction with CO_2 due to a higher mass transfer capability that they exhibit according to Bishnoi and Rochelle (2002).

As it can be seen both in Table 2.1 and Table 2.2, MEA has been the most commonly researched solvent and possibly even the baseline solvent for comparison. Among all known amines, MEA is the most common currently used solvent for the removal of an acid gas from a gaseous stream. Liu et al. (1999) mention that in 1990 MEA comprised up to 40% of the market. It is a weak base with a low molecular weight; therefore it has high CO_2 absorption capacity on a molar basis. Furthermore, it has fast reaction kinetics which means that the CO_2 is bound in the liquid phase in the form of carbamate molecules that are quite stable (see Section 2.4.1). MEA has also a high CO_2 removal efficiency. It works well at low pressure and CO_2 concentrations. It has low price and it is highly water soluble. Its disadvantages are high heat of reaction, hence high energy consumption, high corrosivity, foaming and degradation problems.

2.4 MEA

Monoethanolamine (MEA) is an organic compound that is both a primary amine and a primary alcohol, and acts as a weak base. Aqueous solutions of MEA are used to remove CO_2 from flue gas by weakly dissolving and neutralizing it to turn its molecules into an ionic form making them polar and considerably more soluble in a “cold” MEA solution therefore CO_2 remains bound to MEA. If an aqueous solution of a strong base was used, it would not readily release the CO_2 (weakly acidic gas) upon heating.

2.4.1 Process chemistry

The process chemistry that occurs during the reaction of CO_2 with MEA is described. The general chemical mechanism is the same for primary and secondary amines but the description in this section is made for primary amines and it is shown in Figure 2.5 as presented by Hook, 2007.

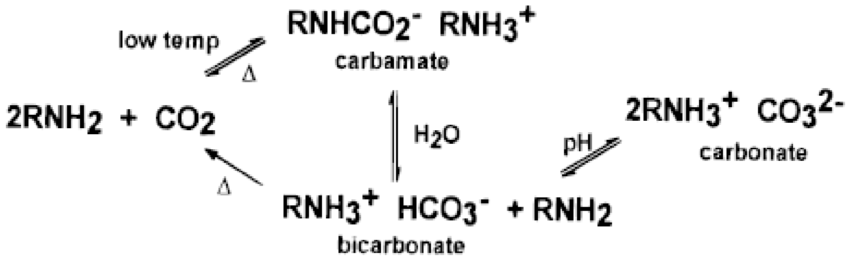


Figure 2.5 Process chemistry of CO_2 absorption by primary or secondary amines (Hook, 1997)

CO_2 reacts with aqueous solutions of primary (RNH_2) amines reaching equilibrium of carbonate, bicarbonate and carbamate. The dissolved CO_2 first reacts with the free amine to form the carbamate ($RNHCO_2^- RNH_3^+$) with a 1:2 (CO_2:amine) stoichiometry. The carbamate then can undergo hydrolysis to produce the bicarbonate ($RNH_3^+ HCO_3^-$) and release a free amine. The lower the pH the more unstable the carbamate is and undergoes through hydrolysis to give bicarbonate (Park et al. 2003). The CO_2 loading of the MEA solution affects the pH, in other words the more CO_2 is absorbed by the MEA the lower the pH of the CO_2-MEA-H_2O solution.

The bicarbonate produced, if the pH conditions are suitable, is converted to produce the carbonate (RNH_3^+ CO_3^{2-}). According to Park et al. (2003) the formation of carbonate ions is not likely to occur because the system pH is normally between 7 and 10 (low basicity) therefore the equilibrium reaction of carbonate-bicarbonate is shifted towards the bicarbonate side.

The maximum absorption of CO_2 is achieved when all of the absorbed carbon dioxide exists as bicarbonate, because the requirement of the carbamate and carbonate species is 2 mol of amine per mol of carbon dioxide reacted, while a one to one ratio exists for bicarbonate. So, maximum hydrolysis of the carbamate is desirable as Hook (2007) mention, however, due to the stability of the carbamate, this reversible reaction (hydrolysis of carbamate) does not occur at an appreciable rate.

For the regeneration stage the absorption by-products are thermally decomposed to release CO_2. Hook (1997) mention that a solution with more bicarbonate, it is more easily regenerated, producing a “leaner” solution (lower total carbamate/bicarbonate/carbonate concentration). Similarly to absorption, the desorption rate of the amine depends on the pH of the solutions. Finally, pH relationship with the degree of crystal formation is important because possible crystallisation of the CO_2 containing ammonium salts can cause problems to the plant.

2.4.2 Solubility of CO_2 in MEA

During the present study, the design and development of a procedure to thermally degrade samples of MEA at elevated temperatures and for prolonged periods of time was deemed necessary (see Section 3.5). Of particular relevance to the thermal degradation rig design and operating protocols were the CO_2 solubility studies in other words the CO_2 partial pressure as a function of the CO_2 molar loading. Therefore, a literature review was performed to have a more clear idea of the CO_2 partial pressures developed above a 30% w/v aqueous MEA solution at elevated temperatures, close to the ones encountered in the stripper.

Shen and Li (1992) presented data of CO_2 solubility in 30 % w/v aqueous MEA solutions. For this study two vapour-liquid equilibrium apparatus were used, a batch equilibrium cell was used for CO_2 partial pressures above 200 kPa and up to 2000 kPa and for partial pressures lower than 200 kPa a vapour recirculation equilibrium cell. The former apparatus was filled by 350 mL of solvent and was purged with CO_2 to remove any O_2 and the partial pressure was adjusted to be between 200 and 2000 kPa; the system was then brought to the desired temperature and the equilibrium was assumed when the total pressure of the cell did not change for 4 hours. At equilibrium three liquid samples were analysed for CO_2 solubility with a titration method and the CO_2 partial pressure was obtained by subtracting the partial pressure of water, calculated by Raoult's law - from the total pressure.

Jou et al (1995) measured the CO_2 solubility in a 30 % w/v MEA solution at temperatures up to 150^oC. 100 mL/min of gas was recirculated and bubbled through the liquid phase in an equilibrium cell mounted in an insulated air bath; the total volume of the system was 250 mL. A 100 mL solution of 30% w/v aqueous MEA was introduced to the evacuated cell and CO_2 was bubbled and absorbed by the MEA. In order to maintain the pressure well above the atmospheric nitrogen was added. The liquid phase analysis was performed by a chromatographic technique and by a precipitation-titration method in which CO_2 was precipitated as $BaCO_3$. The CO_2 partial pressure was calculated by subtracting the amine and water vapour pressures calculated according to Raoult's law. The data were correlated using the model of Deshmukh and Mather (1981), detailed description of the model is not presented here as only the experimental data produced by Jou et al. (1995) were used in the present study. The CO_2 solubility, in a 30 % w/v MEA solution at temperatures up to 150^oC, was measured and the partial pressures of CO_2 were in the range of 0.001-20000 kPa.

The experimental data, as presented by Jou et al. (1995), were used to perform iterative calculations (see Sections 3.5.1.2 and 3.5.1.4), to have an idea of the CO_2 partial pressures that could be developed in the system, before designing the new experimental set up to thermally degrade aqueous MEA solutions for prolonged periods of time at elevated temperatures. For that reason the experimental data points of CO_2 partial pressure versus CO_2 molar loading, as reported by Jou et al. (1995), were used to compare data produced by iterative calculations performed for the experimental conditions intended to use in the present study (see Sections 3.5.1.2 and 3.5.1.4).

Jou et al (1994) presented data for the CO_2 partial pressure distribution of four mixtures of MEA and MDEA with measured CO_2 partial pressures ranging between 100 kPa - 20 MPa at temperatures up to 120 ^oC. The system used and the experimental procedure are described above. These experimental data can serve as a source of information for the modelling of blends of amines.

Ma'mum et al (2005) measured the partial pressures of CO_2 over solutions of 30 % w/v MEA with loadings from 0.16 to 0.42 moles of CO_2 / mole of MEA at 120 ^oC. The experiments were conducted in a vapour liquid equilibrium (VLE) apparatus - with recirculation of the gas phase – which consists of three 300 mL stainless steel cylinders designed to operate at pressures up to 700 kPa and temperatures up to 130 ^oC. 200 mL of loaded MEA solution were added to the first cell while cells two and three held 150 mL each. The cells were heated to the desired temperature by oil baths and, to avoid boiling and vaporization of the solvent, the initial system pressure was set at 300 kPa. When the desired temperature was reached a compressor increased the pressure up to 700 kPa and the vapour was circulated. Equilibrium was obtained when the temperature and the CO_2 concentration in the vapour phase were constant (approximately 2-3 hours including the heating up period). A liquid sample was withdrawn from cell 3, cooled to 10 ^oC and its CO_2 content was determined by IR analysis. The measured CO_2 partial pressures over solutions of 30 % w/v MEA with loadings from 0.16 to 0.42 at 120 ^oC were in the range 7 - 192 kPa.

In addition to the work pre-referenced above, several studies of the partial pressure of CO_2 above its solutions in MEA have been performed, usually at temperatures below 100 ^oC. A wide range of data are reported as summarised in Table 2.3 for 30 % w/v MEA solutions in water with varying loadings up to 1 mole CO_2/ mole MEA.

Table 2.3 CO_2 partial pressures reported in the literature for 30% w/v aqueous MEA at loadings up to 1 mole CO_2/mole MEA (Ma'mum et al. 2005)

Author	Temperature (^oC)	CO_2 Partial Pressure (kPa)
Lyudkovskaya and Leibush (1949)	25, 50, 75	255.3-4124
Atadan (1954)	30, 50, 70	103-3447
Goldman and Leibush (1959)	75, 100, 120, 140	0.5333-472.9
Lee et al. (1974)	40, 100	1.151-6616
Lee et al. (1976)	25-120	0.2-6616
Lawson and Garst (1976)	94	23-453
Nasir and Mather (1977)	100	0.0005-0.52

The maximum loading capacity of MEA is 0.5 moles of CO_2/mole of MEA but this number can be increased at higher CO_2 partial pressures due to free amine liberation from the hydrolysis of the carbamate ions (McLees 2006). After the literature review performed it was concluded that there are considerable differences at the partial pressures measured even at the same temperature and CO_2 molar loading. For example, Nasir and Mathed (1977) measured CO_2 partial pressures of up to 0.52 kPa at 100 ^oC and Lee et al. (1974) at the same conditions up to 6616. These differences are possibly mainly because different experimental setups and rigs were used to perform those experiments.

2.4.3 MEA loss in an amine scrubbing system

During the absorption-stripping process, considerable solvent losses occur. Amine solvents are very volatile and as a result are likely to evaporate from the liquid into the gas phase. MEA volatility, apart from the increase in the process costs because of the solvent losses, has a significant environmental impact as MEA could move into the atmosphere and react producing environmentally hazardous compounds.

Moreover, the irreversible reactions which may occur during the process, that result in products from MEA that can not be recovered, are called degradation. Degradation causes MEA depletion from the system. Firstly, due to the presence of at least 5% of O_2 (e.g. Sexton, 2008) in the flue gas, MEA oxidation is caused in the absorber. Oxidative degradation results in the formation of heat-stable salts and other by-products that decrease the system's efficiency. Apart from solvent losses, they are responsible for equipment corrosion, foaming, fouling and an increase in the solvent's viscosity.

Secondly, thermal degradation which occurs in the cross exchanger, stripper and the thermal reclaiming unit (see Figure 2.1), causes the MEA to form higher molecular weight products. It is estimated that half of the thermal degradation products generated in an industrial unit are produced during the reclaiming process (Blake 1963). At temperatures below 200 ^{o}C and in the presence of CO_2 the thermal degradation occurs by a process termed carbamate polymerization (Davis 2009).

The presence of SO and SO_2 can cause the formation of heat stable corrosive salts that can not be reclaimed. However, the use of a desufurisation system could result in a gas stream that contains less than 70 ppm SO_2 (Abu-Zahran et.al, 2007, Oikawa et al. 2003) that can be installed before the absorber. The NO, also present in the flue gas acts as a inert gas, but NO_2 that is present but at very low concentrations can also form heat stable salts with MEA. Finally, fly ash can cause degradation and foaming resulting in plugging of the process equipment, therefore, wash sections are needed to reduce the fly ash content in the flue gas.

2.4.4 Effect of MEA loss in the amine scrubbing system

Additional equipment - such as reclaimers - are used in the process to remove the by-products generated during the procedure and these by-products are disposed as hazardous chemical wastes which increases the disposal and treatment costs. Solvent make-up is also needed in order to maintain the system's efficiency. Strazisar (2003) mention that due to the degradation of MEA approximately 2.2 kg of MEA per tonne of CO_2 captured require replacement. Additionally, amine solvents are corrosive and the degradation products and heat stable salts, possibly formed in the solvent, can further increase the corrosion rates. Therefore, there is an impact on the process economics and the environmental impact of the disposal of the liquid and solid wastes from the reclaimer that illustrates the need for further research and understanding on the MEA degradation and the degradation products generated.

2.5 MEA DEGRADATION

In this section a literature review on MEA degradation is presented. The parameters that affect the solvent degradation are discussed along with their effects on the solvent, paying special attention to MEA thermal degradation. What it is termed as degradation is defined as the irreversible reactions which may occur during the carbon capture process that result in products, from MEA, that can not be recovered. Oxidative degradation is defined as the reactions of MEA, in the absence or presence of CO_2, with O_2 at conditions that occur during the amine scrubbing process. Oxidative degradation occurs in the absorber. Thermal degradation is defined as the irreversible reactions of MEA with CO_2 that occur due to the elevated temperatures encountered in the stripper, the chemical reaction process is termed carbamate polymerisation. Thermal degradation of MEA itself at temperatures below $200^{o}C$ is inconsiderable.

2.5.1 Oxidative degradation

A number of studies have been performed to assess the effect of O_2, present in the flue gas (approximately 5% Abu-Zahran et. al 2007), on different amine solvents. In this sub-section the effect of O_2 on MEA is discussed, work performed by a number of researchers is presented as far as it concerns both the MEA “disappearance” and the formation of the oxidative degradation products. The focus is to understand the degradation conditions, the parameters that affect the MEA oxidation, identify the major oxidative degradation products and the methods and instruments used to detect and quantify them.

In Table 2.4 some of the studies performed on oxidative degradation are presented. In these studies the oxidative degradation rate is assessed as a function of the MEA concentration changes and NH_3 (ammonia) evolution. It needs to be noted that NH_3 is one of the volatile MEA oxidative degradation products.

Table 2.4 Effects of O_2 on the MEA as reported in the literature

Authors	Parameter measured	Instrument	Observations
Supap et al. (2001)	MEA	GC-MS	Oxidation more sensitive to O_2 concentration increase than MEA concentration increase
Chi and Rochelle (2002)	NH_3 evolution	FT-IR	CO_2 presence and MEA concentration increased oxidation
Goff and Rochelle (2004)	NH_3 evolution	FT-IR	Oxidative degradation rate increased with agitation rate and CO_2 concentration
Bello and Idem (2006)	MEA	GC-MS	MEA concentration, temperature and O_2 increase the degradation rate, CO_2 loading has the opposite effect
Supap (2006)	MEA	HPLC	O_2 and MEA concentration and temperature increases cause an increase in the degradation rates
Uyanga and Idem (2007)	MEA	HPLC	CO_2 loading increase was proved to have an inhibition effect to degradation
Lepaumier et al. (2009) C	MEA	GC-MS, FT-ICR/MS, IC and NMR	20% MEA oxidation, small amounts of amino acids observed

A number of researchers have also performed studies to detect and quantify the generated oxidative degradation products and suggest pathways for their formation.

Sexton (2008) subjected to oxidative degradation aqueous amine solutions in glass jacketed reactors at both low (100ml/min 98%O_2 and 2% CO_2) and high gas rates (7.5 L/min 15%O_2 and 2% CO_2). Samples were analyzed for degradation using ion chromatography (IC) and High Performance Liquid Chromatography (HPLC) with evaporative light scattering detection. A Fourier Transform Infrared Analyzer (FT-IR) collected continuous gas-phase data on amine volatility and volatile degradation products (such as NH_3). Hydroxyethyl-formamide (HEF), hydroxyethylimidazole (HEI), oxalate, acetate, glycolate and formate were found to be the major carbon containing MEA oxidation products. NH_3 and nitrates/nitrites were also detected.

Lepaumier at al. (2010) performed a study to examine degradation of five tertiary polyamines in the presence of O_2 and compared them with MEA. The experiment was performed in a stainless steel 100 ml batch reactor at 140 ^oC under pure O_2 pressure of 2 MPa for 15 days. At the end of the experiment liquid samples were analysed for degradation products using a GC-MS (Gas Chromatograph Mass Spectrometer), an FT-ICR/MS (Fourier Transformation Ion Cyclotron Resonance coupled with a Mass Spectrometer), an IC and an NMR (Nuclear Magnetic Resonance) system. The presence of acetate, formate, oxalate and glycolate was verified in the MEA degraded samples at concentrations of over 100 ppm with highest being the formate concentration which was measured as 2660 ppm. The overall MEA loss due to oxidative throughout the experiment was 21%.

Lepaumier et al. (2011) performed a study to compare, thermal and oxidative degradation of MEA, in pilot-scale plant (Esbjerg plant) samples with samples produced by lab-scale experiments. A lab scale experiment representative of oxidative degradation in the presence of CO_2 and air at absorber conditions (30% w/v aqueous MEA solution with initial CO_2 molar loading of 0.4, sparged with air and CO_2 at 55^oC) was performed. Liquid samples from different parts of the process were taken from the Esbjerg plant during a 20 week experiment with 30% wt aqueous MEA. An LC-MS (Liquid Chromatography Mass Spectrometer) and a GC-MS system were used for the identification and quantification of the main degradation products. In the laboratory experiments, MEA degraded 5.8% after 9 days and the three main degradation products observed were 2-oxazolidone, HEF and HEI. According to the author, the former is formed from the reaction of MEA with formic acid. The oxidative degradation products found in the pilot plant samples are presented in Table 2.5. The presence of acetate, formate, oxalate and glycolate was not verified in any of the samples as no work was performed for the detection and quantification of those compounds. 2-Oxazolidone, which has never before been reported as an MEA oxidative degradation product, was also detected in the laboratory samples and a possible pathway of its formation is also presented.

Table 2.5 Detected MEA degradation products in the samples produced by the Esbjerg pilot plant (Lepaumier et al. 2011)

Oxidative degradation product
2-oxazolidone
HEI
HEF
N-(2-hydroxyethyl)acetamide
2-hydroxy-N-(2-hydroxyethyl)acetamide
N,N'-bis(2-hydroxyethyl)oxalamide
4-(2-hydroxyethyl)piperazine-2-one
N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide

Vevelstad et al. (2011) performed a theoretical study to verify the suggested mechanisms for oxidative degradation, with CO_2, based on the stability of the degradation products generated during the process, in order to explore the possible reaction mechanisms. This was attempted by performing calculations for geometry optimization, frequency and solvation (creation of a compound using a solvent and a solute). It was suggested that oxalic acid, oxalamide and 1-(2-hydroxyethyl)-imidazole (HEI) were the most favourable MEA oxidative degradation products.

Overall, it was noted that an increase in MEA concentration, temperature and O_2 concentration has a positive effect on MEA degradation rate in contrast with the CO_2 molar loading which seems to decrease the MEA loss rate. According to the literature the measured MEA loss due to degradation was up to 20%. It needs to be noted here that in all the studies presented researchers have exposed MEA samples to conditions to accelerate oxidative degradation (elevated oxygen concentrations, pressures and temperatures). The present study attempted to assess the effect of oxygen on the solvent at conditions as close as possible to an actual amine scrubbing plant. It was also attempted to link the formation of oxidation products with the number of absorption/stripping cycles applied to the solvent. In Table 2.6 the major oxidative degradation products that were detected, sometimes quantified as well, and were common in all the studies are shown in Table 2.6.

Table 2.6 Most commonly reported MEA oxidative degradation products.

Oxidative degradation product
NO_2/NO_3 ions
NH_3
Oxalate
Formate
Acetate
HEI
HEF

2.5.2 Thermal degradation

In this section, studies performed to assess the effect of temperature - close to the ones encountered during the stripping and reclaiming - in the presence of CO_2 on MEA are presented. It needs to be noted here that according to Daubert et al. 1987 MEA, in the absence of CO_2, does not decompose at temperatures lower than 350 ^oC. In addition, Lepaumier et al. (2009 (a) and (b)) as well as Eide-Haugmo et al. (2011) measured the MEA decomposition in the absence of CO_2 at 135^o and suggest that it can be considered negligible. Davis (2009) mention that MEA thermal degradation in the presence of CO_2 occurs at stripper temperature conditions (above 100 ^oC). Work performed by a number of researchers on the MEA loss due to thermal degradation, degradation products, their pathways of formation and quantification and corrosion, that was observed due to their presence, is discussed.

2.5.2.1 MEA loss

A number of researchers performed studies on the MEA loss due to carbamate polymerisation at temperatures below 200°C. Davis (2008 & 2009) loaded different MEA solutions with CO_2 and degraded them in sealed bombs in a forced convection oven at 100–150 °C. Amine loss and degradation products were quantified as a function of degradation time by means of IC, HPLC and IC/MS (Ion Chromatograph Mass Spectrometer). It was calculated that the MEA loss rate quadruples for every 17°C increase in the degradation temperature used during these experiments. More specifically when a 7 molal aqueous MEA solution, with 0.4 initial CO_2 molar loading, was heated for less than 4 weeks at 150 °C an MEA loss of approximately 64% occurred. The decrease of loading had a first order effect, in other words if the loading is reduced from 0.4 to 0.2 it could cause a similar decrease in the MEA degradation rate. After 8 weeks of thermal degradation at 135 °C, a 7 molal aqueous MEA solution with initial CO_2 molar loading of 0.2 lost 32% of its initial MEA, whereas when the initial loading was 0.5 the MEA loss was up to 65%. It was also noted that at the beginning of the experiments the MEA loss rate was faster and it slowed down as the experiments progressed.

Lepaumier et al. (2009 (a) and (b)) performed studies on the degradation of MEA in the presence of CO_2 in a 100 ml batch reactor at 140 °C for 15 days. The initial amine concentrations were 4 mol /kg and a CO_2 pressure of 2 MPa was maintained in the reactor. The conditions were chosen to be close to the stripper conditions as CO_2 induced degradation is more likely to occur at these temperature conditions in the stripper. At the end of the experiment liquid samples were analysed for degradation products using a GC-MS, an FT-ICR/MS and an NMR system. It was noted that thermal degradation of MEA in the absence of CO_2 was very low but 42% degradation was measured in the presence of CO_2, which classifies MEA as one of the least stable amines. An aqueous MEA solution of the same concentration was degraded at the same conditions in the absence of CO_2 and its degradation was considered negligible when compared with the MEA loss due to degradation in the presence of CO_2.

Lepaumier et al. (2010) performed a study to examine degradation of five tertiary polyamines in the presence of CO_2 and compared them with MEA. The experiment was performed in a stainless steel 100 ml batch reactor at 140 ^oC under CO_2 pressure of 2 MPa for 15 days. At the end of the experiment liquid samples were analysed for degradation products using a GC-MS, an FT-ICR/MS and an NMR system. The MEA loss due to degradation was measured 42%. A pressure drop in the batch reactor was observed during the experiments which could be attributed to leaks and also the CO_2 consumption by the MEA during the degradation reactions.

Lepaumier et al. (2011) performed a study to compare thermal degradation of MEA in samples produced by a pilot-scale plant (Esbjerg plant) with samples from lab-scale experiments. The pilot plant samples were taken from all the parts of the pilot plant during a 3360 h (20 weeks) test campaign running with 30% wt MEA. A lab scale experiments was performed representative of thermal degradation in the presence of CO_2 at stripper conditions (30% w/v aqueous MEA solution with initial CO_2 molar loading of 0.5 at 135^oC). An LC-MS and a GC-MS system were used for the identification and quantification of the main degradation products. The pilot plant used for comparison was the Esbjerg plant in Denmark. In a 7 ml of a 30% w/v aqueous MEA solution sample with rich initial CO_2 molar loading of (0.5 moles of CO_2/mole of MEA) after degrading at 135^oC for 5 weeks in 316 stainless steel cylinders, 57.6% of MEA loss was measured. It was noted that the degradation rate was linear for the first 4 weeks and then it started slowing down. From the results of the pilot plant the contribution of thermal degradation was limited.

Eide-Haugmo et al. (2011) performed a study on the thermal and chemical stability of new solvents for CO_2 capture, including MEA. Samples of 30% w/v aqueous amine solvents loaded (0.5 moles CO_2/ mole of amine) and in the absence of CO_2 were placed in either at 316 SS cylinders or in glass tubes and were degraded at 135^oC. LC-MS was used to determine the degradation rate as a function of amine loss. The first conclusion of that work was that the selection of the container (glass or metal) did not seem to have any impact on the solvent degradation rates. It was again concluded that thermal degradation of the amine in the absence of CO_2 can be considered negligible under the amine scrubbing process conditions. As far as it concerns MEA, it was measured that, when the sample was degraded for 5 weeks at 135^oC in presence of CO_2 (0.50 initial CO_2 molar loading), the MEA loss due to degradation was 55%. However, it is claimed by the authors that loading plays a significant role in the thermal degradation rates, therefore it was concluded that the degradation rate could be much more considerable if the initial loadings were higher.

To sum up, the CO_2 loading, temperature and degradation time had a considerable effect on MEA loss. The most dramatic MEA loss was reported by Davis as 65% after 8 weeks of thermal degradation at 150^oC. In practice MEA thermal degradation in the presence of CO_2 at stripper temperatures is a slow phenomenon and that is why the temperature conditions chosen were higher to accelerate the degradation. Both Davis (2008&2009) and Lepaumier (2011) noted that the MEA degradation rate was faster at the beginning of the experiment and it started slowing down as the experiment progressed.

2.5.2.2 Degradation products and their concentrations

A few of the studies performed to assess the effect of temperature on MEA in the presence of CO_2, performed work on the quantification of MEA major degradation products. Where % of formation of degradation products is the degradation product concentration divided with the initial MEA concentration and multiplied by 100.

Davis (2008 & 2009) performed a study, as described in Section 2.5.2.1, and found 2-oxazolidone, N,N'-di(2-hydroxyethyl)urea, 1-(2-hydroxyethyl)-2-imidazolidone (HEIA) and N-(2-hydroxyethyl)-ethylenediamine (HEEDA) to be the MEA major thermal degradation products as they make up for the majority of total MEA loss until half the original MEA was degraded, based on a nitrogen balance performed which was used for the purposes of a mass balance. After half the initial MEA is lost, according to Davis (2009) larger polymeric products, which have not been quantified, started being produced at considerable concentrations. The percentage of formation of the degradation products is dependant on temperature as it contributes to faster kinetics, CO_2 loading as more MEA carbamate is available in the samples and the MEA initial concentration. Last but not least, the effect of a decrease of 10% in the MEA initial concentration resulted in a slightly more than 10% decrease in the formation of the degradation products.

Lepaumier et al. (2009 (a)) also examined thermal degradation of MEA in the presence of CO_2 (conditions presented in Section 2.5.2.1). The main degradation proportions due to different reactions were reported to be imidazolidones with percentage of formation 30% (such as the HEIA production) and addition reactions with 5% percentage of formation (such as the 2-oxazolidone production).

Lepaumier et al. (2009 (b) and 2010) reported that the main degradation products identified in the MEA degraded samples were HEIA, monoethanolamine urea and HEEDA and their formation percentages were 12, 3 and 2.6 % respectively.

Lepaumier et al. (2011) compared thermal loss of MEA in samples from the Esbjerg pilot-scale plant in Denmark along with lab-scale experiments. 2-Oxazolidone, HEEDA and HEIA were again identified as the MEA major thermal degradation products in the presence of CO_2 at stripper conditions in the experiments performed in the laboratory (see Section 2.5.2.1). It was noticed that HEIA percentage of formation increased with time reaching approximately 50% after 5 weeks which is a sign of its stability. In contrast, the percentages of formation of 2-Oxazolidone and HEEDA remain stable, up to approximately 32% and 8%, respectively. This shows that they are probably intermediate products of MEA thermal degradation, undergoing further reactions. Very low concentrations of HEIA and no HEEDA were detected in the samples from the pilot plant.

To sum up, from the major degradation products HEIA was the one that was detected in all the samples with formation percentage of 50%, HEEDA was present in most studies, although it was not found in the pilot plant samples. Similar conclusions were drawn for 2-oxazolidone which was not either present in the pilot plant samples and its formation rates were quite different between the different studies, probably due to the different experimental conditions used.

2.5.2.3 Pathways of formation of degradation products

Polderman et al. (1955) performed a study on MEA degradation products in the presence of CO_2 from gas treating plants. Chemical analysis of the degradation products and MEA contents was performed by means of titrations and other analytical procedures such as Kjeldahl and Van Slyke. It was observed that just by heating the carbonate salt, at temperatures encountered in scrubbing systems, MEA is converted into HEIA and HEEDA. A thermal degradation pathway for MEA, shown in Figure 2.6, was proposed according to which the first product generated is 2-Oxazolidone which then, if it reacts with another MEA, is converted into HEIA. HEIA then hydrolyses to give HEEDA. The equilibrium reaction of the HEIA hydrolysis to HEEDA is influenced by the temperature and CO_2 partial pressure. The HEEDA formed restores part of the lost alkalinity but because it is a stronger base than MEA is more difficult to be regenerated when it absorbs CO_2.

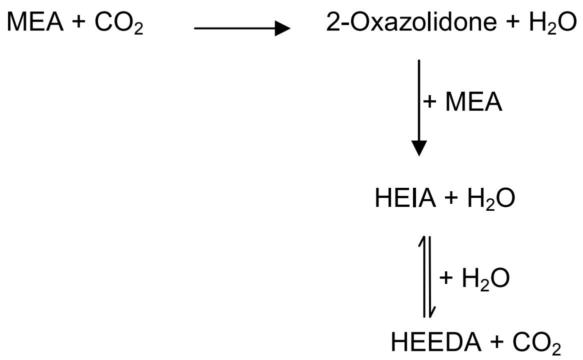


Figure 2.6 MEA thermal degradation pathway in the presence of CO_2 as proposed by Polderman (1955)

Yazvikova et al. (1975) performed a study on the pathways of MEA thermal degradation products in the presence of CO_2 at temperatures encountered in gas treating plants, the temperature used in this study was 200°C and chemical analysis was performed using an IR-spectroscopic method. It was observed that the overall rate of MEA degradation in the presence of CO_2 is limited by the slow rate of formation of 2-Oxazolidone. The reaction of 2-Oxazolidone with

MEA is very rapid and, consequently, it is the reaction that plays the key role in the losses of active MEA. It was noted that the reaction of 2-oxazolidone with MEA does not give as a immediate product HEIA but, a newly introduced product, called N,N'-di(hydroxyethyl)urea. Thereafter, its concentration starts to fall and it is converted to HEIA as an effect of temperature. HEIA then hydrolyses into HEEDA. The proposed pathway is shown in Figure 2.7.

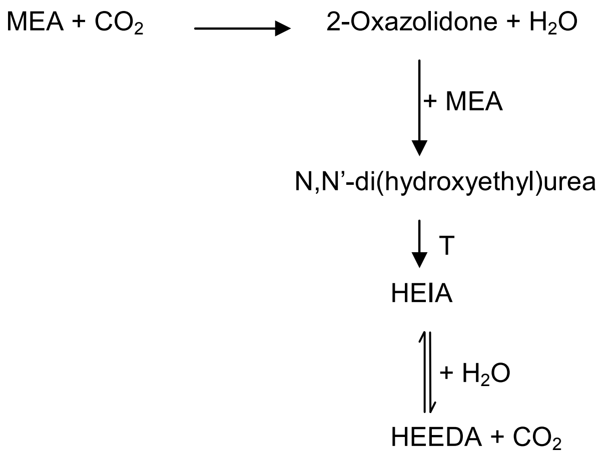


Figure 2.7 MEA thermal degradation pathway in the presence of CO_2 as proposed by Yazvikova (1975)

Davis (2008 & 2009) loaded aqueous MEA solutions with CO_2 and degraded them at temperatures of up to 150 °C and analysed them for degradation products by means of IC, HPLC and IC/MS. It was observed that as far as it concerns MEA, the mechanism for thermal degradation of MEA in the presence of CO_2 at temperatures below 200 °C is called carbamate polymerization. The pathway of formation of degradation products that can be seen in Figure 2.8 is proposed in his PhD thesis (2009). It was observed that the 2-oxazolidone production is a rate-limiting step in the carbamate polymerization procedure and that, contrary to what was previously reported by Polderman (1955) and Yavzikova (1975), HEEDA is a precursor of HEIA.

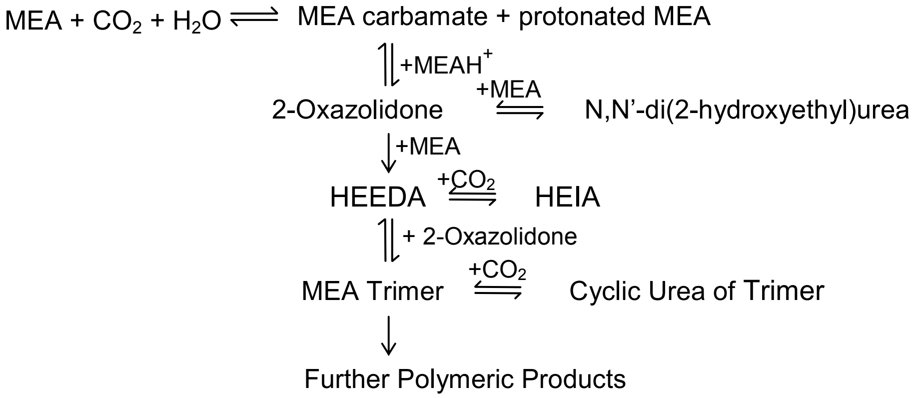


Figure 2.8 MEA thermal degradation pathway in the presence of CO_2 as proposed by Davis (2009)

According to this pathway proposed by Davis (2009) the MEA carbamate can cyclise going through a dehydrolysis step and forms 2-oxazolidone. Another molecule of MEA can attack 2-oxazolidone - at the ketone group - and give MEA urea (N,N'-di(2-hydroxyethyl)urea). 2-Oxazolidone can also react with a molecule of MEA to form N-(2-hydroxyethyl)-ethylenediamine (HEEDA). If HEEDA reacts with a molecule of CO_2 gives a HEEDA carbamate (which like the MEA carbamate) can undergo through ring closure to form 1-(2-hydroxyethyl)-2-imidazolidone (HEIA). HEEDA can also attack 2-oxazolidone (the same way with MEA) to form N-(2-hydroxyethyl)-diethylenetriamine (MEA trimer). The polymerization procedure can be further continued to give other polymeric products.

Lepaumier (2009 (a), 2009 (b) and 2010) performed thermal degradation studies of 40 ml of 4 mol/kg aqueous MEA solutions in the presence of CO_2 (pressures of up to 2 MPa) at 140°C for 15 days in a 100 ml stainless steel batch reactor. The liquid samples were analysed for degradation products using a GC-MS, an FT-ICR/MS and an NMR system. The formation of 2-oxazolidone was observed which is considered to be sensitive and react easily with another amine to give additional products. For MEA the main degradation product is an imidazolidone (HEIA) which is a very stable product. HEEDA, is another degradation product of MEA, which by its structure is favourable to lead to imidazolidones in other words the pathway of formation of degradation products presented agrees with the one presented by Davis (2009), see Figure 2.8.

Lepaumier et al. (2011) performed lab-scale experiments of MEA thermal degradation in the presence of CO_2 at stripper conditions (30% w/v aqueous MEA solution with initial CO_2 molar loading of 0.5 at 135^{o}C) and compared the thermal degradation pathways of MEA in samples from Esbjerg pilot plant in Denmark. An LC-MS and a GC-MS were used for the analysis of the degraded samples. In the samples from the lab-scale experiments 2-Oxazolidone, HEEDA and HEIA were again identified as the MEA major thermal degradation products in the presence of CO_2 at stripper conditions. It was noticed that HEIA concentration increased with time which is a sign of its stability, in contrast with the concentrations of 2-Oxazolidone and HEEDA that remain stable which shows that they are probably intermediate products of MEA thermal degradation, undergoing further reactions. A mechanism is proposed which comes into agreement with the degradation pathway proposed by Davis (2009); see Figure 2.8, for the major degradation products. In the pilot plant results, a very small concentration of HEIA was measured but no HEEDA was detected in the samples.

A theoretical study was performed by Vevelstad et al. (2011). This study was performed in order to verify the suggested mechanisms for thermal degradation with CO_2 based on the stability of the degradation products generated. This was attempted by performing calculations for geometry optimization, frequency and solvation (=creation of a compound using a solvent and a solute). It was suggested that for the thermal degradation of MEA in the presence of CO_2 the key primary degradation product is 2-oxazolidone, which then reacts to form further compounds. The total reaction mechanisms, suggested in this study, for MEA thermal degradation in the presence of CO_2 are, according to the author, energetically favourable.

To conclude, it is shown that the mechanism of formation of thermal degradation products of MEA in the presence of CO_2 below 200^{o}C is carbamate polymerization. Some early studies performed, on the MEA thermal degradation pathways, claimed HEIA was a precursor of HEEDA. Recent studies agree on the contrary. Overall, the MEA major thermal degradation products identified are 2-oxazolidone, HEEDA and HEIA with HEIA presented, by most studies, as the most stable degradation product and 2-oxazolidone as the first and key product that causes the MEA deactivation.

2.5.2.4 Corrosion due to thermal degradation products

Polderman et al. (1955) suggest that the effect of HEIA production in the plant operation is that the viscosity of the solution increases and if its concentration reaches high levels, precipitation of residues in parts of the equipment could be caused. (HEIA can be removed by distillation). Also, studies were performed to assess the effect of HEEDA and HEIA in the corrosion of carbon steel equipment. 20% per wt pure aqueous MEA solutions or spiked with 0.5% HEEDA and HEIA were heated to temperatures up to 150 ^{o}C for 350 hours. It was observed that, in the presence of HEEDA, the average liquid phase penetration in inches per year was 0.048 (1.22 mm/year) as opposed to 0.031 (0.79 mm/year) observed in the pure MEA aqueous solutions. Overall it was observed that the CO_2 is the primary corroding agent in uncontaminated solutions.

According to the study performed by Yazvikova et al. (1975), urea, such as N,N’-di(hydroxyethyl)urea that has been reported as an MEA thermal degradation product in the presence of CO_2 at stripping conditions, and its derivatives are known to form complexes with transition metals such as iron, therefore it could be linked with corrosion signs of steel equipment that has been observed in gas treating plants.

According to DuPart et al. (1993) an increase in CO_2 loading, MEA concentration or temperature has a positive effect on corrosion rates of carbon steel (up to 45 microns/year), 304 SS (up to 10 microns/year) and 316 SS (up to 5 mocrons/year). The study was performed on equipment from pilot plants. It is also suggested that the presence of MEA carbamates - as viable intermediary salts - impacts the corrosivity of MEA.

Kongstein E. O. and B. Schmid (2010) investigated the corrosion rates of 316SS with 5 M aqueous MEA solution saturated with 10% CO_2 in N_2 in a laboratory study at 135°C. A corrosion rate of 0.25 mm/year was measured in the first 10 hours of experimental time, decreasing to 0.15 by 50 hours. The effect of temperature is again highlighted as in the aforementioned studies.

During the years, considerable research has been performed to develop corrosion inhibitors and equipment to remove the degradation products and minimise their effect on the equipment. The most effective inhibitors are heavy metals such as arsenic or vanadium but the environmental concerns associated with them, have had an impact on their popularity.

Some recent studied have tested different additives considered to have an inhibition effect on MEA oxidation and the production of corrosive heat stable salts. Goff and Rochelle (2006) tested different additives to assess their effect on MEA oxidation and found that inhibitor A (a proprietary inorganic compound), Na_2SO_3 (sodium sulphite) and formaldehyde significantly reduced MEA oxidation. Sexton and Rochelle (2009) claim that the proprietary inhibitors A and B as well as EDTA were effective oxidation inhibitors. Supap et al. (2011) investigated compounds such as sodium sulfite (Na_2SO_3), potassium sodium tartrate tetrahydrate ($KNaC_4H_4O_6.4H_2O$), ethylenediaminetetraacetic acid (EDTA), hydroxylamine (NH_2OH) and blends of them which were found to effectively inhibit O_2 induced degradation of MEA during CO_2 capture from coal flue gases

2.5.3 Mixed degradation – Flue gas studies from actual plants

Strazisar et al. (2002) performed experiments to identify and quantify MEA degradation products found in a CO_2 capture plant from a coal-fired boiler used to produce electricity in Trona, California. Three different samples were obtained: virgin concentrated MEA, "lean" MEA (taken before the CO_2 absorption) and from the reclaimer bottoms, therefore after the MEA has been distilled for the degradation products removal. A combination of different analytical tools was used to identify and quantify the compounds present in solutions. A GC-MS along with a GC-FTIR system were used for the analysis of volatile organic compounds with two different GC columns in order to be able to analyses products with different polarities, no information is given on the extraction method used, as water samples can not be imported to the GC. An LVHRMS (low voltage high-resolution mass spectrometry) was used to obtain precise molecular masses for the organic compounds analysed. Finally, an IC system was used for the detection and quantification of inorganic ionic compounds and an ICP-AES system to measure concentrations of metals.

It was observed that 2-oxazolidone and HEIA that are known MEA degradation products due to CO_2 presence and temperature were present in the samples from the reclaimer bottoms. Acetic, propionic and butyric acids, previously reported as oxidative degradation products, were also present. Finally, N-acetylethanolamine and N,N-diacetylethanolamine are presented by the author as products of the reaction of MEA with acetic acid and they are claimed to be the most abundant products. Seven metal cations were present in the analysed reclaimer solutions and it is believed that they manly originated from the coal. Finally, the nitrate and sulphate anions were present amongst others on the reclaimer bottoms samples. Table 2.7 presents the detected organic compounds in the samples taken from the reclaimer bottoms of the pilot plant. It is interesting to note that HEEDA was not present in this pilot plant samples. HEEDA was not detected in the pilot plant studies that Lepaumier et al. 2011 present either.

Table 2.7 Detected organic compounds from MEA reclaimer bottoms (Strazisar et al. 2002)

Compound	Compound
HEIA	NH_3
N-acetylethanolamine	acetic acid
2-oxazolidone	propionic acid
N-glycylglycine	2,6-dimethyl-4-pyridinamine
N-(hydroxyethyl)succinimide	1-methyl-2-imidazolecarboxaldehyde
N,N-diacetylethanolamine	2-imidazolecarboxaldehyde

Strazisar et al (2003) conducted a study to detect the MEA degradation products and their pathways of formation from samples of a CO_2 capture plant from a coal-fired boiler used to produce electricity in Trona, California. The samples were taken from the same parts of the process and the analytical tools were the same as described in Strazisar et al. 2002. In Table 2.8 the degradation products detected in the samples from the reclaimer bottoms of the pilot plant are presented. In this study some new major MEA degradation products were observed. This indicates that there are chemical degradation reactions that occur in the real plant conditions that do not occur in the laboratory experiments where pure gases are used. A new mechanism was proposed according to which carbamate polymerisation (proposed for MEA thermal degradation in the presence of CO_2 at temperatures below 200 ^{o}C) is a minor pathway. According to the proposed pathway, N-acetylethanolamine is believed to be formed as a product of the reaction of acetic acid with MEA, N-acetylethanolamine then may react with another MEA to give 2-hydroxyethylamino-N-hydroxyethyl acetamide. This molecule may then form either 4-hydroxyethyl-2-piperizinone or 1-hydroxyethyl-2-piperazinone. Another similar mechanism starting with the reaction of propionic acid with MEA could justify the formation of 3-hydroxyethylamino-N-hydroxy-ethyl propanamide and 1-hydroxyethyl-3-homopiperazine.

Concerning the rest of the degradation products, 2-oxazolidone and HEIA are the degradation products form by carbamate polymerisation but they are reported as minor components and ammonia, acetic and propionic acid as oxidation products. Once again it is interesting to note again that HEEDA was not present in this pilot plant samples either as well as in the study by Lepaumier et al. 2011.

Table 2.8 MEA degradation products found in reclaimer bottoms samples of a pilot plant (Strazisar et al. 2003)

Compound	Compound	Compound
N-Formylethanolamine	HEIA	NH_3
N-acetylethanolamine	1-hydroxyethyl-2-piperazinone	acetic acid
2-oxazolidone	4-hydroxyethyl-2-piperizinone	propionic acid
N-(hydroxyethyl)-lanthamide	3-hydroxyethylamino-N-hydroxy-ethyl propanamide	2,6-dimethyl-4-pyridinamine
1-hydroxyethyl-3-homopiperazine	2-hydroxyethylamino-N-hydroxyethyl acetamide	1-methyl-2-imidazolecarboxaldehyde

Bello and Idem (2005) conducted experiments under absorption and desorption conditions (55-120 ^{o}C) with MEA in concentrations 5 and 7 mol/L, O_2 pressures 250-350 kPa and CO_2 loading 0-0.44 mol CO_2/mol of MEA. The effects of temperature, MEA concentration, O_2 pressure and CO_2 loading on degradation were examined. For this purpose, a stainless steel rotary-type autoclave reactor and GC/MS were used in order to perform these experiments. The GC-MS system used was equipped with a high polarity poly(ethylene glycol) column. The sample was injected in the column with an autosampler as reproducibility issues were faced during the analysis, problem that was observed in the present study as well. It is claimed that the GC-MS system used had an estimated error of about +/- 3%. Once again no information is given on the extraction method used to partition the organics from water samples into a different solvent, as water samples can not be imported in a GC system.

Table 2.9 presents the oxidative degradation products detected in the degraded samples at 120°C in the presence of O_2 after 135 h without CO_2. As shown in Table 2.9 HEIA is presented as an oxidative degradation product. HEEDA and 2-oxazolidone were not detected in the samples that were degraded in the presence of CO_2. In the experiment performed at similar conditions to the present study, the major degradation products detected in a 7 mol/L aqueous MEA solution at 120°C in the presence of CO_2 after 135 hours were 12-crown-4, 2-(2-ethoxyethoxy)ethanol and 1,4,7,10,13,16-hexaoxacyclooctadecane. These large polymeric compounds could have been formed due to carbamate polymerisation but, as the pathways of CO_2 induced degradation at stripper conditions have not been yet identified, it is difficult to draw a firm conclusion for their formation mechanism. Overall, it is claimed by the authors that the presence of CO_2 causes less oxidation products to be formed.

Table 2.9 Summary of the degradation products detected in samples that degraded at 350 kPa O_2 at 120°C for 135h (Bello and Idem, 2005)

Compound	Compound	Compound
N-(2-hydroxyethyl) acetamide	2,2-dimethyl-3(2H)-furanone	4-methylmorpholine
Formic acid	N-(2-hydroxyethyl) succinimide	HEIA
1H-imidazole	1-piperazineethanol	3-methylpyridine
N-formyl-N-methylformamide	diisopropanolamine	acetamide
1,3-dioxane	(dimethylamino) ethylene tetr-butylamine	nitrosomethane
uracil	2-(2aminoethoxy) ethanol	2-(methylamino) ethanol
4-(hydrazinocarbonyl) imidazole	2-methylpropanitrile	acetic acid
5-(hydrazinocarbonyl) imidazole	ethoxyethene	2-methyl-1H-imidazole

Supap et al. (2006) performed a comparative study between GC-MS, High Performance Liquid Chromatography-Refractive Index Detection (HPLC-RID) and Capillary-Electrophoresis-Diode Array Detection (CE-DAD) for the detection of MEA and its degradation products in systems of MEA/H_2O/O_2, MEA/$H_2O/O_2/CO_2$, MEA/H_2O/CO_2. These experiments were conducted in a 600 ml stainless steel batch reactor using MEA concentrations of 5 kmol/m^3, O_2 pressures of 250 kPa, degradation temperatures of 328 or 393 K and CO_2 loading 0.51 mol of CO_2/mol of MEA for up to 350 hours. The GC-MS system used was equipped with three different columns, a high polarity, a medium polarity and a low polarity column, for the analysis of MEA and its degradation products. An autosampler/autoinjector was used again but no information was given on the extraction method used as no water samples can be imported in a GC-MS system. The same conditions were used to run the samples in all the three columns. The HPLC system was equipped with two different experimental set ups, enabling it to analyse MEA and the degradation products that had the ability to acquire positive charges under acidic conditions. Finally, the CE-CAD system was using a set ups and conditions capable of detecting MEA and its basic and acidic products.

It was found that the GC-MS was the most sensitive technique to detect the greatest number of MEA degradation products in the shortest time and that the sample preparation needed was much less than that for the other methods used. Moreover, in the system that CO_2 was present, the MEA oxidative degradation rate was found to be lower than in the system with no CO_2. Compounds such as HEIA, NH_3, and formic, acitic and oxalic ions were present, amongst many others, in the samples analysed. In Table 2.10 a summary of the compounds found in the degraded samples and have been previously reported in the literature is presented. It is interesting to note that HEEDA and 2-oxazolidone were not detected in these samples either. The author is not classifying the compounds under the categories of thermal and oxidative degradation.

Table 2.10 Summary of the compounds found in the degraded samples in the $MEA/H_2O/O_2/CO_2$ system (Supap et al. 2006)

Compound	Compound	Compound	Compound
1-methylazetidine	N(2-hydroxyethyl) succimide	4,5 dimethyloxazole	acetic acid
imidazole	1-amino-4-methyl piperazine	18-crown-6	pyrimidine
D,L homoserine lactone	2-pyrolidinone	ethylurea	acetamide
N-(2-hydroxyethyl) acetamide	N-methylene ethanamine	N-glycylgycine	acetamide
1,3-dioxane	5-aminovaleric acid	dimethylhydrazone-2-propanone	2-methylaminoethanol
N-methyl formamide	D,L-aspartic acid	HEIA	acetaldehyde
2-ethyl-1H-imidazole	2-[(2-aminoethyl)amino] ethanol	NH_3	ethanol
uracil	ethylamine	formic acid	oxalic acid

To conclude, a wide range of degradation products are presented both in the samples from a pilot plant and the samples produced by a lab procedure. The commonly reported known MEA oxidative degradation products were oxalic and formic acids and NH_3, whereas from the known MEA thermal degradation products only HEIA was detected in all the samples. HEEDA was not detected in any of the samples and 2-oxazolidone in some of them, which could lead to the conclusion that at actual plant conditions different reactions may occur than those encountered in controlled laboratory experiments or that HEEDA is one of the intermediate degradation products in the carbamate polymerisation process as indicated by Davis 2009, Lepaumier (2009 (a), 2009 (b), 2010 and 2011) and as observed in the present study as well.

The presence of other gases in the actual plant inlet gas, such as SO, SO_2 and NO_x, in combination with O_2 and the elevated temperatures encountered in the stripper might cause different interactions between the degradation products and lead into different degradation pathways. Note also here that at the experiments performed in laboratory environments the conditions were accelerated to produce highly degraded samples within a reasonable timescale. Therefore, a need for further research to explore the pathways of formation of degradation products under actual plant conditions is illustrated as well as developing chemical analysis methods for the identification and quantification of the degradation products.

2.6 SUMMARY

Amine scrubbing has been an established technology over the past several decades for removal of acid gases (such as CO_2 and H_2S) from gaseous streams in the chemical and oil industries. The key issues concerning the design and the technical and economic operation of an amine scrubbing system for a coal fired power plant, include the selection of the appropriate solvent and its management for a specific system, the system's design characteristics and the energy requirements that have a detrimental effect on the cost of the technology.

Primary, secondary, tertiary and sterically hindered amines are the most common solvents for CO_2 removal from gaseous streams but still MEA is the solvent of choice and the baseline solvent for comparison due to good characteristics over other amines and the experience developed due to its wide use. Issues such as solvent volatility losses, degradation due to the presence of CO_2 at elevated temperatures, O_2, SO_x, NO_2 and fly ash, that are addressed with additional equipment and solvent make up, cause the technology costs to rise and need further research because of the potential environmental impact of the disposal of the by-products generated.

The irreversible reactions which may occur during the carbon capture process that result in products, from MEA, that can not be recovered are called degradation. Oxidative degradation is defined as the reactions of MEA, in the absence or presence of CO_2, with O_2 at absorber conditions. The O_2 effect on MEA is quite considerable with reported MEA losses due to oxidation up to 20%. The major MEA oxidation products reported in the literature are NO_2/NO_3 ions, NH_3, oxalate, formate, acetate, HEI and HEF.

Thermal degradation is defined as the irreversible reactions of MEA with CO_2 that occur due to the elevated temperatures encountered in the stripper, the chemical reaction process is termed carbamate polymerisation. The effect of CO_2 loading, temperature and degradation time had a considerable effect on MEA with reported MEA loss of up to 65%. The major MEA thermal degradation products, in the presence of CO_2 at temperatures below 200^oC, reported are

HEIA, HEEDA and 2-oxazolidone. HEIA is reported as the most stable with formation percentages that reach 50% whereas 2-oxazolidone as the first step to MEA thermal degradation and its formation as a critical reaction. Some discussion on the pathways of formation due to some early studies that presented HEEDA as the MEA most stable degradation product and as a HEIA precursor are challenged by new studies that claim the opposite. Last but not least, some issues of corrosion of different types of steel due to temperature, MEA concentration and MEA degradation products presence are presented.

Finally, a few studies presenting a mixture of oxidative and thermal degradation are presented as well as some studies with analyses of samples from actual plants. Most of the major oxidative degradation products were present in those samples whereas HEEDA (major thermal degradation product) was not detected in any of the samples and 2-oxazolidone that was detected in a few cases. A wide list of degradation products detected by these studies is also presented.

CHAPTER 3
EXPERIMENTAL

3.1 INTRODUCTION

In this chapter the materials, methods and systems used to perform this research work are discussed and the results processing procedures are detailed.

Section 3.2: The chemicals and materials used in the present study are presented.

Section 3.3: The analytical equipment used to perform the present study is described.

Section 3.4: The absorption/stripping rig built, capable of applying repeated cycles of absorption/stripping to different amine solvents, is presented. The important parameters, calculations and course of action taken to design and commission this rig are also detailed.

Section 3.5: The thermal treatment rig and the experimental procedure developed in order to thermally degrade MEA samples by exposing them to high temperatures for prolonged periods of time are presented. The parameters considered, the calculations, the design and process developed are also described.

Section 3.6: The procedure followed and the results processing to determine the CO_2 volume at the absorption/stripping rig's outlet by means of microGC is detailed.

Section 3.7: The inorganic carbon content measurement procedure, used to determine the CO_2 molar loading of MEA, and the results processing methods and calculations are described.

Section 3.8: The analytical procedure for the detection and quantification of the major oxidative degradation products of MEA is presented. The method development and final procedure are described along with the calibration curves and the method detection limits.

Section 3.9: The GC-MS available equipment is described along with the changes made on the instrument setups and the procedures followed in order to develop and apply the appropriate method for the analysis of the MEA and its major thermal degradation products. The calibration curves produced are also presented.

Section 3.10: Presents the description of the experimental procedure followed for the generation of thermally degraded samples and the procedure developed to assess the effect of thermal treatment on the solvent.

Section 3.11: The summary section of the experimental chapter.

3.2 MATERIALS

All the chemicals used in the laboratory work are listed in Table 3.1.

Table 3.1 Chemicals and associated materials used and their sources

Chemical	Function	Supplier and Cat. No.
Paraffin oil	Oil bath medium	Fisher Scientific P/0320/17
Ethanolamine 99.5%	CO_2 solvent	Fisher Scientific E/0701/17
SulfaVer 4 pillows	Sulphate analysis	HACH® 2106769
NitraVer 5 pillows	Nitrate analysis	HACH® DR/890
NitriVer 2 pillows	Nitrite analysis	HACH® DR/890
OnGuard II H cartridges	IC sample pre-treatment	Dionex 057086
TraceCERT Nitrate standard	Chemical analysis by IC	Sigma-Aldrich 74246-100mL
TraceCERT Nitrite standard	Chemical analysis by IC	Sigma-Aldrich 67276-100mL
Potassium nitrite 97%	Chemical analysis by IC	Acros Organics 222702500
Sodium nitrate	Chemical analysis by IC	Fisher Scientific S/5560/53
Formic acid 98+%	Chemical analysis by IC	Fisher Scientific F/1850/PB08
Acetic acid glacial 99.7%	Chemical analysis by IC	Fisher Scientific A/040/PB08
Oxalic acid 99.5-100.5%	Chemical analysis by IC	Fisher Scientific O/0600/53
2-Oxazolidone 98%	Product of degradation	Sigma-Aldrich 09409-5G
1-(2-Hydroxyethyl)-2-imidazolidinone 75% in H_2O	Product of degradation	Sigma-Aldrich 378658-250mL

Chemical	Function	Supplier and Cat. No.
N,N-(2-Hydroxyethyl) formamide	Product of degradation	Sigma-Aldrich S617296-1EA
N-(2-Hydroxyethyl) ethylenediamine	Product of degradation	Sigma-Aldrich 127582
17% O_2, 15% CO_2 (w/w)/ 16% O_2, 10% CO_2 (v/v) in N_2	Micro-GC calibration	Scientific and Technical Gases
Diethyl ether	GC-MS analysis	Fisher Scientific

All aqueous dilutions where necessary were performed with deionised water.

3.3 ANALYTICAL EQUIPMENT

The analytical equipment and specifications for each instrument are listed below:

1. *Ion Chromatography, IC*

The IC system was used for the analysis of the major MEA oxidative degradation products. It was the Dionex ICS-2000 fitted with the IonPac AS11-HC anion exchange column with a conductivity-dependant detector.

2. *Gas Chromatography – Mass Spectrometry, GC-MS*

The GC-MS system was used for the analysis of MEA and its major thermal degradation products. All work was performed on a Perkin Elmer CLARUS 500 GC-MS. The GC columns used were the Elite-5MS by Perkin Elmer and the Rtx 5 Amine from Restek with different extraction methods and instrument conditions until good responses were obtained.

3. *The Micro Gas Chromatograph, micro-GC*

The micro-GC (Varian CP-4900 running Galaxie software with a thermal conductivity detector and the packed column M5A BF with helium as a carrier gas) was used to measure CO_2 concentrations at the exit of the gas absorption/desorption rig described in one of the following sections.

4. *Inductively Coupled Plasma Optical Emission Spectrometry, ICP-OES*

For the analysis of the corrosion products an ICP-OES system was used. The instrument used was the Perkin Elmer Optima 2100DV ICP-OES running the WinLab 32 software.

5. *Carbon Contents of Aqueous Solutions*

The CO_2 molar loadings of the MEA samples were determined by means of the inorganic carbon measurement with a TOC instrument. These measurements were made with a Total Organic Carbon Analyser TOC-500(A) by Shimadzu using the TOC-control-V software.

6. *Colorimetric Determinations of Anions*

These were performed with the HACH portable data logging colorimeter DR/890

3.4 ABSORPTION/STRIPPING RIG

In this section the absorption stripping rig design and commissioning are described. The purpose of this system was to be able to apply repeated cycles of absorption/stripping to different amines using conditions as close as possible to the conditions used on an actual amine scrubber. The solvent behaviour, the parameters that affect its operational lifetime and its CO_2 loading capacity were assessed using this system. The system parts are also listed.

3.4.1 Absorption/stripping rig development

The design of the experimental rig involved the literature review, presented in Chapter 2, and a visit to the University of Texas to attend the Rochelle meeting in January 2008. Also present at the meeting were researchers from the University of Regina Canada and the NTNU University, Norway.

The salient points of the visit are presented here.
The subjects presented fell into four categories:

- Solvent Management
- Thermodynamics and Solvent Development
- Rates and Absorber Modelling
- System Modelling and Sequestration

The main area of interest in the current project is solvent management and in this category the subjects presented were as follows:

- Oxidative and thermal degradation of MEA, blends of MEA and aqueous Piperazine (PZ), and AMP.
- Theoretical study of amine degradation using computational chemistry
- The oxidative degradation and oxidative reduction potential of the solvent ROC20.
- Degradation of the solvent ROC16 (which is a novel amine solvent) and on the solubility of potassium sulphate (K_2SO_4) in CO_2 - loaded MEA/PZ solutions.

- Environmental impacts and various aspects of the absorbents used for the carbon dioxide capture

The main purpose of the trip was to visit the laboratories used for the experiments. The first apparatus used for the oxidative degradation experiments is shown in Figure 3.1 and is called the "low gas flow" apparatus. In this system the O_2 and CO_2 mixture, which is controlled by a rotameter, is fed to the saturator.

Figure 3.1 Low flow gas apparatus at Austin

Then, the saturated mixture enters the reactor from the top and it is agitated to be mixed with the solvent. The system is stopped once a day to take samples. Analysis for amino acids and aldehydes are performed by IC and HPLC. The second system used for these sets of experiments is the "modified low gas flow" apparatus which is the same system but the reactor is fed with CO_2 and O_2 gases from different bottles. This is done because the pure O_2 speeds up the degradation. Finally, the third system used is the "high gas flow" apparatus which can be seen in Figure 3.2.

Figure 3.2 High gas flow apparatus in Austin

This system is again similar to the “low gas flow” system but the gas inlet is from the bottom of the glass reactor, the gas and the amine being mixed in the reactor. From the top of the reactor there is a heated line which takes samples at specific time intervals and transfers them to an FT-IR system. This apparatus is used for continuous measurements, so there is no need to stop the system to take samples. The main difference between the low and high gas systems is the gas flow rates, which are low and high respectively.

For the thermal degradation experiments, which are carried out under stripper conditions, high pressure sample containers of 316L stainless steel tubing and endcaps were used at Austin. These containers are put in a forced convection oven at constant temperature, so as to maintain the CO_2 loading at high temperature and pressure to accelerate the degradation. Two different sizes of containers are used; the 2 ml sample containers for the tests at 100°C and 150°C, and the 10 ml sample containers which are used for the 120°C and 135°C tests. A high pressure reactor could be used but this experimental design is simpler and allows for many samples to be tested in the same time. A combination of two different measuring devices is used because as it was claimed that:

i. with the GC results can be altered at the high temperatures, because of the high injection temperatures that the instrument is using to evaporate the sample before it is injected to the GC column.

ii. with HPLC it is difficult to detect amines with standard detectors and

iii. with cation ion chromatography (IC) it is not possible to detect non-ionic compounds

In order to conduct studies for kinetic and volatility data a wetted wall column was being used as can be seen in Figure 3.3.

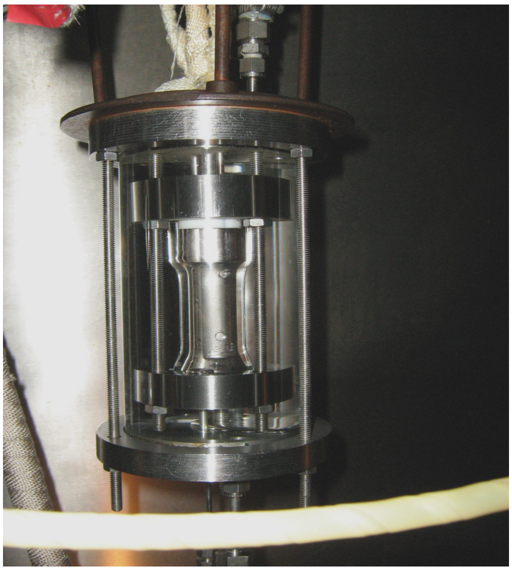


Figure 3.3 Wetted wall column for kinetic and volatility studies at Austin

Around the external wall of the column paraffin oil flows to ensure that the temperature is kept constant and to enable experiments to be conducted both for absorption and desorption. The measuring system is as seen in Figure 3.4.

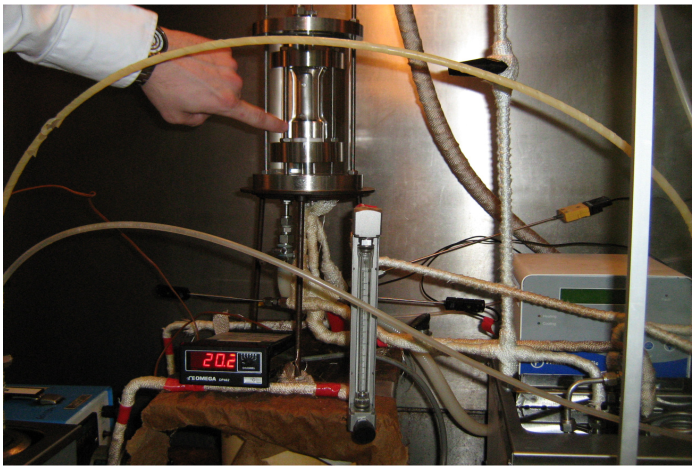


Figure 3.4 Experimental apparatus for absorption and desorption studies at Austin

3.4.2 Absorption/stripping rig description and experimental protocol

The constructed absorption/stripping rig at Cardiff is shown in diagrammatic form in Figure 3.5 and a photograph is shown in Figure 3.6 with the system placed in a fume cupboard. The system is capable of applying repeated cycles of absorption/stripping to different amine solvents using different inlet gas compositions. The initial purpose of this rig was to be able to assess the performance of different solvents and the key parameters that affect their operational lifetime. Exact details of the component parts are included in Section **Σφάλμα! Το αρχείο προέλευσης της αναφοράς δεν βρέθηκε.** (Rig Components) but the following gives an outline of the apparatus and initial experimental protocol.

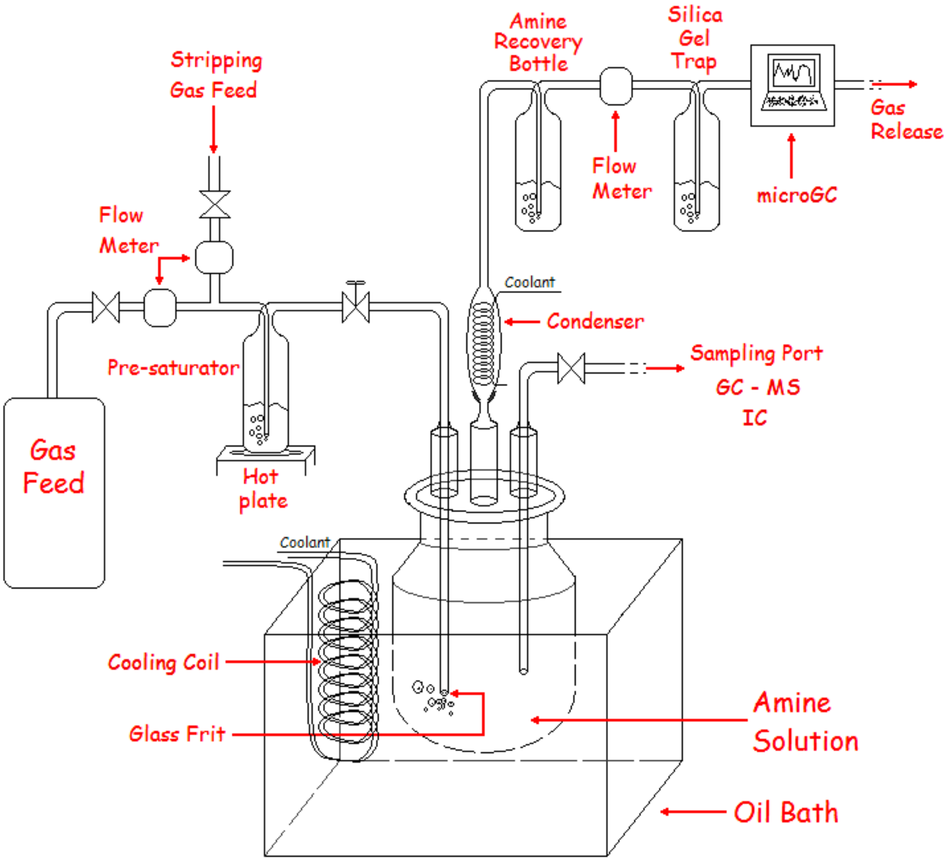


Figure 3.5 Schematic of the Cardiff Absorption/Stripping Rig

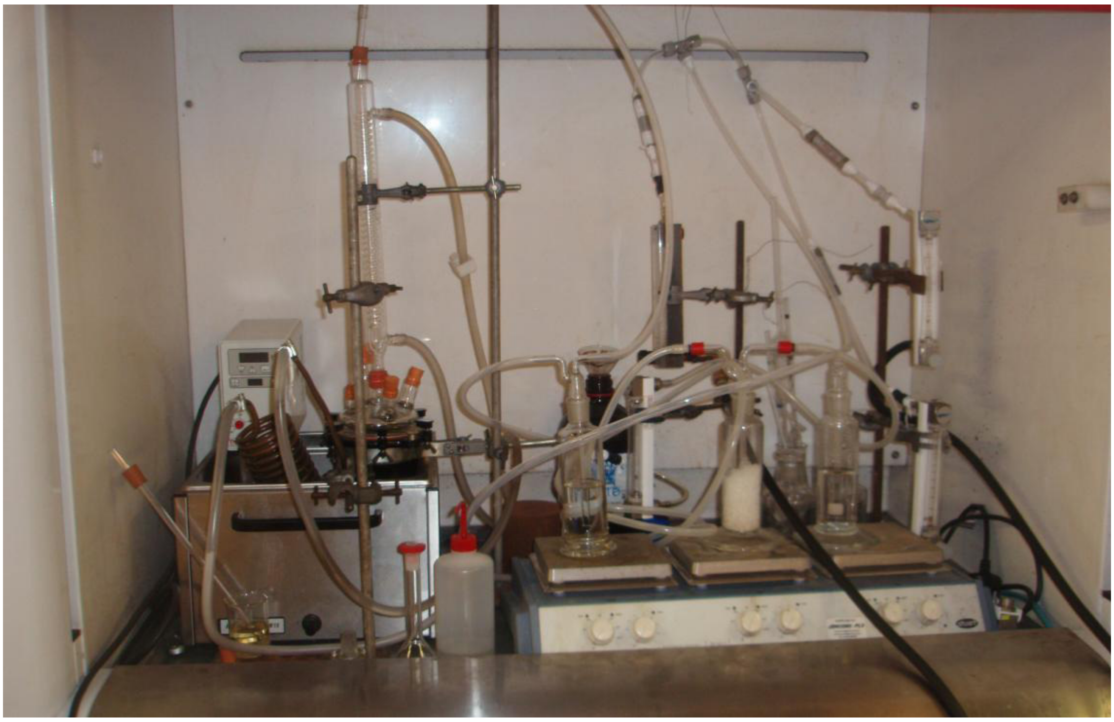


Figure 3.6 **Photograph of the Cardiff Absorption/Stripping Rig in a Fume Cupboard**

This experiment was a cyclic process of two stages, absorption and desorption. Unless otherwise stated, the procedure was as follows:

Absorption: The glass reactor filled with the aqueous MEA solution had to be at a stable temperature, so the oil bath temperature was raised at 50 ^{o}C. The gas feed valve was opened (at this point the stripping gas feed is closed) and the CO_2 gas was fed to the pre-saturator, through a flow controller, in order to maintain the water balance in the system. Then, it was bubbled to the glass reactor using a sintered gas distribution tube to ensure good distribution of the gas in the solvent. The excess gas was vented to the fume cupboard through a condenser and an amine recovery bottle to avoid the escape of any amine or water vapours from the system. Whilst the amine was being loaded, measurements of the excess gas flow rate and its CO_2 content were taken with a CO_2 rotameter and a microGC system, respectively. When the desired CO_2 molar loading was achieved, the valve of the CO_2 gas feed was closed.

Desorption: The oil bath temperature was raised to 120 ^{o}C. The stripping gas feed valve was opened and the N_2 was fed to the glass reactor through the glass frit to ensure good agitation. While the amine was releasing the captured CO_2, which was vented to the fume cupboard through a condenser and an amine recovery bottle, measurements of the CO_2 content at the system's outlet were taken with a microGC system and an air/nitrogen flow meter gives the volumetric gas flow rate. A cooling coil was also available in order to cool down the oil bath and the reactor after the end of the stripping in order to reduce the experimental time and be able to perform more than one absorption/stripping cycles per day.

A Dreschel bottle filled with silica gel was also placed at the system's outlet in order to avoid any water vapours, carried by the gas, to be transferred to the microGC system. Samples of the amine were taken from the reactor in order to measure the amine losses and detect and quantify any degradation products generated from the process by means of Gas Chromatography Mass Spectrometry (GCMS) and Ion Chromatography (IC). The CO_2 molar loading was determined by means of inorganic carbon content measurement.

3.4.3 Absorption/stripping rig components

The principal components were all commercially sourced and are listed as follows:

1. A gas feed system with three large gas canisters for pure CO_2, O_2-free N_2 and air together with their regulators, and in the case of CO_2 an in-line heater, purchased from BOC
2. 3 Pneumatic in line non-return valves, ¼" from RS (product no 486-8945)
3. Four rotameters, two for CO_2 and two for N_2, purchased from Fischer Scientific Ltd with the following specifications:
    - Flow meter air/nitrogen variable 0.1-1.2 L/min Influx (product no FJC-625-035V)
    - Flow meter air/nitrogen variable 0.02-0.25 L/min Influx (product no FJC-625-015E)
    - Flow meter carbon dioxide variable 10-100 cm^3/min Influx (product no ENGFIS1-CO_2)

    - Flow meter carbon dioxide variable 50-750 ml/min Influx (product no ENGFIS14-CO_2)
4. Three gas wash bottles, Quickfit Dreschel borosilicate glass 250 ml (item no QWF-360-X) with bottle heads Quickfit Dreschel sintered (item no BTF-900-090K).
5. A circulator oil bath Thermo Scientific Haake, DL30-W15/B purchased by Fisher Scientific (product no CLR-420-020N)
6. A glass reactor purchased from Fisher Scientific consisting of:
    - Vessel SLV reactor cylindrical borosilicate glass 1 L (product no SLV-110-110Y)
    - Lid SLV multipoint (product no SLV-110-050A)
    - Ring SLV sealing (product no SLV-110-230V)
    - Collar SLV for 100 mm flange (product no SLV-110-250P)
7. Gas distribution frit Pyrex with pore size 1, 14mm dia - Fisher Scientific (item number TUL-410-020A)
8. A coil condenser, Pyrex glass 207 mm length and cone 40/38 (item no QCJ-240-J)
9. FEP tubing 10mm OD, 8mm ID purchased from RS (product no 486-8945)
10. Tubing silicone rubber translucent 6.5 mm x 1.5 mm purchased from Fisher Scientific (product no FB50869)
11. 9 ¼” BSP 10 mm Pneufit straight adaptors purchased from RS (product no 210-2316)
12. 1 male BSPT straight connector ¼” x 10 mm purchased from RS (product no 287-3327)
13. 1 Diff dia str push-in fitting 8 to 10 mm purchased from RS (product no 617-4078)
14. 2 Tee piece 10 mm OD from RS (product no 739-180)

3.5 THERMAL DEGRADATION RIG

During the course of this project, and after realising that it would not be feasible to produce degraded samples in the gas absorption/stripping rig within reasonable timescales, it was decided to focus on thermal degradation. For that reason, an extended literature review was performed and based on the information gathered during the visit to the University of Texas; it was decided to design a new experimental procedure and a thermal degradation process/rig to be able to thermally degrade samples quickly enough. The purpose of the new thermal degradation rig described in the following Sections was to produce thermally degraded samples, which would then be tested in the gas absorption/stripping rig to assess the solvent deterioration in CO_2 uptake capacity due to thermal degradation.

3.5.1 Thermal degradation rig development

The purpose of the thermal degradation rig development was to assess the behaviour of 500 ml of 5 molal aqueous MEA solution loaded with CO_2 if it is exposed to temperatures of 150 ^oC and above and for a long period of time (up to 8 weeks). The produced thermally degraded samples were then tested using the absorption / desorption rig (Figure 3.5) to investigate the solvent deterioration in CO_2 uptake against the performance of a known pure amine sample and to try to identify and quantify any degradation products. For that reason, 500 ml samples of solutions needed to be thermally degraded so as to be able to test them in the gas absorption/stripping rig.

The experimental design used by Davis (2008) was thought to be the most appropriate in order to degrade amine samples in an easy and quick way. Davis (2008) loaded with CO_2 amine solutions of different concentrations and thermally degraded them in 10 ml stainless steel pressure vessels in a forced convection oven. The only difference was that the sample volumes that needed to be prepared were 500 ml and that meant that the gas volumes absorbed by the amine would be much higher and as a result the pressures built would be much higher as well.

Therefore, before ordering any equipment for use in these experiments, for safety reasons, some initial calculations needed to be performed in order to estimate what kinds of pressures should be expected.

3.5.1.1 Worst case scenario

The first step was to determine the worst case scenario, which means to calculate the CO_2 partial pressure developed in a 600 ml vessel if 590 ml of 5 molal MEA almost fully loaded with CO_2 were degraded at 150 ^{o}C for up to 8 weeks, i.e. if the available headspace was 10 ml. According to Davis J. and G. Rochelle (2008) if a 7 molal MEA solution with initial CO_2 loading of 0.4 moles of CO_2 / mole of MEA is degraded for 8 weeks at 150 ^{o}C the final MEA concentration will be 0.8 molal, in other words 89% of the MEA is lost.

Taking the aforementioned information into account, it was calculated that 590 ml of 5 molal MEA, if its initial loading is 0.4, can absorb 0.91 moles or 20.26 L of CO_2. If then, 89 % of the MEA was lost, which means that the number of moles of MEA in the final solution would be 0.25, only 0.125 moles of CO_2 or 2.78 L could stay in solution. This means that 17.48 L of CO_2 could need to be in the 10 ml headspace. The CO_2 partial pressure was calculated, using the ideal gas law, to be 2743.451 bar (274.35 MPa). It is important to note here that CO_2 does not behave as an ideal gas. The ideal gas law was used to perform those calculations in order to have an estimation of the pressures that they were going to be built up. For more accurate calculations a CO_2 compressibility factor should have been used.

Of course, quite a considerable amount of this CO_2 would be absorbed by the water - at these pressure and temperature conditions (Dodds et al. 1956) - and HEEDA, which is being reported (Davis 2009, Lepaumier 2009 (a), Lepaumier 2009 (b), Leapumier 2010 and Lepaumier 2011) as one of the major thermal degradation products of MEA.

From these calculations, the possibility existed of extremely high pressures (274.35 MPa) to be developed in the vessel headspace. At this stage it was decided to purchase the high pressure vessels and to carefully monitor any pressure increase and use it as a measure of degradation. The experiment would be terminated if the pressures approached safety limits.

3.5.1.2 Iterative calculations with various CO_2 loadings

In order to have a clearer idea of what pressures to expect a journal paper with similar experimental conditions, to those planed in the present work, was found in the literature for 150 °C by Jou et al (1995). It was assumed that the same CO_2 solubilities can be applied to less concentrated MEA solutions (5 molal) than the 30 % w/v (7 molal). Based on the information available, the CO_2 partial pressures versus the CO_2 loading were plotted and Excel was used for curve fitting for the results (Figure 3.7). The equation of the curve at 150 °C is Equation 3.1.

$$y = 8884.4x^{2.4688} \qquad \text{Equation 3.1}$$

where y is the CO_2 partial pressure and x is the CO_2 molar loading. All the calculations were performed for 590 ml of 5 molal aqueous MEA solution at 150 °C with 10 ml available headspace and for four different CO_2 loadings. Different numbers of moles were assumed to be released into the headspace, and then the resulting pressure build-up was calculated with the ideal gas law and compared with the values that resulted from the study of Jou et al (1995).

In Table 3.2 the results for initial loading 0.25 moles of CO_2 / mole of MEA are shown, the total number of moles of CO_2 in MEA is 0.5675 or 12.63 L. The partial pressure from the literature was calculated using the aforementioned Equation 3.1. In order to calculate the CO_2 partial pressure in the headspace the Ideal Gas Equation 3.2 was used.

$$P_{CO2} = \frac{[molesofCO_2inheadspace] \times 0.08315 \times 423}{0.01} \qquad \text{Equation 3.2}$$

It should be noted here again that CO_2 does not behave as an ideal gas and the Ideal Gas Law was used as a tool to have a rough estimation of the pressures. As already mentioned a CO_2 compressibility factor should have been used for more accurate results.

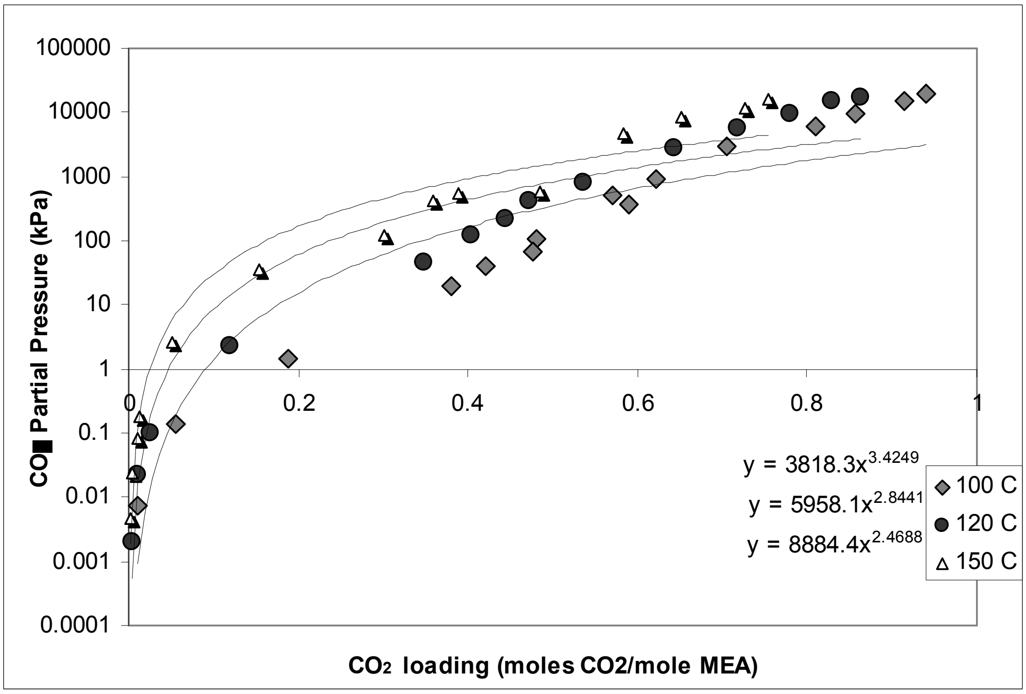


Figure 3.7 Experimental data for CO_2 partial pressure versus CO_2 molar loading presented by Jou et al. (1995) for 100, 120 and 150 °C.

Table 3.2 Calculated CO_2 partial pressures for a 5 molal aqueous MEA solution with initial molar loading 0.25 and comparison with literature values.

Assumed CO_2 released in the headspace (moles*10^{-5})	Calculations		Jou et al. (1995)
	Loading after the CO_2 released	P_{CO2} headspace (kPa)	P_{CO2} (kPa)
80	0.249648	281.38	288.9
81	0.24964	284.9	288.89
82	***0.249639***	***288.41***	***288.88***
83	0.249634	291.93	288.86
84	0.24963	295.45	288.85

Note: 590 ml of 5 molal aqueous MEA solution, 10 ml available headspace, initial loading 0.25 moles CO_2 / mole MEA, 0.5675 moles of CO_2 initially in solution, temperature 150 °C

As the loading increases the CO_2 partial pressure in the headspace increases as well. The bold data refer to where agreement between the calculated values (based on the ideal gas law) and those reported by Jou et al. (1995) were obtained.

In Table 3.3 the CO_2 partial pressure when the initial sample loading is 0.3 moles of CO_2 / mole of MEA is shown, the total number of moles of CO_2 absorbed by the MEA is 0.681 or 15.16 L. The results were calculated in the same way as described above. The bold data refer to agreement between the calculated values - based on Equation 3.2 - and those reported by Jou et al. (1995).

Table 3.3 Calculated CO_2 partial pressures for a 5 molal aqueous MEA solution with initial molar loading 0.30 and comparison with literature values.

Assumed CO_2 released in the headspace (moles*10^{-4})	Calculations		Jou et al. (1995)
	Loading after the CO_2 released	P_{CO2} headspace (kPa)	P_{CO2} (kPa)
12.6	0.299445	443.17	452.65
12.7	0.299441	446.69	452.63
12.8	***0.299436***	***450.21***	***452.61***
12.9	***0.299432***	***453.72***	***452.60***
13	0.299427	457.24	452.58
13.1	0.299423	460.76	452.56

Note: 590 ml of 5 molal aqueous MEA solution, 10 ml available headspace, initial loading 0.30 moles CO_2 / mole MEA, 0.681 moles of CO_2 initially in solution, temperature 150 ^oC

As the loading increases the CO_2 partial pressure in the headspace increases as well, so from 288.41 kPa became 452.72 kPa when the initial loading was increased by 0.05 moles of CO_2 / mole of MEA.

Table 3.4 and Table 3.5 show the calculated values for MEA initial loadings 0.4 and 0.5 respectively**.** For initial loading 0.4 moles of CO_2 / mole of MEA, the total number of moles of CO_2 absorbed by the MEA is 0.908 or 20.21 L.

Table 3.4 Calculated CO_2 partial pressures for a 5 molal aqueous MEA solution with initial molar loading 0.40 and comparison with literature values.

Assumed CO_2 released in the headspace (moles*10^{-4})	Calculations		Jou et al. (1995)
	Loading after the CO_2 released	P_{CO2} headspace (kPa)	P_{CO2} (kPa)
25.9	0.398859	910.97	918.61
26	0.398855	914.48	918.58
26.1	***0.398850***	***918.00***	***918.56***
26.2	0.398846	921.52	918.53
26.3	0.398841	925.04	918.51

Note: 590 ml of 5 molal aqueous MEA solution, 10 ml available headspace, initial loading 0.40 moles CO_2 / mole MEA, 0.908 moles of CO_2 initially in solution, temperature 150 °C

As can seen in Table 3.4 the CO_2 partial pressure which could potentially be developed in the headspace is almost 3 times higher than the partial pressure developed when the initial loading is 0.25 or 0.30 moles of CO_2 / mole of MEA. Finally, for the data shown in Table 3.5, the initial loading is 0.5 moles of CO_2 / mole of MEA which means that in total there are 1.135 moles or 25.27 L of CO_2 absorbed by the MEA.

Table 3.5 Calculated CO_2 partial pressures for a 5 molal aqueous MEA solution with initial molar loading 0.50 and comparison with literature values.

Assumed CO_2 released in the headspace (moles*10^{-4})	Calculations		Jou et al. (1995)
	Loading after the CO_2 released	P_{CO2} headspace (kPa)	P_{CO2} (kPa)
45	0.498018	1582.76	1589.23
45.1	0.498013	1586.28	1589.19
45.2	***0.498009***	***1589.79***	***1589.16***
45.3	0.498004	1593.31	1589.12
45.4	0.498000	1596.83	1589.09

Note: 590 ml of 5 molal aqueous MEA solution, 10 ml available headspace, initial loading 0.50 moles CO_2 / mole MEA, 1.135 moles of CO_2 initially in solution, temperature 150 °C

Iterative calculations were performed with various CO_2 loadings to explore when agreement occurs between predicted headspace pressure and values reported in the literature. It was concluded that reasonable agreement is shown between the calculated data and those of Jou et al. (1995) at different loadings. From these calculations is shown that as the loading increases the CO_2 partial pressure in the headspace increases rapidly and that not very much CO_2 release from a given loading is required to give the agreed pressures.

Due to the wide range of results found in the literature and the high calculated CO_2 partial pressures, it was decided to purchase 600 ml vessels with maximum working pressure 2950 psi (20 MPa) and temperature 350 ^oC. All three vessels have safety rupture disks which would burst if the pressure in the vessels exceeds 1800 psi (about 12 MPa). Therefore, overall, the calculated values gave some confidence that it was safe to perform the thermal degradation experiments as the predicted expected pressure was approximately 1.6 MPa which is much lower than the maximum operating pressure of the pressure vessels.

3.5.1.3 Chosen experimental conditions

During the literature review it was noted that there is a gap in systematic data for CO_2 solubility over aqueous MEA solutions of different concentrations at high temperatures, over 150 ^oC. For this reason too many assumptions needed to be made in order to design the thermal degradation experiment.

First of all, it was noted that there are no data available for 5 molal MEA solutions, so the next step was to decide to change the MEA concentration to 30 % w/v (approximately 7 molal) for the thermal degradation experiments.

Then, it was noted that most of the studies measured the CO_2 solubility over 30 % w/v aqueous MEA solutions at temperatures of up to 120 ^oC and only one study presented data at 150 ^oC. Due to the fact that the generation of thermally degraded samples needed to be accelerated, in the present work the experimental temperature was desired to be 160 ^oC (Davis 2009 observed that the major degradation products generated in the MEA as the temperature changes, but below 200 ^oC, are the same but their formation is accelerated as the temperature rises). In practice, this meant that data at different temperatures needed to be extrapolated. Thus, it was decided to repeat some of the CO_2 solubility experiments reported in the literature, to build confidence in the system before starting the actual degradation experiments for which the vessels need to be left in the oven for long periods of time.

When the pressure vessels were eventually purchased, it was noted that, according to the manufacturer's guidelines for safe operation, the maximum volume of sample in the vessel must not exceed 400 ml. As a result, the sample volume needed to be reduced and the headspace needed to be increased from the 10 ml, used in the iterative calculations, to 200 ml which meant that more CO_2 could be released in a 200 ml headspace which would cause a drop in the pressures originally expected.

At this stage it was decided to operate the degradation experiments as a function of the total system pressure (or partial CO_2 pressure as it is the one that is changing) and not as a function of time as it was done in previous studies. It was decided that attempts would be made to assess whether the increase of pressure above the MEA solution, caused by the release of CO_2, could be considered as a degradation indicator.

Finally, it was agreed that for the first set of degradation experiments the initial loading of the MEA would be about 0.25 moles of CO_2 / mole of MEA, in other words lean loading and for the second set of experiments the initial molar loading would be rich close to 0.50.

3.5.1.4 Pressure calculations for the chosen experimental conditions

For the thermal degradation of MEA 400 ml of 30 % w/v aqueous MEA solution were degraded at 160 ^{o}C. The initial loading was 0.25 moles of CO_2/mole of MEA. As loading is expected to have an effect on the MEA thermal degradation, as suggested by Davis 2009 and Eide-Haugmo et al. 2011, higher loading experiments were also performed. 0.25 moles of CO_2/mole of MEA initial loading means that in practice the MEA will initially have absorbed 0.44 moles of CO_2 or 9.80 L. The CO_2 partial pressure values as a function of the CO_2 loading for 160 ^{o}C were extrapolated from the data given by Jou et al. (1995). Using Excel to process the extrapolated values, (see Figure 3.8), the resulting

Equation 3.3 was used to calculate the results shown in the last column in Table 3.6.

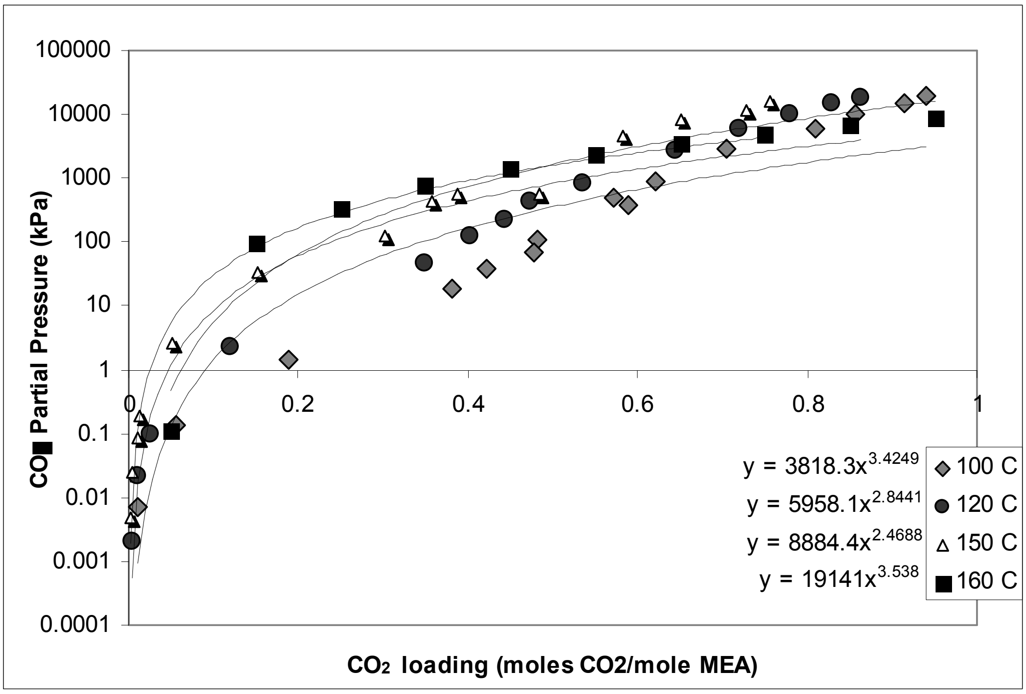


Figure 3.8 Experimental data for CO_2 partial pressure versus CO_2 molar loading presented by Jou et al. (1995) for 100, 120 and 150 °C and extrapolated data for 160 °C.

$$y = 19141x^{3.538}$$ Equation 3.3

For the calculated CO_2 partial pressure, the Ideal Gas law was used and then the result was converted to kPa from bar. Note here that for more a more accurate estimations a CO_2 compressibility factor should have been used as CO_2 does not behave as an ideal gas.

$$P_{CO2} = \frac{[molesofCO_2inheadspace] \times 0.08315 \times 433}{0.2}$$ Equation 3.4

As can be seen from Table 3.6 the CO_2 partial pressure above a 30 % w/v aqueous MEA solution is almost half the calculated value for a 5 molal MEA solution (Table 3.2) with the same loading, because the headspace, the MEA concentration and the temperature have changed. Therefore, bearing in mind that a large number of assumptions were made, the calculated pressures were much lower than the pressure vessels' operating pressures so it was deemed safe to use the vessels for the thermal degradation experiment under the described conditions. Part of the CO_2 solubility studies was decided to be repeated to build confidence with the designed system and its operation; the results are presented in Section 4.5.

Table 3.6 Calculated CO_2 partial pressures for a 30% w/v aqueous MEA solution with initial molar loading 0.25 and comparison with literature values.

Assumed CO_2 released in the headspace (moles*10^{-4})	Calculations		Literature
	Loading after the CO_2 released	P_{CO2} headspace (kPa)	P_{CO2} (kPa)
74	0.24579	133.22	133.6
74.1	0.245789	133.4	133.59
74.2	***0.245784***	***133.58***	***133.58***
74.3	0.24577841	133.76	133.57
74.4	0.245773	133.94	133.56

Note: 400 ml of 30% w/v aqueous MEA solution, 200 ml available headspace, initial loading 0.25 moles CO_2 / mole MEA, 0.44 moles of CO_2 initially in solution, temperature 160 °C

3.5.2 Thermal degradation rig description and operating protocols

As already mentioned, three 600 ml vessels with maximum working pressure 2950 psi (20 MPa) and temperature 350 °C were purchased from the Parr Instrument Company. These are illustrated in Figure 3.9. All three have safety rupture disks which would burst if the pressure in the vessels exceeded 1800 psi (about 12 MPa). Initially just one of the vessels was equipped with a pressure gauge with range 0-2000 psi (0 – 14 MPa) and later on a digital pressure gauge was purchased and placed on the second vessel (description of all the equipment is presented in Section 3.5.3, Thermal Degradation Rig Components). These vessels, filled with 400 ml of a CO_2 loaded MEA solution, were placed in a forced convection oven which could reach temperatures up to 350 °C and the whole system was placed under a fan to extract any gas released if the rupture disk bursts.

Figure 3.9 Two of the pressure vessels used for MEA degradation

Before thermally treatment the samples were loaded with CO_2 and this was done in the absorption/stripping rig. For that reason,1200 ml of a 30 % w/v aqueous MEA solution were loaded with CO_2 in the gas absorption/stripping rig (Figure 3.5) with initial molar loading as determined by an inorganic carbon content measurement (method described in Section 3.7).

In order to be thermally treated, the CO_2 loaded MEA sample was distributed between the three vessels (400 ml in each), sealed and placed in the forced convection oven at 160 ^oC. In the first set of thermal treatment experiments, the pressure change inside one of the vessels was continuously monitored with an analogue pressure gauge for safety reasons; it was assumed, as the experimental conditions were the same, that the pressure changes were the same in all the three vessels. In the second set of experiments the analogue and a digital pressure gauge were used, therefore two out of the three vessels were equipped with a pressure measurement device. The vessels equipped with the pressure gauges came last out of the oven.

The samples were left inside the high pressure vessels in the oven sealed at 160 ^oC for 2, 3 and 8 weeks to thermally degrade. Each one of the samples was taken out of the oven and remained sealed at room temperature until the beginning of the absorption-stripping experiment. All the three samples were tested and compared against a pure known MEA sample of the same initial concentration

(30 % w/v) to determine how thermal degradation affects the solvent's CO_2 up take capacity.

3.5.3 Thermal degradation rig components

These vessels and associated equipment were designed in order to thermally degrade samples of different solvents quickly, meaning that it was necessary to operate at high temperatures and thus high pressures. The whole system consists of:

1. Three 0.6 L high pressure vessels with maximum working pressure of 20 MPa (2950 psi) and temperature range from -10 to 350 ^{o}C (product no 453HC3) all equipped with a rupture disk in case the pressure in the vessel exceeds 2000 psi (product no 526HCPF) purchased from Parr Instrument Company Ltd in the USA.
2. A needle pressure gauge 0-2000 psi (0 to 13.6 MPa) purchased from Parr Instrument Company Ltd (product no 593HCPF)
3. A digital pressure gauge purchased from OMEGA Ltd with the following specifications:
    a. a pressure transducer with accuracy 0.08% and range 2500.0 psig (17 MPag) (part no PX419-2.5KG5V)
    b. a 0-15.0 V voltage logger (part no OM-CP-VOLT101)
    c. a USB interface cable/SW (part no OM-CP-IFC200)
    d. OMEGASOFT for OM-CP series data logging software, version 2.02.5
4. A fan-assisted oven (Binder, see Figure 3.9) capable of maintaining temperatures up to 300 ^{o}C +/- 1 ^{o}C.

3.6 MICROGC ANALYTICAL PROCEDURE AND RESULTS PROCESSING

The microGC system available at Cardiff School of Engineering was used in order to measure the gas composition at the absorption/stripping rig outlet. The CO_2 concentration was then used to calculate the CO_2 volume at the system's outlet.

The system is a Varian CP-4900 microGC, operating with two channels enabling the simultaneous measurement of the gases of interest (O_2, N_2, and CO_2). The system operates with an electric conductivity dependant detector.

The conditions under which the system runs were as follows:

- Sample line temperature 55 ^{o}C
- Cabinet T= 31 ^{o}C and P= 101.0 kPa
- Both channel 1 and channel 2 run under the same conditions.
  Injector T= 55.0 ^{o}C, column T= 105.0 ^{o}C and P= 103.4 kPa
- Channel 1 balance gas argon
- Channel 2 balance gas helium

From Channel 1 measurements of the percentage of O_2 and N_2 present in the flue gas were taken whereas Channel 2 was used to detect CO_2. The system was calibrated using a calibration gas which contained 10% CO_2 and 16 % O_2 (v/v) in N_2.

Unless otherwise stated the microGC results processing was as follows:

The initial plan was to examine the solvent behaviour during absorption using the microGC, but later in the project it was decided that the assessment of the solvent behaviour during absorption was going to be performed with the TOC instrument (the process is described in Section 3.7). At the stage of the project that the microGC was used to assess the solvent's behaviour during absorption a reading of the CO_2 concentration was taken along with a measurement of the exit flow rate every 20 minutes. A CO_2 flow meter was used at the system's outlet when a changing mixture of air and CO_2 was released. For that reason a flow correction was needed and the Equation 3.5 was used to calculate the corrected flow.

$$Q_m = Q_{measured}\sqrt{\frac{\rho_{CO2}}{\rho_m}} \qquad \text{Equation 3.5}$$

where $Q_{measured}$ = the flow meter reading and ρ_m is the density of the mixture of the gases. The density of the mixture of the gases was calculated using the Equation 3.6.

$$\rho_m = \frac{\rho_{CO2}V_{CO2} + \rho_{air}V_{air}}{V_m} = \rho_{CO2}\left(\frac{V_{CO2}}{V_m}\right) + \rho_{air}\left(\frac{V_{air}}{V_m}\right) = \rho_{CO2}\left(\frac{V_{CO2}}{V_m}\right) + \rho_{air}\left[\left(\frac{V_m - V_{CO2}}{V_m}\right)\right]$$

Equation 3.6

where V_m = the volume of the mixture = 1, V_{CO2} = CO_2 volume = microGC response and V_{air} = air volume. Finally, the CO_2 volume at the system's outlet was calculated by multiplying the microGC response with the corrected flow and the time for the twenty minute time intervals (Equation 3.7).

$$V_{CO2} = microGCresponse \times Q_m \times 20 \qquad \text{Equation 3.7}$$

Similarly, during the course of the stripping experiments, as 200 ml/min of N_2 were bubbled in the reactor, an air/nitrogen flow meter was used at the system's outlet. For that reason a flow correction was needed and Equation 3.8 was used to calculate the corrected flow.

$$Q_m = Q_{measured}\sqrt{\frac{\rho_{air}}{\rho_m}} \qquad \text{Equation 3.8}$$

where $Q_{measured}$ = the flow meter reading and ρ_m is the density of the mixture of the gases. The density of the mixture of the gases was calculated using Equation 3.6 and the volume of CO_2 for the twenty minute time intervals was calculated using Equation 3.7.

The readings of the volumetric flow and CO_2 concentration at the system's outlet were taken every 20 min; therefore, the CO_2 volumes absorbed and released were calculated assuming that the volume of CO_2 released or absorbed remained stable for 20 minutes. It needs to be noted here that the volume of CO_2 calculated using this integration might not be as accurate as a continuous measurement of the CO_2 volume at the system's outlet. Note also that observing the raw data during absorption the CO_2 concentrations and flows did not change considerably in twenty minutes, more gradual changes were observed. It was just at the beginning of the stripping experiment and for the first 30-40 minutes that the CO_2 concentrations had a more considerable increase.

3.7 INORGANIC CARBON MEASUREMENT FOR CO_2 CONTENT DETERMINATION

Before starting to measure unknown samples a calibration curve was created for the instrument (Shimadzu TOC-500(A)) and saved in the software used (TOC_control_V). Three different standards of concentrations 1, 10 and 100 mg of C/L were prepared. For the highest standard, 0.350 g of sodium hydrogen carbonate and 0.441 g of sodium carbonate were added in a 100 ml volumetric flask which was filled with DI water and the other two were prepared by 10 times dilution. The calibration curve was created and saved following the steps given by the software.

In order to make sure that the measurement of the unknown sample was accurate, before each measurement a DI water sample and a standard of concentration 100 mg/L in inorganic carbon were run. New standard solutions were prepared every week. Each sample was measured twice and if the difference between the two responses was more than 2%, the sample was automatically measured again. If the response for the standard was within 5% of the expected value it was considered to be accurate and then the unknown samples were measured.

For the unknown samples produced by the absorption/stripping rig, their CO_2 content was analysed using the TOC instrument for inorganic carbon measurement. Firstly, a pure MEA sample was measured to determine its inorganic carbon content. Then, each sample produced by the reactor was diluted by 100 and further diluted in the instrument by a factor of 10. The diluted sample was then analysed and compared against the saved calibration curve. It might be argued that the MEA releases some CO_2 on dilution but this is likely to be very small, also negated by the reduction in temperature with dilution. Moreover, according to the instrument manual the sample was introduced in a H_3PO_4 solution which reverses the MEA + CO_2 reaction and releases the CO_2, which is then detected by an NDIR sensor. According to Pacheco 1998, Chi 2000, Bishnoi 2000, Hilliard 2008 and Freeman et al. 2010 phosphoric acid can be used to acidify the CO_2 loaded amine samples to release aqueous CO_2, carbamate and bicarbonate as gaseous CO_2.

In order to calculate the CO_2 molar loading and the volume of CO_2 in a loaded solution from the instrument response the procedure was as follows:

- The instrument gave the responses in mg of inorganic carbon per L of solution. The responses needed to be multiplied by 100 as all the solutions were diluted by 100 (the dilution in the instrument was accounted by it). The result was then divided by 1000 to be converted into g/L
- The results were then converted into moles of carbon per L of solution by dividing the result above with the carbon atomic weight which is 12.011.
- Each CO_2 molecule contains one atom of carbon, therefore, the moles of C/L of solution equals the moles of CO_2 per L of solution.
- The moles of CO_2/L were then multiplied by 0.4 to be converted into moles of CO_2 per 400 ml of solution (as the sample volume was 400 ml).
- The maximum theoretical MEA absorption capacity is 0.5 moles of CO_2/mole of MEA or 0.98 moles of CO_2 in 400 ml of 30% w/v aqueous MEA solution.
- Thus, if 0.98 moles of CO_2 is 0.5 loading, then the molar loading of the unknown solution can be calculated.

After all the above calculations were performed the resulting Equation 3.9 was the one that was used to process all the values.

$$\text{Molar Loading} = 0.0017 \times \text{Instrument Response} \qquad \text{Equation 3.9}$$

3.8 COLORIMETRIC DETERMINATION OF IONS

The HACH portable data logging colorimeter DR/890 available at Cardiff School of Engineering was used to verify and quantify the presence of nitrite, nitrate and sulphate ions in some of the degraded samples (see Sections 4.2.3 and 4.4.4).

For the analysis of nitrite ions the method used was the ferrous sulphate for high range (0 to 150 mg/l NO_2^-) with the method number 8153. The first step was to choose the stored program in the instrument for the analysis of nitrites, the program number was 59. According to that method, a sample cell (HACH meter equipment) was filled with 1

0 ml of 0.5 molal aqueous fresh MEA solution (not degraded); the cell was cleaned and placed in the HACH meter sample holder. The cap was placed on the instrument; when the measurement reading showed on its screen, the 0 button was pressed in order to perform an automatic reagent blank adjust. Thereafter, another cell was filled with 10 ml of the degraded sample. The contents of one NitriVer 2 nitrite reagent powder pillow were added and mixed with the sample in the cell. The sample was let to rest for 10 minutes, which is the reaction period of the sample with the powder added. After the end of the 10 minute period, the cell was gently inverted a couple of times, it was cleaned and placed into the HACH meter’s sample holder. The cap was put on the instrument and the reading was taken.

The cadmium reduction method in the high range from 0 to 30 mg/L with method number 8039 was used for the analysis of nitrate ions. The first step, as described in the paragraph above, was to choose the stored program in the instrument which was program number 51. Then, a 10 ml blank sample, 5 molal aqueous MEA solution, was again used to perform an automatic reagent blank adjust. Thereafter, 10 ml of degraded sample were placed to one of the instrument cells and the contents of one NitraVer 5 nitrate reagent powder pillow were added to the sample and the contents of the cell were vigorously shaken for 1 minute. After 1 minute, the sample was left to rest for a five minute reaction period and then, after it was cleaned, the sample cell was placed in the instruments cell holder. The cap is placed on the instrument and a reading was taken.

It was not originally expected to detect sulphate anions in the degraded sample but, as it was detected by Dionex was used the HACH portable data logging colorimeter was again used to analyse the sample in Cardiff to verify their presence. The SulfaVer 4 method (method number 8051) in the range from 0 to 70 mg/L was used for the analysis. Again the analysis program number (91) was selected and a blank of 0.5 molal aqueous MEA was used to perform an automatic reagent blank adjust. The contents of a SulfaVer 4 sulphate reagent powder pillow were added to the sample cell and it was mixed with 10 ml of sample. The sample was left to stand for five minutes; the cell was cleaned, placed in the instrument and measured.

3.9 ION CHROMATOGRAPHY (IC) - ANALYTICAL PROCEDURE

A considerable period of time during the present study was spent on development of analytical procedures for IC, for the analysis of the ionic oxidative degradation products of MEA. Work was performed to assess whether it was possible first to detect and then quantify them with the IC system available. It was decided to focus on the major MEA degradation products, in other words, the most commonly reported in the literature (Strazisar 2002, Strazisar 2003, Bello 2005, Supap 2006, Davis & Rochelle 2008, Lepaumier 2010 and Lepaumier 2011). Methods were developed to pre-process the samples to deactivate any MEA observed, produce calibration curves and calculate the method detection limits.

3.9.1 Method development

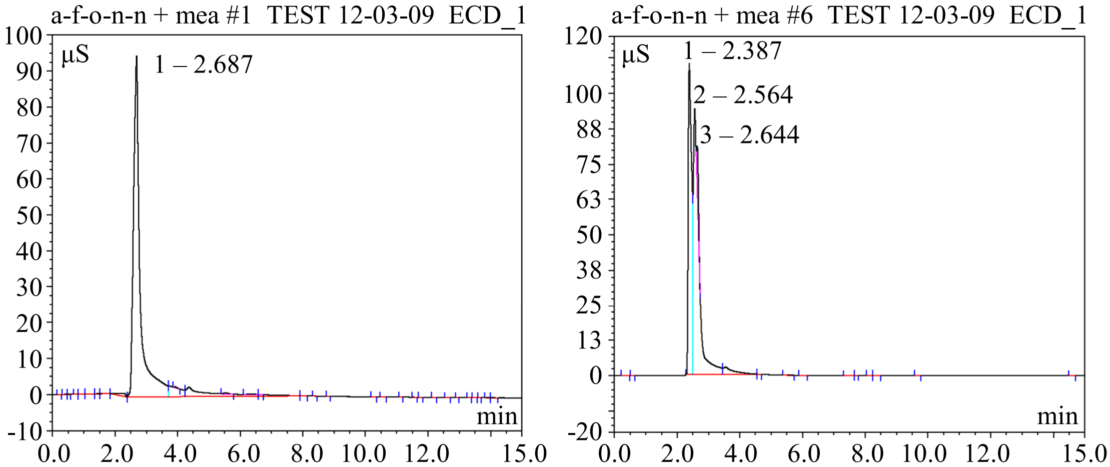
3.9.1.1 Major MEA oxidative degradation products analysis

The first step was to find in the literature the most commonly detected MEA oxidation products and purchase them. Potassium nitrite, sodium nitrate, formic acid, acetic acid and oxalic acid were analysed using the available system with the IC column IonPac AS11-HC anion exchange with a conductivity dependant detector. The operating conditions for the system were as follows:

- eluent - potassium hydroxide 30 mM,
- flow rate - 1.2 ml/min,
- temperature - 30 °C,
- injection volume - 10 µl and
- suppressor current - 100 mA.

1. *Acetic Acid*

A solution of acetic acid in DI water with concentration 1040 mg/L was prepared by adding 0.1 ml of acetic acid to 100 ml of water. Then, 5 ml of sample were taken and measured in the IC system under the conditions described above. Moreover, in order to assess the effect of the background, samples with the same concentrations were prepared in 0.5 molal aqueous MEA solutions. As for the water samples, 1 ml of acetic acid was added to 100 ml of a 5 molal aqueous MEA solution. The sample was further diluted by 10 (1 ml of sample into 9 ml of water) in order to avoid overloading of the IC column. Then, 5 ml of sample were introduced to the IC and measured under the same conditions (Described in Section 3.9.1.1). The resulting chromatographs are shown in Figure 3.10.



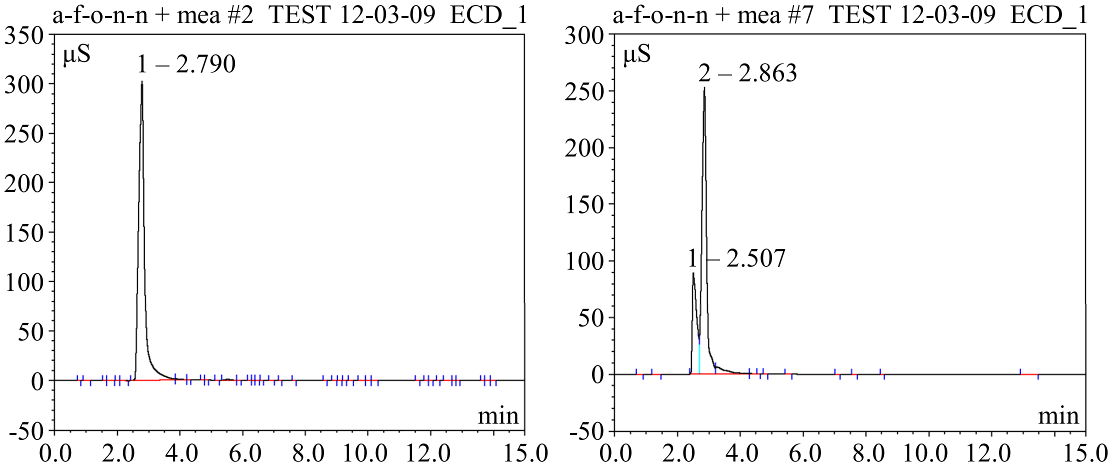
(a) (b)

Figure 3.10 Acetic acid of concentration 1040 mg/L (a) in water and (b) 0.5 molal aqueous MEA solution

As shown in Figure 3.10 (a) a clear response was obtained for acetic acid in water. Figure 3.10 (b) shows the response for acetic acid in MEA, as it can be seen the peaks of MEA and acetic ion are almost overlapping. This means that in the degraded MEA samples when analysed with the IC it is difficult to identify acetic acid and quantify it from a similar response.

2. Formic Acid

Samples of formic acid with concentration 1220 mg/L in water and in 0.5 molal aqueous MEA were prepared in a similar way to the acetic acid samples. For the first sample 0.1 ml of formic acid was added to 100 ml of DI water. For the second sample, 1 ml of formic acid was added to 100 ml of a 5 molal aqueous MEA solution. The second sample was further diluted by 10 (1 ml of sample into 9 ml of water). Then, 5 ml of each sample were run with the IC under the same conditions (Described in Section 3.9.1.1). Figure 3.11 presents the resulting chromatographs.



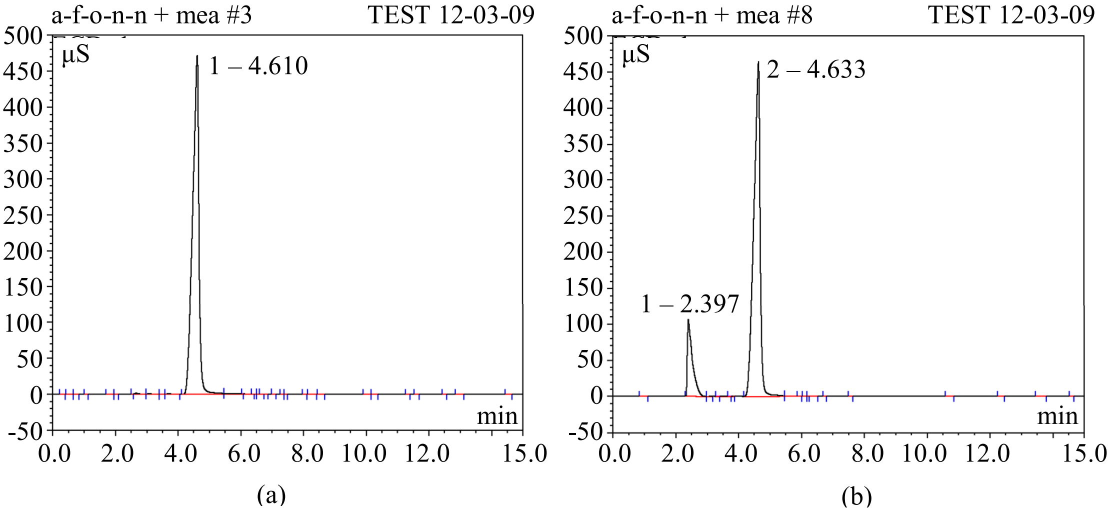
(a) (b)

Figure 3.11 Formic acid of concentration 1220 mg/L (a) in water and (b) 0.5 molal aqueous MEA solution

A similar conclusion to the one drawn above for acetic acid can be drawn in the case of formic ion as well. In Figure 3.11 (a) a clear response was obtained for the aqueous solution of formic acid. Figure 3.11 (b), though shows the response for formic acid in an aqueous MEA solution, the retention times for MEA and the formic ion are very close again and as a result the peaks are almost overlapping again.

3. *Oxalic Acid*

Samples of oxalic acid with concentration 1653 mg/L in water and in 0.5 molal aqueous MEA were prepared in a similar way to the acetic acid samples. For the first sample 0.1 ml of oxalic acid was added to l00 ml of water. For the second sample, 1 ml of oxalic acid was added to 100 ml of a 5 molal aqueous MEA solution. The second sample was further diluted by 10 (1 ml of sample in to 9 ml of water). Then, 5 ml of each sample were run with the IC under the same conditions (see in Section 3.9.1.1). In Figure 3.12 the IC response for the oxalic acid samples are shown.



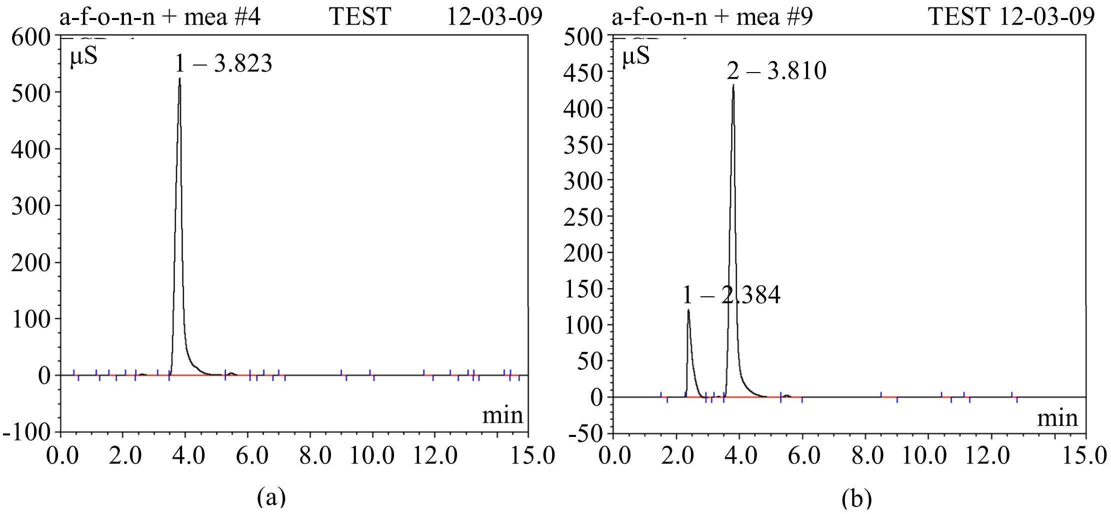
(a) (b)

Figure 3.12 Oxalic acid of concentration 1653 mg/L (a) in water and (b) 0.5 molal aqueous MEA solution

As shown in both Figure 3.12 (a) and Figure 3.12 (b) clear responses are obtained for both the aqueous oxalic acid and oxalic acid in aqueous MEA samples.

4. *Potassium Nitrite*

Samples of potassium nitrite with concentration 999.9 mg/L in water and in 0.5 molal aqueous MEA were prepared. For the first sample 0.1 g of potassium nitrite was added to l00 ml of water. For the second sample, 1 g of potassium nitrite was added to 100 ml of 5 molal aqueous MEA solutions. The second sample was further diluted by 10 (1 ml of sample in to 9 ml of water). Then, 5 ml of each sample were run with the IC under the same conditions (Described in Section 3.9.1.1). See Figure 3.13 for the IC chromatographs.



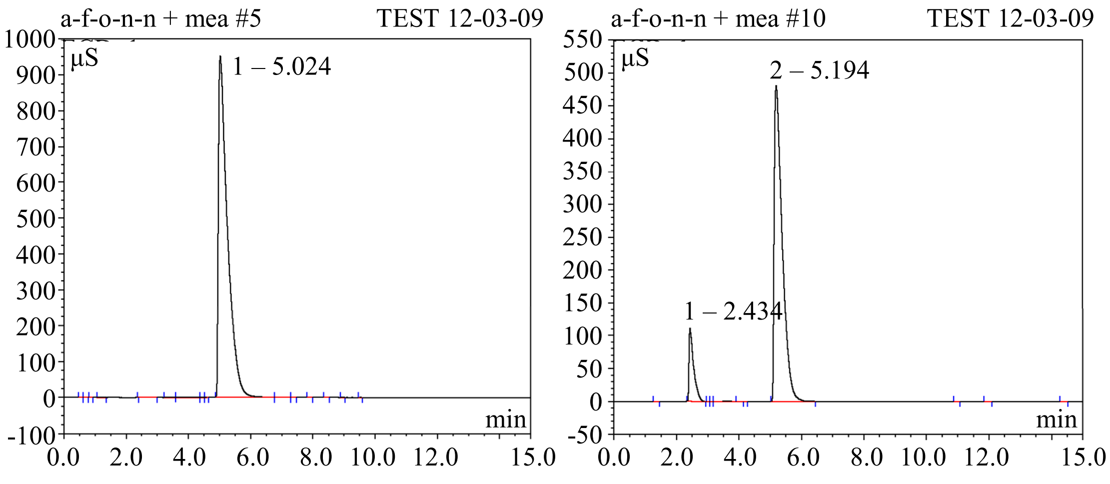
(a) (b)

Figure 3.13 Potassium nitrite of concentration 999.9 mg/L (a) in water and (b) 0.5 molal aqueous MEA solution

It needs to be noted here that the concentrations were calculated considering the density of the final mixtures to be 1, as the mass of potassium nitrite was small compared to the volume of solvent (water and MEA - water mixture) in which it was diluted. Moreover, the density of MEA is 1.012 g/cm^3 which is close to the water density. As observed in Figure 3.13 (a) and Figure 3.13 (b) the peaks that resulted from the analysis of both solutions are clear and quantifiable.

5. *Sodium Nitrate*

Samples of sodium nitrate with concentration 1996 mg/L in water and in 0.5 molal aqueous MEA were prepared in a similar way to the potassium nitrate. For the first sample 0.2 g of sodium nitrate was added to 100 ml of water. For the second sample, 2 g of sodium nitrate was added to 100 ml of 5 molal aqueous MEA solutions. The second sample was further diluted by 10 (1 ml of sample into 9 ml of water). Then, 5 ml of each sample were run with the IC under the same conditions (see Section 3.9.1.1). The resulting chromatographs are shown in Figure 3.14. For the concentration calculations the same assumptions as described for potassium nitrite were made.



(a) (b)

Figure 3.14 Sodium nitrate of concentration 1996 mg/L (a) in water and (b) 0.5 molal aqueous MEA solution

Figure 3.14 (a) and Figure 3.14 (b) presents quantifiable peak responses for both nitrate in water and nitrate in the aqueous MEA solution. As seen it can be seen in Figure 3.10, Figure 3.11, Figure 3.12, Figure 3.13 and Figure 3.14, the available IC system can give quantifiable peak responses for all good responses for all the MEA major oxidative degradation products. Figure 3.10 (b) and Figure 3.11 (b) show that MEA peak response almost overlaps with the other analytes present in solutions which in practice means that in the unknown samples it might be difficult to identify and quantify the peaks. Note here that an MEA response should not be taken at the available IC system, therefore further investigation was needed to assess the effect of MEA on the system.

3.9.1.2 Effect of background (MEA) in the IC analysis

As it is shown in Figure 3.10 (b), Figure 3.11 (b), Figure 3.12 (b), Figure 3.13 (b) and Figure 3.14 (b) a clear peak response was obtained for MEA in all the IC chromatographs where it was present. The column used at Cardiff for this study is an anionic column and as MEA acts as a weak base, it should not be detected by the current set up. Moreover, these peaks have a considerably high conductivity response which means that some other small peaks may appear like noise and affect the accuracy of the results. The presence of MEA could also cause the degradation of the IC column material. Most importantly, as shown in

Figure 3.10 (b) and Figure 3.11 (b), the MEA peak almost overlaps with the acetic and formic acid peaks, therefore, a positive identification of acetates and formates might not be possible with the current system.

For these reasons the Dionex On Guard II H cartridges 2.5 cc were purchased in order to pre-process the samples and deactivate the amine and its effect on the IC system. These cartridges have the effect of removing the large diffuse peaks that were present at low residence times on the IC chromatographs by selectively sorbing the MEA onto the solid resins in the column whilst leaving the anions of interest unaffected. The cartridge tube was fitted to the bottom of a 25 ml syringe. In order to clean the cartridge 15 ml of DI water, with flow of approximately 2 ml/min, were passed through the cartridge and discarded. Then, 10 ml of 5 molal aqueous MEA solution were passed through the cartridge the same way, the first 5 ml were discarded and the rest of the sample was analyzed in the IC and run under the conditions described in Section 3.9.1.1 Major MEA Oxidative Degradation Products.

Figure 3.15 (a) presents the IC response for a 0.5 molal aqueous MEA sample and Figure 3.15 (b) the response of an aqueous MEA solution after the use of the deactivation cartridge. It is clear that there is no clear peak response for MEA in Figure 3.15 (b), the peaks shown are background noise and the peak size is not bigger than 0.100 µS. In Figure 3.15 (a) the peak height for the sample of 0.5 molal aqueous MEA was close to 110 µS.

The effect of MEA in the analysis and the accuracy of the results after the use of the amine deactivation cartridges need to be further assessed. This is because the selective material which is used in these cartridges might also deactivate other degradation products generated from the system.

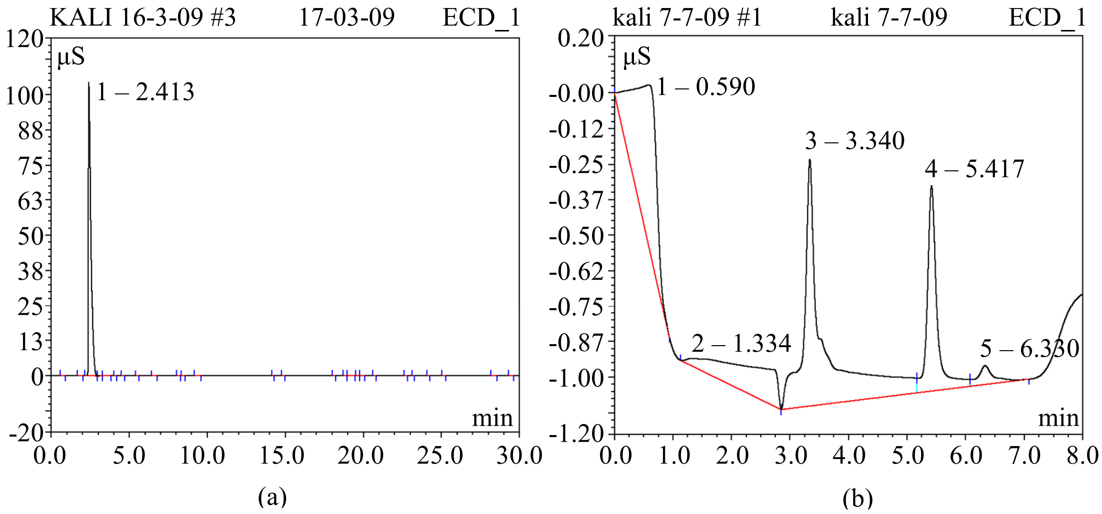


Figure 3.15 Aqueous MEA sample (a) not filtered and (b) filtered

3.9.1.3 IC Column AS-11 HC CHECK

It was noted that in the chromatographs generated by the IC system in Cardiff University, the peak retention times were different to the ones expected based on the information given by the manufacturers and contamination of the column was suspected. For this reason, it was decided to run a clean-up cycle of the column using 1M NaOH solution and then to run a 7 anion standard solution to check if the resulting chromatograph is close to the one given by the manufacturer (Figure 3.16).

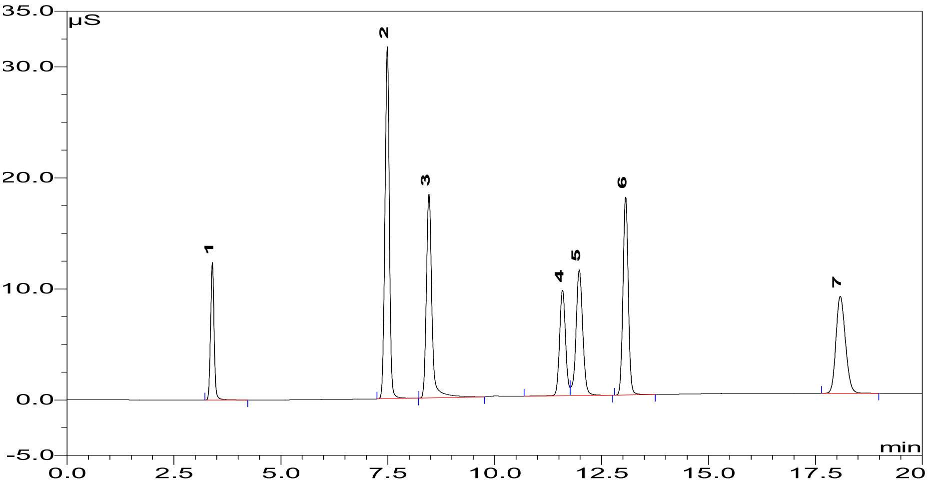


Figure 3.16 7 anions standard solution run provided by the IC system's manufacturer

For that reason a sample with the concentrations presented in Table 3.7 was prepared in DI water and run in the IC system.

Table 3.7 Expected results of the 7 anion standard solution

Analyte	Concentration (mg/L)	Expected Peak Height (μS)
Peak1: Fluoride	2.0	8.0
Peak 2: Chloride	10.0	20.0
Peak 3: Nitrite	10.0	11.5
Peak 4: Bromide	10.0	6.0
Peak 5: Nitrate	10.0	7.0
Peak 6: Sulphate	10.0	11.0
Peak 7: Phosphate	20.0	5.5

The IC system and column used for the system check was as normal (IonPac AS11-HC anion exchange with a conductivity dependant detector) but the operating conditions were changed to the following:

- Flow rate 1.5 ml/min,
- Temperature 30 ^{o}C,
- Injection volume 10 μl and
- Suppressor current 150 mA.
- Experimental run time was 25 min
- Eluent used was potassium hydroxide but the concentration was changing as follows:

Time (min)	Eluent Concentration (mM)
-5.0	5.0
0.0	5.0
2.0	5.0
13.0	30.0
20.0	30.0

Figure 3.17 presents the response obtained by the available IC system at Cardiff School of Engineering.

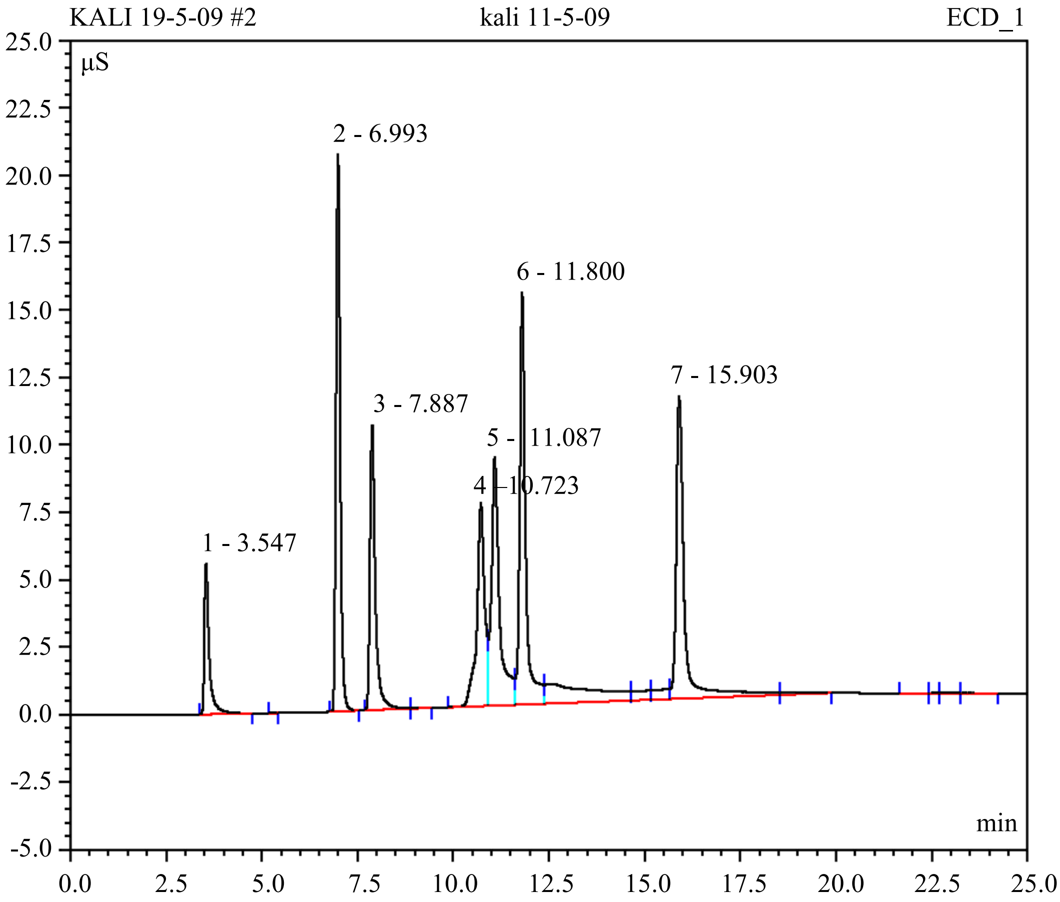


Figure 3.17 7 anions standard solution run in the Cardiff University IC system

It was concluded that the resulting chromatograph (Figure 3.17) was very close to the expected results presented in Table 3.7 in terms of their conductivity response and the retention times presented in Figure 3.16. Therefore, the system used is capable of detecting and quantifying accurately some of the compounds of interest namely nitrite, nitrate and sulphate.

3.9.2 Ion Chromatography (IC) final method

After extensive experimentation, mostly in collaboration with Dionex specialists in the UK and Switzerland, it was resolved to deactivate the MEA and its effect on the IC chromatographs and for that reason the Dionex On Guard II H cartridges (2.5 cc) were purchased in order to pre-process all the samples. The cartridge tube is fitted to the bottom of a 25 ml syringe. In order to clean the cartridge 15 ml of DI water, with flow of approximately 2 ml/min, were passed through the cartridge and discarded. Then, 10 ml of the aqueous MEA solutions were passed through the cartridge, the first 5 ml are discarded and the rest of the sample is analysed in the IC using the following conditions:

- eluent - potassium hydroxide, 30 mM,
- flow rate - 1.2 ml/min,
- temperature - 30 ^{o}C,
- injection volume - 10 μl
- suppressor current - 100 mA

3.9.3 Calibration curves and method detection limits

In Table 3.8 the retention times determined for the major oxidative degradation products when analysed with the available IC system can be seen.

Table 3.8 Retention times in the IC system for the major oxidative degradation products

Analyte	Retention time (min)
Acetate	2.56
Formate	2.86
Oxalate	4.63
Nitrite	3.81
Nitrate	5.19
Sulfate	4.30

Work was also performed to produce calibration curves and determine the detection limits of the IC system. Samples, of different concentrations of each compound in 5 molal MEA, were prepared. The samples were run in the IC system after being pre-processed to avoid the MEA effect on the chromatograms and run under the decided IC conditions, the procedure followed is described in the Section 3.9.2, Final Ion Chromatography (IC) method.

The calibration curves for acetic, formic, oxalic, nitrate and nitrite ions are plotted in Figure 3.18, Figure 3.19, Figure 3.20, Figure 3.21 and Figure 3.22, respectively and the raw data can be seen in *Appendix 1.1*. The calibration curves produced from the IC system gave an R^2 of over 0.97 and were considered quite linear over the range of concentrations examined. Note here that none of the curves crosses zero, which means that the procedure used is not very accurate for very low concentrations close to zero. Moreover, if the highest concentration is excluded from the curves there is a slight increase to R^2, which could be attributed to the fact that the IC column might get overloaded when high sample concentrations are passed through it. As at that stage of the project it was not clear what range of concentrations would be detected in the degraded samples, a calibration curve including a wider range of concentrations was considered more appropriate.

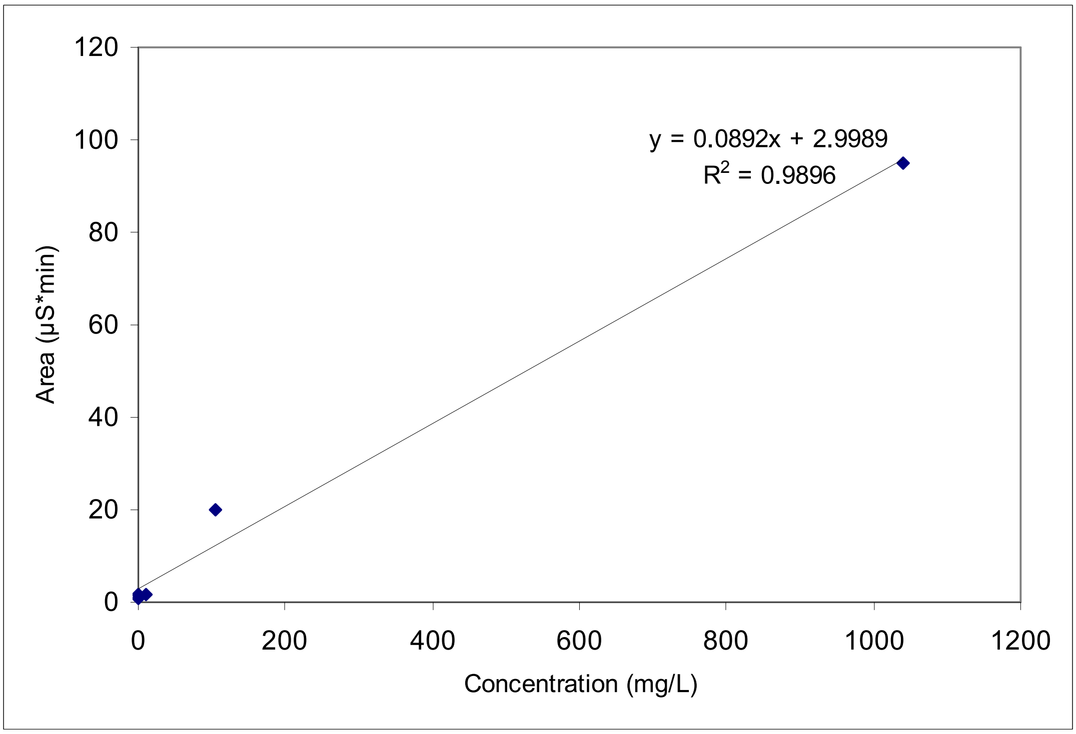


Figure 3.18 Calibration curve for acetic ion produced by the IC system

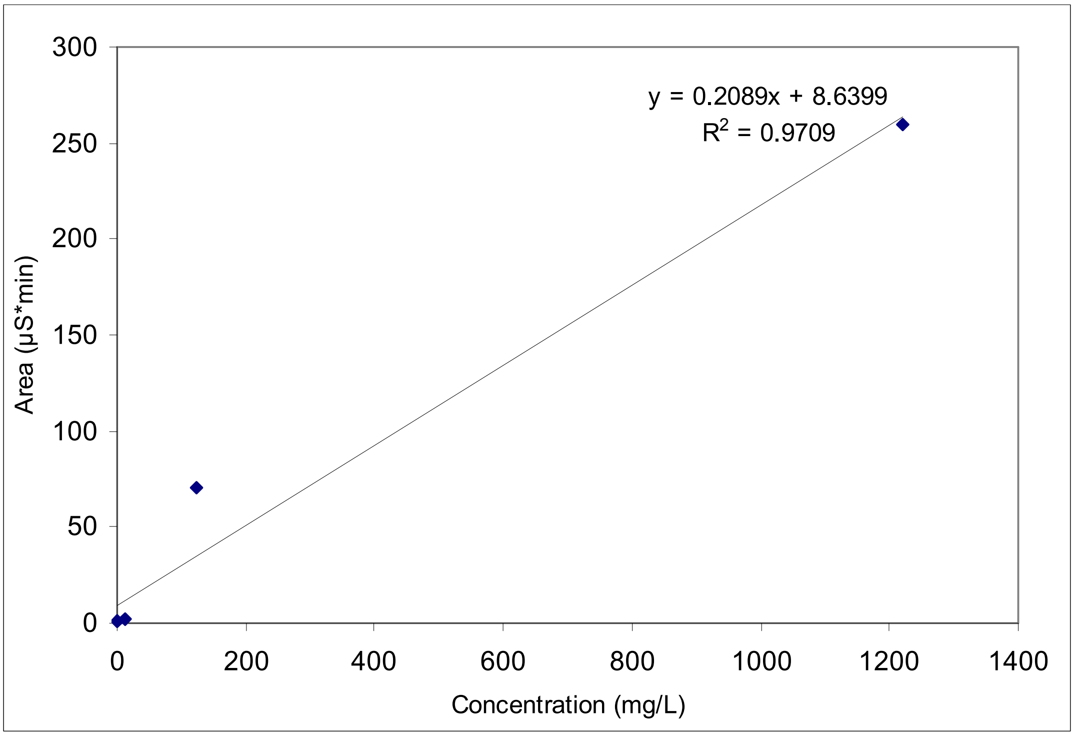


Figure 3.19 **Calibration curve for formic ion produced by the IC system**

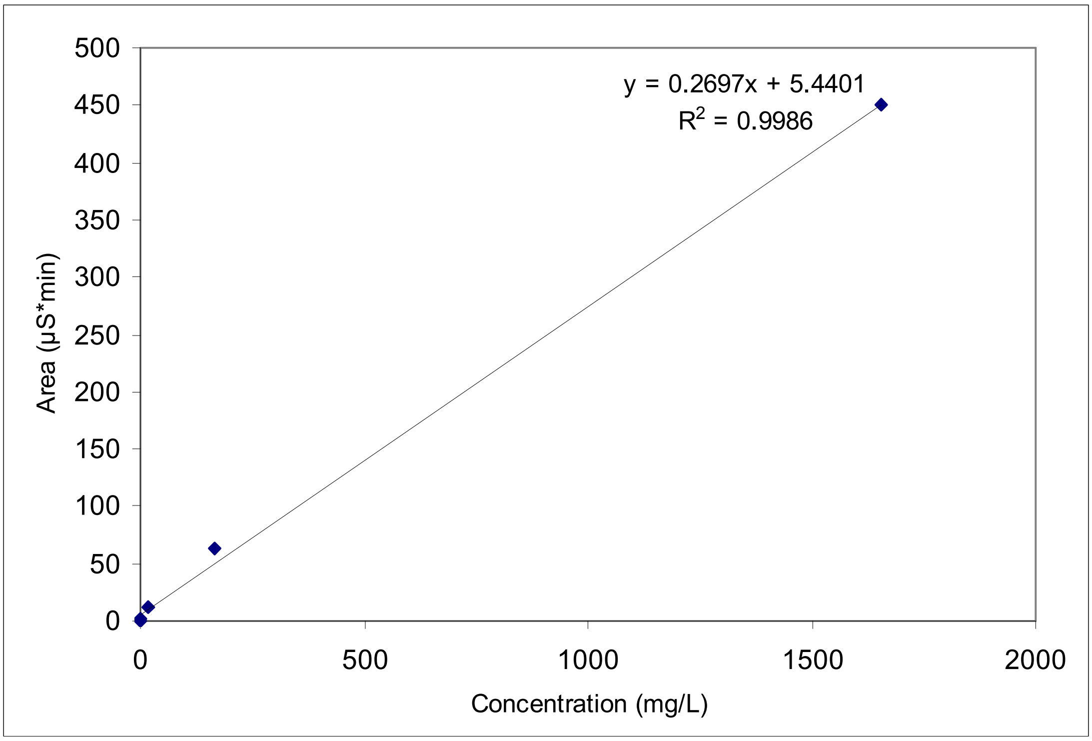


Figure 3.20 **Calibration curve for oxalic ion produced by the IC system**

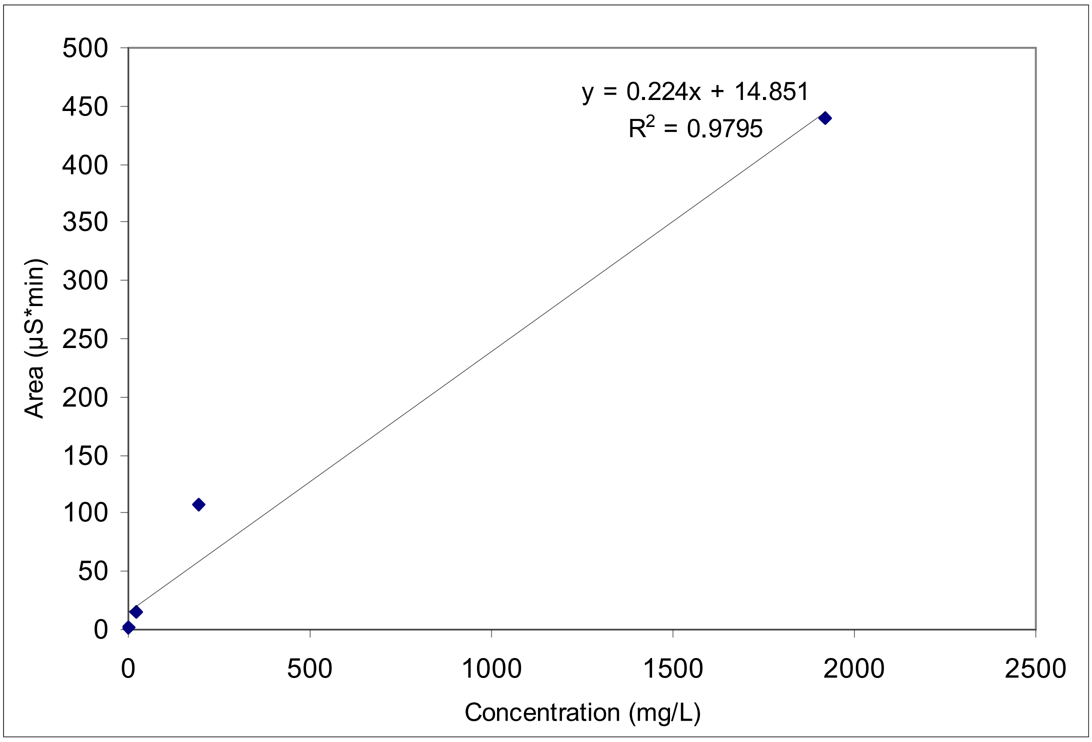


Figure 3.21 **Calibration curve for nitrate ion produced by the IC system**

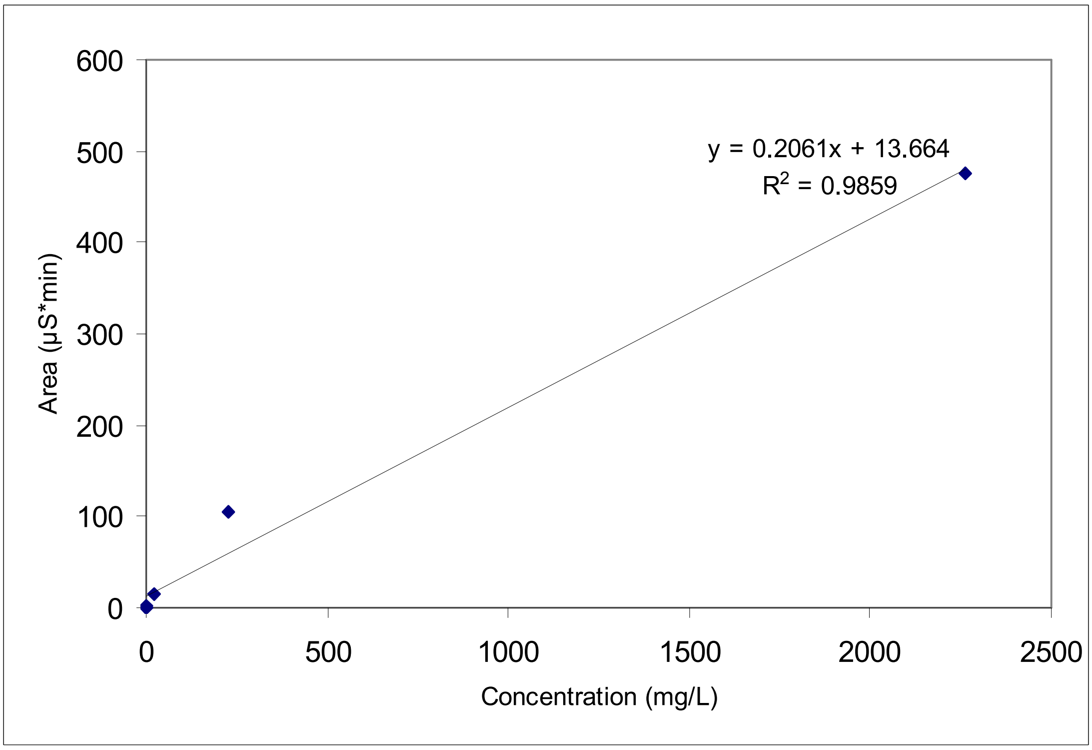


Figure 3.22 **Calibration curve for nitrate ion produced by the IC system**

The procedure followed to calculate the MDLs was the EPA method ["Definition and Procedure for the Determination of the Method Detection Limits" described in the Appendix B - Revision 1.11 of the part 136 "Guidelines establishing test procedures for the analysis of pollutants" in subchapter D "Water Programs"]. All the samples were preprocessed with the MEA deactivation cartridges and run using the method described in Section 3.8.2 Final Ion Chromatography (IC) method. According to the MDL used, the first step was to calculate the instrument detection limit (IDL). The IDL was calculated by filtering 10 samples of a 5 molal aqueous MEA samples with the MEA deactivation preprocessing cartridges and run the in the IC system. Thereafter, based on the retention times, the noise level for each compound was determined by measuring its response (if any) in the blank sample. The IDL is three times the standard deviation of the noise for each compound in the blank sample and can be seen in Table 3.9.

Table 3.9 Instrument Detection limit for each of the analytes in the IC system

Analyte	IDL (mg/L)
Acetic ion	0.23
Formic ion	0.19
Oxalic ion	0.22
Nitrite ion	0.24
Nitrate ion	0.13

The next step was to run 7 samples of each analyte with concentration 5 times the instrument detection limit (approximately 1 mg/L) in the IC and calculate the relative standard deviation, RSD (which is the standard deviation divided by the average) from the instrument responses. The samples were prepared in a matrix of a 5 molal aqueous MEA solution and preprocessed with the MEA deactivation cartridges before run in the IC. The RSD for all compounds is shown in Table 3.10.

Table 3.10 Relative standard deviation as calculated by the IC responses for each analyte

Analyte	RSD
Acetic ion	0.19
Formic ion	0.22
Oxalic ion	0.29
Nitrite ion	0.13
Nitrate ion	0.21

Finally, the MDL was calculated by multiplying the RSD with the concentration (1mg/L) and the students' t value for a 99% confidence level with 6 degrees of freedom which was found from the one sided table to be 3.143. Table 3.11 shows the MDLs for all the inorganic ions analysed in the available IC system. The raw data and all the calculations procedure can be seen in *Appendix 1.2*.

Table 3.11 Method detection limits for anions in the IC

Analyte	MDL (mg/L)
Acetic ion	0.6
Formic ion	0.7
Oxalic ion	0.9
Nitrite ion	0.4
Nitrate ion	0.7

The resulting MDL are all lower than 1 mg/L, especially for the acetic and nitrite ions.

3.10 GC-MS ANALYTICAL PROCEDURE

In this section the work performed to detect and quantify the MEA major thermal degradation products is presented. HEIA, HEEDA and 2-oxazolidone were considered to be the MEA major thermal degradation products the most commonly encountered in the literature as reported by Strazisar 2002, Strazisar 2003, Bello 2005, Supap 2006, Davis & Rochelle 2008, Davis 2009, Lepaumier 2009 (a), Lepaumier 2009 (b), Lepaumier 2010 and Lepaumier 2011. Opinions differ on whether the GC-MS is the best analytical tool to measure thermal degradation products due to the fact that the high injection temperatures that can be experienced in a GC system might cause the MEA to thermally degrade. Saha et al. (1977) reported that alkaloamines do not undergo rapid thermal decomposition at injection temperatures up to $375^{o}C$, therefore, based on that information it was decided that the GC-MS was the most appropriate available piece of equipment for this work.

A GC-MS system combines a GC with an MS together; it is a very powerful piece of equipment when it comes to analysing organic compounds even at very low concentrations. Its use allows a much more accurate and precise detection of elements as combining the two methods together can minimise the possibility of two different compounds behaving exactly the same way in both the GC and MS.

During the present study, a few challenges were faced concerning the analysis of MEA and its major thermal degradation products with the GC-MS. Firstly, the samples needed to be analysed were aqueous MEA samples, either with pure fresh MEA or degraded MEA samples containing degradation products. Therefore, a selective method to partition MEA and its degradation products into an organic solvent, which could be introduced to the GC, was the first step to be taken. As MEA and most of its degradation products were ionic compounds and highly water soluble, quite a few solvents and a solid extraction method (as described in detail in Section 3.10.1) were used before finding the one that was more appropriate for the analysis in question.

At the same time, as samples of those compounds were analysed in the system, attempts to find the optimum conditions for the analysis of those specific compounds with the available set up for both the GC and MS needed to be found. For both the GC and MS analysis the conditions were changed based on the experience gained. Changing the conditions could result in enabling the system to detect a compound or could change the retention times or obtain more easily quantifiable peaks, for example:

- The initial and final oven temperatures as they need to be different as different compounds have different boiling points and physicochemical characteristic as well as the column material.
- The rate in which the temperature would increase in order to achieve clear responses for each compound.
- The split ratio, in other words the flow of carrier gas through the system, according to the sample concentration in order to get clearer peak responses, not to overload the column with highly concentrated samples or to improve tailing problems (not good quantifiable peaks).
- The experimental time to be long enough for the compounds in question to be eluted from the column and short enough to reduce the analysis time.

The MS conditions were also changed based on the experience gained, for example:

- The starting and final masses were changed in order to be able to analyse for compounds of different sizes and molecular weights depending on the accuracy that is needed to be achieved. For example if two compounds have mass specs very close to each other
- The experimental time also needed to be adapted to be at least as long as the GC experimental time in order to characterise the compounds that were exiting the GC system.

Finally, it was realised that the GC column used was not the appropriate one for the analysis that needed to be performed. As the column packing material needs to be selective for the analysis needed to be performed, studying the chemical characteristics of the compounds in question was important to make a selection between different kinds of columns based on the polarity and the family of chemical compounds that they belonged. The length and diameter of the GC column is another important factor as it plays a role in the selectivity and separation of the different components in the samples. In the following Section 3.10.1, a detailed explanation of the GC-MS method development based on the GC-MS responses and the experience gained during the present study is presented.

3.10.1 Method development

3.10.1.1 Initial instrument set up

The original GC system set up comprised of a low polarity (slightly acidic) column (the Elite-5MS by Perkin Elmer).

1. MEA

The first step was to become familiar with the system and its operation and then run MEA samples until a clear MEA peak was obtained to be used as a starting reference point. For that reason, samples of 5 molal MEA aqueous solutions were analysed in the GC-MS. The methods chosen for the MEA analysis were the U.S. Environmental Protection Agency (EPA) method 8260B for volatile organic compounds (VOCs) with low boiling points below 200^{o}C, GC_VOC for the GC and MS_VOC for the MS.

Due to the fact that water samples can not be introduced to the GC-MS, the samples needed to be pre-processed using a liquid to liquid extraction method. Therefore, a known volume of the sample was mixed with dichloromethane (DCM) in a separator flask, in order to partition the organics from the water sample to DCM (initially 50 ml of DCM and 50 ml of sample). Then, the water phase was separated from the organic solvent phase and the DCM with the organics was evaporated down with a N_2 blow-down at 40 °C.

Then, the samples were run in the GC-MS but no peak was identified see Figure 3.23.

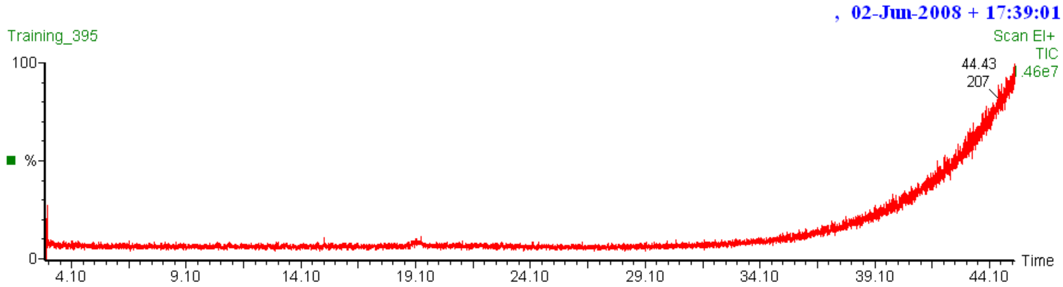


Figure 3.23 GC-MS response for MEA in DCM

MEA is a low molecular weight volatile compound, so it is possible that it could not be detected because the pre-processing method was not the appropriate one. It could be either that the MEA would not partition into DCM or that, because MEA is volatile, it evaporated during the concentration process where the N_2 blow-down was used. For that reason it was decided to use the headspace trap auto sampler (Heaspace Autosampler Turbomatrix 40 Trap Perkin Elmer). This way, an extraction method was not needed as the auto sampler was taking samples from the headspace, created inside the sampling vessels, above an aqueous MEA solution. The sample preparation technique provided by the EPA for the method 8260B is the 5030, which recommends purge and trap. The method chosen for the MEA analysis was again the U.S. Environmental Protection Agency (EPA) method 8260B for volatile organic compounds (VOCs) with low boiling points below 200°C, GC_VOC for the GC and MS_VOC for the MS. No Peak response was obtained using this method either.

For the next measurements a solid phase extraction method was used. In this method, a silica-based non-polar sorbent - Cyclohexyl CH(EC)a - was used for the extraction of basic compounds from aqueous solutions using non-polar interactions. Moreover, the method for the analysis was slightly changed based on information found in the literature. First of all, in the GC method the oven starting temperature was changed from 100 °C to 40 °C. Moreover, the oven temperature was raised from 40 to 240 °C with heating rate 7 °C/min and it was held there, in contrast with the first method used, in which the starting temperature was 100 °C and in hold for 2 minutes and then raised to 310 °C and hold for another 4 min with heating rate 4 °C/min. Additionally, in the MS method the mass range was changed so as to start from 10 and not from 50 m/z because the MEA is a low molecular weight compound and volatile so the characteristic peak comes before 50 m/z.

The resulting chromatograph and mass spectrum are shown in Figure 3.24 and Figure 3.25, respectively.

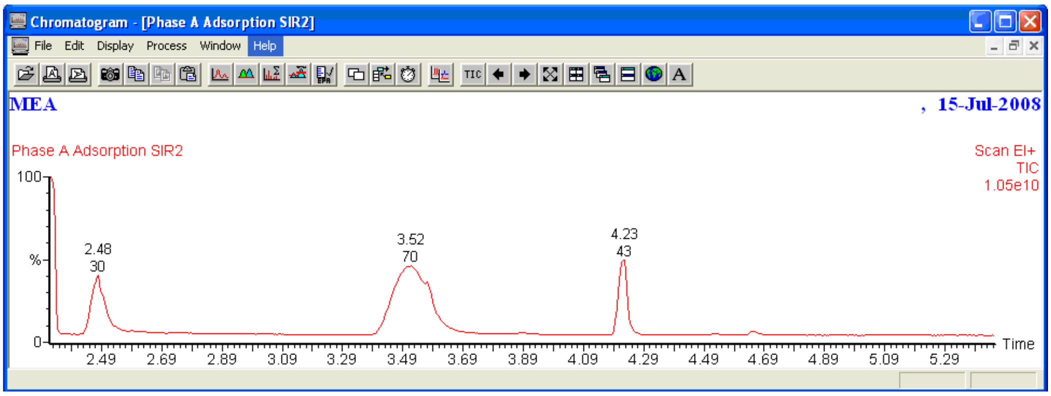


Figure 3.24 **Chromatograph for MEA after using a solid phase extraction method**

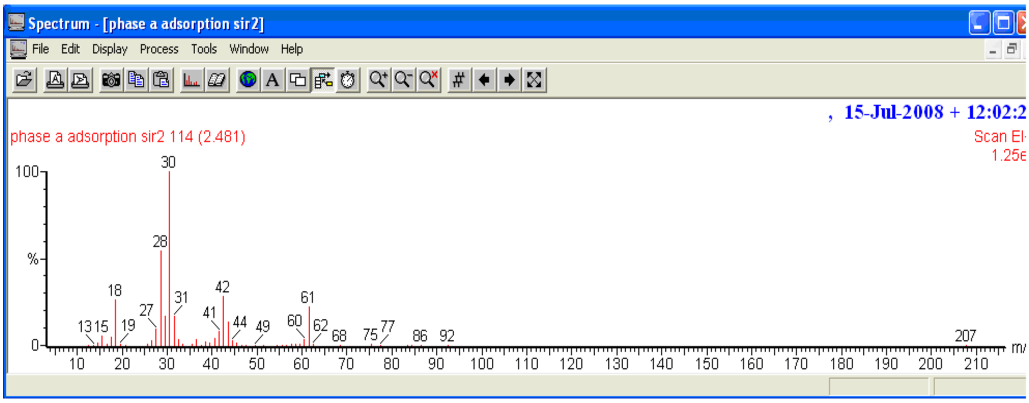


Figure 3.25 **Mass Spectrum of MEA**

When the same procedure was repeated, it was realised that it was not possible to reproduce the results and it was decided to work on developing a more appropriate method for the analysis of MEA.

In the next phase of the project it was decided to use a liquid to liquid extraction method but using different organic solvents. Therefore, the GC and MS conditions described in the paragraph above (used in the analysis of the samples that were processed with the solid extraction method) were used for the GC-MS analysis but using a different organic solvent for the liquid to liquid extraction. The solvents used were DCM, mixtures of DCM and methanol and acetone changing the solvent/samples ratios as well. All this work performed was inconclusive as no consistent clear quantifiable MEA peaks were produced.

The next step was to change the GC operating conditions (shown in *Appendix 1.3*) so parameters such as split ratio, oven initial and final temperatures, holding times and rate of temperature increase were changed and most of the times no considerable changes were applied to the MS method apart from the duration times (*Appendix 1.4*). The procedure followed was to change the conditions observing the GC-MS response when each sample was run. GC and MS conditions found in the literature were also used (Supap et al 2001, Strazizar et al. 2003 and Bello&Idem 2005) the systems and set ups were different between those studies and the system used in this study, but it was considered important to consult other studies to have a clearer idea of what conditions could the appropriate ones for the analysis. The same solvents described in the paragraph above were used for the liquid to liquid extractions but again no consistent MEA quantifiable (tailing problems) peaks were achieved.

At that stage it was concluded that the GC column used was not the appropriate one for the analysis needed. The column used was a neutral – slightly acidic column for compounds of higher molecular weights (large compounds). The MEA is a small compound and acts as a weak base and its thermal degradation products have different polarities and large variation in sizes. Therefore, after working for a while with MEA using the original system set up, it was decided to work on the analysis of its thermal degradation products using the available set up.

2. HEIA (1-(2-hydroxyethyl)-2-imidazolidinone)

A large number of trials were performed to assess whether it was possible to detect and quantify HEIA with the available GC-MS set up as it was done for MEA as well. Solvents such as DCM, mixtures of DCM with ethanol, hexane, isopropanol and chloroform were used as solvents to perform the liquid to liquid extractions with and without a N_2 blow-down. All the GC and MS conditions used can be seen in the *Appendix 1.3* and *Appendix 1.4*, respectively. The procedure described below was the one followed in one of the successful attempts.

In order to measure using the GC-MS, a solution of 100 mg/L HEIA in 5 molal aqueous MEA was prepared; 0.013 ml of the 75% aqueous HEIA solution and 23.18 ml MEA were added to 76.82 ml of H_2O. Due to the fact that water samples can not be introduced to the GC-MS, the organics were partitioned into DCM. For this reason 50 ml of the sample was mixed in a separating funnel with 50 ml of DCM. Then, the resulting sample of the DCM with the organics was evaporated down to volumes of approximately 2 ml, using a nitrogen blow-down at 40 ^{o}C.A second liquid to liquid extraction was performed on the water sample left after the first extraction in order to check if there is any HEIA remaining.

The sample was then introduced to the GC-MS and run at different GC conditions until a clear peak response was achieved using this GC method:

Experimental time 17.83 min
Split ratio 20 ml/min
Initial temperature 50 ^{o}C, hold for 0.50 min
Final temperature 280 ^{o}C, hold for 2 min
Rate 15^{o}C/min.

The MS method is Kali6 that is shown in *Appendix 1.4*. Figure 3.26 presents the chromatograph showing the peak of HEIA from the first extraction. No peak at all was observed in the samples resulting from the second extraction.

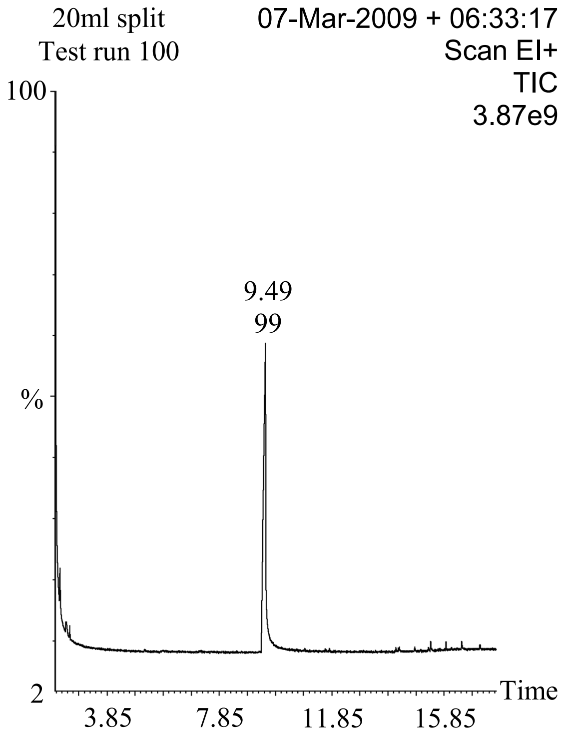


Figure 3.26 GC-MS response of 100 mg/L HEIA in 5 molal aqueous MEA solution

3. HEEDA (N-(2-hydroxyethyl) ethylenediamine)

A similar process was followed for HEEDA. A sample of 100 mg/L HEEDA in 5 molal MEA was prepared by adding 0.09 ml of HEEDA in 99.9 ml of 5 molal aqueous MEA solution (23.2 ml MEA and 76.89 ml of H_2O). A number of solvents were used in the liquid to liquid extractions such as DCM, DCM and ethanol mixtures, hexane, isopropanol and chloroform. It was noted that the best response was given when 50 ml of the sample was mixed in a separating funnel with 25 ml of DCM and 25 ml of isopropanol.

The sample was then introduced to the GC-MS and run at different GC (*Appendix 1.3*) and MS (*Appendix 1.4*) conditions until a clear peak response was achieved using the following conditions:

- experimental time - 20 min
- split - 50 ml/min
- initial temperature - 50 ^{o}C

- final temperature - 280 °C
- rate - 20 °C/min.

The MS method is Kali6 that is shown in *Appendix 1.4*. The resulting response for the 100 mg/L HEEDA in 5 molal aqueous MEA is shown in Figure 3.27

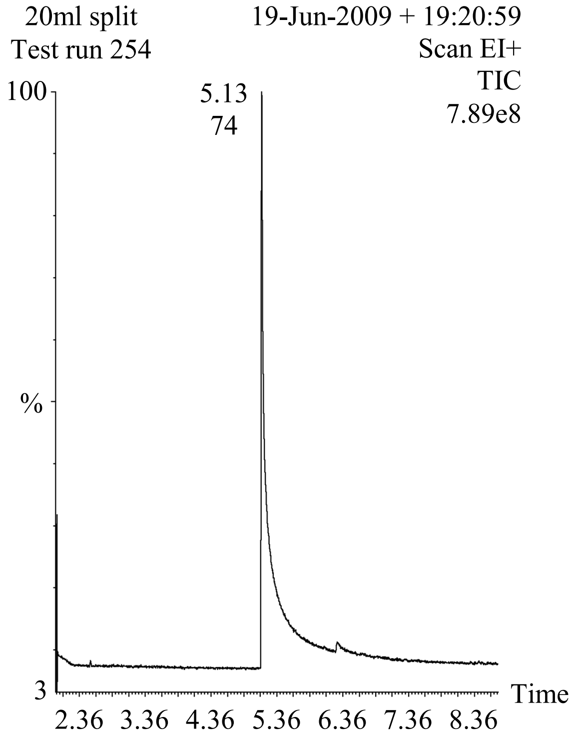


Figure 3.27 **GC-MS Chromatograph of 100 mg/L HEEDA in 5 molal aqueous MEA solution**

Unfortunately, the same problem that was faced with the MEA was faced with HEEDA in that no consistent peaks were achieved. This could be attributed to the fact that, as MEA, HEEDA is an amine as well and the available set up is not the appropriate for its detection and quantification.

4. 2-Oxazolidone

Similarly to what it was described for HEEDA and HEIA (Figure 3.26 and Figure 3.27), work needed to be performed for 2-Oxazolidone as well for its detection and quantification with the GC-MS. A100 mg/L 2-Oxazolidone solution in 5 molal aqueous MEA was prepared by adding 10 mg of 2-Oxazolidone and 20.9

ml of MEA in 68.9 ml of H_2O. A liquid to liquid extraction was needed to partition the organics into a mixture of DCM and isopropanol (50:50). 50 ml of the sample was mixed in a separating funnel with 25 ml of DCM and 25 ml of isopropanol. The sample was then introduced to the GC-MS and run at different GC (*Appendix 1.3*) and MS (*Appendix 1.4*) conditions, until a clear peak response was achieved using the following GC conditions:

Experimental time was 17.83 min
Split was 20 ml/min
Initial temperature was 50 ^{o}C, hold for 0.50 min
Final temperature was 280 ^{o}C, hold for 2 min
Rate was 15 ^{o}C/min.

The MS method is Kali6 (*Appendix 1.4*). The resulting response for the 100 mg/L 2-Oxazolidone in 5 molal aqueous MEA is shown in Figure 3.28.

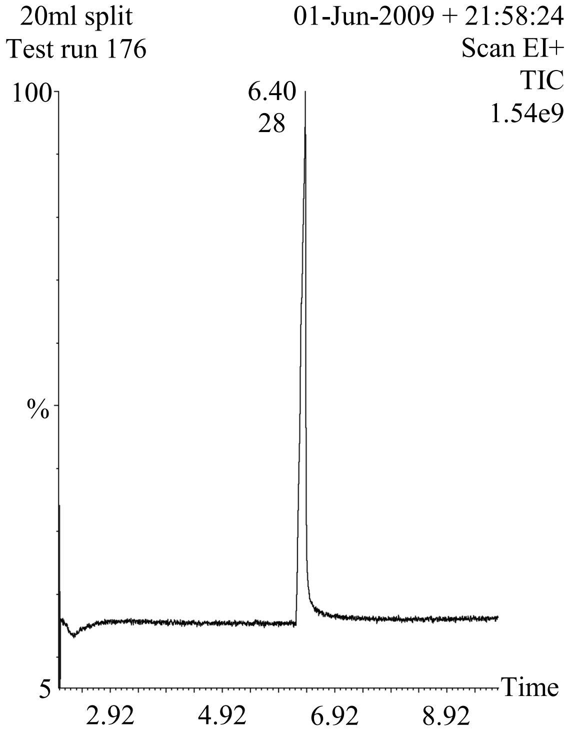


Figure 3.28 **GC-MS Chromatograph of 100 mg/L 2-Oxazolidone in 5 molal aqueous MEA solution**

3.10.1.2 Final instrument set up

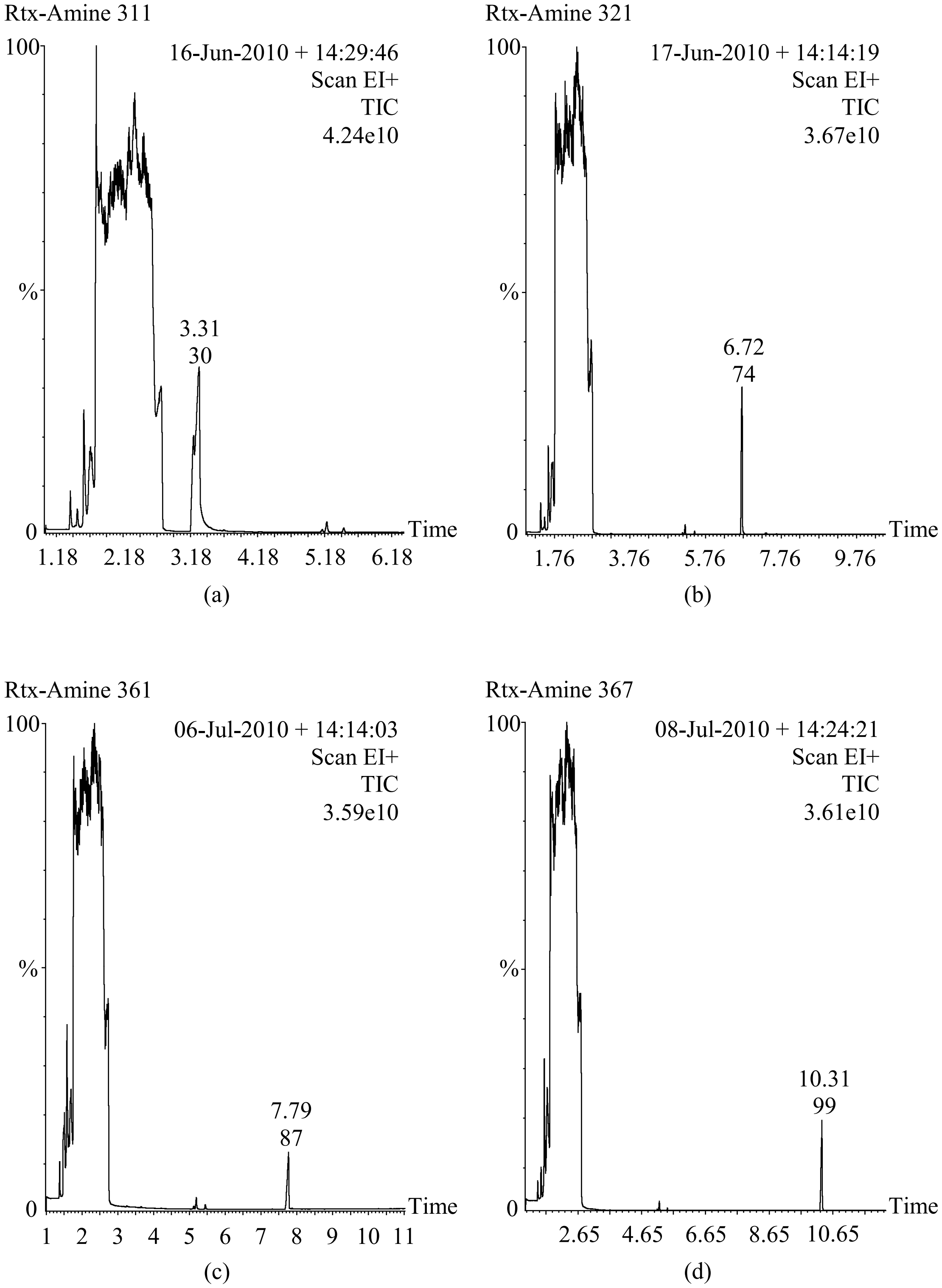
From all the previous work done by the author with the GC-MS for the analysis of MEA and its major thermal degradation products, it was concluded that it was not possible to identify and quantify them with the available set up. For that reason it was decided to purchase a different GC column (Rtx 5 Amine from Restek) more appropriate for the analysis needed to be performed.

With the new column it was initially necessary to conduct a systematic calibration exercise in the same way as was done for the previous column. Initially samples of pure MEA, HEEDA, HEIA and 2-Oxazolidone diluted in MTBE, DCM, toluene and acetone were run in the system. For the extractions, 50 ml of sample were mixed with 50 ml of the solvent in a separating funnel, the funnel was placed in a rotating bed for approximately 3 hours and then it was left to stand until the layers were clearly separated. Finally, about 2 ml of the organic solvent were taken and imported to the GC-MS system. The sample list can be seen in *Appendix 1.5* the conditions chosen can be seen in *Appendix 1.6* and *Appendix 1.7*, and the more appropriate conditions for the analysis of those compounds were found to be GC-MS.

GC (method kz3 *Appendix 1.6*)
Experimental time 14.50 min
Split is 50 ml/min
Initial temperature 50 ^{o}C hold for 0.5 min, rate 20 ^{o}C/min to 320 ^{o}C hold for 0.5min

MS (Method MEA4 *Appendix 1.7*)
Duration 17 min
Start mass 10 m/z
End mass 200 m/z

Armed with encouraging results from the DCM samples a programme of work was undertaken with a range of organic solvents to extract the target compounds from their aqueous solutions. DCM, acetone, toluene, MTBE and diethyl ether were used to perform liquid to liquid extractions and it was found that diethyl ether was the solvent that gave the best responses for all the 4 compounds that needed to be analysed. The peak responses produced are presented in Figure 3.29.



(a) (b)

(c) (d)

Figure 3.29 GC-MS responses for (a) MEA in ether (b) HEEDA in ether (c) 2-Oxazolidone in ether and (d) HEIA in ether

3.10.2 GC-MS-Final method

The experimental procedure that, after the extensive preliminary work, gave the best responses for all the 4 compounds of interest is described. The same procedure was used to produce the calibration curves for all analytes and to measure the unknown samples.

Due to the fact that aqueous samples could not be introduced to the GC-MS, the first step was to partition the organics from the water samples into diethyl ether. 50 ml of the sample were mixed in a volumetric flask with 50 ml of diethyl ether and shaken on a rotating bed for 2 days. 2 ml of the ether with the dissolved organics were then introduced to the GC-MS and run under the following conditions:

GC
Experimental time 14.50 min
Split is 50 ml/min
Initial temperature 50 ^{o}C hold for 0.5 min, rate 20 ^{o}C/min to 320 ^{o}C hold for 0.5min

MS
Duration 17 min
Start mass 10 m/z
End mass 200 m/z

In Table 3.12 the retention times for MEA, HEEDA, HEIA and 2-Oxazolidone when analyzed with the available GC-MS system can be seen.

Table 3.12 Retention time of each analyte in the GC-MS

Analyte	Retention Time (min)
MEA	3.31
HEEDA	6.72
HEIA	10.31
2-Oxazolidone	7.79

3.10.3 Calibration curves

Good consistent responses were obtained for all compounds using the method described in Section 3.10.2, so the next step was to produce calibration curves for all the 4 compounds. Samples of different concentrations of each compound were prepared in diethyl ether (not extracted from water samples) and peak responses were integrated to produce the calibration curves reported in Figure 3.30 and Figure 3.31 for HEEDA and 2-Oxazolidone, respectively (raw data can be seen in *Appendix 1.8*). The calibration curves produced for all the four compounds were quite linear over the concentration range examined, with R^2=0.98 and above. It is important to note here that (0, 0) point was not used when the curves were plotted, none of the lines crosses zero which means that the method is not very accurate at very low concentrations close to 0.

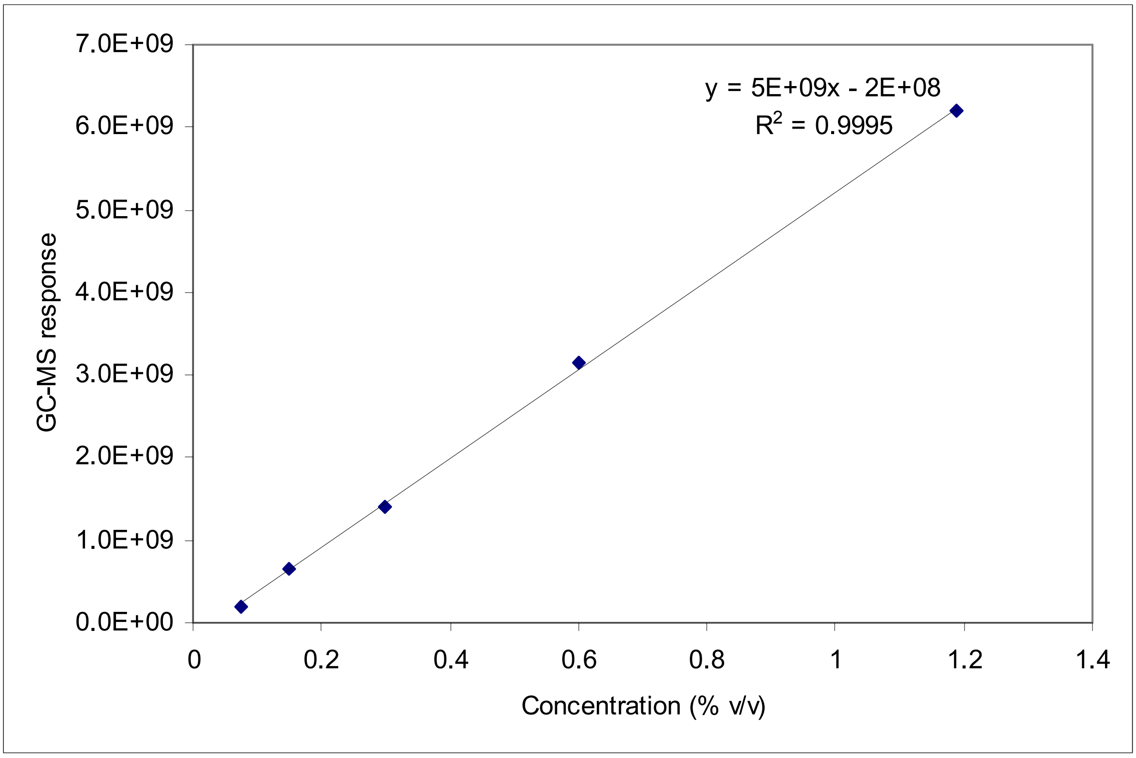


Figure 3.30 GC-MS responses for different concentrations of HEEDA in Diethyl Ether

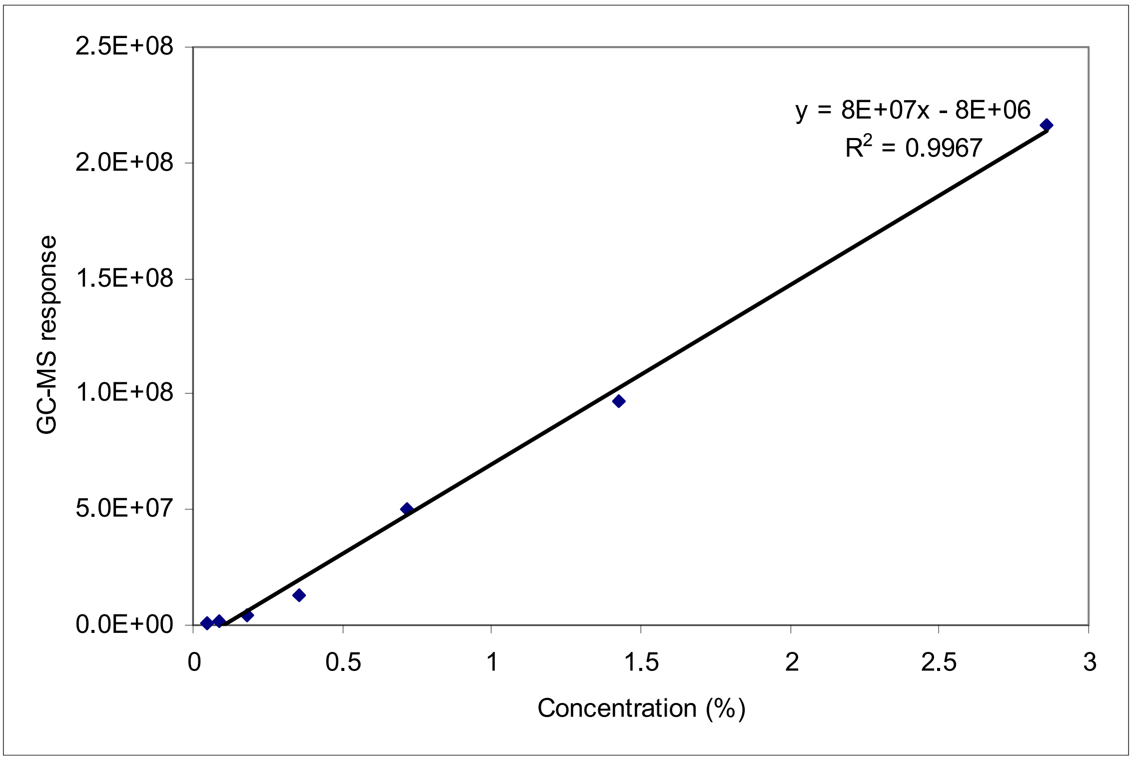


Figure 3.31 **GC-MS responses for different concentrations of 2-Oxazolidone in Diethyl Ether**

It was noted very early in this work that not all of the analytes were recovered by the liquid/liquid extraction process. At this point it was realised that it was important to perform more work in order to be able to quantify with more accuracy the MEA and HEIA which is considered the major MEA thermal degradation product (it accounts for most of the MEA loss) as reported in the literature (Davis 2009, Lepaumier 2009 B, Lepaumier 2009 A, Lepaumier 2010 and Lepaumier 2011). Therefore new calibration curves following the process described in Section 3.10.2 (GC-MS - final Method) were produced performing liquid to liquid extractions for every sample (raw data shown in *Appendix 1.9*). In total three calibration curves were produced for MEA and two for HEIA and the ones with the highest R^2 for each compound were used to determine the concentrations in the unknown samples. The produced calibration curves are shown in Figure 3.32 and Figure 3.33.

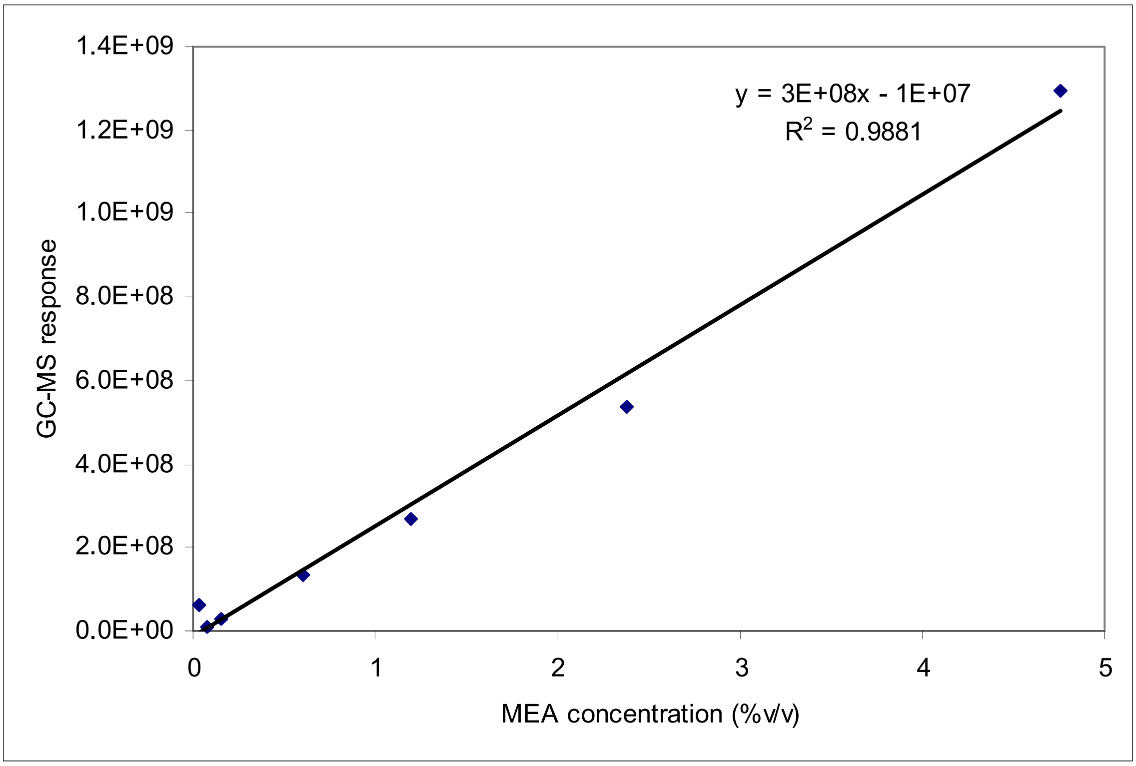


Figure 3.32 **GC-MS responses for different concentrations of MEA extracted in Diethyl Ether**

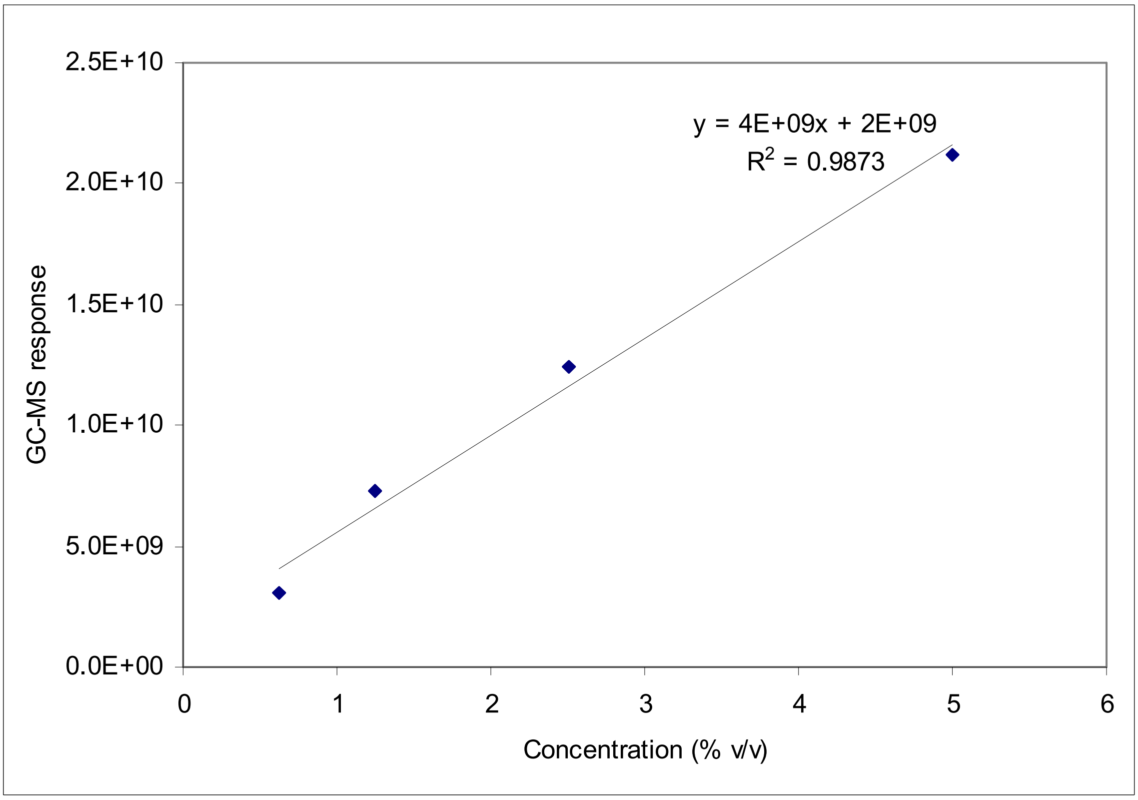


Figure 3.33 **GC-MS responses for different concentrations of HEIA extracted in Diethyl Ether**

It was necessary though to quantify the partitioning of HEEDA and 2-Oxazolidone into the diethyl ether and work with the calibration curves already produced. Solutions containing a known concentration of each of the two compounds (one sample for each compound) were prepared and the liquid/liquid extractions performed. The resulting solutions of the compounds in the diethyl ether were then measured by the GC-MS and the concentration determined from the calibration curve detailed in Figure 3.30 and Figure 3.31 (raw data and calculations presented in *Appendix 1.8*). The ratio of this concentration to the known concentration is termed the Partition Coefficient in the present work. Values of these coefficients expressed as a percentage for 2-oxazolidone and HEEDA are presented in Table 3.13.

Table 3.13 Partition coefficients for HEEDA and 2-oxazolidone into diethyl ether

Analyte	Partition Coefficient %
HEEDA	20
2- oxazolidone	100

3.11 DETERMINATION OF THE EFFECT OF THERMAL DEGRADATION ON CO_2 ABSORPTION AND DESORPTION-EXPERIMENTAL PROCEDURE

Unless otherwise stated the procedure was as follows.

A volume of 1200 ml of 30% w/v aqueous MEA solution was contacted with pure CO_2 at a rate of 100 ml/min in the gas absorption/stripping rig (Figure 3.5), until the desired loading was achieved, as determined by the inorganic carbon content measurement performed by the TOC instrument (see Section 3.7).

The resulting sample was put into the three high pressure vessels (Figure 3.9), 400 ml in each, and then the vessels were placed in the oven to be thermally degraded at 160°C. The pressure change in two of the three vessels was continuously monitored, for safety reasons.

The vessels were removed from the oven at predetermined times, 2, 3 and 8 weeks. Repeated absorption/stripping cycles were applied to samples of pure MEA in the absorption/stripping apparatus (Figure 3.5) in order to determine the pure solvent's behaviour and its capacity for CO_2 uptake for a given period of time (approximately 6.5 hours for absorption and the same for stripping).

For the absorption: the temperature in the oil bath was raised to 50 °C and the feed gas inlet valve opened. 100 ml/min of pure CO_2 were bubbled into the reactor through a pre-saturator to maintain the water balance in the system. Any excess CO_2 gas that is not absorbed by the solvent is vented to a fume cupboard through a condenser and an amine recovery bottle. In order to determine the loading, samples of 0.1 ml were taken every 30 min and measured for their inorganic carbon content (see Section 3.7). After the absorption has finished the feed gas valve is closed.

For the stripping: the temperature in the oil bath was raised to 120 °C, the feed gas inlet valve opened and 200 ml/min of pure N_2 were bubbled into the reactor to ensure good agitation. At those conditions the CO_2 is released by the MEA and is again vented to the fume cupboard through a condenser and an amine recovery bottle. The outlet gas flow and composition were measured every 20 to 30 min with a flow meter and microGC system (see Section 3.6). Repeated absorption/stripping cycles were then applied to the degraded samples so as to determine how thermal degradation affects the solvent's CO_2 uptake capacity. During the absorption the CO_2 loading of the sample was determined by measuring the carbon content of the sample with the TOC analyser (see Section 3.7). During stripping the microGC system was used to determine the CO_2 concentration at the outlet of absorption / stripping rig. The samples were analysed for thermal degradation products with the GC-MS (see Section 3.10.2).

3.12 SUMMARY

The procedures followed to design and commission the absorption/stripping rig have been described in detail along with its operating protocols and details of its components. The system was designed to be capable of applying repeated cycles of absorption/stripping to different amine solvents and identifying the key parameters that affect the operational lifetime of the solvents. The screening of the solvent behaviour in terms of its CO_2 uptake capacity and how this is affected by solvent deterioration, though, was the most important use of that system.

After realising that solvent degradation was a very slow phenomenon at the chosen conditions and it would not be feasible to degrade MEA samples within a reasonable timescale, a second experimental procedure was designed. A more focused approach on the MEA thermal degradation was taken and a procedure to degrade samples of amines loaded with CO_2, by exposing them to elevated temperatures for prolonged periods of time, was developed. Description of the system and information for its components has also been included in this chapter.

Descriptions of all the analytical equipment used to perform this research work were also presented in this chapter; a detailed description of the results processing tools and procedures is also included. As a the detection and quantification of MEA and its major degradation products was of utter importance for this research project, a considerable amount of time was spent to develop techniques and procedures to be able to perform the analysis needed by means of GC-MS and IC. The approach followed and the course of action taken to develop and improve the methods and analytical equipment setups has been discussed. The calibration curves were also presented for all the analytes tested. It can be concluded that with the systems and methods developed throughout this project, the identification and quantification of MEA and its major oxidative and thermal degradation products is feasible.

Last but not least, the procedure followed to thermally degrade samples and assess the effect of thermal degradation on the solvent operational lifetime was detailed. This section links all the rigs, methods and procedures together and explains how these were used to assess the solvent deterioration.

CHAPTER 4
RESULTS-DISCUSSION

4.1 INTRODUCTION

In this chapter the results generated during this study are presented and discussed. This chapter is split into the following sections:

Section 4.2: Non-systematically degraded sample experiments, performed in order to get more familiar with the absorption/stripping rig equipment, try to degrade samples and detect any degradation products generated.

Section 4.3: MEA full loading experiment, to assess the solvent's behavior during absorption in the absorption/stripping rig.

Section 4.4: The 14 repeated full cycles experiment, as an initial systematic effort to degrade an MEA sample with mixtures of CO_2 and O_2 in the gas absorption/stripping rig, assess the solvent's behavior in terms of CO_2 uptake and detect and quantify any degradation products generated in it.

Section 4.5: After it was realized that it would not have been feasible to degrade samples within timescale in the existing rig, the CO_2 solubility experiments were performed in order to build confidence with the new designed experiment for MEA thermal degradation in the presence of CO_2.

Sections 4.6 and 4.7: Thermal degradation experiments with lean and rich initial molar loading, respectively. The solvent behavior was assessed in terms of the effect of degradation on the solvent's CO_2 uptake capacity and thermal degradation products generation.

Section 4.8: A brief discussion of the effect of the initial molar loading on the solvent thermal degradation.

Section 4.9: A summary section of the results and discussion chapter.

4.2 NON-SYSTEMATICALLY DEGRADED SAMPLE

The first step in order to gain experience with the absorption/stripping rig (Figure 3.5) was to make an effort to degrade a sample of MEA. 500 ml of a 5 molal aqueous MEA solution was put in the absorption/stripping rig and degraded for about 5 days in a random fashion by bubbling air and CO_2 through it and at high temperatures (over 100^oC), in order to expose the sample to conditions to accelerate the degradation. No record of the exact experimental conditions was kept as it was an initial effort to see how the absorption/stripping rig works and how fast samples can be degraded in that system. The degraded sample was then analyzed both in the GC-MS and in the IC in order to check if the sample contained any of the compounds reported in the literature as MEA major oxidative and thermal degradation products.

4.2.1 Cardiff University analysis

After a certain experience was gained with the GC-MS and IC equipment the non-systematically degraded sample was analysed. It needs to be noted here that the methods described in Section 3.8.2 and Section 3.9.2 were not fully developed when this sample was generated. Therefore, the experimental procedures and results processing are as described in the following paragraphs.

4.2.1.1 GC-MS

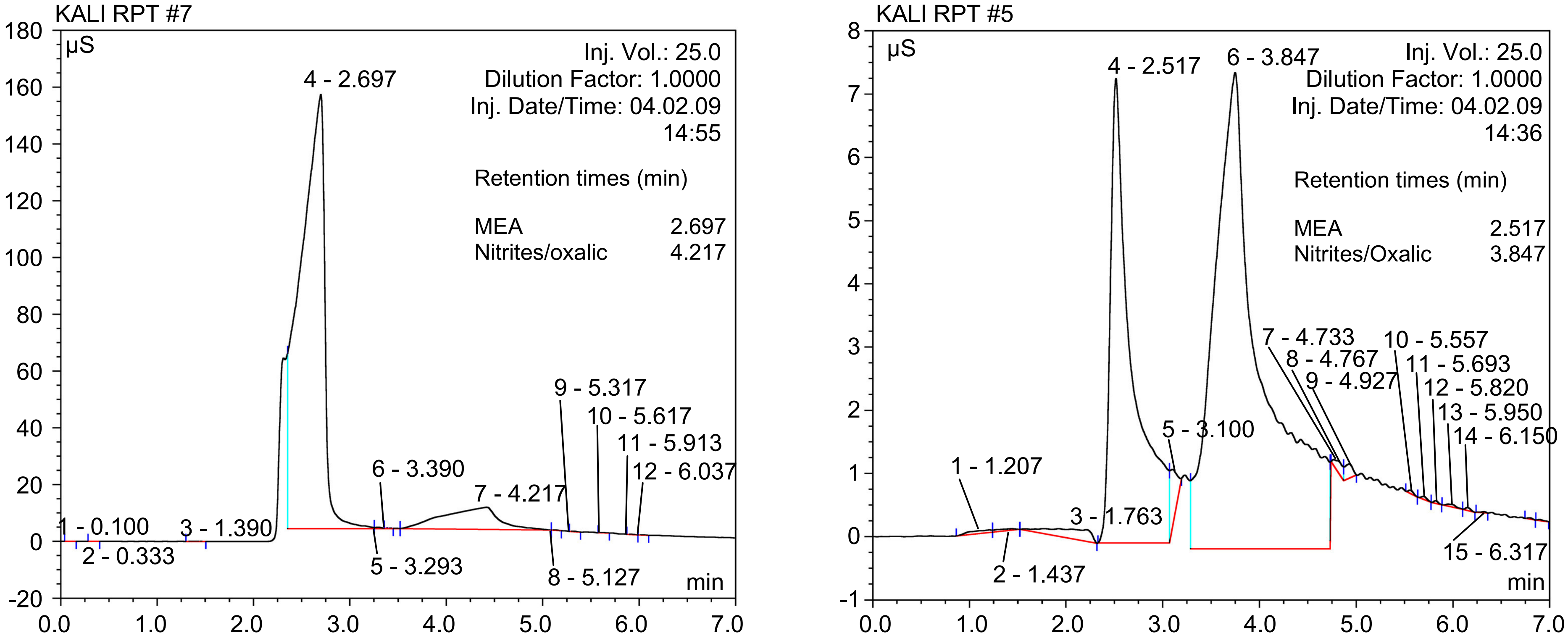
For the GC-MS measurements the old system set up was used (see Section 3.9.1.1), due to the fact that water samples can not be introduced to the GC-MS, the organics were partitioned in to DCM (dichloromethane) using the liquid to liquid extraction method. For this reason 50 ml of each solution were mixed in a separating funnel with 50 ml of DCM. Then, the resulting sample containing the DCM with the organics was evaporated down to volumes of approximately 2 ml, using a nitrogen blow down. The sample was run under different conditions changing the initial and final temperatures, the split ratio and the hold times but a clear peak response was not achieved (*Appendix 1.3* and *Appendix 1.4)*. Thus, it was concluded that this sample did not contain any compounds which could be detected with the set up available at the time in the lab or it contained lower concentrations than the minimum detectable concentrations from the available GC-MS system. As mentioned in Section 3.9.1, a modified procedure was developed at a later stage of the project.

4.2.1.2 IC

For the IC measurements a uniform sample of 10 ml was taken from the reactor and it was diluted by 10 (1 ml of sample in 9 of water) and by 100 (1 ml of sample in to 99 of water) and they were measured in the IC, Figure 4.1 (a) and (b) respectively. The samples were not pre-processed with the amine deactivation cartridges; therefore the first peak observed is MEA (with retention time 2.697 min Figure 4.1 (a) in and 2.517 min in Figure 4.1 (b)) The IC conditions to run the samples were as follows:

- eluent - potassium hydroxide, 30 mM,
- flow rate - 1.2 ml/min,
- temperature - 30 °C,
- injection volume - 10 μl
- suppressor current - 100 mA.

As shown in Figure 4.1 (a) and (b) the resulting chromatographs consist of two peaks. Based on information from the other sample runs the first peak seems to be MEA. For the second peak based on the retention times of the separate compound samples which were run, acetic, formic and nitrate anions are excluded. It could either be due to nitrite or oxalic anions. For this reason another method for the measurement of nitrite ions was used in order to detect if the sample contains nitrite anions see Section 4.2.3. It should be noted here that samples of 0.5 molal fresh aqueous MEA solutions have been run in the IC system (see Figure 3.14 (a)) and no considerable peaks close to the nitrite or oxalic retention times have been observed.



(a) (b)

Figure 4.1 5 molal aqueous MEA sample degraded in a non-systematic way (a) x10 dilution and (b) x100 dilution

4.2.2 Non-systematically degraded Dionex IC analysis

4.2.2.1 Anion IC analysis

The same degraded sample as was analyzed in Cardiff was also sent to Dionex Ltd in Switzerland to be analyzed in an IC system at their laboratories. An ICS-3000 system with a suppressed conductivity detector was used.

The anions were separated on an IonPac AS24 column and analyzed in 25 minutes using the following conditions:

- Eluent KOH 0.3 ml/min via eluent generator
- System pressure less than 2,800 psi
- Suppressor current 50 mA
- Temperature 15 ^{o}C
- Injection volume 25 µL.

The resulting chromatograph is shown in Figure 4.2.

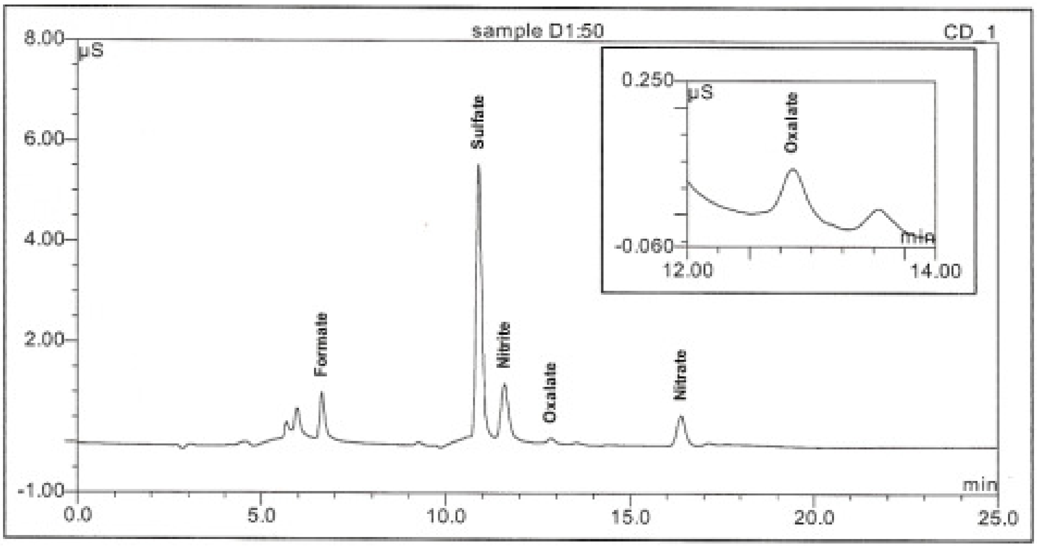


Figure 4.2 Anionic analytes in the degraded sample analyzed by Dionex Ltd

The concentrations of the anionic analytes in the original sample determined by Dionex are shown in Table 4.1.

Table 4.1 Concentrations of the anionic analytes in the degraded sample as determined by Dionex Ltd

Analytes	Amount (mg/L)
Formate	11.97
Sulphate	64.37
Nitrite	18.23
Oxalate	2.091
Nitrate	14.44

The presence of 5 analytes was verified in the samples and the highest concentration observed was that of sulphate, with nitrite following. Nitrites were also detected by the IC system and the colorimetric method used at Cardiff School of Engineering. There is a difference in the measured values between laboratories and different equipment; more research would be needed to assess those differences. Moreover, peaks of formate, oxalate and nitrate were not observed in the IC chromatographs produced by the system used in this study. It should be noted here that the presence of sulphate ions was not expected but they were detected in the degraded samples. As no sulphate ions were detected in the pure MEA, the air used during the process came from a bottle and no obvious contamination source was noted in any part of the process, their presence could possibly be attributed to the dish-washer detergent used to wash all glassware used throughout the process. Note here that the glassware was rinsed with DI water before their use.

4.2.2.2 Cation IC analysis

For the detection and analysis of the amines the IonPac CS17 column, using gradient elution in combination with a suppressed conductivity detector, was used by the Dionex Ltd laboratories in Switzerland. The chosen conditions for the analysis are as follows:

- Gradient MSA 0.3 ml/min via eluent generator
- System pressure less than 2,640 psi
- Suppressor current 40 mA
- Temperature 30 ^{o}C
- Injection volume 10 μL

The resulting chromatograph is shown in Figure 4.3.

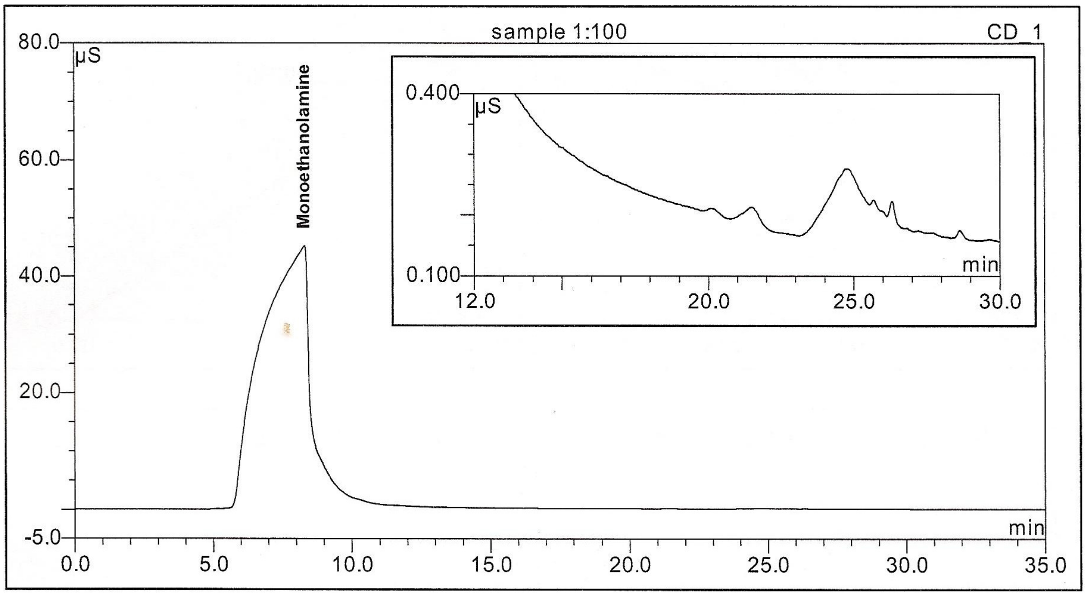


Figure 4.3 Cationic analytes of the degraded sample analyzed by Dionex Ltd

No analysis was performed to detect amines or any cationic products at Cardiff School of Engineering. The chromatograph shown in Figure 4.3 presents a peak response for MEA and no other identified cationic analyte is present in considerable amounts.

4.2.3 Colorimetric analysis with HACH meter

The HACH portable data logging colorimeter DR/890 available at Cardiff School of Engineering was used to verify and quantify the presence of nitrite, nitrate and sulphate ions in the non-systematically degraded sample, as they were detected in the sample that was analysed by Dionex (Section 4.2.2).

The first step was to determine if the second peak response present in the degraded sample's chromatograph (see Figure 4.1 (a) and Figure 4.1 (b)) was due to oxalic or nitrite ions. For that reason, the HACH meter was used for the analysis of nitrite ions with the ferrous sulphate method for high range (0 to 150 mg/l NO_2^-) with the method 8153 (see Section 3.8). In the first measurement made, the sample was not diluted and it was noted that the reading was outside the range of the method, for that reason the measurement was repeated after the sample was diluted by 10 (1 ml of degraded sample in 9 ml of DI water). The instrument reading was multiplied by 10 and it was determined that it contained 600 mg/L nitrite anions.

As nitrate anions were also detected in the sample in the Dionex laboratories, the HACH portable data logging colorimeter was used to analyse the sample and quantify any nitrates present in solution. The cadmium reduction method in the high range from 0 to 30 mg/L with method number 8039 was used (see Section 3.8). The presence of 8 mg/L nitrate anions was determined using this method.

It was not originally expected to detect sulphate anions in the degraded sample but, as it was detected by Dionex in their system, another method was used in Cardiff to verify their presence. The HACH portable data logging colorimeter was again used to analyse the sample, with the SulfaVer 4 method (method number 8051) in the range from 0 to 70 mg/L (see Section 3.8). The first sample analysed was not diluted and the reading was outside the range of the method, therefore the sample was diluted by 10 and the measurement was repeated and the final instrument reading was multiplied by 10. It was determined that the sample contains 130 mg/L of sulphate anions.

Table 4.2 shows the concentrations of each analyte as measured by Dionex Ltd and the HACH meter at Cardiff University. The peaks identified in the sample analysed by the anion IC system used in this study, were not quantified as no calibration curve was available at the time that this sample was analysed. The calibration curves produced at a later stage of the project were prepared using a different procedure for the IC analysis.

Table 4.2 Anion quantification in the randomly degraded sample with O_2, comparison of the Dionex Ltd IC system and the HACH meter

	HACH meter Cardiff University	IC Dionex Ltd
Analytes	Concentration (mg/L)	
Formate	-	11.97
Sulphate	130	64.37
Nitrite	600	18.23
Oxalate	-	2.091
Nitrate	8	14.44

Clearly, there is a need for further work in order to explore the differences between results at different laboratories and using different equipment. However, there is clear demonstration that sulphate (unexpectedly and unexplained), nitrate and nitrite ions have been generated during this initial degradation process. As already mentioned in the case of the randomly degraded sample (Section 4.2.2.1), one possible source of sulphate contamination could be the dish-washer detergent, no other apparent source could be identified.

4.3 FULL LOADING EXPERIMENTS

The next step for the commissioning of the absorption/stripping rig and to develop a method to assess the MEA behavior during the process was to attempt a full loading experiment in the developed system and with the chosen operating conditions.

It was theoretically calculated that 500 ml of a 5 molal aqueous MEA solution can absorb 27.83 L of CO_2 considering that the maximum loading that could be achieved is at absorber conditions is 0.5 moles of CO_2/mole of MEA. The CO_2 inlet flow for this initial experimental run was chosen to be low, 20 ml/min and 180 ml/min of air. The CO_2 inlet flow was adjusted in such way so as the solvent could absorb all the CO_2 at the beginning of the experiment. In other words, the inlet flow was low so the CO_2 bubbled into the solvent would not reach the liquid surface. This was done in order to be able to assess the solvent's behavior in terms of CO_2 uptake. Taking into account the CO_2 inlet flow, it was calculated that the aforementioned MEA solution needs 23.2 hours until fully loaded. In order to check the system's behavior an experiment to fully load the amine was performed.

Samples of the outlet gas were taken every 15 minutes using the microGC system during the period of absorption (see Section 3.6 for the microGC procedure) it needs to be noted here that the data presented in this section are just CO_2 concentrations (% w/w) and not volumes of CO_2 (see *Appendix 2.1* for raw data). In Figure 4.4 the % (w/w) of CO_2 in the outlet gas over time during absorption can be seen. The vertical grey line shows the time where, according to the theoretical calculations, the loading is supposed to be finished (23 hours). The horizontal black line shows the CO_2 concentration (15.84 %) which was calculated from the inlet flow, whereas the grey horizontal line shows an average value of all the CO_2 inlet concentrations measured during the experimental time. From Figure 4.4 it can be concluded that the system operates as expected. For the first 8.5 hours the MEA seems to absorb all the CO_2. After this and until the end of the 33rd hour the absorption rate falls but the CO_2 percentages fluctuate. It needs to be noted here that at this initial experiment, the gas flow rate at the absorption/stripping rig's outlet was not measured; therefore the solution breakthrough capacity could not be calculated.

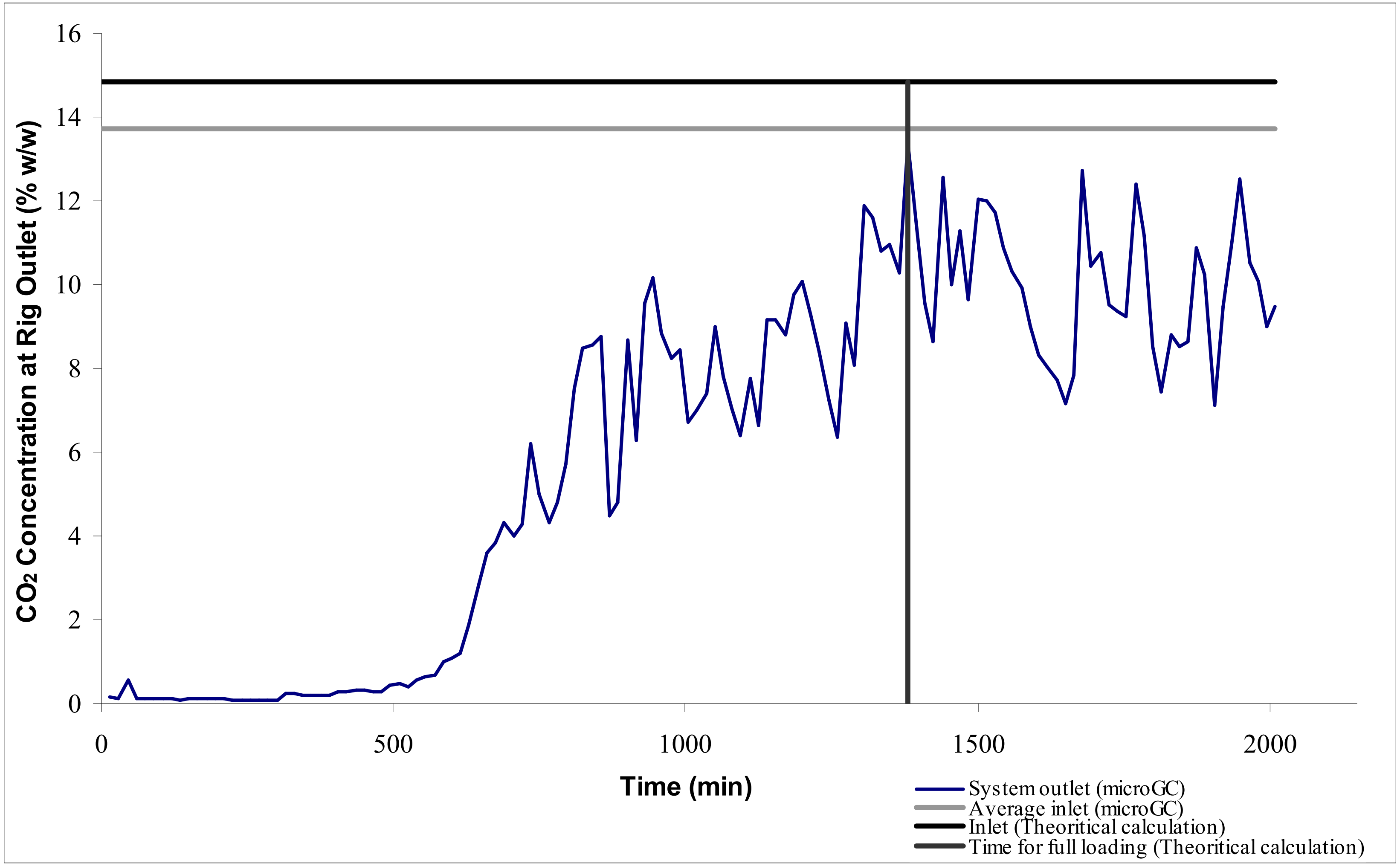


Figure 4.4 CO_2 concentration with time in the laboratory absorption/stripping rig during the full loading experiment

4.4 14 FULL CYCLES OF ABSORPTION/STRIPPING WITH O_2/ CO_2 MIXTURE

After the full loading experiment was performed, a more systematic exercise to degrade a sample of MEA, by exposing it to repeated cycles of absorption/stripping at conditions as close as possible to a real amine scrubber, was attempted.

4.4.1 Solvent behaviour accessed with the microGC

In order to assess the effect of the presence of O_2 on the solvent and the system operation, 500 ml of 5 molal aqueous MEA solution was prepared and subjected to repeated cycles of absorption and stripping in the absorption/stripping rig, under such conditions to achieve MEA oxidation (Figure 3.5). The feed gas composition was 20 ml/min CO_2 and 180 ml/min air or 66.4% N_2, 17.7% O_2 and 15.84% CO_2 % w/w. The microGC system was used at the rig's outlet to measure the gas composition with the method described in Section 3.6, the data presented are CO_2 concentrations % w/w and not volumes of CO_2.

Each absorption cycle lasted 2 hours and stripping 1 hour, the system was run for 14 full (absorption-stripping) cycles. The experiments were run over a period of 7 days, which means that 2 full cycles were performed each day. The absorption temperature (50 ^{o}C) in the oil bath was reached in 10 minutes and the stripping temperature (from 50 to 120 ^{o}C) in 20 minutes.

Samples of the outlet gas were taken every 10 minutes for all the period of absorption and stripping. The measurements were initiated after the desired temperature was achieved in the oil bath and they are plotted in Figure 4.5 and Figure 4.6 for absorption and stripping respectively. These graphs represent the CO_2 concentrations at the system's outlet (microGC response) over time. Due to technical difficulties some of the absorption values were missing (absorption 3, day 2, cycle 1 from 09:00:00 to 09:40:00 and absorption 5, day 3, cycle 1 from 09:00:00 to 09:50:00), these values were found by performing linear interpolation using the values from the other curves. This was done by calculating the average values of the microGC responses obtained by the other cycles at the specific times missing (see *Appendix 2.2* and *Appendix 2.3*)

As already mentioned, it was theoretically calculated that 500 ml of a 5 molal aqueous MEA solution can absorb 27.83 L of CO_2 (see Figure 4.4). Taking into account that the inlet CO_2 flow for the experimental run was chosen to be 20 ml/min, it was also calculated that the aforementioned MEA solution needs at least 23.2 hours until fully loaded. Moreover, as it was also chosen to run the absorption experiments for 2 hours to be able to perform more than one cycles per day. Thus, based on theoretical calculations, the highest loading which could be achieved in 2 hours is up to 8.6 %.

From Figure 4.5, which shows the absorption curves resulting from all 14 cycles, it can be seen that at all the 14 runs the sample absorbs all the CO_2 after about 30 minutes and is still absorbing CO_2 till the end of the absorption experiment. It was therefore concluded that with the available system, being capable to achieve maximum loading of 8.6% in 2 hours, it would take a very long time to observe a difference in the MEA breakthrough curve, if no difference is observed after 14 full cycles. As shown in Figure 4.4, it took about 500 minutes to observe CO_2 exiting the system's outlet and in Figure 4.5 no CO_2 exits the system after 120 min when 14 cycles of absorption/stripping in the presence of O_2. Therefore, it can be concluded that a measurable effect of MEA oxidation on the solvent's CO_2 uptake capacity would take a long time to be observed with the available system and conditions. It must also be noted here that these lines just represent CO_2 percentage at the system's outlet, in other words no measurement of the exit flow was taken, and thus not safe conclusions can be drawn on the CO_2 volumes absorbed.

During the stripping, as shown in Figure 4.6 the curves have similar trends which shows that the system has the expected behavior as far as stripping is concerned for all the 14 cycles. The system starts to almost fully release the CO_2 after approximately 40 minutes, which could be also attributed to the fact that the measurements started after the temperature in the oil bath reached the desirable

120 ^{o}C but the temperature inside the reactor takes longer to be reached. Overall, the curves are essentially identical within experimental error.

Therefore, it could be concluded that many more full cycles of absorption-stripping should be applied to the MEA in order to start observing the effect of O_2 on the solvent CO_2 uptake capacity at those conditions and in the available absorption/stripping rig. Note here again that a more accurate way to assess the effect of O_2 on MEA and how it affects its capability to absorb the CO_2 would be by performing mass balances in the system. This was not possible at this experiment as the CO_2 volumetric flow at the system's outlet was not measured during these experiments. Moreover, the effect might have been more prominent at a later stage of the absorption process, when the solution has absorbed volumes closer to its maximum capacity. It would take a very long time though to perform full cycles of absorption/stripping as with the available rig took about 500 minutes to breakthrough (see .

Based on the literature review (see Section 2.5.1) the oxidative degradation rate is enhanced as the MEA and O_2 concentrations are increased whereas there is a disagreement on whether the CO_2 molar loading has an inhibition effect or increased the degradation rates. Therefore, it was concluded that many more full cycles of absorption/stripping should be applied to the MEA, or introduce higher O_2 concentrations in order to start observing a more dramatic effect of O_2 on the solvent.

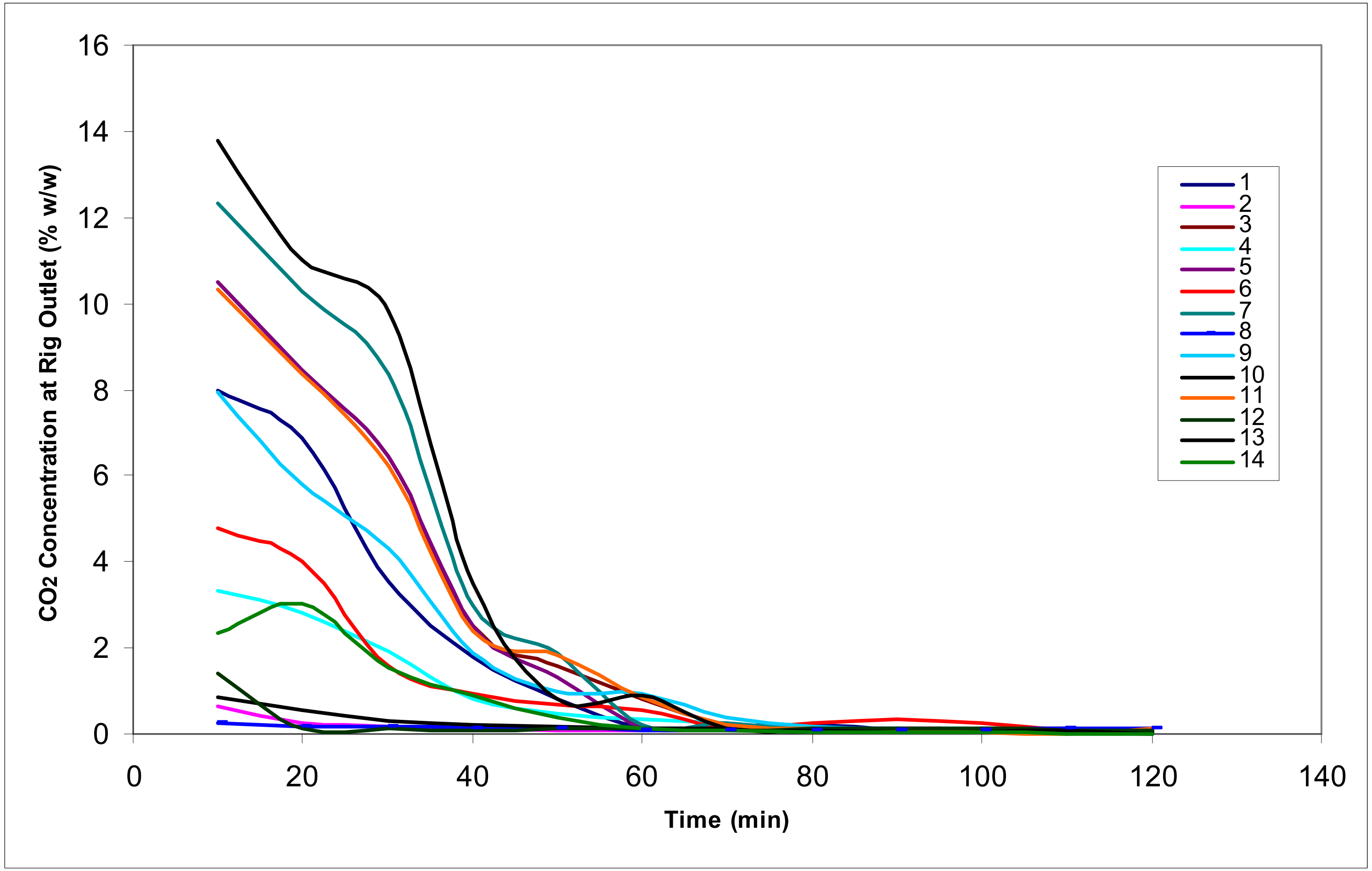


Figure 4.5 CO$_2$ concentration during absorption with time in the laboratory absorption/stripping rig for each of the 14 absorption-stripping cycles

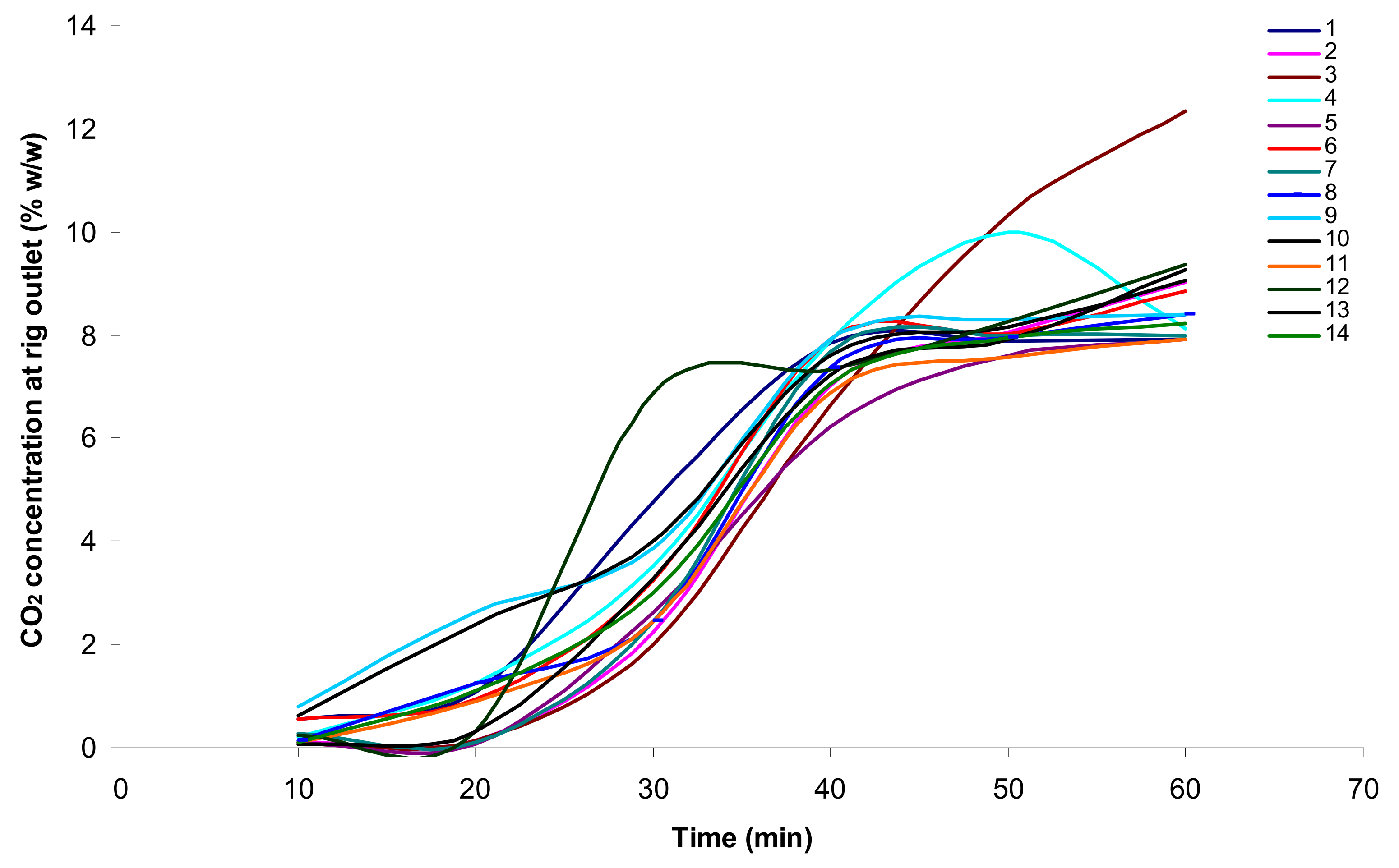


Figure 4.6 CO$_2$ concentration during stripping with time in the laboratory absorption/stripping rig for all the 14 absorption-stripping cycles

4.4.2 Sample analysis with the GC-MS

The MEA sample which resulted from the repeated absorption/stripping experiment described in the previous paragraph, was also analyzed in the GC-MS using different conditions -for both the GC and the MS (*Appendix 1.3* and *Appendix 1.4*) and organic solvents (DCM, hexane, isopropanol and chloroform) for the liquid to liquid extraction but no clear response was obtained for this sample. This means that the sample did not contain any of the compounds which can be detected with the available system setup (HEEDA, HEIA or 2-Oxazolidone) or that they were present at concentrations lower than the minimum detectable by this GC-MS system. It needs to be noted here that a more appropriate procedure for the analysis of those compounds was developed at a later stage of the project (see Section 3.9.1).

4.4.3 Sample analysis with the IC

The same sample was preprocessed with the MEA deactivation cartridges and was analyzed with the available IC system using the conditions described in Section 3.8.1.3.

The resulting chromatograph can be seen in Figure 4.7. In this chromatograph 4 clear peaks can be noted and based on the retention times for each of the compounds (See Table 3.8) it can be concluded that MEA, nitrite and nitrate anions were in the solution. Two of the peaks were quantified and the presence of 111 mg/L nitrites and 1350 mg/L nitrates was determined.

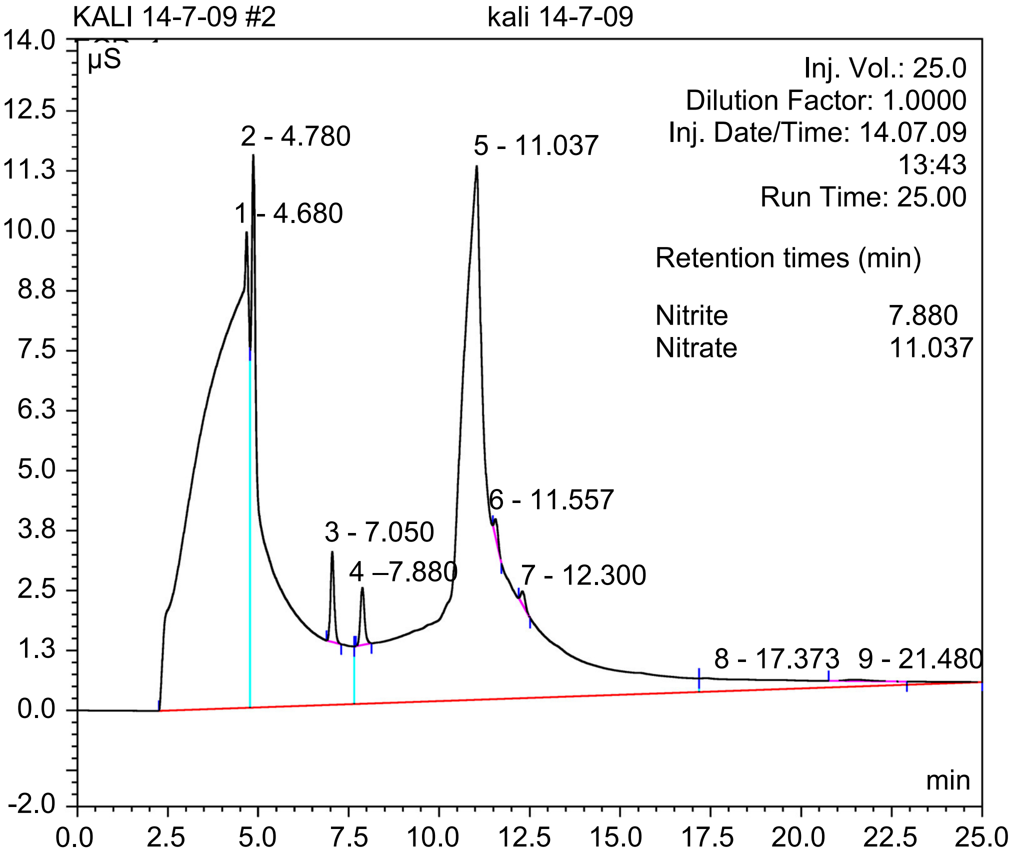


Figure 4.7 IC chromatograph of the degraded MEA sample after 14 cycles of absorption-stripping

As seen in Figure 4.7, the resulting chromatograph is not very good, the base line is slightly raised and there are two major peaks and other small ones. At 11.557 min a small peak (number 6) can be observed at the side the nitrates peak that could be sulphate (based on the retention times). Again as in the randomly degraded sample (see Section 4.2.1.2) it was not expected to detect sulphate anions but because they were detected in the previous sample (by both the Dionex IC system and Cardiff University analytical equipment) and there is a small peak observed in Figure 4.7, another method was used to verify their presence.

4.4.4 Sulphate, nitrite and nitrate anions HACH meter measurement

The HACH portable colorimeter was again used to verify the IC results and to compare the values measured by the two instruments, as at this stage of the study the calibration curves and method detection limits had been produced for all the five analytes. The analytical procedure followed is described in Section 3.8.

The SulfaVer 4 method in the range from 0 to 70 mg/L was used again and it was determined that the sample contains 6 mg/L of sulphate anions. Nitrate anions were also detected in the sample by the IC and the HACH colorimeter with the cadmium reduction method in the range from 0 to 30 mg/L was also used to crosscheck the results. The presence of 560 mg/L nitrate anions was verified using also this method (the sample was diluted by 10 to perform this measurement). Finally, the ferrous sulphate method for high range (0 to 150 mg/L NO_2^-) was used to verify the presence of nitrite ions. It was observed that the sample contains 29.6 mg/L nitrite anions. Table 4.3 presents a comparison of the measured analytes by the two different methods.

Table 4.3 Anion quantification in the degraded MEA sample with the IC system and the HACH meter.

	Nitrate (mg/L)	Nitrite (mg/L)	Sulphate (mg/L)
Anion IC	1350	111	-
HACH meter	560	29.6	6

5 molal aqueous MEA after14 cycles of absorption/stripping in the presence of O_2

As clearly seen in Table 4.3, there are differences between the absolute values of concentrations found by the two instruments but the trends are similar. Reconciliation of these differences in absolute concentrations would require further analytical investigation work. However, these results confirm the earlier findings of the randomly degraded sample presented in Section 4.2.3. Note here that there were 1.92 moles of nitrogen in the initial MEA solution, therefore, according to the IC analysis, approximately 0.5% of the nitrogen was converted to nitrates and 0.041% was converted to nitrites.

4.5 CO_2 SOLUBILITY EXPERIMENT AT 100 ^{O}C

As concluded in Section 4.4.1, it would not have been feasible to degrade MEA samples in the absorption/stripping rig (Figure 3.5) within reasonable timescale in this study. For that reason a more focused approach on thermal degradation and a new set of experiments needed to be developed. For that reason, it was deemed necessary to repeat part of the CO_2 solubility experiments in order to get more familiar with the new system built (see Figure 3.9) and the new operating protocols as presented in Section 3.5.2.

Samples of 400 ml of 30% w/v aqueous MEA solutions were placed in the absorption/stripping rig (Figure 3.5) and were loaded with pure CO_2. Thereafter, the initial CO_2 loading was determined (see Section 3.7) and each sample was placed in the high pressure vessel (the one equipped with the needle pressure gauge) shown in Figure 3.9. The measured inorganic carbon content for each sample can be seen in Table 4.4, the CO_2 molar loading was determined using Equation 3.9 (see Section 3.7).

Table 4.4 CO_2 loading determination

Date	Measured Inorganic Carbon (mg/L)	Loading (molesCO_2/mole MEA)
02/03/2010	23.26	0.039
03/03/2010	133.78	0.225
04/03/2010	245.7	0.414
05/03/2010	264.88	0.446
09/03/2010	209	0.352
18/03/2010	167.9	0.283

400 ml of 30 % w/v aqueous MEA solution samples, loaded in the absorption-stripping rig at 50^{o}C, 500 ml/min pure CO_2

The vessel was sealed and placed in the oven at 100 ^{o}C until equilibrium was reached (it was assumed that equilibrium was reached when the pressure reading of the pressure gauge was stable for more than an hour). The measured total pressure and the time to reach equilibrium for each sample are presented in Table 4.5 (raw data presented in *Appendix 2.4: Raw Data CO_2 Solubility Experiment*).

Table 4.5 Total Pressure Data for MEA – CO_2 – Water system at 100 °C

Initial Loading (molesCO_2/mole MEA)	Measured Total Pressure (kPa)	Time to equilibrium (hours)
0.039	240.7	3
0.225	275.08	5
0.283	550.16	6
0.352	584.54	7
0.414	618.93	8
0.446	861.85	10

400 ml of 30% w/v aqueous MEA solution, 200 ml available headspace, temperature 100 °C

The CO_2 partial pressure was then calculated by subtracting from the total pressure the partial pressures of MEA, H_2O (both calculated using Raoult's law) and the air partial pressure (calculated assuming ideal gas behaviour). In Figure 4.8 the relationship between the initial CO_2 loading and the time that it took for the system to reach equilibrium is shown and it can be seen that as the initial loading increases the time to equilibrium increases as well. Figure 4.9 presents the measured total pressure during the solubility experiments at 100 °C versus the CO_2 initial molar loading.

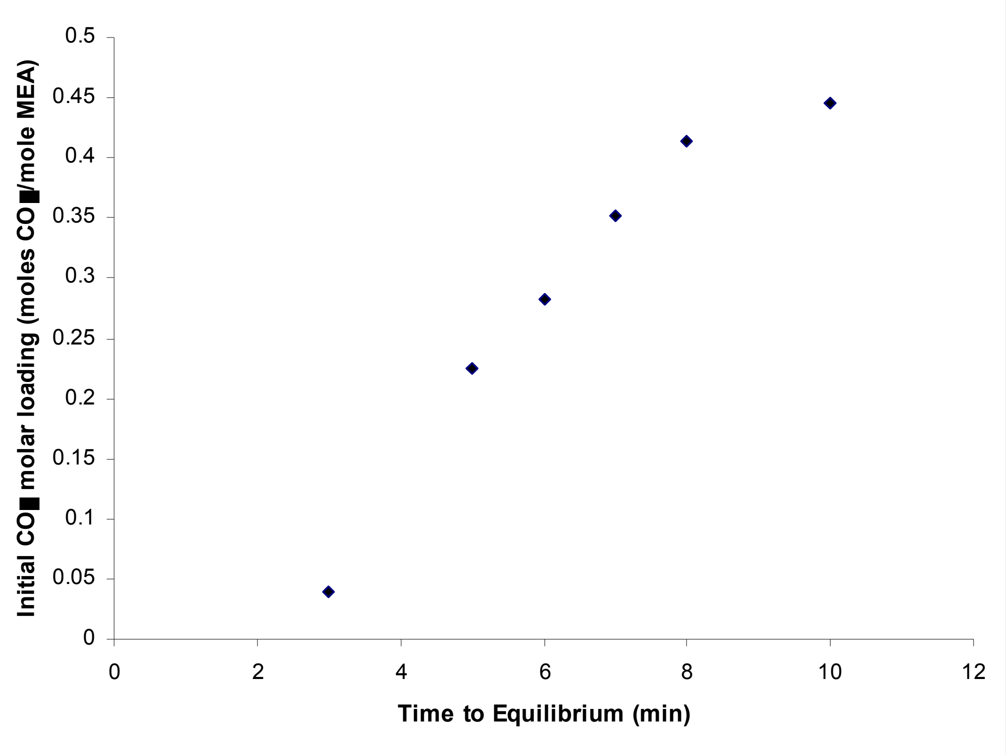


Figure 4.8 Time to equilibrium during the CO_2 solubility experiments at 100°C

Equilibrium between 400 ml of 30 % w/v aqueous MEA solution and the CO_2 released in the headspace of the pressure vessel versus the initial CO_2 molar loading of the MEA solution.

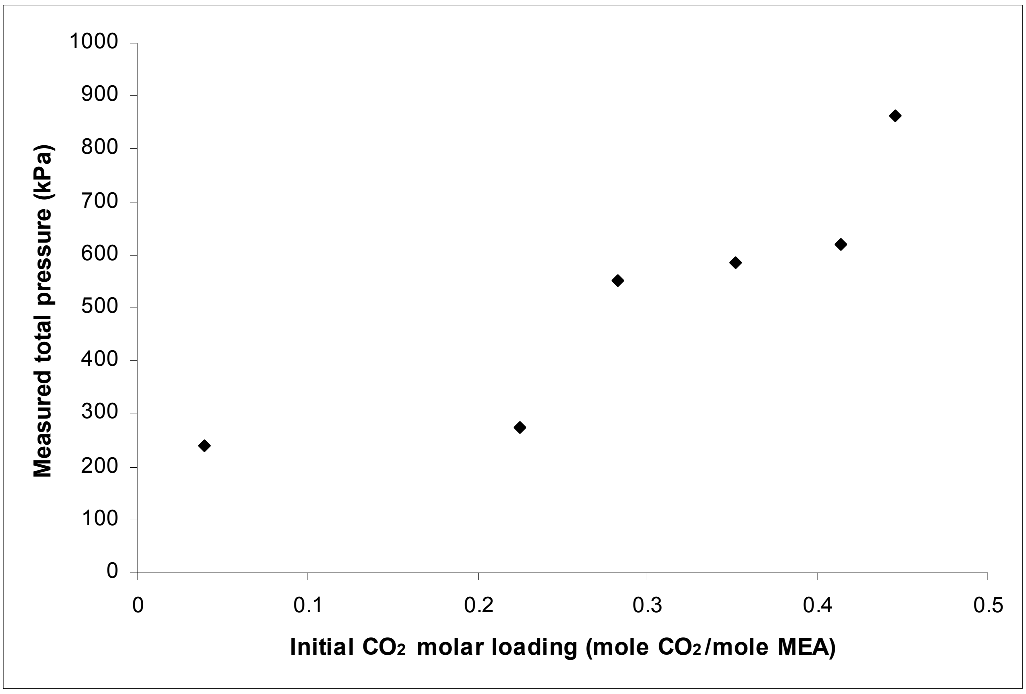


Figure 4.9 Measured total pressure versus initial CO_2 molar loading of the MEA.

Total pressure developed between 400 ml of 30 % w/v aqueous MEA solution and the CO_2 released on the headspace of the pressure vessel during CO_2 solubility experiments at 100 °C.

From this measured total pressure the CO_2 partial pressure can be calculated using the method followed by Jou et al. (1995). Based on information found in the literature from Daubert et al (1987), the vapour pressure of the pure MEA at 104.44 °C is P^o_{MEA}= 8.010 kPa. Moreover, from the steam tables, the pressure of water at 100 °C is P^o_{H2O} = 101.35 kPa. In 400 ml of 30 % w/v aqueous MEA solution there are 1.964 moles of MEA and 15.62 moles of water. There were 0.008 moles of air in the 200 ml headspace at the beginning of the experiment, thus P^o_{AIR} = 373*101.35/298= 126.86 kPa. The CO_2 partial pressure was calculated by subtracting the water, MEA and the air partial pressures from the total measured pressure. The partial pressures are calculated by Raoult's law. So the formula used to calculate the CO_2 partial pressure is:

$$P_{total} = P_{H2O} + P_{MEA} + P_{CO2} + P_{AIR} \qquad \text{Equation 4.1}$$

Where, P_{total} is the measured pressure during the experiment,

$$P_{H2O} = X_{H2O} * P^o_{H2O} \qquad \text{Equation 4.2}$$

$$P_{MEA} = X_{MEA} * P^o_{MEA} \qquad \text{Equation 4.3}$$

where, X_{H2O} and X_{MEA} the mole fractions of water and MEA, respectively, in the initial solution. The calculated mole fractions and partial pressures for MEA and H_2O are presented in Table 4.6 and Table 4.7 (see *Appendix 2.4: Raw Data CO_2 Solubility Experiment*).

Table 4.6 Calculated mole fractions for MEA and H_2O for each sample of the CO_2 loaded solutions

Initial Loading (molesCO$_2$/mole MEA)	X_{MEA}	X_{H2O}
0.039	0.111	0.884
0.225	0.109	0.866
0.283	0.108	0.861
0.352	0.107	0.855
0.414	0.107	0.849
0.446	0.106	0.846

Table 4.7 Calculated partial pressures for MEA and H_2O for each sample of the CO_2 loaded solutions

Initial Loading (molesCO$_2$/mole MEA)	P_{MEA} (kPa)	P_{H2O} (kPa)
0.039	0.000891	89.636
0.225	0.000873	87.806
0.283	0.000867	87.257
0.352	0.000861	86.604
0.414	0.000855	86.029
0.446	0.000852	85.731

In Table 4.8 the calculated CO_2 partial pressures are shown. From the calculated CO_2 partial pressures, the number of moles of CO_2 that were released by the MEA at this temperature and moved to the headspace can be determined and as a result the CO_2 loading when the system was in equilibrium can be calculated using the ideal gas law as a tool to have an approximate value (as CO_2 is not behaving as an ideal gas therefore for more accurate results a correction factor would need to be used). In Table 4.8 the loadings during equilibrium are presented.

Table 4.8 **Calculated CO_2 partial pressures for MEA solutions with various CO_2 loadings at 100 °C**

Initial Loading (molesCO$_2$/mole MEA)	Total Pressure (kPa)	CO$_2$ Partial Pressure headspace (kPa)	CO$_2$ in the headspace (moles*10^{-3})	Loading during equilibrium (moles CO$_2$/mole MEA)
0.039	240.7	60.064	3.874	0.037
0.225	275.08	96.274	6.209	0.222
0.283	550.16	371.903	23.984	0.270
0.352	584.54	406.937	26.243	0.338
0.414	618.93	441.902	28.498	0.399
0.446	861.85	685.119	44.183	0.423

400 ml of 30% w/v aqueous MEA solution, 200 ml available headspace, temperature 100 °C

In Figure 4.10 the graphical representation of the CO_2 partial pressure versus the CO_2 molar loading resulting from the experimental data is shown.

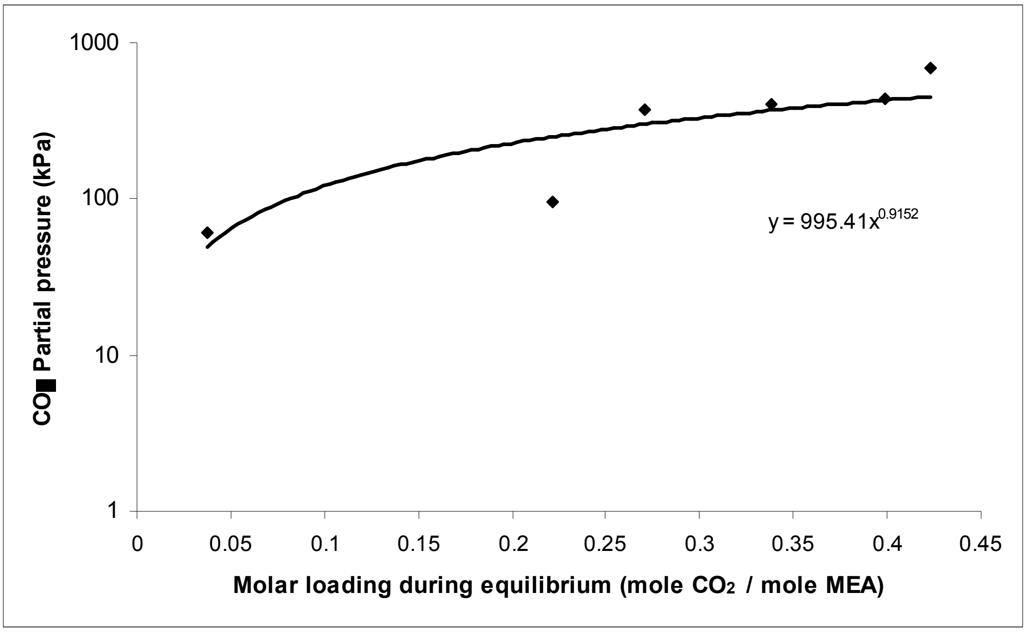


Figure 4.10 **CO_2 partial pressure versus CO_2 loading for 30 % w/v aqueous MEA solution at 100 °C**

An example of calculations of the CO_2 compressibility factor (Z_{CO2}), for the sample with the highest measured total pressure (see Table 4.8 last line), is presented. This was done in order to have an idea of how the CO_2 molar loading during equilibrium would change if the compressibility factor was taken into account. According to Çengel Y. A. and M. A. Boles (2007) in order to calculate the compressibility factors for a mixture of non-ideal gases, the reduced pressure and temperature for CO_2 need to be calculated. The reduced pressure was calculated to be 0.117 by dividing the total measured pressure (P_m = 861.85 kPa) with the critical pressure of CO_2 (P_{cr} = 7390 kPa). Similarly, the reduced temperature was calculated to be 1.23 by dividing the temperature, 373 K, with the critical temperature of CO_2, T_{cr} = 304.2 K. The compressibility factor was then determined using the Nelson-Obert generalised compressibility chart and it was found to be approximately 0.52. Then, the number of moles of CO_2 in the vessel's headspace was recalculated to be 0.10 by dividing the calculated number of moles, as presented in Table 4.8, with the compressibility factor (Z_{CO2}), thus, 0.044/0.52. Finally, the loading was calculated again to be 0.392 instead of 0.423 that was calculated without taking into account the compressibility factor. Therefore, it can be concluded that a smaller number of moles of CO_2 is needed, under those experimental conditions, to cause the same pressure if a corrections factor is not used.

Table 4.9 shows a comparison between the experimental data generated in this work and experimental data found in the literature under the same conditions (30% w/v aqueous MEA solutions at 100 °C).

Table 4.9 Comparison of the CO_2 solubility data at 100°C between the literature values and the experimental data from the present study

Present Study		Shen & Li (1992)		Jou et al (1995)		Ma'mum et al (2005)	
Molar Loading	CO_2 Partial Pressure (kPa)	Molar Loading	CO_2 Partial Pressure (kPa)	Molar Loading	CO_2 Partial Pressure (kPa)	Molar Loading	CO_2 Partial Pressure (kPa)
0.039	60.064	0.227	2.8	0.0117	0.00724	0.155	7.354
0.225	96.274	0.279	8.5	0.0566	0.136	0.2326	19.62
0.283	371.903	0.305	19.9	0.188	1.43	0.2901	39.18
0.352	406.937	0.348	99.9	0.381	19	0.3594	92.79
0.414	441.902	0.427	379	0.422	39	0.38882	137.9
0.446	685.119	0.457	772	0.477	69	0.4182	191.9

30% w/v aqueous MEA solutions, temperatures 100 °C

From the results of the present experiment (Figure 4.10 and Table 4.8), if compared with the data shown in the literature review (see Table 4.9) it can be concluded that the solubility data seem to differ when different rigs are used to obtain them. In general the data produced by this set of experiments show higher

CO_2 partial pressures. The values obtained by the study performed by Shen and Li (1992) seem to come to close agreement with the data from the present work at high CO_2 loadings. In all the literature studies presented the aqueous MEA solution volume was smaller than in this study as well as the total system volumes (description of the rigs and conditions used in these studies is presented in Section 2.4.2 of the literature review entitled Solubility of CO_2 in MEA). Last but not least, it is possible that the pressure measurements – especially at the lower values – were not very accurate as they were estimated by eye. The needle pressure gauge used was numbered every 10 psi and it is noted that 1 psi = 6.895 kPa. Therefore, a second digital pressure gauge was purchased at a later stage of this project for more accuracy (see Section 3.5.2).

After comparing the CO_2 solubility data produced for 100^oC with the values found in the literature and after recalculate the loading taking into account the compressibility factor, it was concluded that it was safe to place the high pressure vessels in the oven at 160^oC for up to 8 weeks. The calculated pressures were within the operating limits of the pressure vessels purchased and at the higher end of the pressures reported in the literature at similar CO_2 solubility experiments.

4.6 THERMAL DEGRADATION EXPERIMENT - LEAN INITIAL MOLAR LOADING

The purpose of this experiment was to expose the CO_2-loaded MEA sample to conditions to accelerate its thermal degradation in the presence of CO_2. Then, the effect of thermal degradation on the solvent CO_2 uptake capacity as well as the build up of thermal degradation products was assessed. A detailed description of the entire procedure followed in this section is presented in Section 3.10. It needs to be noted here that the temperature was chosen to be 160 °C (higher than in an actual stripper) to accelerate the production of degraded samples. Polderman et al. (1955) suggests one mechanism of MEA thermal degradation in the presence of CO_2 below 200 °C, which is called carbamate polymerisation. Moreover, according to Davis & Rochelle (2008) and Lepaumier et al. (2009 & 2010) the MEA degradation products are the same at 100, 120, 135, 140 and 150°C; it is the rate of their production that increases with the temperature.

4.6.1 Pressure changes – Thermal degradation rig

For the degradation experiment, three 400 ml samples of 30 % w/v aqueous MEA solutions were loaded into the absorption/stripping rig (Figure 3.5) with initial molar loading of 0.19 (moles of CO_2/mole of MEA) as determined by an inorganic carbon content measurement. The samples were sealed in the high pressure vessels (Figure 3.9) and placed in the oven at 160 °C. The pressure change inside one of the vessels was continuously monitored with an analogue pressure gauge with range 0-2000 psi (0 – 14 MPa) (see Section 3.5.3) for safety reasons; it was assumed – as the experimental conditions were the same – that the pressure changes were the same in all the three vessels. The vessel equipped with the pressure gauge came last out of the oven. The samples were left in the oven at 160 °C for 2, 3 and 8 weeks to thermally degrade. Each one of the samples was taken out of the oven and remained sealed at room temperature until the beginning of the absorption/stripping experiment.

The total pressure change versus time during the 8 weeks of the thermal degradation experiment can be seen in Figure 4.11 and the raw data in *Appendix 2.5: Pressure Changes During Thermal Degradation – Lean Samples*. As it can be seen, the system reaches its highest pressure (3034 kPa) after 24 hours. The pressure then starts dropping at a fast rate initially and then slower until it stabilises at 965 kPa after 480 hours (20 days).

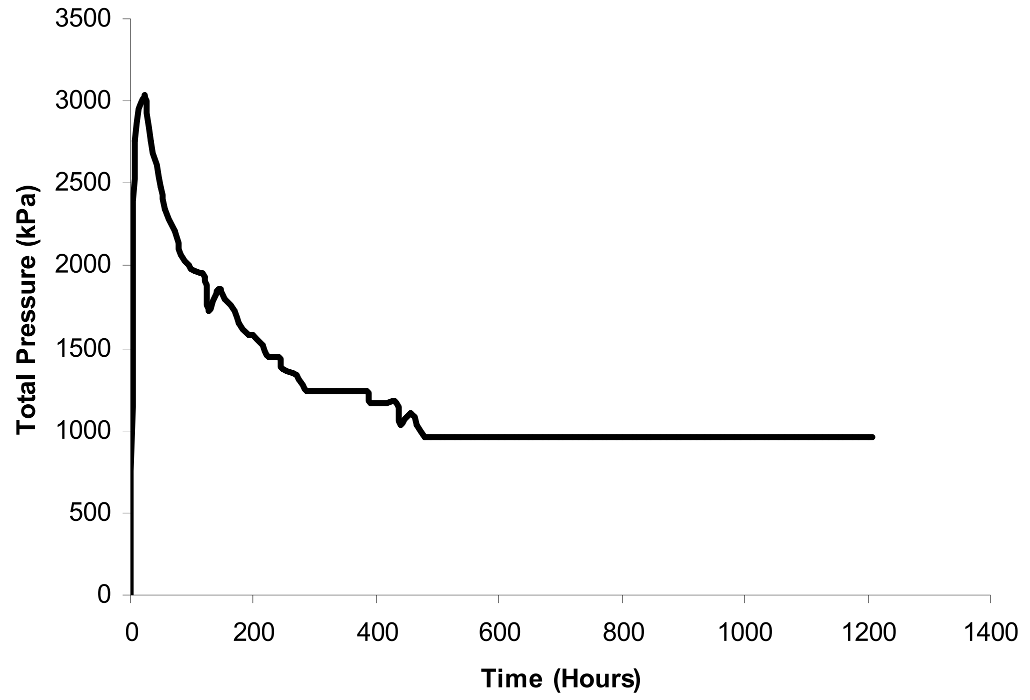


Figure 4.11 Total pressure change versus time during the thermal degradation experiment at 160 °C

400 ml of 30 % w/v aqueous MEA solution

The system's behaviour – in terms of pressure – was not as originally predicted from vapour pressure calculations. It was believed that as the MEA degrades the CO_2 initially captured would have been released to the vessel's headspace. In practice, after the initial expected rapid increase, the pressure started dropping almost immediately and it kept dropping for 420 hours. Of course quite a considerable amount of it would have been absorbed by the water at these temperatures and pressures but this can not explain the constant pressure drop for 20 days.

The first thing that was checked to ensure that the pressure change was not affected by any external influence was the oven temperature. For this reason a mercury thermometer was used to verify that the oven temperature was actually at 160 ^{o}C and that the temperature was stable. Another reason which could have caused the pressure drop would have been if there was a leak from the vessels. For that reason the first action taken after the samples were taken out of the oven - and before they were tested in the absorption-stripping rig – was to measure the sample volumes at room temperature using the same volumetric tube used to measure the initial sample volumes (400 ml). The measured volumes can be seen on Table 4.10.

Table 4.10 Volumes of the MEA samples before and after thermal degradation at 160 °C

Sample	Initial Volume (ml)	Final Volume (ml)
Week 2	400	396
Week 3	400	398
Week 8	400	397

30 % w/v aqueous MEA solution

The volume changes are very small, and whilst not being conclusive proof that no leak has occurred, they do at least support the hypothesis that the pressure changes might be attributable to other effects as well. It is interesting to note that when one of the vessels was known to have leaked in another test a considerable volume of liquid escaped with the exhaust gases. It has also been verified that the vessels can indeed sustain the high pressures experienced in these tests and that the pressure gauge is working correctly. 400 ml of DI water were placed in the vessels and heated at 160°C; the pressure reading was the as expected from the steam tables and remained stable for approximately 8 hours.

Clearly, if it is considered that the system was not leaking, the considerable change in the vessel's total pressure was caused by the change in CO_2 partial pressure as the partial pressures of air and water remain the same (if the conditions are considered stable throughout the experiment) and the MEA partial pressure change was too small to have caused such a change in the total pressure. Therefore, another reason of this pressure change could also be explained by the fact that MEA uses CO_2 in order to degrade which can be seen in the schematic representation of the thermal degradation products proposed by Davis (2009) (see Figure 2.8).

Of course further investigation would be needed in order to be able to draw firm conclusions on what is the actual cause of this pressure change and it could, in fact ,be a combination of all the aforementioned explanations that resulted in that pressure drop. Lepaumier et al. (2010 and 2009 (b)) mention that CO_2 needed to be added in their system throughout the 15 days of their experiment due to the fact that MEA was using the CO_2 to degrade but also due to leaks from their equipment.

In Section 4.6.2 a conceptual model that could explain how the MEA uses CO_2 in order to degrade is presented.

4.6.2 Thermal degradation of MEA using CO_2

At the beginning of the degradation experiment, the 400 ml sample of loaded MEA put in the reactor was comprised of MEA carbamate (MEA associated with CO_2), some molecules of “free” MEA and water. When the temperature reached 160^{o}C, the MEA carbamate was converted into MEA and CO_2 molecules (expected MEA behaviour during stripping) that accumulate in the vessel’s headspace and that could explain the initial pressure built up that was observed. The high pressure developed in the vessel probably caused a considerable amount of the CO_2 from the headspace to be dissolved MEA and in the water. Carroll et al. (1991) presents experimental data from three sources at 160 ^{o}C and at CO_2 partial pressure of about 1 MPa (smaller than the one experienced during the experiments of the present study) with a measured CO_2 solubility of about 0.07 mol % in water.

Later on, when the system in the vessel would have normally reached equilibrium, the MEA started degrading and in order to explain how degradation might affect the CO_2 partial pressure in the headspace, the development of a conceptual model has been attempted. For this initial attempt at elucidating the mechanisms at play, the model of MEA degradation proposed by Davis (2009) has been used. The suggested pathway agrees with the thermal degradation pathways presented by Lepaumier (2009 (a) and (b), 2010 and 2011). Davis (2009) schematic representation of the degradation is presented in Figure 4.12.

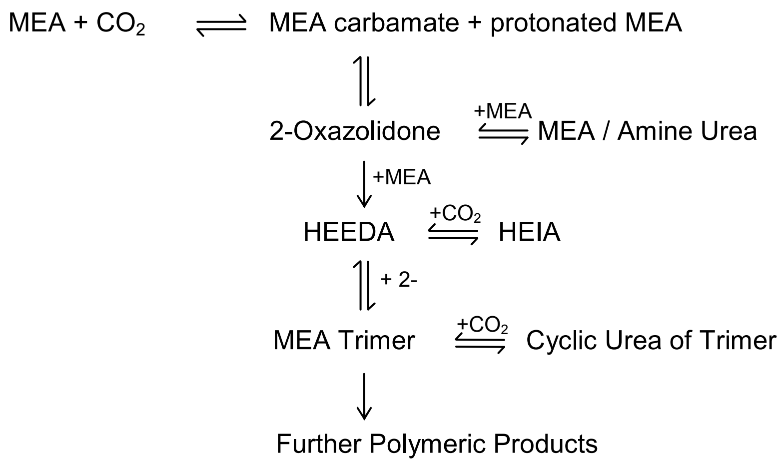


Figure 4.12 Schematic of the pathway of formation of MEA carbamate polymerization degradation (Davis, 2009)

According to this model the first step for the MEA degradation (at those conditions) is when the MEA carbamate reacts to form 2-Oxazolidone reversibly. The formation of 2-Oxazolidone causes the equilibrium of the MEA carbamate production to be displaced. This means that more MEA will react with CO_2 to form MEA carbamate in order to balance the equilibrium, for that reason molecules of CO_2 from the headspace will be used and this will cause its partial pressure to drop.

Consequently the 2-Oxazolidone produced is “used” to produce other degradation products, which cause the equilibrium of the carbamate formation to be shifted again. Therefore the available MEA reacts with more available molecules of CO_2 and the CO_2 partial pressure drops more. Other degradation products formed such as HEEDA and MEA Trimer also react with the available CO_2 and cause the pressure to drop more. At the beginning of the experiment the amounts of CO_2 and MEA available are higher so the reactions move faster. As a result the pressure drop in the beginning of the experiment is more dramatic.

As time passes the rate of 2-oxazolidone production (first step of MEA degradation) slows down as there is not that much available CO_2 and MEA. Davis (2009) also reports that “once the solution becomes more highly degraded, a compound effect of MEA loss starts to become important” which slows the overall MEA loss. If the MEA loss slows it probably means that not much CO_2 is used irreversibly anymore for MEA degradation. This is consistent with the fact that the rate of pressure drop (after 300 hours) slowed until it stabilised or could not be measured with the available pressure gauge. A similar conclusion is drawn by Lepaumier et al. (2011) that states that "At 135 °C in the presence of CO_2, MEA degraded 57.6 % after 5 weeks; the slope of the degradation rate was quite linear during the first four weeks, and then started to slow down".

It is believed that, some of the pressure drop during the course of the 8 weeks experiment could be attributed to the mechanism described above. If no CO_2 gas was used by the MEA then the MEA would not have degraded. Moreover, after the samples were taken out of the oven they were put in the absorption/stripping rig (Figure 3.5) to release any CO_2 left and all the three contained CO_2 (see Section 4.6.3.1). That means that even if there was a leak from the vessels, there was still CO_2 available in the sample for the MEA to degrade.

4.6.3 Effect of degradation on MEA CO_2 uptake capacity

All the three samples after having thermally degraded for 2, 3 and 8 weeks at 160°C were tested in the absorption-stripping rig (Figure 3.5) to assess the effect of degradation on the solvent's CO_2 uptake capacity when compared with a pure fresh MEA solution of the same concentration (for description of the experimental procedure see Section 3.10).

4.6.3.1 1st stripping

After the vessels were opened and the sample volume was measured, the next step was to release all the CO_2 that was still in the solution. For that reason each sample was placed in the absorption/stripping rig and after 20 minutes, when the temperature in the oil bath reached 120°C, the stripping gas feed valve was opened and N_2 (200 ml/min) was fed to the reactor for good agitation. The exit flow and the outlet gas composition were measured every 20 minutes with the microGC. The volume of CO_2 was then calculated by multiplying the CO_2 percentage with the exit flow rate and the time (20 minutes). A flow correction was needed as during the stripping the exit flow meter is calibrated for nitrogen when a mixture of CO_2 and N_2 is coming out of the system as a result of displacement of the initial contents of the vessels and connecting lines (see Section 3.6).

In Figure 4.13 the cumulative CO_2 volume released by the degraded samples at 160 °C can be seen (see raw data and calculations in *Appendix 2.6: MicroGC Raw Data – 1st Stripping Lean Samples*).

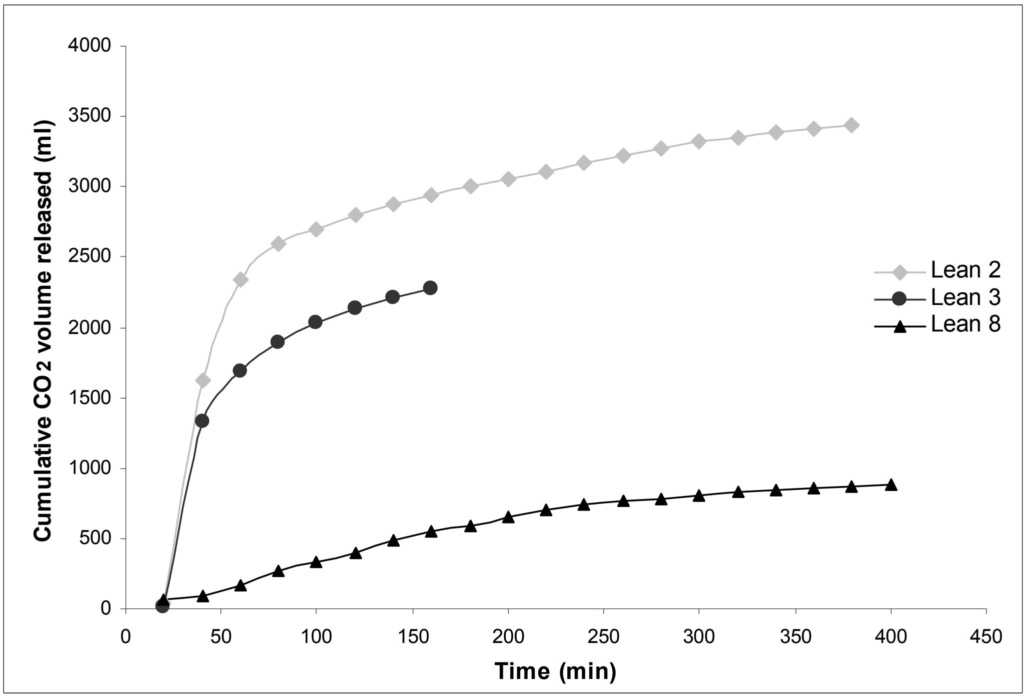


Figure 4.13 Cumulative CO_2 volume released during the 1st stripping – "lean" samples

Initial concentration 30% w/v aqueous MEA solution, 0.19 initial molar loading, degradation temperature 160 °C

As shown in Figure 4.13, the longer the sample degraded the more CO_2 disappeared from the solution. This is consistent with the expectation that the formation of degradation products requires CO_2 (see Section 4.6.2) and even if a leak occurred during the experiment there was still CO_2 available for the MEA to degrade. Table 4.11 shows the volumes of CO_2 released by all the three degraded samples with initial concentration of 30% w/v aqueous MEA and initial molar loading of 0.19 after being kept at 160°C for the allocated times of 2, 3 and 8 weeks.

Table 4.11 Volume of CO_2 released during 1st stripping following degradation

Sample	CO_2 volume released (L)	Experimental Time (min)
Lean 2	3.4	380
Lean 3	2.3	180
Lean 8	0.9	400

Initial concentration 30% w/v aqueous MEA solution, 0.19 initial molar loading, degradation temperature 160 °C

It should be noted here that the samples were initially loaded with 8.3 L of CO_2 and that CO_2 evolution was still happening when stripping was stopped for the 2 week and 3 week samples. What is clear is that the sample held in the oven for 8 weeks has "lost" 7.4 litres of CO_2.

4.6.3.2 Absorption - microGC

After the first stripping the samples were loaded with CO_2 in the absorption-stripping rig (Figure 3.5). For the absorption the temperature in the oil bath is raised to 50 °C and it takes up to 10 minutes for this temperature to be reached. At that point the inlet gas feed valve is opened and pure CO_2 is bubbled inside the reactor at a flow rate of 100 ml/min. The outlet gas composition and the exit flow rate were again measured every 20 minutes. The volume of CO_2 absorbed was calculated by subtracting the amount of CO_2 at the system's outlet from the amount of CO_2 put in the system. The flows needed again to be corrected as a pure CO_2 flow meter is used at the system's outlet when a mixture of air and CO_2 are coming out of the system.

In Figure 4.14 the graphical representation of the volume of CO_2 absorbed by the system versus time can be seen (raw data presented in *Appendix 2.7*). The degraded samples are compared with a pure fresh MEA sample of the same initial concentration (30%wt). The first observation that can be made is that the pure MEA continues to absorb consistently throughout the period whilst the sample held at 160°C for 8 weeks showed a distinct drop in performance at 300 minutes. The data are not quite as conclusive for the 2 and 3 week samples but it can be observed that the more degraded the samples are the less CO_2 they can absorb. Careful examination of the volumes of CO_2 calculated by this method shows a considerable overestimate and loss of gas before entry to the absorber is suspected. This was investigated in the next phase of experimentation.

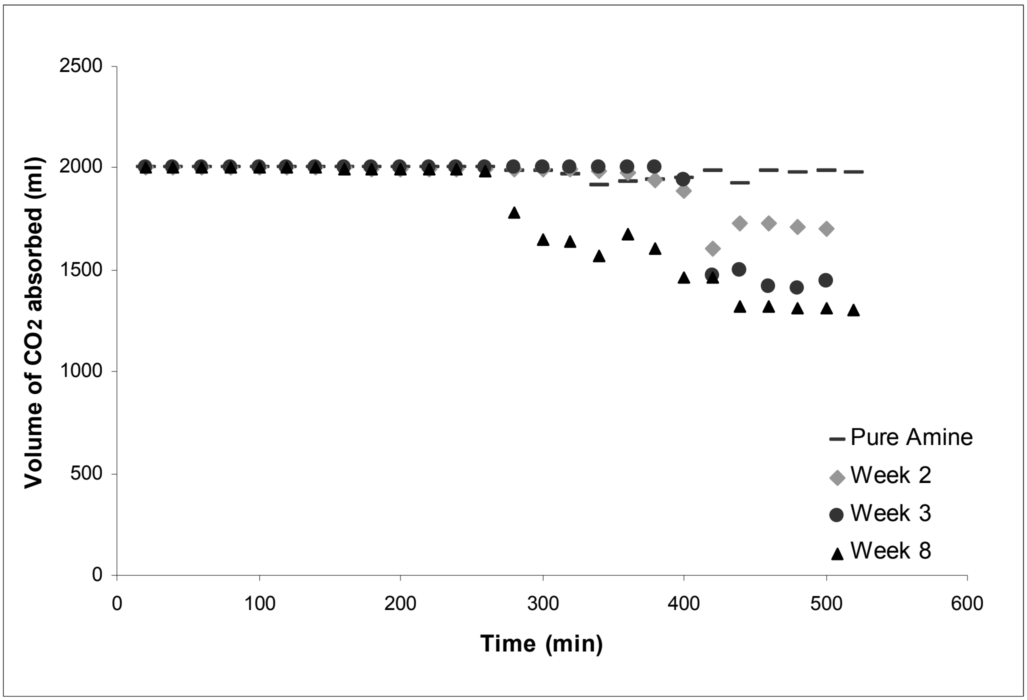


Figure 4.14 Volume of CO_2 absorbed by the degraded samples compared with a pure fresh MEA sample of the same concentration

400 ml 30% w/v aqueous MEA solution, initial molar loading 0.19, degradation temperature 160°C

After the absorption was finished the samples were measured in the TOC apparatus to determine the inorganic carbon content of the samples and calculate how much CO_2 was absorbed. The results can be seen in Table 4.12.

Table 4.12 CO_2 concentration, as measured by inorganic carbon content measurement, after absorption for the degraded and the pure MEA samples

Sample	Volume of CO_2 in solution (L)
Pure MEA	9.3
Lean 2	2.9
Lean 3	2.8
Lean 8	1.9

400 ml 30% w/v aqueous MEA solution, initial molar loading 0.19, degradation temperature 160°C

The results from Table 4.12 support the conclusion that was drawn from the measurements performed with the microGC during absorption in the absorption-stripping rig, that the more degradation the sample undergoes, the less CO_2 it can absorb. A loss of MEA of the order of 80% after 8 weeks is suggested by these data.

After performing those experiments it was realised it was not possible to perform a mass balance in the absorption/stripping rig during absorption. Further investigation was needed, therefore, it was deemed necessary to perform an experiment to assess the situation and investigate the possibility of a leak in the system.

For that purpose 400 ml of acidified DI water (pH= 5 approximately) were put in the absorption/stripping rig and an absorption cycle, as described in Section 3.4.2, was performed. The microGC was used to measure the CO_2 percentage at the rig's outlet (raw data shown in *Appendix 2.8*). It was noted that approximately 170 minutes passed before a volume of CO_2 exited from the rig and even at that point and until after 330 minutes the outlet volume was not equal with the inlet CO_2 volume. The next step was to investigate from which part of the system the CO_2 gas losses occurred. Therefore, while the rig was operating, as described above, the joints were sprayed with water and soap solution and it was observed whether bubbles were created. The activity started from the system's outlet and proceeded towards the inlet. During this test it was noted that there were leaks at the part in between the inlet (after the CO_2 flow meter) and the reactor. It was verified that the presence of the glass frit was causing a pressure built up which was resulting in gas escaping from the connections.

In the part of the system after the reactor and to the rig's outlet no leaks were observed that is why no problems were observed during the stripping. Thus, it was considered necessary to find a different way to assess the solvent behaviour during the absorption. The inorganic carbon measurement, using the TOC instrument, was determined to be the most appropriate to determine the CO_2 content in a CO_2 loaded amine solution. The procedure followed is as described in Section 3.7.

4.6.3.3 Absorption – Inorganic Carbon Measurement (TOC instrument)

The CO_2 was released by the degraded samples and the loading was repeated using the inorganic carbon measurement to assess the solvent's behaviour during absorption in the absorption/stripping rig. For the absorption the temperature in the oil bath is raised to 50 °C and it takes up to 10 minutes for this temperature to be reached. At that point the inlet gas feed valve was opened and pure CO_2 was bubbled into the reactor at a flow rate of 100 ml/min. The amount of CO_2 captured by the MEA was determined by measuring the inorganic carbon content of the solution using the TOC instrument as described in Section 3.7. Figure 4.15 shows the graphical representation of the volume of CO_2 captured by the degraded samples over time for all three samples, *Appendix 2.9* shows all of the data.

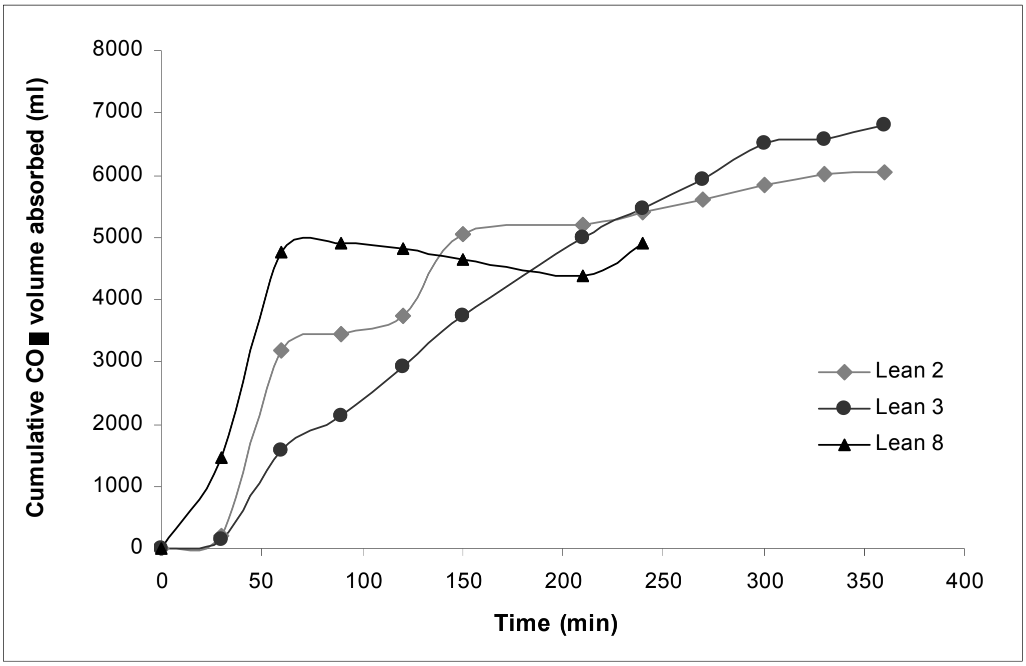


Figure 4.15 Cumulative volume of CO_2 absorbed – "lean" samples after thermal degradation

400 ml 30% w/v aqueous MEA solution, initial molar loading 0.19, degradation temperature 160°C

From Figure 4.15 it can be observed that the 8-week sample stops absorbing CO_2 after approximately 1 hour of bubbling and it absorbs about 4.9 L of CO_2. Moreover, it can be observed that the 8 weeks "lean" sample seems to have a faster CO_2 uptake than the other samples which could be explained if it is considered that some of the degradation products, possibly present in higher concentrations in the highly degraded samples, might have the capability to absorb CO_2. The samples after 2 and 3 weeks of thermal treatment seem to stop absorbing at almost the same time (after about 300 minutes). At this point it is important to consider the volumes of CO_2 that remained in the degraded samples after the first stripping. These were determined by TOC and were 2.7 L, 0.9 L and 0.9 L for the 2, 3 and 8 week degraded samples respectively

A pure MEA solution with 30% w/v initial concentration has the potential to absorb about 23 L of CO_2 and on this basis it is concluded that the "lean" solution after 8 weeks of thermal degradation has lost approximately 75% of its ability to absorb the gas i.e. 5.8 L of gas absorbed compared to a theoretical capacity of 23 L. According to Davis (2009) a 7 molal (30% w/v) aqueous MEA solution with initial molar loading of 0.25 after degrading for 8 weeks at 135 ^{o}C has an approximately 29% MEA loss. The MEA loss determined by the present study is much higher possibly due to the much higher temperature used.

4.6.3.4 Stripping

After the end of the absorption, stripping was performed in the normal manner (see Section 4.6.3.1). In Figure 4.16 the cumulative CO_2 released from the three degraded samples is shown (see *Appendix 2.10* for raw data and calculations). The resulting curves are compared with the one produced for a 400 ml pure fresh 30% w/v aqueous MEA sample. The degraded samples release less CO_2 than the pure sample and this is especially shown for the sample that was degrading for 8 weeks. It can also be seen that the degraded samples are releasing the CO_2 at a faster rate than the pure MEA sample. The precise reason for the increase in stripping rate exhibited by the degraded samples needs to be further assessed.

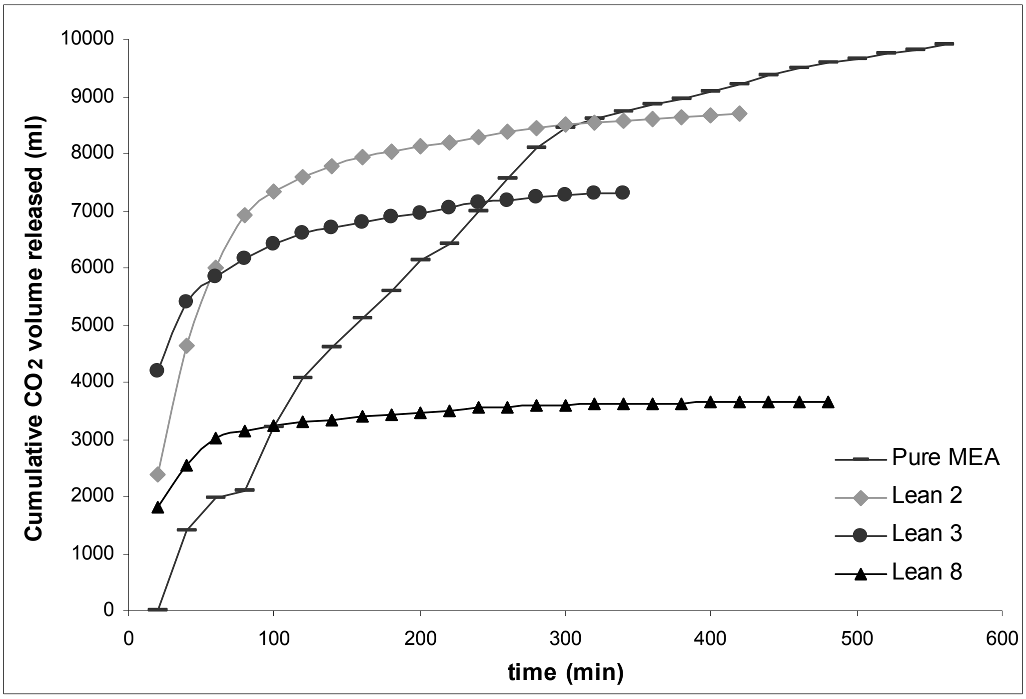


Figure 4.16 Cumulative CO_2 volume released - "lean" samples test compared with a pure fresh MEA sample

400 ml 30% w/v aqueous MEA solution, initial molar loading 0.19, degradation temperature 160^oC

4.6.3.5 Summary solvent's CO_2 uptake capacity - Lean loading

Table 4.13 summarises the absorption and stripping results for the samples with "lean" loading after being subjected to the thermal degradation process.

Table 4.13 Absorption/Stripping behaviour of thermally degraded, "lean" samples after removal of residual CO_2

Sample and degradation time (weeks)	Volume of CO_2 absorbed in 400 min (L)	Volume of CO_2 stripped in 400 min (L)
Pure MEA (no thermal treatment)	9.9*	9.9
Lean 2	8.8	8.7
Lean 3	7.8	7.3
Lean 8	5.8	3.7

400 ml 30% w/v aqueous MEA solution, initial molar loading 0.19, degradation temperature 160^oC
** Inferred – not measured*

In Table 4.13 it can be observed that there is a tendency for the CO_2 to be retained in solution during the stripping stage and that this trend is more prominent for the

8 week sample. However it is recalled that the absorption data were obtained by TOC instrument measurement and the stripping by microGC, hence further cycles of absorption and stripping would be necessary to explore this phenomenon in more detail.

4.6.4 Corrosion

After the end of the degradation experiment and when the pressure vessels were opened, it was noted that quite considerable amount of solids were present in all the 3 degraded samples. At that point after an inspection of the pressure vessels, corrosion was suspected. For that reason after the absorption-stripping experiment, all the three samples were filtered in order to be analysed for metals in the ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

As the amount of solids in solutions was not enough for the ICP-OES analysis (at least 0.10 gr of dried solids needed), only the solids from the sample of 8 weeks degradation was analysed, as well as liquid samples (not filtered) from the degraded samples of 2, 3 and 8 weeks. The entire volume of the 8 weeks sample was filtered passing it through as funnel with filter Whatman, 90 mm dia (product number 1440090), the filter was then dried in the oven at 100 ^oC for 2 days. 0.101 gr of dried solids were recovered from the sample and were then analysed with the ICP-OES. The results can be seen in
Table 4.14 for the solid sample and Table 4.15 for the liquid samples.

Table 4.14 Analysis of metal content of the solids in the sample that degraded for 8 weeks

Sample name	Cr (g/Kg)	Fe (g/Kg)	Mn (g/Kg)	Mo (g/Kg)	Ni (g/Kg)
Lean 8	112.5	722	0.5	4.3	2.4

Sample of 0.101 g of dried solids filtered from the 400 ml of 30% w/v aqueous MEA solution with initial CO_2 molar loading of 0.19 after degrading for 8 weeks at 160 ^oC in the pressure vessels.

Table 4.15 Analysis of metal content of the degraded samples compared with a sample of fresh MEA.

Sample name	Cr (mg/L)	Fe (mg/L)	Mn (mg/L)	Mo (mg/L)	Ni (mg/L)
Fresh MEA	0	0	0	0.1	0
Lean 2	16.6	19.7	0	20.0	149.3
Lean 3	16.5	27.3	0	24.3	224.7
Lean 8	20.4	366.2	0.4	67.6	929.2

400 ml 30% w/v aqueous MEA solutions with initial CO_2 molar loading of 0.19 degraded for 2, 3 and 8 weeks at 160 ^oC compared with a 30% w/v aqueous fresh MEA, volume of the analysed sample 2 ml.

From the data shown in Table 4.14 and Table 4.15 , it can be concluded that the samples of loaded MEA are causing the stainless steel vessels to corrode. For the solid sample found in the 8 weeks degraded sample - as shown in Table 4.14 – quite high concentrations of metals were measured. From the data shown in Table 4.15, it can be seen that the more the sample stays in the vessels, at these temperatures and pressures, the higher the amount of metals found in the analysed liquid samples.

The metal losses per unit area and per unit area over time of the degradation experiments, based on the liquid sample metal analysis shown in Table 4.15, were determined. These calculations were performed considering the vessel's surface area as 282.6 cm^2 and the time as the degradation experiment duration in days and are shown in Table 4.16.

Table 4.16 Corrosion rates of the high pressure vessels during the degradation experiments of MEA

	mg Cr/cm^2	mg Cr/cm^2/day
Lean 2	0.023	0.002
Lean 3	0.024	0.001
Lean 8	0.029	0.0005
	mg Fe/cm^2	mg Fe/cm^2/day
Lean 2	0.028	0.002
Lean 3	0.039	0.0018
Lean 8	0.518	0.0093
	mg Mo/cm^2	mg Mo/cm^2/day
Lean 2	0.028	0.002
Lean 3	0.034	0.0016
Lean 8	0.096	0.0017
	mg Ni/cm^2	mg Ni/cm^2/day
Lean 2	0.211	0.015
Lean 3	0.318	0.015
Lean 8	1.315	0.024

400 ml 30% w/v aqueous MEA solutions with initial CO_2 molar loading of 0.19 degraded for 2, 3 and 8 weeks at 160 °C

As it can be seen in Table 4.16 the metal loss per surface area increased as the time progressed. It can also be concluded that the rate of metal loss remained almost stable throughout the time of the thermal degradation experiment, as shown in the 3rd column of Table 4.16 except for Fe and Ni in the lean 8 sample.

In Table 4.17 the nominal chemical composition of the pressure vessel materials is shown as provided by the manufacturer (Parr Instrument Company).

Table 4.17 Percentage of major elements of the high pressure vessels

Material	Fe (%)	Ni (%)	Cr (%)	Mo (%)	Mn (%)
T316 Stainless Steel	65	12	17	2.5	2.0

In the 8 weeks lean sample (

Table 4.14) high amounts of Fe and Cr were measured in the solid sample and a small concentration of Ni, whereas Ni and then Fe were the highest concentrations detected in the liquid samples (Table 4.15). Noticing the major elements of the high pressure vessels provided by the manufacturer, see Table 4.17, the highest metal percentages are those of Fe, Ni and then Cr. Thus, it seems that the vessels do not corrode uniformly.

Kongstein and Schmid (2010) determined the corrosion rate and corrosion potential for bare 316 L Steel in 5 M MEA solution at 135 °C with 10 % CO_2. The corrosion rate started at 0.35 mm/y and droped to 0.15 after 50 hours of experiment. Based on metal content in solution determined in the 8-weeks liquid sample (see Table 4.16) it is calculated that the overall corrosion rate in the present work is 1.95 mm/y, a value somewhat higher than theirs. This could be in part due to the operating temperature and also to differences in the stainless steels used in the studies.

4.6.5 Thermal degradation products identification and quantification

After the end of the tests to assess how degradation affects the solvent's CO_2 uptake and stripping capacity, the degraded samples were analysed in the GC-MS to identify and quantify any thermal degradation products generated. In addition to this the concentration of the MEA left in solution was also determined. Figure 4.17, Figure 4.18 and Figure 4.19 show the peak responses produced by the GC-MS when the samples that degraded for 2, 3 and 8 weeks were analysed.

In Table 4.18 all of the compounds present in the 3 samples, as determined by the GC-MS analysis, have been listed. The ones in bold have been previously reported in the literature as MEA degradation products (Strazisar B. R. et al. 2002, Strazisar B. R. et al. 2003, Supap T. et al. 2006, Davis PhD thesis 2009, Lawal O. et al. 2005, Bello A. et al. 2005).

Table 4.18 Degradation products found in the lean samples

Degradation Product	Lean 2	Lean 3	Lean 8
HEEDA	+	+	+
HEIA	+	+	+
2-oxazolidone	+	+	
1,2-ethanodiol	+		+
1-amino-2-propanol			+
piperazine	+	+	+
1-(2-aminoethyl)imidazole			+
2-methylpiperazine			+
2,5-dimethylpiperazine			+
2-methyl-3-oxazolidine		+	+
4-methylmorpholine			+
4-morpholineethanol	+	+	
diisopropanolamine	+		+
2-imidazolidinone	+		+
3-methyl-oxazolidone	+	+	
Tris(2-aminoethyl)amine			+
1-piperazineethanol			+
1,3-propanediame			+
1,4-bis(2-hydroxyethyl)piperazine	+	+	+
N,N'-bis(2-aminoethyl)-1,2-ethanediamine	+	+	+
1-(2-(2-hydroxyethoxy)ethyl)piperazine	+	+	+
3-(2-hydroxyethyl)-2-oxazolidinone	+	+	+

Initial concentration 30% w/v aqueous MEA solution, initial molar loading of 0.19, degradation temperature 160^oC

It is interesting to note that the present study has identified piperazine and other related compounds in all three of the degraded samples. Full quantification was not possible during the project but a preliminary determination of piperazine alone gave a concentration lower that 0.2% w/v.

The calibration curves and partition coefficients detailed in Section 3.9.3 were used to quantify MEA, HEIA, HEEDA and 2-oxazolidone.

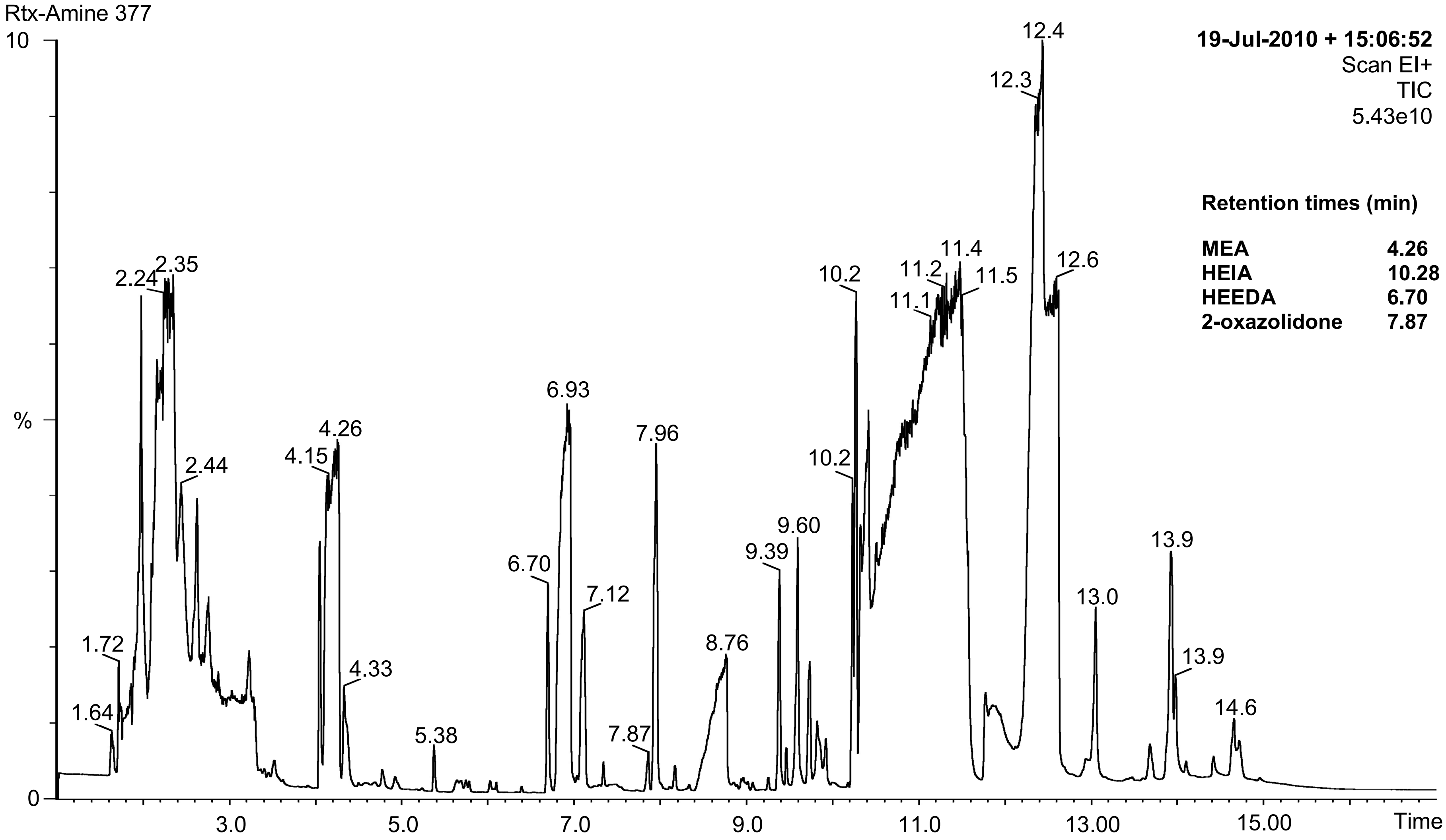


Figure 4.17 GC-MS response for the 2 weeks degraded sample – “lean” loading test

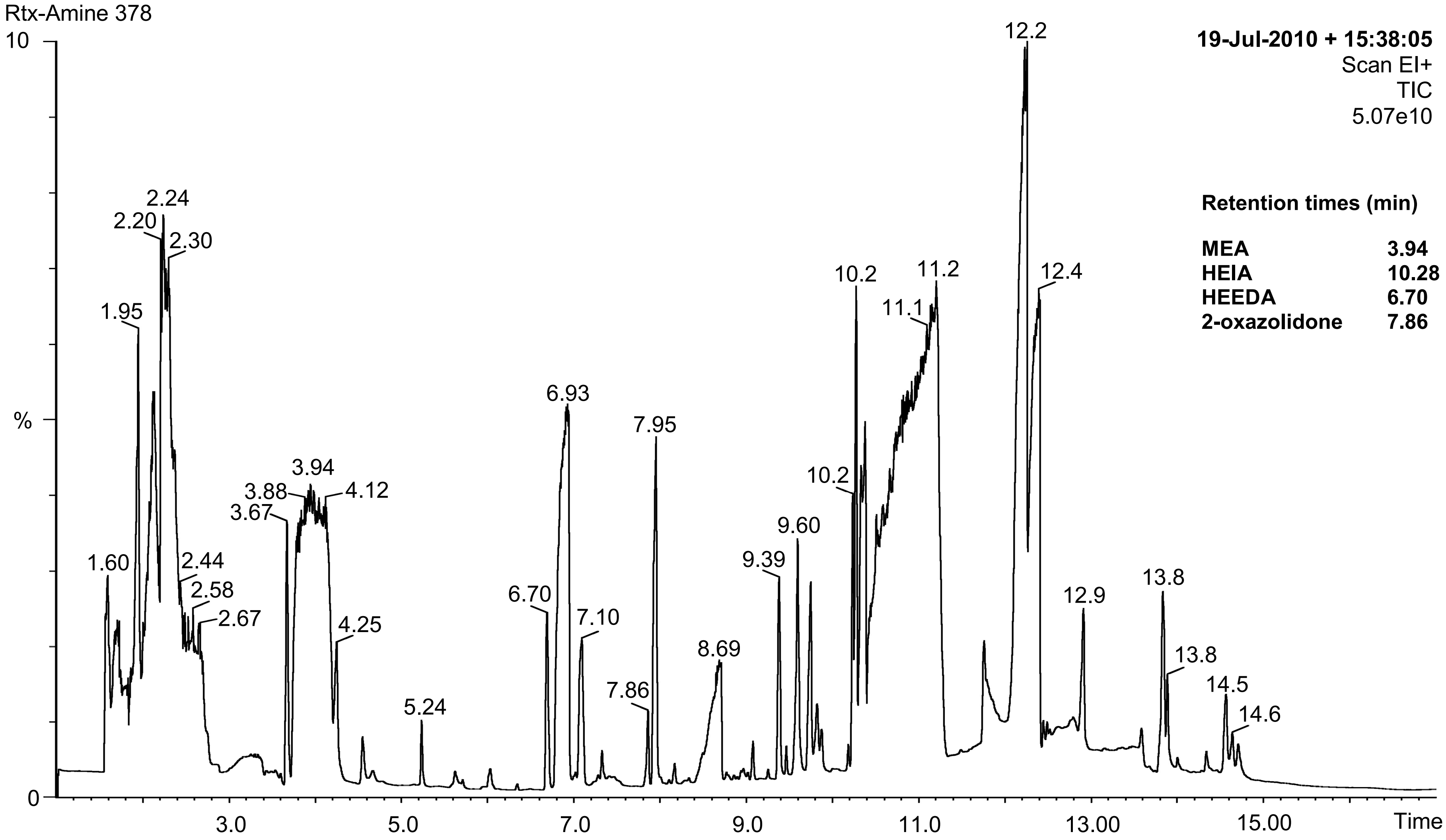


Figure 4.18 GC-MS response for the 3 weeks degraded sample – "lean" loading test

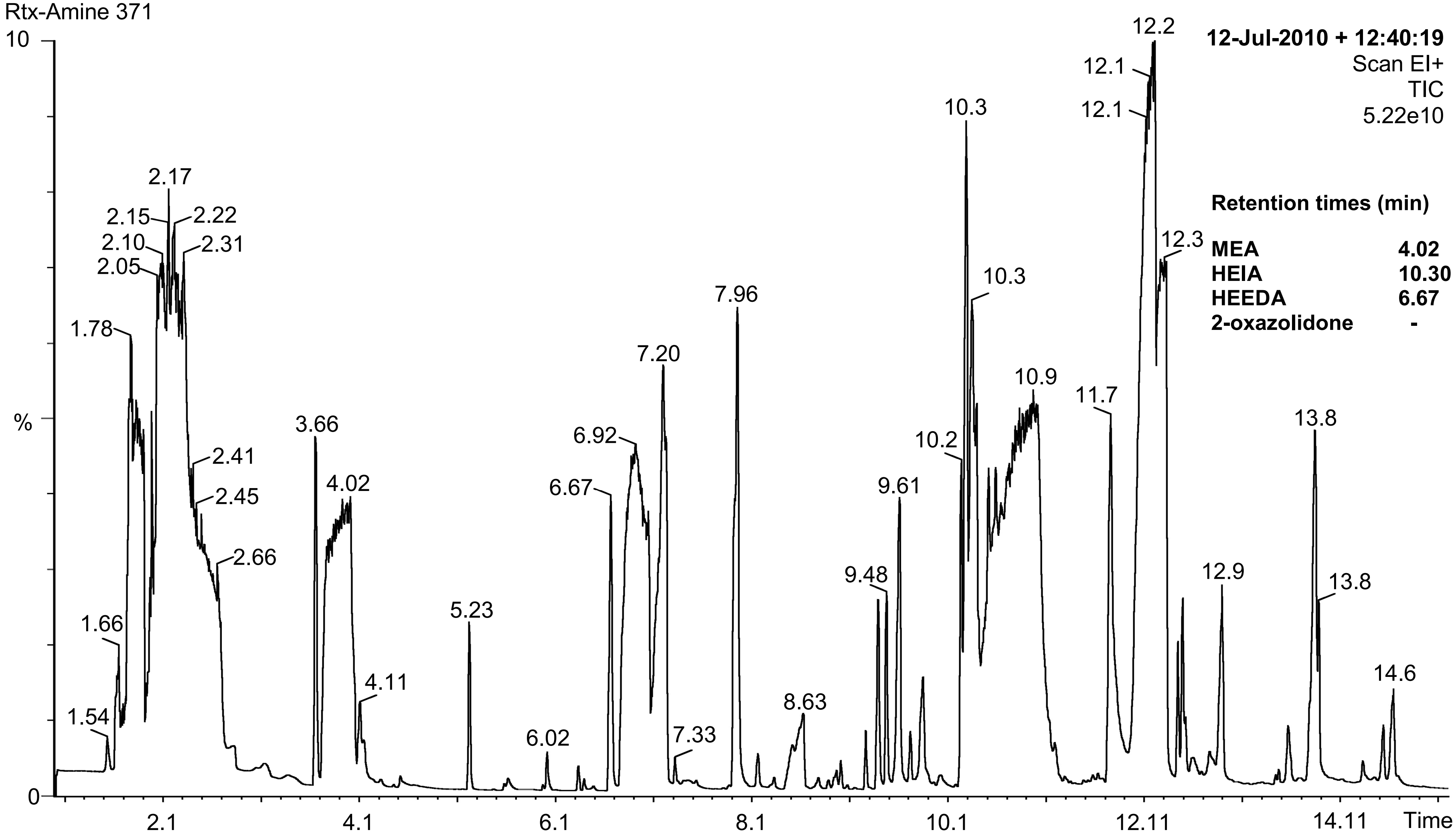


Figure 4.19 GC-MS response for the 8 weeks degraded sample – "lean" loading test

Table 4.19 shows the concentrations of MEA, HEIA, 2-oxazolidone and HEEDA in the three degraded samples with the "lean" initial loading (0.19 moles of CO_2 / mole of MEA).

Table 4.19 MEA and its major thermal degradation products concentrations– "lean" samples

Compound	Sample		
	Lean 2 (% v/v)	Lean 3 (% v/v)	Lean 8 (% v/v)
MEA	14.8	12.7	5.2
HEIA	0.3	3.2	11.9
HEEDA	0.3	0.3	0.9
2-Oxazolidone*	1.6	0.9	-

Initial concentration 30% w/v (or 29.6 % v/v) aqueous MEA solution, 0.19 initial molar loading, degradation temperature 160^{o}C
**The 2-oxazolidone concentrations are in % w/v*

These data show that as the degradation experiment progresses, the MEA concentration decreases steadily from 29.6 % v/v to about 5% v/v. The 2-oxazolidone appears during the first two weeks and is then reduced over time, whereas HEEDA is almost stable for the first 3 weeks and then it slightly increases. According to Davis (2009) the first degradation product produced from MEA is 2-oxazolidone (see Figure 2.8). Lepaumier et al. (2009) suggests that oxazolidones react very easily with another amine to give addition products. Therefore, the absence of 2-oxazolidone from the 8 weeks sample is what would be expected from these previous studies. HEIA concentrations grew as the degradation time increases and it is the major product in the 8 week sample as also noted by Lepaumier et al. (2009, 2010 (a) and (b)) and Davis 2009.

For mass balance purposes for the GC-MS analysis of degradation products, a nitrogen balance was performed as N_2 is more stable in solution according to Davis (2009) and Lepaumier et al. (2011). Table 4.20 presents the calculations done for the nitrogen balance between the initial number of N atoms in the fresh 400 ml of 30% w/v aqueous MEA solution and the N atoms in the 400 ml of degraded MEA, HEIA, HEEDA and 2-oxazolidone. The concentrations detected by the GC-MS were converted into ml of each analyte in the final volume of the degraded sample (see Table 4.10) and then into moles of each analyte in the final sample volume. Considering that 1 molecule of MEA contains 1 atom of N, 1 molecule of HEIA contains 2 N atoms, 1 molecule of HEEDA contains 2 atoms of N and 1 molecule of 2-oxazolidone contains 1 N atom, the total N atoms in the degraded samples were calculated. Note that 400 ml of 30% w/v aqueous MEA solution contain in total 1.9 atoms of N.

Table 4.20 Nitrogen balance in the degraded samples with lean initial molar loading, based on the concentrations detected by the GC-MS

Sample	Volume of analyte (ml)	Moles of analyte	Nitrogen moles
MEA			
Lean 2	59.2	0.981	0.981
Lean 3	50.8	0.842	0.842
Lean 8	20.8	0.345	0.345
HEIA			
Lean 2	1.2	0.011	0.022
Lean 3	12.8	0.117	0.234
Lean 8	47.6	0.435	0.870
HEEDA			
Lean 2	1.2	0.012	0.024
Lean 3	1.2	0.012	0.024
Lean 8	3.6	0.036	0.071
2-Oxazolidone			
Lean 2	6.4*	0.075	0.075
Lean 3	3.6*	0.041	0.041
Lean 8	-	-	-
Total nitrogen moles			
	Initial		Measured
Lean 2	1.9		1.1
Lean 3	1.9		1.2
Lean 8	1.9		1.4

400 ml of aqueous MEA solution with i*nitial concentration 30% w/v (or 29.6 % v/v), 0.19 initial molar loading, degradation temperature 160^{o}C*
* 2-Oxazolidone mass in gr

Clearly only three of the MEA thermal degradation products (see Table 4.18) detected in the degraded samples were quantified. Therefore it was not possible to account for all the N, but based on the data shown in Table 4.20, HEIA seems to account for a considerable amount of the MEA loss (55%) in the 8 weeks degraded sample (total MEA loss approximately 83% or 1.64 moles of MEA loss). HEEDA follows accounting for 5% of the MEA loss but with no considerable changes in its concentration throughout the course of the experiment, which supports the claims by Davis (2008&2009) and Lepaumier (2008, 2009, 2010 (b)) that HEEDA is an intermediate MEA thermal degradation product and it is HEIA's precursor.

4.7 THERMAL DEGRADATION EXPERIMENT – RICH INITIAL MOLAR LOADING

The detailed description of the experimental procedure has been presented in Section 3.10.

4.7.1 Pressure changes – Thermal degradation rig

Three 400 ml samples of 30 % w/v aqueous MEA solutions were loaded in the absorption/stripping rig to an initial molar loading of 0.37 as determined by inorganic carbon content measurement. The pressure change inside two of the vessels was continuously monitored with an analogue pressure gauge (3-weeks sample vessel) and a digital gauge (8-weeks sample vessel) for safety reasons. The total pressure changes throughout the experiment are shown in Figure 4.20 (raw data can be seen in *Appendix 2.11*). The final pressure readings of both the gauges were quite close to each other, but it is interesting to note that the needle pressure gauge shows an initial rapid increase then a slight decrease in pressure until they converge after approximately 200 hours, this trend is similar, but of a much smaller magnitude, to that noted for the "lean" sample (see Figure 4.10).

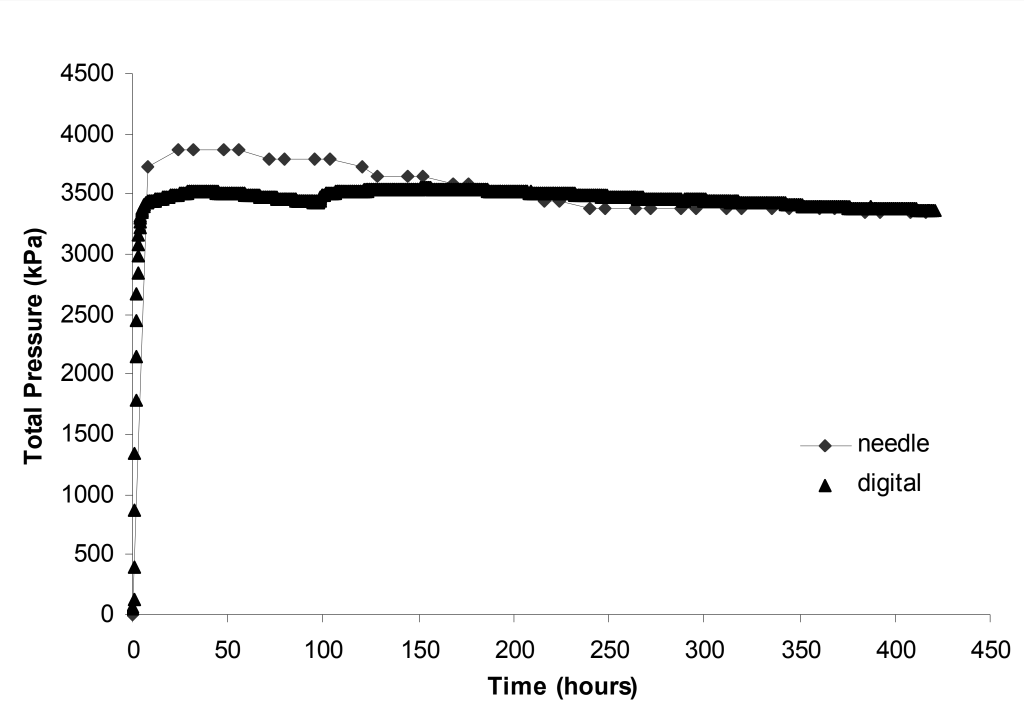


Figure 4.20 Total headspace pressure measured in two pressure vessels – "rich" samples

The samples were left in the oven sealed at 160 °C for 2, 3 and 8 weeks to thermally degrade. Each one of the samples was taken out of the oven and remained sealed at room temperature until the beginning of the absorption/stripping experiment.

After the end of the degradation experiment, each of the three samples was taken out of the high pressure vessels and its volume was measured at room temperature using the same volumetric tube used to measure the initial sample volumes (400 ml).

Table 4.21 Volumes of the degraded samples after the end of the degradation experiments

Sample	Volume (ml)
Rich 2	396
Rich 3	399
Rich 8	401

Initial volume 400 ml, initial concentration 30% w/v aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 °C

The volumes were almost identical and showed little change compared to the initial value of 400 ml (see Table 4.21).

4.7.2 Effect of degradation on MEA CO_2 uptake capacity

4.7.2.1 1st Stripping

The first step was to remove the CO_2 left in the solutions and the microGC was used to determine the volume released by the samples (stripping procedure as done in Section 4.6.3.1). The CO_2 volume was calculated described in Section 3.6 and in Figure 4.21 the cumulative CO_2 volume released by the degraded samples can be seen. The raw data are shown in *Appendix 2.12: MicroGC Raw Data – 1st Stripping – Rich Samples*.

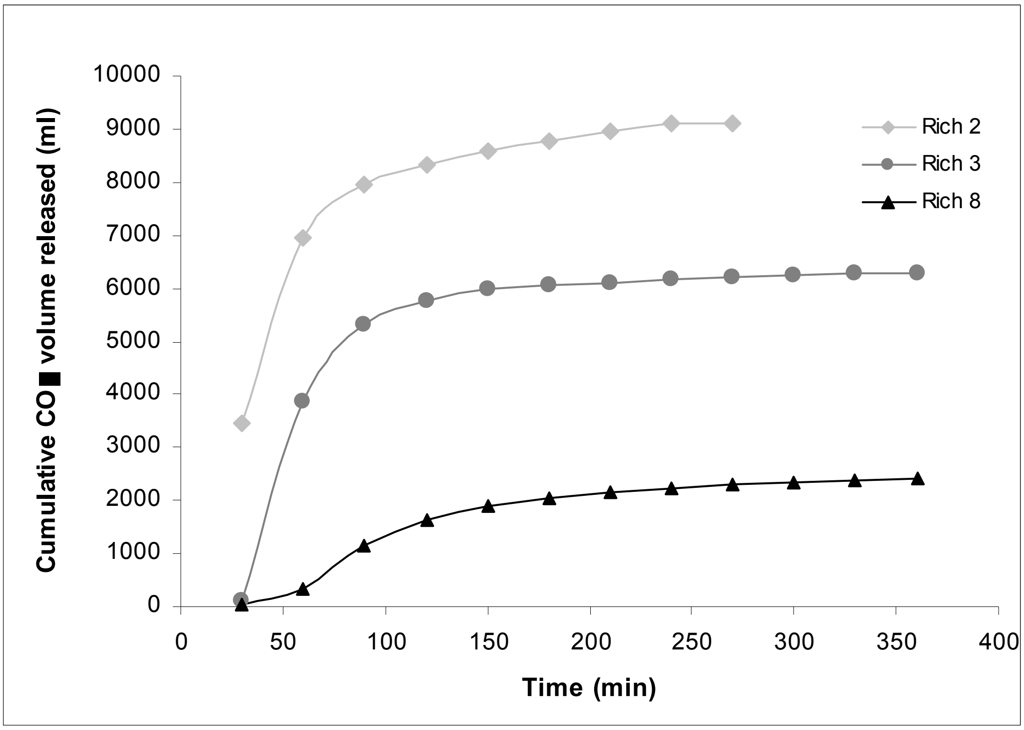


Figure 4.21 **Cumulative CO_2 volume released during the 1st stripping – "rich" samples**

Initial concentration 30% w/v aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 °C

Once again it is observed that the longer the thermal treatment the less CO_2 is released. In this case the pressure reduction in the vessels was very small and little if any CO_2 could have been lost by leakage. The loss of CO_2 probably corresponds to its uptake in forming the degradation products. Table 4.22 shows the volumes of CO_2 released by the three degraded samples with initial concentration of 30% w/v aqueous MEA and initial rich molar loading of 0.37 after treatment at 160°C.

Table 4.22 **Volume of CO_2 released during 1st stripping of the degraded "rich" samples**

Sample	CO_2 volume released (L)	Experimental Time (min)
Lean 2	9.1	390
Lean 3	6.3	390
Lean 8	2.4	330

Initial concentration 30% w/v aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 °C

Note that the samples were initially loaded with 16.1 L of CO_2; therefore quite a considerable amount of CO_2 is lost by the samples.

4.7.2.2 Absorption – Inorganic Carbon Content

After the first stripping the samples were loaded with CO_2 in the absorption/stripping rig, the procedures followed both during the experiment and the results processing is the same as followed for the lean sample, see Section 4.6.3.3. Figure 4.22 shows the graphical representation of the volume of CO_2 captured by the degraded samples over time for all the three degraded samples (raw data in *Appendix 2.13: Inorganic Carbon Measurement – Absorption – Rich Samples*).

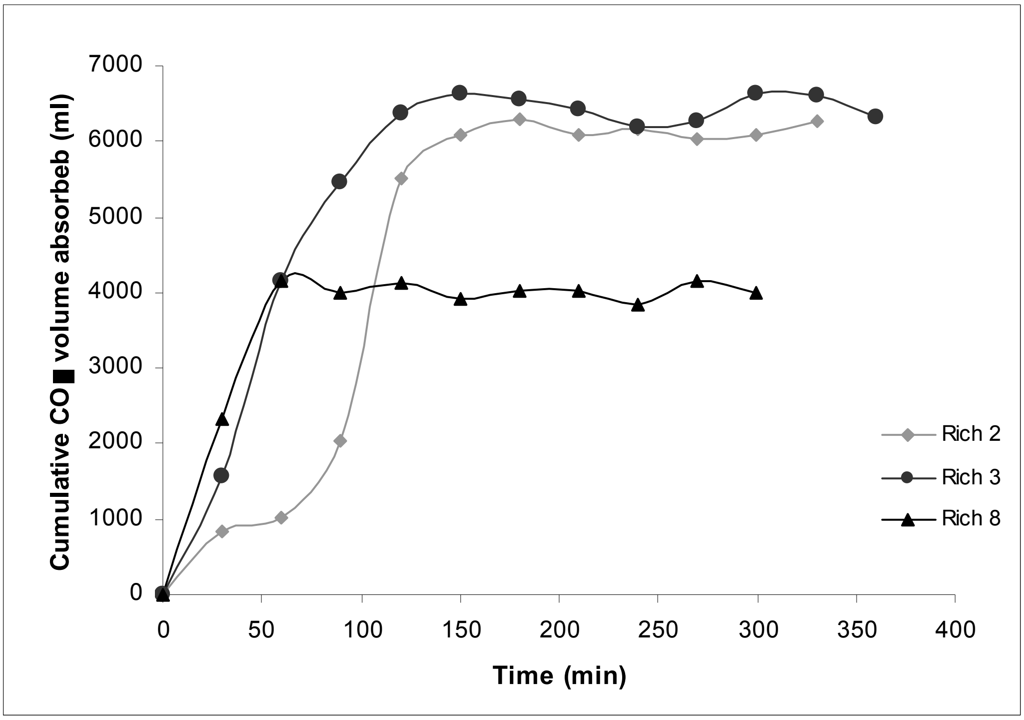


Figure 4.22 Cumulative volume of CO_2 absorbed – "rich" samples

Initial concentration 30% w/v aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 ^oC

The sample after 8 weeks of degradation (Rich 8) stops absorbing after about 50 minutes whereas the samples of 2 and 3 weeks duration continue absorbing for almost 150 min. Once again it is important to consider the volumes of CO_2 that remained in the degraded samples after the first stripping. These were determined by TOC and were 2.3 L, 1.1 L and 0.9 L for the 2, 3 and 8 weeks degraded samples respectively. As expected, Rich 8 absorbs less CO_2 than the other two, whereas the sample after 2 weeks of thermal treatment absorbs the most CO_2 (see Table 4.23). Recalling that about 23 L of CO_2 could potentially be absorbed it is estimated that the "rich" solution after 8 weeks of thermal degradation has lost approximately 78 % of its ability to absorb the gas, a value slightly in excess of that found for the "lean" case.

4.7.2.3 Stripping

After the end of the absorption, stripping was performed in the normal manner (Section 4.6.3.1). In Figure 4.23 the cumulative CO_2 released from the three degraded samples when compared with a pure MEA sample of the same initial concentration can be seen (see *Appendix 2.14*).

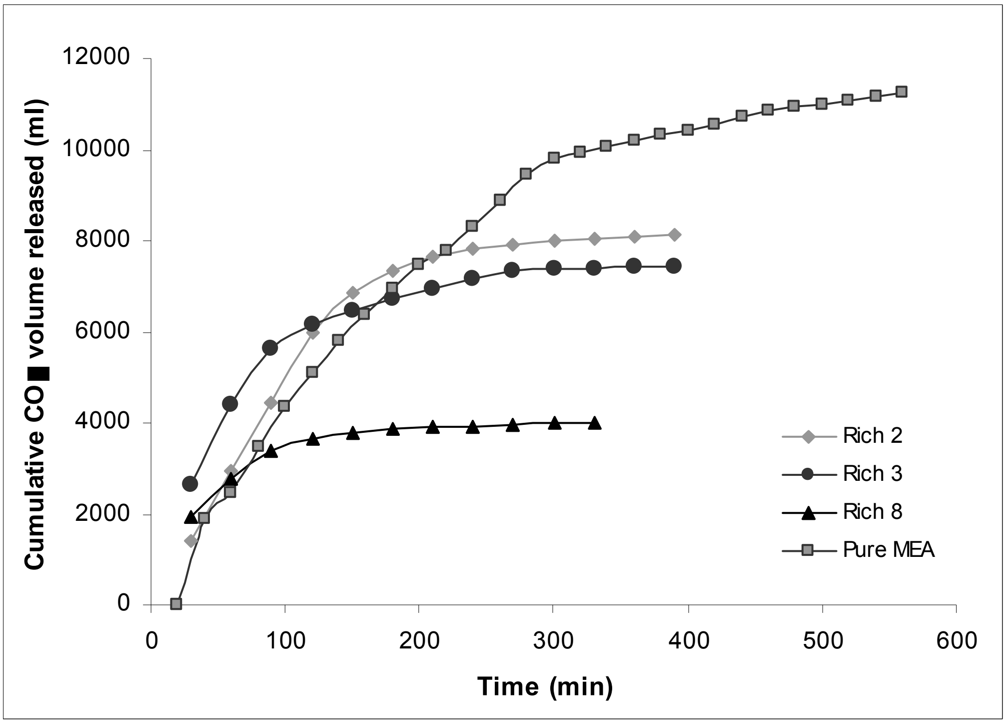


Figure 4.23 Cumulative volume of CO_2 released – "rich" samples

Initial concentration 30% w/v aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 ^oC

It is observed that the samples of 2 and 3 weeks degradation stop releasing CO_2 almost at the same time, but the sample of 2 weeks releases a little more (see Table 4.23). The 8 weeks sample releases considerably less CO_2 than the other two.

4.7.2.4 Summary solvent's CO_2 uptake capacity

Table 4.23 summarises the absorption and stripping results for the degraded samples with rich initial molar loading.

Table 4.23 Absorption/Stripping behaviour of thermally degraded, rich samples after removal of residual CO_2

Sample and degradation time (weeks)	Volume of CO_2 absorbed in 400 min (L)	Volume of CO_2 stripped in 400 min (L)
Pure MEA (no thermal treatment)	9.9*	9.9
Rich 2	8.6	8.1
Rich 3	7.6	7.4
Rich 8	5.1	4.0

Initial concentration 30% w/v aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 °C

** Inferred – not measured*

It is interesting to note that like the "lean" sample (Table 4.13) there is evidence of retention of CO_2 after absorption, suggesting a different mechanism than for pure MEA. More work is required to confirm this observation. However, it needs to be noted here that the data were obtained using two different pieces of equipment, i.e. the TOC instrument to determine the CO_2 concentration in the degraded solutions by measuring the inorganic carbon content during absorption and the microGC to determine volume of CO_2 released by the samples during stripping.

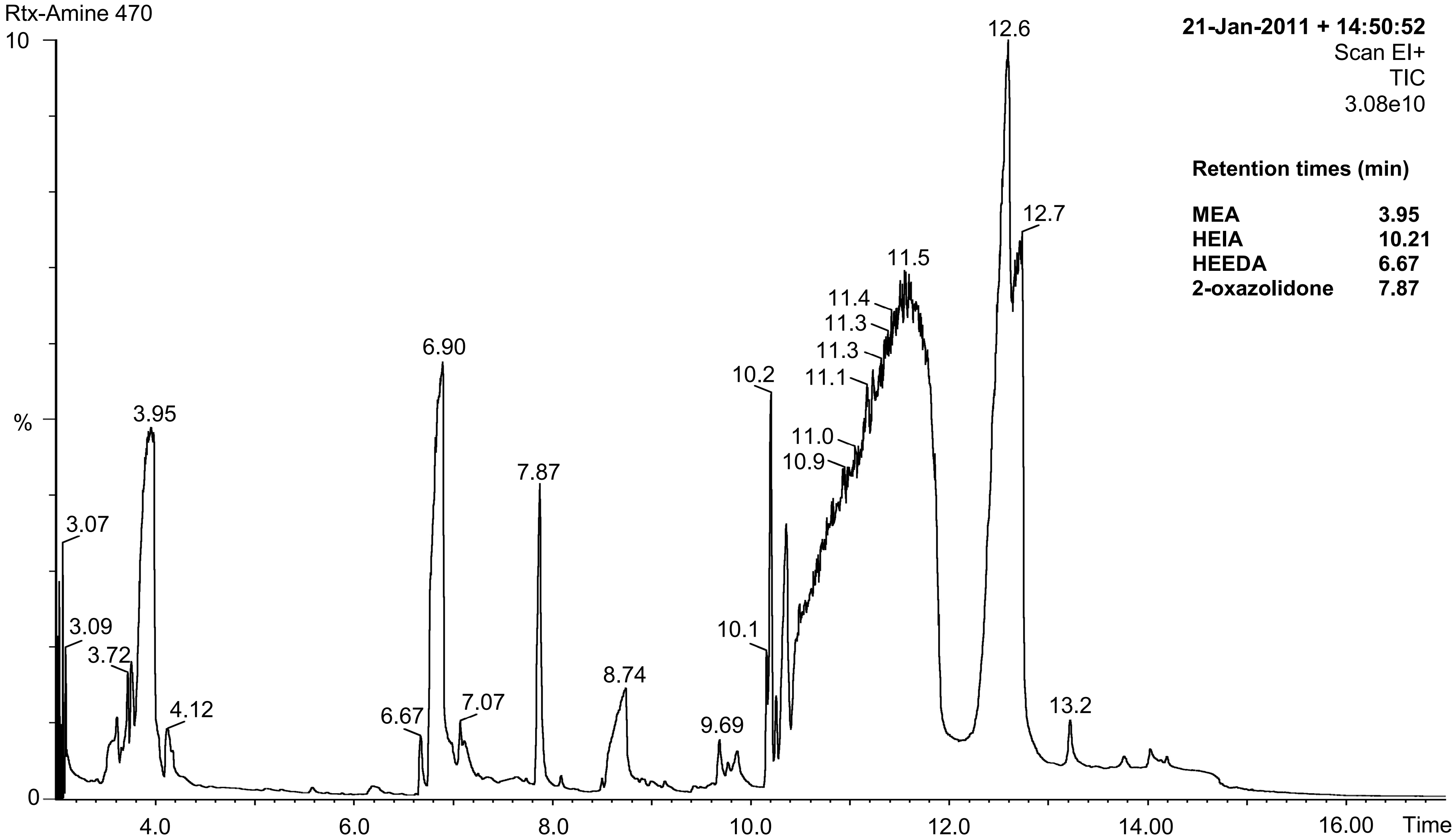
Recalling that about 23 L of CO_2 could potentially be absorbed it is estimated that the "rich" solution after 8 weeks of thermal degradation has lost approximately 78 % of its ability to absorb the gas, a value slightly in excess of that found for the "lean" case. It can be concluded here that, based on the solvent's CO_2 uptake capacity, the initial molar loading of the samples did not have a serious effect on their degradation on the highly degraded samples. However, the effect of loading was more prominent in the 2 and 3 weeks degraded samples.

4.7.3 Thermal degradation products identification and quantification

After the end of the test to assess how degradation affects the solvent's CO_2 uptake capacity, the degraded samples were analysed in the GC-MS to identify and quantify any thermal degradation products generated. In addition to this the concentration of the MEA left in solution was also determined. Figure 4.24, Figure 4.25 and Figure 4.26 show the peak responses produced by the GC-MS when the samples that degraded for 2, 3 and 8 weeks were analysed, respectively.

In Table 4.24 all of the compounds detected by the GC-MS software in the 3 samples are listed. The ones in bold have been previously reported in the literature as MEA degradation products (Strazisar et al. 2002, Strazisar et al. 2003, Supap et al. 2006, Davis, PhD thesis 2009, Lawal et al. 2005, Bello et al. 2005, Lepaumier 2009, 2010 (a) and (b) and 2011)

As for the "lean" sample it is again interesting to note that this study has identified piperazine and other related compounds in all three of the degraded samples. Full quantification was not feasible during the project but a preliminary determination of piperazine alone gave concentration lower that the detection limit of 0.1% w/v. However, in view of the large molecular masses of some of these compounds, very small concentrations are sufficient to account for the carbon originally present in the MEA.



Retention times (min)

MEA	**3.95**
HEIA	**10.21**
HEEDA	**6.67**
2-oxazolidone	**7.87**

Figure 4.24 **GC-MS response for the 2 weeks degraded sample – "rich" samples**

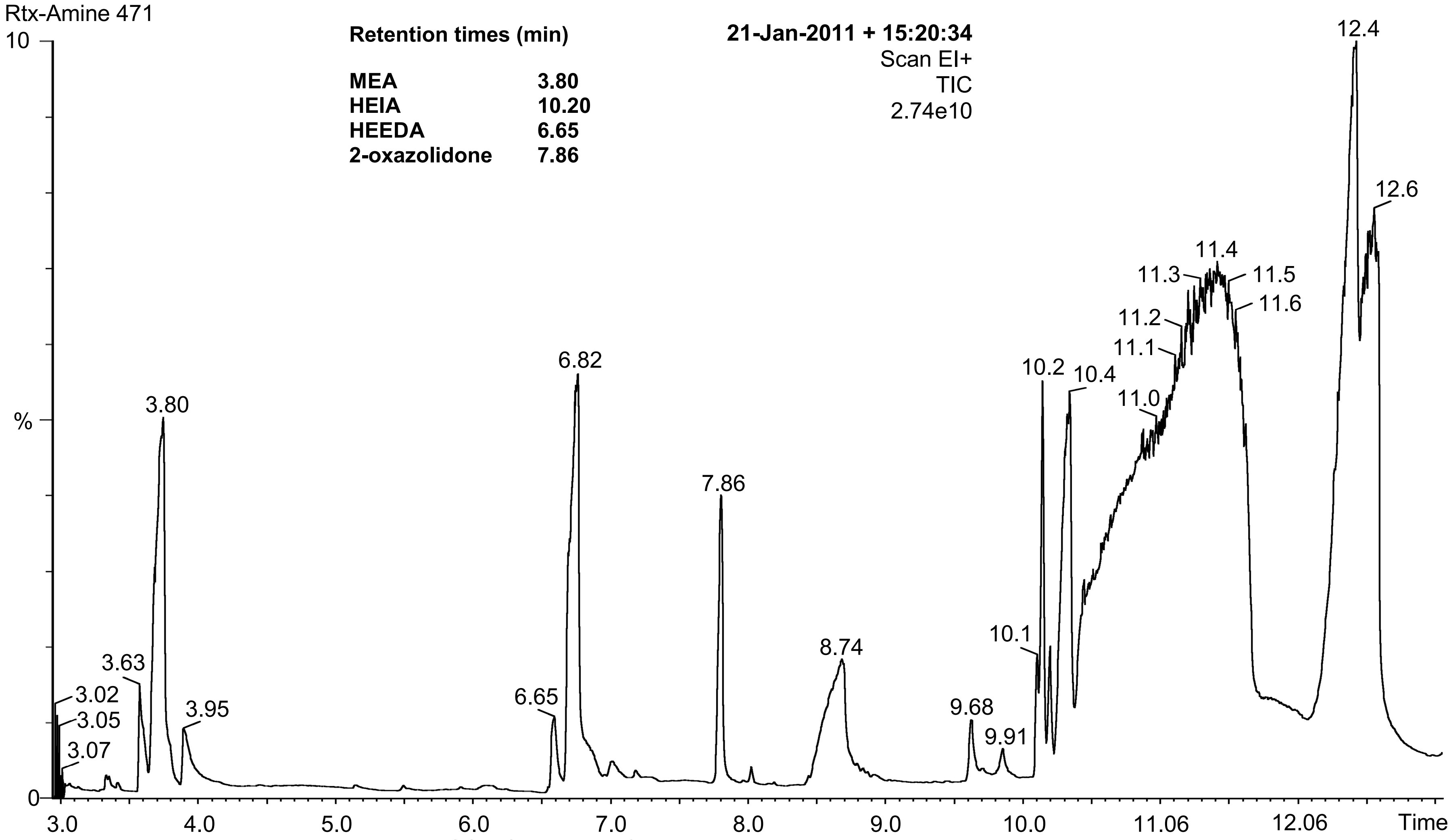


Figure 4.25 GC-MS response for the 3 weeks degraded sample – “rich” samples

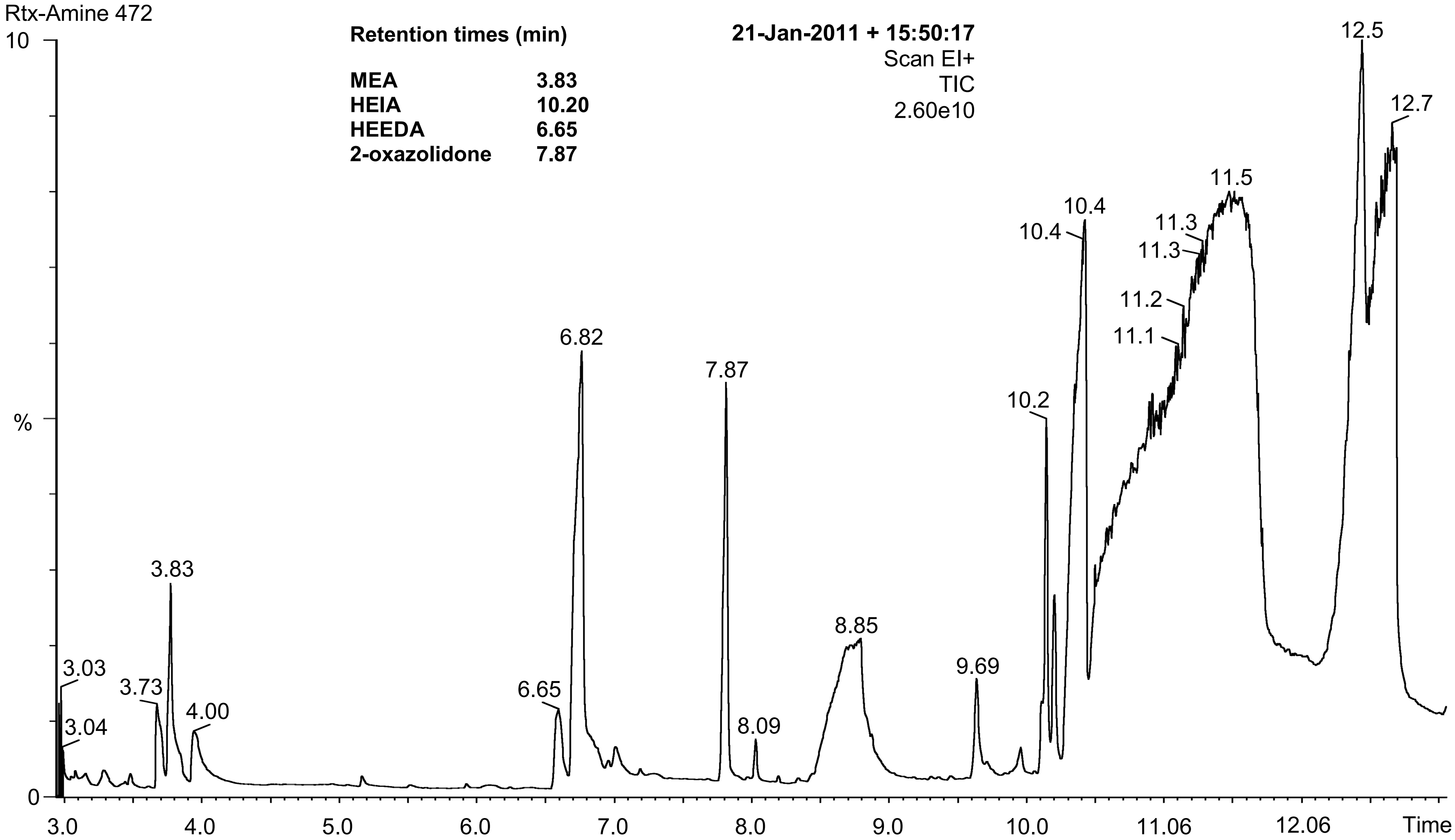


Figure 4.26 GC-MS response for the 8 weeks degraded sample – “rich” samples

Table 4.24 Degradation products found in the degraded samples with initial "rich" loading

Degradation Product	Rich 2	Rich 3	Rich 8
HEEDA	+	+	+
HEIA	+	+	+
2-oxazolidone	+	+	+
1,2-ethanodiol		+	+
1-amino-2-propanol	+		
piperazine*	+	+	+
1-(2-aminoethyl)imidazole		+	+
2-methyl-3-oxazolidine	+		
4-methylmorpholine			+
diisopropanolamine			+
2-imidazolidinone	+	+	+
3-methyl-oxazolidone		+	+
1-piperazineethanol			+
1,3-propanediame		+	+
1,4-bis(2-hydroxyethyl)piperazine	+	+	+
N,N'-bis(2-aminoethyl)-1,2-ethanediamine	+	+	+
1-(2-(2-hydroxyethoxy)ethyl)piperazine		+	+
3-(2-hydroxyethyl)-2-oxazolidinone		+	+

Initial concentration 30% w/v aqueous MEA solution, initial molar loading of 0.37, degradation temperature 160°C

Table 4.25 shows the concentration of MEA, HEIA, 2-oxazolidone and HEEDA determined in the three degraded samples with the "rich" initial loading (0.37 moles of CO_2 / mole of MEA).

Table 4.25 MEA and its major thermal degradation products concentrations– "rich" samples

Compound	Sample		
	2 weeks (% v/v)	3 weeks (% v/v)	8 weeks (% v/v)
MEA	9.3	4.6	0.6
HEIA	2.0	4.5	17.0
HEEDA	1.1	1.2	2.2
2-Oxazolidone*	6.3	5.9	4.5

Initial concentration of 30% w/v (or 29.6 % v/v) aqueous MEA solution and 0.37 initial molar loading

**The 2-oxazolidone concentrations are in % w/v*

The trends in this table are similar to those found for the "lean" sample and reported in Table 4.19. Of note are the very low final concentrations of MEA determined by the analysis procedure developed in the present work, showing degradations of the original amine in excess of 95% in 8 weeks at 160 ^{o}C. The absorption/stripping study suggested a somewhat lower degradation of the MEA as evidenced by the ability of the degraded solvents to remove CO_2 from the feed gas streams. However, this may be a reflection of the ability of some of the degradation products to absorb and release CO_2. Despite this difference both approaches demonstrate that there is very significant destruction of MEA at this elevated temperature.

However, in order to add confidence to the stated analytical results a nitrogen balance was again performed for each of the degraded samples.

Table 4.26 Nitrogen balance in the degraded samples with lean initial molar loading, based on the concentrations detected by the GC-MS

<table>
<tr><th>Sample</th><th>Volume of analyte (ml)</th><th>Moles of analyte</th><th>Nitrogen moles</th></tr>
<tr><td colspan="4">MEA</td></tr>
<tr><td>Rich 2</td><td>45.2</td><td>0.749</td><td>0.749</td></tr>
<tr><td>Rich 3</td><td>38.4</td><td>0.636</td><td>0.636</td></tr>
<tr><td>Rich 8</td><td>6.4</td><td>0.106</td><td>0.106</td></tr>
<tr><td colspan="4">HEIA</td></tr>
<tr><td>Rich 2</td><td>8</td><td>0.073</td><td>0.146</td></tr>
<tr><td>Rich 3</td><td>18</td><td>0.165</td><td>0.329</td></tr>
<tr><td>Rich 8</td><td>68</td><td>0.622</td><td>1.244</td></tr>
<tr><td colspan="4">HEEDA</td></tr>
<tr><td>Rich 2</td><td>4.4</td><td>0.044</td><td>0.087</td></tr>
<tr><td>Rich 3</td><td>4.4</td><td>0.044</td><td>0.087</td></tr>
<tr><td>Rich 8</td><td>8.8</td><td>0.087</td><td>0.174</td></tr>
<tr><td colspan="4">2-Oxazolidone</td></tr>
<tr><td>Rich 2</td><td>27.6*</td><td>0.317</td><td>0.317</td></tr>
<tr><td>Rich 3</td><td>23.6*</td><td>0.271</td><td>0.271</td></tr>
<tr><td>Rich 8</td><td>18*</td><td>0.207</td><td>0.207</td></tr>
<tr><td colspan="4">Total nitrogen moles</td></tr>
<tr><td></td><td colspan="2">Initial</td><td>Measured</td></tr>
<tr><td>Rich 2</td><td colspan="2">1.9</td><td>1.3</td></tr>
<tr><td>Rich 3</td><td colspan="2">1.9</td><td>1.4</td></tr>
<tr><td>Rich 8</td><td colspan="2">1.9</td><td>1.7</td></tr>
</table>

400 ml of aqueous MEA solution with i*nitial concentration 30% w/v (or 29.6 % v/v), 0.19 initial molar loading, degradation temperature* $160^{o}C$

* 2-Oxazolidone mass in gr

As seen in Table 4.26, it was not possible in general to account for all the N initially present in the MEA by the limited number of compounds that were quantified (see Table 4.24). On this basis it is entirely feasible that the thermal degradation products; 2-oxazolidone, HEEDA and HEIA represent the vast majority of the species in solution after intense degradation. In this case as in the case of the 8 weeks “lean” sample HEIA concentration accounts for most of the MEA loss (76%).

4.8 LEAN-RICH SAMPLE COMPARISON

The main observation is that, although most of the MEA has almost "disappeared" (95%) from the samples after 8 weeks of thermal treatment according to the GC-MS measurements, the samples still retain their capacity to absorb and release a considerable amount of CO_2, compared to what it was considered to be the case at the beginning of this study.

Moreover, there is an indication that both the "lean" and "rich" samples retained some of the CO_2 during stripping (Section 4.6.3.5 and Section 4.7.2.4), which could mean that some of the degradation products are capable of absorbing CO_2 but they can not be regenerated or they are regenerated at different conditions. According to Polderman et al. (1955) HEEDA, that is one of MEA thermal degradation products, is a stronger base than MEA is more difficult to be regenerated when it absorbs CO_2.

It was estimated that the "rich" solution after 8 weeks of thermal degradation lost approximately 78 % of its ability to absorb the gas, which is slightly in higher that that found for the "lean" sample (see Figure 4.16 and Figure 4.22). Eide-Haugmo et al. (2011) claim in their study that CO_2 loading plays a significant role in the thermal degradation rates. Moreover, Davis (2009) states that "doubling the concentration of CO_2 from 0.2 to 0.4 roughly doubles the initial degradation rate" at 135°C which is a conclusion that does not quite agree with the findings of the present study. In the present work, both in the 2 and 3 weeks samples, a roughly 20% more MEA loss is observed in the "rich" samples when compared with the "lean". It seems that the temperature increase (135°C to 160°C in this work) has a more dramatic effect on the MEA loss than the initial CO_2 molar loading. Davis (2009) also suggests that an increase in the temperature by 15 °C, quadruples the MEA loss.

The integrated form of the rate equation was plotted based on the MEA concentrations, as determined by the GC-MS, in order to determine the order of the degradation reaction and obtain an estimate of the rate constants. The equations, as presented by Langmuir (1997), are shown in Table 4.27.

Table 4.27 Reaction order, rate law and rate constants (Langmuir, 1997)

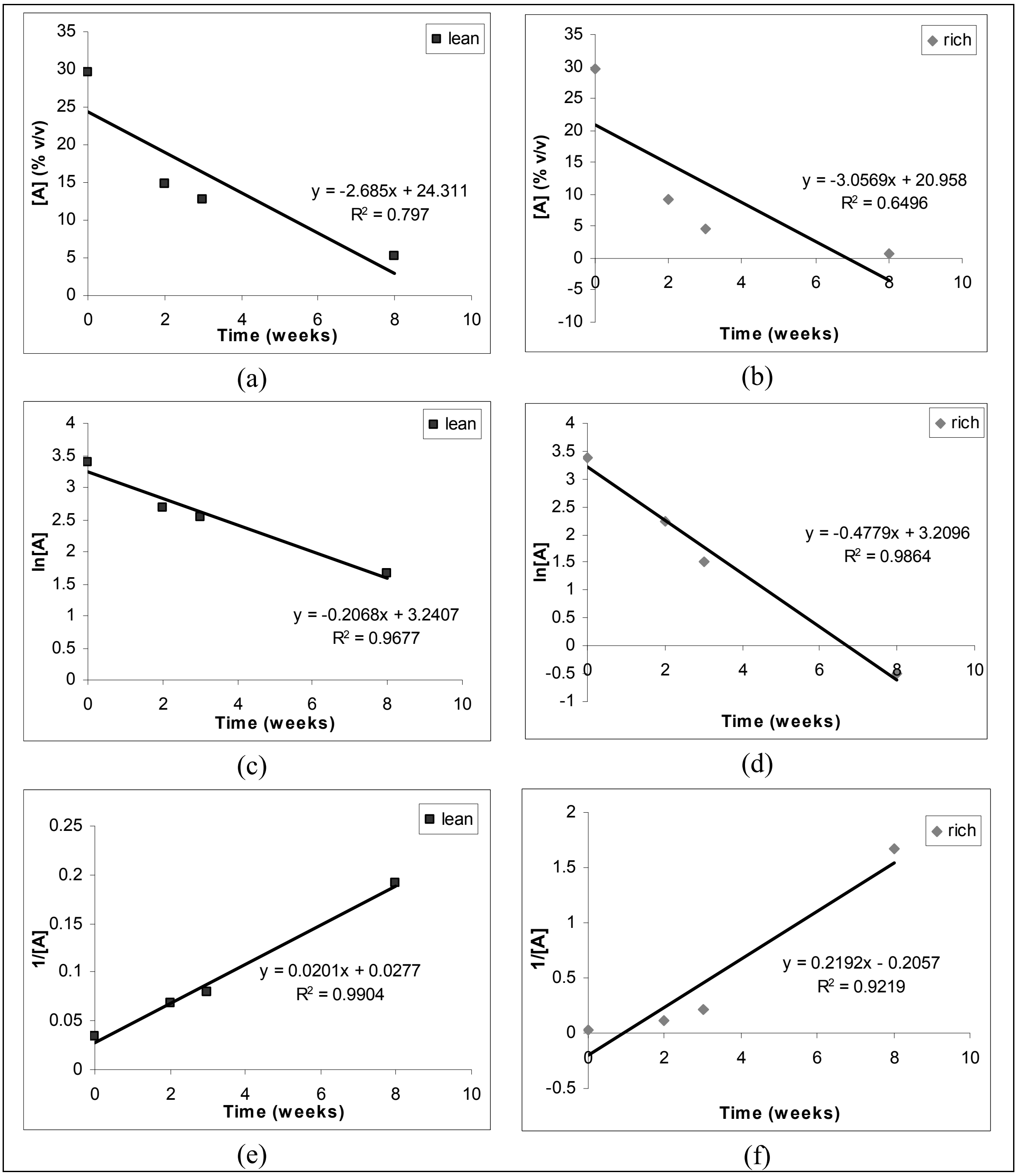
Reaction Order	Differential Rate Law	Integrated Rate Law	Kinetic Plot
0	$-\frac{d[A]}{dt}=k$	$[A]=[A]_0-kt$	$[A]$ vs t
1st	$-\frac{d[A]}{dt}=k[A]$	$[A]=[A]_0 e^{-kt}$	ln $[A]$ vs t
2nd	$-\frac{d[A]}{dt}=k[A]^2$	$[A]=\frac{[A]_0}{1+kt[A]_0}$	$\frac{1}{[A]}$ vs t

where [A] the MEA concentration in % v/v, $[A]_0$ the initial MEA concentration = 29.6 % v/v, t the time in weeks and k the rate constant.

Based on Table 4.27 the characteristic kinetic plots were drawn in excel for the lean and rich samples for zero, first and second reaction order reactions, using the integrated rate law. The resulting lines are presented in Figure 4.27.

As shown in Figure 4.27 (d) and Figure 4.27 (e), based on the R^2 as calculated by excel, it seems that the "lean" sample has 2nd order kinetics whereas the "rich" sample has 1st order kinetics with respect to MEA. This could mean that there is a different reaction scheme between the two samples. Note that the line equation was given from only 4 data points; therefore, more work would be needed to be able to draw firm conclusions. The calculated rate constants are 0.0201 for the "lean" sample and 0.4779 for the "rich" sample.

Based on these data shown in Figure 4.27 (d) and Figure 4.27 (e), it seems that the change in the CO_2 initial concentration has an effect in the MEA thermal degradation pathway described by Davis (2009) (see Figure 4.12). This could be explained because, according to Davis (2009) at many different parts of the proposed pathway, equilibrium reactions of the produced degradation products with MEA or CO_2 occur. As a result a change in the initial CO_2 concentration could favour different degradation reactions, for example the reaction of MEA trimer with CO_2 to give cyclic urea of trimer or the reaction of 2-oxazolidone with MEA to give amine urea (see Figure 4.12).



(a) (b)

(c) (d)

(e) (f)

Figure 4.27 Characteristic kinetic plot (a) "lean" sample – zero order reaction, (b) "rich" sample – zero order, (c) "lean" sample – 1st order, (d) "rich" sample 1st order, (e) "lean" sample – 2nd order and (f) "rich" sample - 2nd order.
*** [A] = MEA Concentration in % v/v**

400 ml of aqueous MEA solutions with i*nitial concentration 29.6 % v/v, 0.19 "lean" and 0.37 "rich" initial molar loadings, degradation temperature 160°C*

It needs to be noted here that, as evidence of the chemical analysis, the MEA major thermal degradation products (namely HEIA, HEEDA and 2-oxazolidone) were quantified in all the degraded samples at high concentrations. Moreover, no quantification was performed for any of the other degradation products detected in the samples (see Table 4.18 and Table 4.24) so as to be able to draw more accurate conclusions.

Davis (2009) suggests that a 25% increase in the molar loading can cause the HEIA concentration to almost double. Figure 4.28 presents the increase in HEIA concentration over time for both the lean and rich samples, these graphs were drawn assuming that during the degradation experiments the conditions inside the three vessels were the same. As it can be seen HEIA concentration increased considerably but not as much as described in the literature, it is possible that the temperature has a more detrimental effect on the HEIA production than the CO_2 concentration.

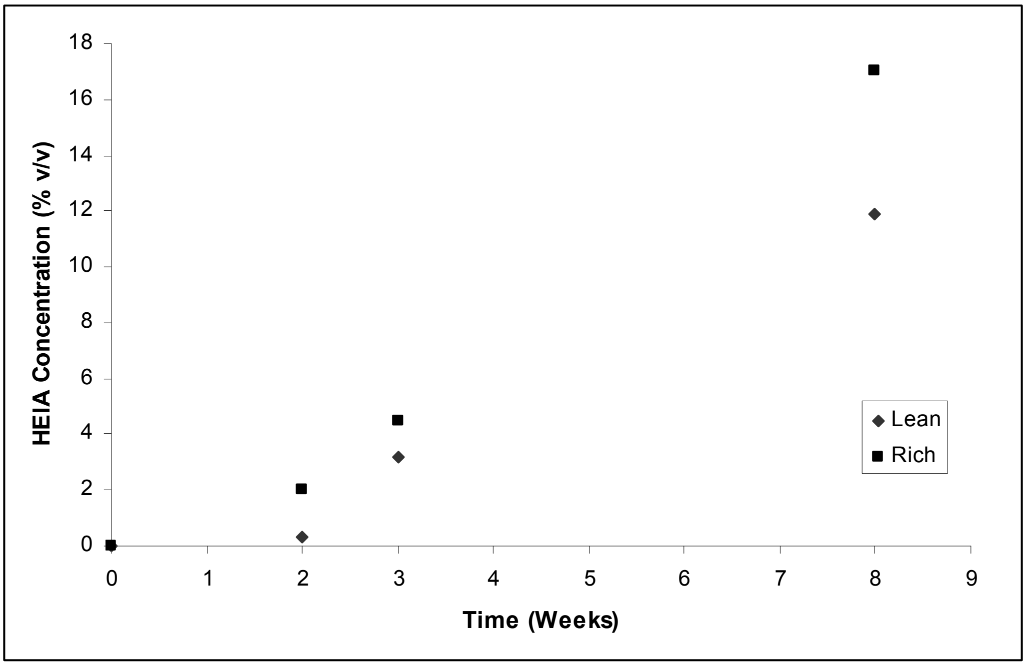


Figure 4.28 HEIA concentration versus time- Comparison between the "lean" and "rich" samples

According to Lepaumier et al. (2010 b), when a sample of 4 mol/kg (24.5 % w/v) aqueous MEA solution is degraded at 140 ^{o}C under 2 MPa of CO_2 pressure for 2 weeks 40 % MEA loss is observed. In the present study the MEA loss in the first two weeks in the "lean" sample is about 56% and 68.2% in the "rich" but with higher experimental temperature (160^{o}C) and higher MEA initial concentration, therefore the MEA degradation is considered to be in the same range.

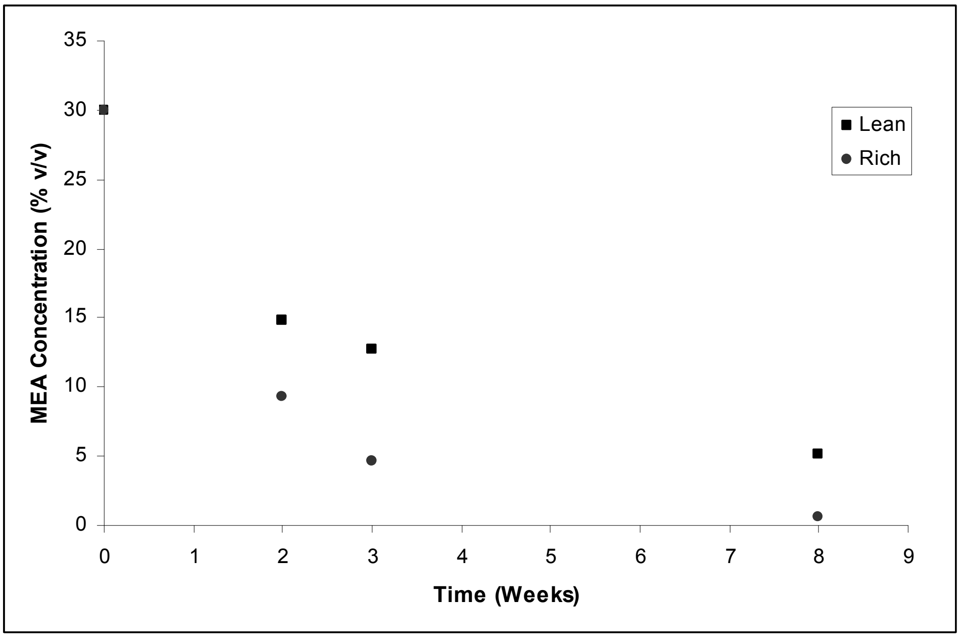


Figure 4.29 MEA concentration during the thermal degradation experiment – Comparison between the "lean" and "rich" samples

Davis (2009) also reports that "once the solution becomes more highly degraded, a compound effect of MEA loss starts to become important" which slows the overall MEA loss. Figure 4.29 presents a similar trend to that as at the beginning of the experiment the MEA concentration reduction is more dramatic than at the end. Lepaumier et al. (2011) also observed the same, it is mentioned in the study that it was noted that the degradation rate was linear for the first 4 weeks and then it started slowing down.

Last but not least, it is interesting to note here that, according to the literature, low concentrations of HEIA and 2-oxazolidone but no HEEDA were detected in samples from actual pilot plants as reported by Lepaumier et al. (2011), Strazisar et al. (2002), Strazisar et al. 2003. Bello and Idem (2005) only detected HEIA and Supap et al (2006) detected HEIA and 2-oxazolidone in some of the samples.

4.9 SUMMARY

In this chapter the results produced for the MEA degradation in the present study are reported and discussed. Some initial experiments were performed to get familiar with the absorption/stripping rig equipment, assess the solvent behavior during absorption and the effect of O_2 on it by bubbling air and CO_2 through an aqueous MEA sample in a random fashion. In addition to this, the "degraded" MEA sample was analysed using the available IC system at Cardiff University, an IC system at another laboratory and a colorimetric method. The presence of nitrites, nitrates and sulphates was verified. Concentrations of the three analytes were detected by all methods in the samples but the differences in the values between laboratories and methods were considerable. Nitrites and nitrates are MEA oxidative degradation products previously reported in the literature but sulphates were not originally expected to be present and their origin is unclear.

The next step was to perform a more systematic exercise and attempt to degrade an aqueous MEA sample in the absorption/stripping rig with an air and CO_2 mixture. The gas concentration was continuously monitored with the microGC for 14 repeated cycles of absorption/stripping and the resulting sample was analysed with the GC-MS and IC systems and a colorimetric method. The resulting sample contained nitrite, nitrate and sulphate ions but again, although the trends were similar, considerable differences in the concentrations were observed between the different methods used. Therefore, further analytical work would be needed to investigate the differences between the absolute quantified concentrations. Another conclusion drawn was that the MEA degradation is a slow phenomenon because, despite having detected degradation products in the sample, no apparent trend was observed in the solvent's absorption and stripping behavior after 14 full cycles of absorption/stripping.

At that stage and in order to be able to degrade samples within a reasonable timescale, a more focused approach on thermal degradation was taken. A new set of experiments was designed and some initial experiments were performed to gain confidence with the equipment. The CO_2 partial pressure data versus the CO_2 molar loading of MEA indicated that the CO_2 solubility data are rig dependant. Moreover, the CO_2 partial pressures measured in this work are higher than those reported in most studies with one study showing a close agreement with the measured values at high CO_2 molar loadings. Most importantly, it was concluded that it was safe to use the new rig to thermally degrade MEA samples for prolonged periods of time at elevated temperatures.

Samples of 30% w/v aqueous MEA solution with two different initial molar loadings (0.19 and 0.37 moles of CO_2/mole of MEA) were thermally treated at 160 ^oC for 2, 3 and 8 weeks. The samples were assessed in terms of their CO_2 uptake capacity, absorption and stripping behavior, and the presence of degradation products in them. The first observation was that even though almost 95% MEA loss was measured (GC-MS in the Rich 8 sample), the solvent still retained 22% of its maximum capacity to absorb CO_2. Moreover, it was noticed that in both the samples with “lean” and “rich” initial molar loading, the solvent after the stripping still retained some of the CO_2 that it had absorbed, especially observed in the 8 weeks samples in both cases (see Table 4.13 and Table 4.23), more cycles would be needed though to assess this observation.

The effect of the initial molar loading was more considerable in the 2 and 3 weeks samples as an approximately 20% higher MEA loss was measure for the “rich” samples. The effect was not as considerable as described in the literature and it is believed that this is due to the fact that temperature has a more detrimental effect in the production of degradation products. HEIA, HEEDA and 2-oxazolidone, previously reported in the literature as the major MEA thermal degradation products, were detected in all samples. Their concentrations and the nitrogen balance performed indicated that HEIA has the higher concentration of all degradation products and it increases with time, whereas 2-oxazolidone and HEEDA concentrations were almost stable throughout the experiment. Note here that it was not possible to account for all the nitrogen in the nitrogen balance as only 3 of the detected degradation products were quantified. Last but not least, signs of corrosion were observed in both “lean” and “rich” samples, ICP-OES was used to detect and quantify a considerable quantity of metals in the “lean” samples. Finally, there is some evidence that there might be a different reaction pathway that occurs, between the “lean” and “rich” case, but further investigation is needed to assess this observation.

CHAPTER 5
CONCLUSIONS – FUTURE RECOMMENDATIONS

This chapter presents the conclusions drawn from this research study and some future recommendations.

Oxidative Degradation

Considerable degradation products concentrations of nitrites and nitrates in particular and also sulphates were detected by the IC and the HACH meter in both the samples, non-systematically degraded and the 14 full cycles even at limited exposure to O_2. The differences in concentrations of ions between the different laboratories and analytical equipment noticed need to be further explored. The presence of sulphate anions detected both in the sample analysed by Dionex Ltd and by the HACH meter needs also further assessment as it was not expected.

The analysis performed with the GC-MS at that stage of the project was inconclusive; the samples though could have been analysed with the "new" analytical protocol developed for thermal degradation products.

In terms of the MEA CO_2 uptake capacity deterioration, after 14 full cycles of absorption/stripping in the presence of approximately 16% O_2 no considerable effect was observed for the CO_2 percentages of absorbed or released by the sample as measured with the microGC. Now that the equipment has been developed, this study could be extended to assess the effect of oxidative degradation and oxidative degradation products on the MEA CO_2 uptake capacity, by applying more cycles of absorption/stripping in the presence O_2 at possibly higher concentrations. Additionally, more gases, such as NO_x or SO_2 or a synthetic flue gas could be added to assess their effect on MEA behaviour and degradation products.

CO_2 Solubility in MEA

The solubility data obtained at 100°C in 400 ml of 30% w/v aqueous MEA solutions seem to differ when different rigs are used to obtain them. In general the data produced in the present of experiments show higher CO_2 partial pressures at a given molar loading to those reported in the literature, apart from one study that show close agreement at higher CO_2 molar loadings.

Corrosion

An overall corrosion rate of 1.95 mm/y was calculated in the present work. It is somewhat higher that available literature values which could be attributed to the fact that higher temperatures were used during the degradation experiments and the different type of steel.

Thermal degradation

From the 1st stripping after the thermal treatment experiment it was concluded that the more degraded the solution, the less CO_2 was left in it. In all cases there was still CO_2 available in the samples to use in the carbamate polymerisation process and thus continue degrading the MEA.

The 8 weeks sample with "lean" initial molar loading lost approximately 75% and the "rich" 78 % in terms of its CO_2 absorption capacity. The MEA concentration, as evidence of the GC-MS analysis, at the end of the 8 weeks thermal treatment was approximately 82 % and 95% less for the "lean" and "rich" samples, respectively. It can be concluded that, despite having lost most of their MEA, the samples still retained some of their capacity to remove CO_2. This may indicate the ability of some of the degradation products to remove CO_2. Therefore, the requirement for MEA make-up may not be quite as serious as initially believed. More work should be performed in order to quantify the MEA make-up needed to maintain the system's efficiency during the process as MEA is "lost" due to degradation.

Observing the deterioration in the CO_2 volume absorbed by the degraded samples after 8 weeks of thermal treatment (82 % “lean” and 95% “rich”), it can be concluded that the initial molar loading of the samples did not have such a serious effect as in both cases the MEA has almost disappeared. The effect of the initial molar loading was more considerable in the 2 and 3 weeks samples where roughly 20% more MEA loss was determined for the “rich” samples. The effect was not as considerable as described in the literature.

Observing the CO_2 volumes absorbed and released from both the “lean” and “rich” samples, there is evidence of retention of CO_2 after absorption, especially in the 8 weeks samples in both cases. This could be due to the fact that the some of the degradation products have the ability to absorb CO_2 and not release it or they release it but under different conditions. More absorption/stripping cycles are required though in order to confirm this observation.

In terms of the major MEA thermal degradation products, 2-oxazolidone, HEEDA and HEIA represent the vast majority of the species in solution after intense degradation based on the N_2 balance performed for all samples. The MEA concentration loss is more dramatic at the beginning of the experiment which probably indicates that the degradation slows down as the sample degrades more.

Based on the calculated reaction rates, as estimated by the four experimental data points available for each sample (“lean” and “rich”), it seems that the “lean” sample has 2nd order kinetics and the “rich 1st order kinetics. It is therefore suggested that there might be a different reaction pathway occurring between the “lean” and “rich” initial molar loading. More work would be needed to assess this observation and draw firm conclusions.

In both the 8 weeks samples, HEIA concentration accounts for most of the MEA loss and seems to be the most stable degradation product based on the concentrations measured in both samples over time. The HEEDA and 2-oxazolidone concentrations had very little change over time, which indicates that they are intermediate products to HEIA.

Finally, it is interesting to note that, according to the literature, low concentrations of HEIA and 2-oxazolidone but no HEEDA were detected in the samples from pilot plants. Therefore, more work could be done to assess why in all the studies performed in laboratories for “controlled” thermal degradation by carbamate polymerisation, HEIA is the most stable degradation product and 2-Oxazolidone and HEEDA are always detected, whereas the same is not observed in samples from an actual plant. It could either mean that in the actual process thermal degradation by carbamate polymerisation is not as considerable or that the proposed pathway of thermal degradation at those conditions is not the one believed or that other interactions between the produced by products occur during the process.

Overall, the present study uniquely assessed the effect of thermal degradation on the solvent’ operational lifetime. More specifically, it was found that even with an MEA loss of up to 95% due to thermal degradation, the sample still retained 22% of its capacity to remove and release CO_2. In other words, although it has not been fully quantified, the requirement for monoethanolamine make-up may not be quite as serious as initially believed which in practice means lower solvent costs.

Moreover, there was some evidence to support some of the available literature that the rate of thermal degradation was enhanced as CO_2 loading increased and a 20% higher MEA loss was determined in the samples with the rich initial molar loading. The effect of loading on thermal degradation is important as, by slightly reducing the loading of the sample entering the stripper in an actual plant, MEA thermal degradation could potentially be controlled.

A range of degradation products were quantified that suggest a pathway of formation that verifies the one recently cited in the literature suggesting HEEDA as a precursor of HEIA. According to this pathway, 2-oxazolidone and HEEDA are intermediate products and HEIA is indicated as the most stable MEA thermal degradation product with measured concentrations of up to 17% v/v. Moreover, a few other degradation product reported in the literature were also detected in these samples. The description and verification of the thermal degradation pathways is important for the actual plant to understand how the solvent deteriorates, how its degradation products interact between them, different solvents could be screened and compared in terms of degradation as well as the reclaimer wastes that need to be treated before disposed. Last but not least, the development of analysis methods for the detection and quantification of the major degradation products is very important as the chemical analysis of degraded samples has been a challenging issue in the field of solvent degradation.

This work could be further extended to:

- include other gases such as O_2, SO_2, NO_x or synthetic flue gas and degrade samples at elevated temperatures and pressures, then assess the effect on the solvent CO_2 uptake capacity and detect any additional degradation products generated.
- perform experiments with synthetic flue gas and conditions as close to the actual ones as possible and apply repeated cycles of absorption/stripping to assess how the MEA deterioration progresses with time and detect the degradation products generated.

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APPENDIX 1: EXPERIMENTAL

Appendix 1.1: IC Calibration Curves

Raw data used to produce the calibration curves:

Samples of different concentrations (in mg/L) for each compound and the area response (in μS*min) in the IC. The samples were prepared in 5 molal aqueous MEA solutions and pre-processed with the cartridges.

Acetic Acid		Formic Acid		Oxalic Acid		Potassium Nitrite		Sodium Nitrate	
mg/L	μS*min	mg/L	μS*min	mg/L	μS*min	mg/L	μS*min	mg/L	μS*min
1040	95	1220	260	1653	450	1920	440	2260	475
104	20	122	70	165.3	62.5	192	108	226	105
10.4	1.8	12.2	1.75	16.53	12	19.2	15	22.6	15
1.04	1.75	1.22	1.25	1.653	1.75	1.92	2	2.26	2.5

Appendix 1.2: IC Method Detection Limits

IC method detection limits for all compounds raw data

- IDL Calculation:

Noise level response from 10 IC chromatograms (of a preprocessed 5 molal aqueous MEA solutions) for each compound, determined by measuring its response (if any) in the blank sample.

Acetic	Formic	Oxalic	Nitrate	Nitrite
0.0065	0.0164	0.0254	0.0164	0.12
0.0828	0.031	0.1215	0.041	0.081
0.0765	0.119	0.097	0.0148	0.089
0.1515	0.0254	0.1232	0.0047	0.326
0.2173	0.2173	0.031	0.1272	0.1219
0.045	0.0431	0.072	0.0847	0.0452
0.05	0.0469	0.0008	0.0147	0.026
0.041	0.0354	0.301	0.0827	0.1066
0.0378	0.0401	0.1311	0.0022	0.0036
0.0354	0.325	0.0036	0.0956	0.1815

The IDL is three times the standard deviation of the noise for each compound in the blank sample

Acetic	Formic	Oxalic	Nitrate	Nitrite
STD				
0.063671	0.10267	0.089287	0.045116	0.091821

IDL				
Acetic	Formic	Oxalic	Nitrate	Nitrite
3*STD				
0.191013	0.308011	0.26786	0.135348	0.275462

- MDL calculation

7 Solutions with concentrations 5*IDL (approximately 1 mg/L) for each compound were prepared in a 5 molal aqueous MEA solution matrixes and run in the IC:

Acetic	Formic	Oxalic	Nitrate	Nitrite
Area (µS*min)	Area (µS*min)	Area (µS*min)	Area µS*min	Area µS*min
0.723	0.3994	1.2887	1.3361	1.2381
0.6019	0.2495	1.3026	1.375	1.249
0.783	0.2368	1.2933	1.3882	1.3639
0.932	0.3473	1.7	1.05	0.89
0.979	0.4226	1.55	1.2101	1.14
1.054	0.381	0.9088	1.1794	1.17
0.8803	0.3994	0.6322	0.6869	1.0447

The STD (Standard Deviation) was calculated along with the average and % RSD (Relative Standard Deviation). Finally, the MDL was calculated by multiplying the RSD with the concentration (1mg/L) and the students' t value for a 99% confidence level with 6 degrees of freedom which was found from the one sided table to be 3.143.

Acetic	Formic	Oxalic	Nitrate	Nitrite
Average				
0.850457143	21.63339	0.198179779	1.1751	1.156528571
STD				
0.157092986	0.075284	0.364221282	0.247158977	0.15395105
% RSD				
18.47159344	21.63339	29.38758098	21.03301652	13.31147829
MDL (mg/L)				
0.580008034	0.679288	0.922770043	0.660436719	0.417980418

Appendix 1.3: GC Conditions – Old Set Up

GC Conditions

Kali method

Turbochrom Method File : C:\TURBOMASS\KALI.PRO\ACQUDB\Kali.mth
Created By : Mathew
Edited By : Mathew
Number of Times Edited : 3
Number of Times Calibrated : 0

GC Control
Instrument Name: inst1
Experiment Time: 38.57 min
Delay Time : 0.00 min
Run Time : 38.57 min

Injection : AUTO Injection
Volume: 1.0µL
Sampling Rate : 1.56250 pts/s
Channel : NONE

Inlet A : PSSI
Inlet B : NONE
Detector A: NONE
Detector B: NONE

Oven Temperature Program:
Initial Temperature: 40 deg for 5.00 min
Ramp 1: 7.0 deg/min to 240 deg, hold for 5.00 min

Kali 1 method

Turbochrom Method File : C:\TURBOMASS\KALl.PRO\ACQUDB\kali1.mth
Created By : Mathew
Edited By : Mathew
Number of Times Edited : 1
Number of Times Calibrated : 0

GC Control
Instrument Name: inst1
Experiment Time: 38.57 min
Delay Time : 0.00 min
Run Time : 38.57 min

Injection : AUTO Injection
Volume: 1.0µL
Sampling Rate : 1.56250 pts/s
Channel : NONE

Inlet A : PSSI
Inlet B : NONE
Detector A: NONE
Detector B: NONE

Oven Temperature Program:
Initial Temperature: 40 deg for 5.00 min
Ramp 1 : 7.0 deg/min to 240 deg, hold for 5.00 min

Kali 2 method

Turbochrom Method File : C:\TURBOMASS\KALl.PRO\ACQUDB\kali2.mth
Created By : Mathew
Edited By : Mathew
Number of Times Edited : 1
Number of Times Calibrated : 0

GC Control
Instrument Name: inst1
Experiment Time: 20.00 min
Delay Time : 0.00 min
Run Time : 20.00 min

Injection : AUTO Injection
Volume: 1.0µL
Sampling Rate : 1.56250 pts/s
Channel : NONE

Inlet A : PSSI
Inlet B : NONE
Detector A: NONE
Detector B: NONE

Oven Temperature Program:
Initial Temperature: 100 deg for 1.00 min
Ramp 1 : 10.0 deg/min to 240 deg, hold for 5.00 min

Kali 3 method

Turbochrom Method File : C:\TURBOMASS\KALI.PRO\ACQUDB\kali3.mth
Created By : Mathew
Edited By : Mathew
Number of Times Edited : 0
Number of Times Calibrated : 0

GC Control
Instrument Name: inst1
Experiment Time: 34.00 min
Delay Time : 0.00 min
Run Time : 34.00 min

Injection : AUTO Injection
Volume: 1.0μL
Sampling Rate : 1.56250 pts/s
Channel : NONE

Inlet A : PSSI
Inlet B : NONE
Detector A: NONE
Detector B: NONE

Oven Temperature Program:
Initial Temperature: 100 deg for 10.00 min
Ramp 1 : 10.0 deg/min to 240 deg, hold for 10.00 min

Kali 4 method

Turbochrom Method File : C:\TURBOMASS\KAL1.PRO\ACQUDB\kali4.mth
Created By : Mathew
Edited By : Mathew
Number of Times Edited : 0
Number of Times Calibrated : 0

GC Control
Instrument Name: inst1
Experiment Time: 75.00 min
Delay Time : 0.00 min
Run Time : 75.00 min

Injection : AUTO Injection
Volume: 1.0μL
Sampling Rate : 1.56250 pts/s
Channel : NONE

Inlet A : PSSI
Inlet B : NONE
Detector A: NONE
Detector B: NONE

Oven Temperature Program:
Initial Temperature: 100 deg for 10.00 min
Ramp 1 : 7.0 deg/min to 240 deg, hold for 45.00 min

Kali 5 method

Turbochrom Method File : C:\TURBOMASS\KAL1.PRO\ACQUDB\kali5.mth
Created By : Mathew
Edited By : Mathew
Number of Times Edited : 1
Number of Times Calibrated : 0

GC Control
Instrument Name: inst1
Experiment Time: 17.00 min
Delay Time : 0.00 min
Run Time : 17.00 min

Injection : AUTO Injection
Volume: 1.0µL
Sampling Rate : 1.56250 pts/s
Channel : NONE

Inlet A : PSSI
Inlet B : NONE
Detector A: NONE
Detector B: NONE

Oven Temperature Program:
Initial Temperature: 50 deg for 2.00 min
Ramp 1: 10.0 deg/min to 180 deg, hold for 2.00 min

Kali 6 method

Turbochrom Method File : C:\TURBOMASS\KALI.PRO\ACQUDB\kali6.mth
Created By : Mathew
Edited By : Mathew
Number of Times Edited : 0
Number of Times Calibrated : 0

GC Control
Instrument Name: inst1
Experiment Time: 17.83 min
Delay Time : 0.00 min
Run Time : 17.83 min

Injection : AUTO Injection
Volume: 1.0µL
Sampling Rate : 1.56250 pts/s
Channel : NONE

Inlet A : PSSI
Inlet B : NONE
Detector A: NONE
Detector B: NONE

Oven Temperature Program:
Initial Temperature: 50 deg for 0.50 min
Ramp 1 : 15.0 deg/min to 280 deg, hold for 2.00 min

Appendix 1.4: MS method – Old Set Up

MS methods

Kali 1 method

Experiment Report
Experiment File: c:\turbomass\kali.pro\acqudb\kali 1.exp
Printed: Tue Nov 11 17:06:03 2008

Name	Default Experiment
Creation Time	Mon 03 Nov 2008 17:54:03
Instrument Identifier	
Version Number	1.0
Duration (min)	39.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 2.00 to 39.00, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	2.00
End Time (min)	39.00

Kali 2 method

Experiment Report
Experiment File: c:\turbomass\kali.pro\acqudb\kali2.exp
Printed: Tue Nov 11 17:11 :15 2008

Name	Default Experiment
Creation Time	Fri 10 Oct 2008 14:22:07
Instrument Identifier	
Version Number	1.0
Duration (min)	21.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 2.00 to 21.00, Mass 30.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	30.00
End Mass	300.00

```
Scan Time (sec)                    0.20
InterScan Time (sec)               0.05
Start Time (min)                   2.00
End Time (min)                     21.00
```

Kali 3 method

```
Experiment Report
Experiment File: c:\turbomass\kali.pro\acqudb\kali3.exp
Printed: Tue Nov 11 17:20:50 2008

Name                               Default Experiment
Creation Time                      Wed 08 Oct 2008 16:33:04
Instrument Identifier
Version Number                     1.0
Duration (min)                     34.0
No Solvent Delays
Number Of Functions

Function 1 : MS Scan, Time 0.00 to 34.00, Mass 30.00 to 300.00 EI+

Type                               MS Scan
Ion Mode                           EI+
Data Format                        Centroid
Start Mass                         10.00
End Mass                           300.00
Scan Time (sec)                    0.20
InterScan Time (sec)               0.05
Start Time (min)                   0.00
End Time (min)                     34.00
```

Kali 4 method

```
Experiment Report
Experiment File: c:\turbomass\kali.pro\acqudb\kali4.exp
Printed: Tue Nov 11 17:21 :21 2008


Name                               Default Experiment
Creation Time                      Wed 08 act 2008 17:10:59
Instrument Identifier
Version Number                     1.0
Duration (min)                     75.0
No Solvent Delays
Number Of Functions                1

Function 1 : MS Scan, Time 0.00 to 75.00, Mass 10.00 to 300.00 EI+

Type                               MS Scan
Ion Mode                           EI+
Data Format                        Centroid
Start Mass                         10.00
End Mass                           300.00
```

Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.00
End Time (min)	75.00

Kali 5 method

Experiment Report
Experiment File: c:\turbomass\kali.pro\acqudb\kali5.exp
Printed: Tue Nov 11 17:20:13 2008

Name	Default Experiment
Creation Time	Fri 10 Oct 2008 14:35:52
Instrument Identifier	
Version Number	1.0
Duration (min)	17.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 0.87 to 17.00, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.87
End Time (min)	17.00

Kali 6 method

Experiment Report
Experiment File: c:\turbomass\kali.pro\acqudb\kali6.exp
Printed: Tue Nov 11 17:20:20 2008

Name	Default Experiment
Creation Time	Fri 10 Oct 2008 15:13:29
Instrument Identifier	
Version Number	1.0
Duration (min)	18.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	1.0
Number Of Functions	1

Function 1 : MS Scan, Time 0.92 to 18.00, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid

Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.92
End Time (min)	18.00

Appendix 1.5: GC-MS Sample Runs – New Set Up

GC-MS sample runs GC and MS conditions and sample description

TurboMass - Sample List

Sample List: C:\TURBOMASS\KALI.PRO\SampleDB\Test runs.SPL
Printed: Tue Jul 26 16:23:57 2011

	File Name	MS Method	GC Method	Sample ID
1	Test Run 469	kali2	kali6	Isopropanol
2	Test Run 469	kali2	kali6	Isopropanol
3	Test Run 470	kali2	kali6	DCM
4	Test Run 471	kali2	kali6	Oxazolidone
5	Test Run 472	kali5	kali6	Oxazolidone
6	Test Run 473	kali6	kali6	Oxazolidone
7	Test Run 474	MEA 1	MEA 1	Isopropanol
8	Test Run 475	MEA 1	MEA 1	DCM
9	Test Run 476	MEA 1	MEA 1	HEIA
10	Test Run 477	MEA 1	kali1	HEIA
11	Test Run 478	MEA 1	kali2	HEIA
12	Test Run 479	MEA 1	kali3	HEIA
13	Test Run 480	MEA 1	kali4	HEIA
14	Test Run 481	MEA 1	kali5	HEIA
15	Test Run 482	MEA 1	kali6	HEIA
16	Test Run 483	kali6	kali1	HEIA
17	Test Run 484	kali6	kali2	HEIA
18	Test Run 485	kali6	kali3	HEIA
19	Test Run 486	kali6	kali4	HEIA
20	Test Run 487	kali6	kali5	HEIA
21	Test Run 488	kali6	kali6	HEIA
22	Test Run 489	kali6	Kali	HEIA
23	Test Run 490	kali6	MEA 1	HEIA
24	Test Run 491	kali2	kali3	Isopropanol
25	Test Run 492	kali2	kali3	DCM
26	Test Run 493	kali2	kali3	HEEDA
27	Test Run 494	kali2	kali6	HEEDA
28	Test Run 495	kali2	Kali	HEEDA
29	Test Run 496	kali2	kali1	HEEDA
30	Test Run 497	kali2	kali1	Isopropanol
31	Test Run 498	kali5	Kali	DCM
32	Test Run 499	kali5	Kali	DCM
33	Test Run 500	kali5	Kali	Isopropanol
34	Test Run 501	kali5	Kali	Oxazolidone
35	Test Run 502	kali5	kali1	Oxazolidone
36	Test Run 503	kali5	kali2	Oxazolidone
37	Test Run 504	kali5	kali3	Oxazolidone
38	Test Run 505	kali5	kali4	Oxazolidone
39	Test Run 506	kali5	kali5	Oxazolidone
40	Test Run 507	kali5	kali6	Oxazolidone
41	Test Run 508	kali6	Kali	Oxazolidone

	File Name	MS Method	GC Method	Sample ID
42	Test Run 509	kali6	kali1	Oxazolidone
43	Test Run 510	kali6	kali2	Oxazolidone
44	Test Run 511	kali6	kali3	Oxazolidone
45	Test Run 512	kali6	kali4	Oxazolidone
46	Test Run 513	kali6	kali5	Oxazolidone
47	Test Run 514	kali6	kali6	Oxazolidone
48	Test Run 515	MEA 1	Kali	DCM
49	Test Run 516	MEA 1	Kali	Isopropanol
50	Test Run 517	MEA 1	Kali	Oxazolidone
51	Test Run 518	MEA 1	kali1	Oxazolidone
52	Test Run 519	MEA 1	kali2	Oxazolidone
53	Test Run 520	MEA 1	kali3	Oxazolidone
54	Test Run 521	MEA 1	kali4	Oxazolidone
55	Test Run 522	MEA 1	kali5	Oxazolidone
56	Test Run 523	MEA 1	kali6	Oxazolidone
57	Test Run 524	Kali.mth	Kali	Oxazolidone
58	Test Run 525	Kali.mth	kali1	Oxazolidone
59	Test Run 526	Kali.mth	kali2	Oxazolidone
60	Test Run 527	Kali.mth	kali3	Oxazolidone
61	Test Run 528	Kali.mth	kali4	Oxazolidone
62	Test Run 529	Kali.mth	kali5	Oxazolidone
63	Test Run 530	Kali.mth	kali6	Oxazolidone
64	Test Run 531	kali2	Kali	Oxazolidone
65	Test Run 532	kali2	kali1	Oxazolidone
66	Test Run 533	kali2	kali2	Oxazolidone
67	Test Run 534	kali2	kali3	Oxazolidone
68	Test Run 535	kali2	kali4	Oxazolidone
69	Test Run 536	kali2	kali5	Oxazolidone
70	Test Run 537	kali2	kali6	Oxazolidone
71	Test Run 538	kali3	Kali	DCM
72	Test Run 539	kali3	Kali	Isopropanol
73	Test Run 540	kali3	Kali	Oxazolidone
74	Test Run 541	kali3	kali1	Oxazolidone
75	Test Run 542	kali3	kali2	Oxazolidone
76	Test Run 543	kali3	kali3	Oxazolidone
77	Test Run 544	kali3	kali4	Oxazolidone
78	Test Run 545	kali3	kali5	Oxazolidone
79	Test Run 546	kali3	kali6	Oxazolidone
80	Test Run 547	kali4	Kali	Oxazolidone
81	Test Run 548	kali4	kali1	Oxazolidone
82	Test Run 549	kali4	kali2	Oxazolidone

	File Name	MS Method	GC Method	Sample ID
83	Test Run 550	kali4	kali3	Oxazolidone
84	Test Run 551	kali4	kali4	Oxazolidone
85	Test Run 552	kali4	kali5	Oxazolidone
86	Test Run 553	kali4	kali6	Oxazolidone
87	Test Run 554	kali5	Kali	DCM
88	Test Run 555	kali5	Kali	Isopropanol
89	Test Run 556	kali5	Kali	HEIA
90	Test Run 557	kali5	kali1	HEIA
91	Test Run 558	kali5	kali2	HEIA
92	Test Run 559	kali5	kali3	HEIA
93	Test Run 560	kali5	kali4	HEIA
94	Test Run 561	kali5	kali5	HEIA
95	Test Run 562	kali5	kali6	HEIA
96	Test Run 563	Kali.mth	Kali	HEIA
97	Test Run 564	Kali.mth	kali1	HEIA
98	Test Run 565	Kali.mth	kali2	HEIA
99	Test Run 566	Kali.mth	kali3	HEIA
100	Test Run 567	Kali.mth	kali4	HEIA
101	Test Run 568	Kali.mth	kali5	HEIA
102	Test Run 569	Kali.mth	kali6	HEIA
103	Test Run 570	kali2	Kali	HEIA
104	Test Run 571	kali2	kali1	HEIA
105	Test Run 572	kali2	kali2	HEIA
106	Test Run 573	kali2	kali3	HEIA
107	Test Run 574	kali2	kali4	HEIA
108	Test Run 575	kali2	kali5	HEIA
109	Test Run 576	kali2	kali6	HEIA
110	Test Run 577	kali3	Kali	HEIA
111	Test Run 578	kali3	kali1	HEIA
112	Test Run 579	kali3	kali2	HEIA
113	Test Run 580	kali3	kali3	HEIA
114	Test Run 581	kali3	kali4	HEIA
115	Test Run 582	kali3	kali5	HEIA
116	Test Run 583	kali3	kali6	HEIA
117	Test Run 584	kali4	Kali	HEIA
118	Test Run 585	kali4	kali1	HEIA
119	Test Run 586	kali4	kali2	HEIA
120	Test Run 587	kali4	kali3	HEIA
121	Test Run 588	kali4	kali4	HEIA
122	Test Run 589	kali4	kali5	HEIA
123	Test Run 590	kali4	kali6	HEIA

	File Name	MS Method	GC Method	Sample ID
124	Test Run 591	kali5	Kali	DCM
125	Test Run 592	kali5	Kali	Isopropanol
126	Test Run 593	kali5	Kali	HEEDA
127	Test Run 594	kali5	kali1	HEEDA
128	Test Run 595	kali5	kali2	HEEDA
129	Test Run 596	kali5	kali3	HEEDA
130	Test Run 597	kali5	kali4	HEEDA
131	Test Run 598	kali5	kali5	HEEDA
132	Test Run 599	kali5	kali6	HEEDA
133	Test Run 600	kali6	Kali	HEEDA
134	Test Run 601	kali6	kali1	HEEDA
135	Test Run 602	kali6	kali2	HEEDA
136	Test Run 603	kali6	kali3	HEEDA
137	Test Run 604	kali6	kali4	HEEDA
138	Test Run 605	kali6	kali5	HEEDA
139	Test Run 606	kali6	kali6	HEEDA
140	Test Run 607	MEA 1	Kali	DCM
141	Test Run 608	MEA 1	Kali	Isopropanol
142	Test Run 609	MEA 1	Kali	HEEDA
143	Test Run 610	MEA 1	kali1	HEEDA
144	Test Run 611	MEA 1	kali2	HEEDA
145	Test Run 612	MEA 1	kali3	HEEDA
146	Test Run 613	MEA 1	kali4	HEEDA
147	Test Run 614	MEA 1	kali5	HEEDA
148	Test Run 615	MEA 1	kali6	HEEDA
149	Test Run 616	Kali.mth	Kali	HEEDA
150	Test Run 617	Kali.mth	kali1	HEEDA
151	Test Run 618	Kali.mth	kali2	HEEDA
152	Test Run 619	Kali.mth	kali3	HEEDA
153	Test Run 620	Kali.mth	kali4	HEEDA
154	Test Run 621	Kali.mth	kali5	HEEDA
155	Test Run 622	Kali.mth	kali6	HEEDA
156	Test Run 623	kali2	Kali	HEEDA
157	Test Run 624	kali2	kali1	HEEDA
158	Test Run 625	kali2	kali2	HEEDA
159	Test Run 626	kali2	kali3	HEEDA
160	Test Run 627	kali2	kali4	HEEDA
161	Test Run 628	kali2	kali5	HEEDA
162	Test Run 629	kali2	kali6	HEEDA
163	Test Run 630	kali3	Kali	DCM
164	Test Run 631	kali3	Kali	Isopropanol

	File Name	MS Method	GC Method	Sample ID
165	Test Run 632	kali3	Kali	HEEDA
166	Test Run 633	kali3	kali1	HEEDA
167	Test Run 634	kali3	kali2	HEEDA
168	Test Run 635	kali3	kali3	HEEDA
169	Test Run 636	kali3	kali4	HEEDA
170	Test Run 637	kali3	kali5	HEEDA
171	Test Run 638	kali3	kali6	HEEDA
172	Test Run 639	kali4	Kali	HEEDA
173	Test Run 640	kali4	kali1	HEEDA
174	Test Run 641	kali4	kali2	HEEDA
175	Test Run 642	kali4	kali3	HEEDA
176	Test Run 643	kali4	kali4	HEEDA
177	Test Run 644	kali4	kali5	HEEDA
178	Test Run 645	kali4	kali6	HEEDA
179	Test Run 646	kali4	kali6	DCM
180	Test Run 647	kali4	kali6	Isopropanol
181	Test Run 648	MS VOCs	VOCs	HEIA
182	Test Run 649	MS VOCs	VOCs	2-Oxazolidone
183	Test Run 650	MS VOCs	VOCs	HEEDA
184	Test Run 651	MS_VOCs	VOCs	Test
185	Test Run 652	MS VOCs	VOCs	HEIA
186	Test Run 653	MS VOCs	VOCs	HEEDA
187	Test Run 654	MS_VOCs	VOCs	2-Oxazolidone
188	Test Run 655	MS_VOCs	VOCs	HEIA
189	Test Run 656	MS VOCs	VOCs	HEEDA
190	Test Run 657	MS VOCs	VOCs	2-Oxazolidone
191	Rtx-Amine 1	Kali.mth	Kali	MTBE
192	Rtx-Amine 2	Kali.mth	Kali	MEA in MTBE
193	Rtx-Amine 3	MEA 1	kali2	MTBE
194	Rtx-Amine 4	MEA 1	kali2	MEA in MTBE
195	Rtx-Amine 5	MEA 1	kali2	MTBE
196	Rtx-Amine 6	MEA 1	kali2	Oxazol MEA in MTBE
197	Rtx-Amine 7	MEA 1	kali2	MTBE
198	Rtx-Amine 8	MEA 1	kali2	HEEDA MEA in MTBE
199	Rtx-Amine 9	MEA 1	kali2	MTBE
200	Rtx-Amine 10	MEA 1	kali2	HEIA MEA in MTBE
201	Rtx-Amine 11	MEA 1	kali2	MTBE
202	Rtx-Amine 12	MEA 1	kali2	DCM
203	Rtx-Amine 13	MEA 1	kali2	MEA in DCM
204	Rtx-Amine 14	MEA 1	kali2	DCM
205	Rtx-Amine 15	MEA 1	kali2	Oxazol MEA in DCM

	File Name	MS Method	GC Method	Sample ID
206	Rtx-Amine 16	MEA 1	kali2	DCM
207	Rtx-Amine 17	MEA 1	kali2	HEEDA MEA in DCM
208	Rtx-Amine 18	MEA 1	kali2	DCM
209	Rtx-Amine 19	MEA 1	kali2	HEIA MEA in DCM
210	Rtx-Amine 20	MEA 1	kali2	DCM
211	Rtx-Amine 21	MEA 1	kali2	Toluene
212	Rtx-Amine 22	MEA 1	kali2	MEA in tolue
213	Rtx-Amine 23	MEA 1	kali2	Tolue
214	Rtx-Amine 24	MEA 1	kali2	Oxazol MEA in Tolue
215	Rtx-Amine 25	MEA 1	kali2	Tolue
216	Rtx-Amine 26	MEA 1	kali2	HEEDA MEA in Tolue
217	Rtx-Amine 27	MEA 1	kali2	Tolue
218	Rtx-Amine 28	MEA 1	kali2	HEIA MEA in Tolue
219	Rtx-Amine 29	MEA 1	kali2	Tolue
220	Rtx-Amine 30	MEA 1	kali5	MTBE
221	Rtx-Amine 31	MEA 1	kali5	MEA in MTBE
222	Rtx-Amine 32	MEA 1	kali5	MTBE
223	Rtx-Amine 33	MEA 1	kali5	Oxazol MEA in MTBE
224	Rtx-Amine 34	MEA 1	kali5	MTBE
225	Rtx-Amine 35	MEA 1	kali5	HEEDA MEA in MTBE
226	Rtx-Amine 36	MEA 1	kali5	MTBE
227	Rtx-Amine 37	MEA 1	kali5	HEIA MEA in MTBE
228	Rtx-Amine 38	MEA 1	kali5	MTBE
229	Rtx-Amine 39	MEA 1	kali5	DCM
230	Rtx-Amine 40	MEA 1	kali5	MEA in DCM
231	Rtx-Amine 41	MEA 1	kali5	DCM
232	Rtx-Amine 42	MEA 1	kali5	Oxazol MEA in DCM
233	Rtx-Amine 43	MEA 1	kali5	DCM
234	Rtx-Amine 44	MEA 1	kali5	HEEDA MEA in DCM
235	Rtx-Amine 45	MEA 1	kali5	DCM
236	Rtx-Amine 46	MEA 1	kali5	HEIA MEA in DCM
237	Rtx-Amine 47	MEA 1	kali5	DCM
238	Rtx-Amine 48	MEA 1	kali5	Toluene
239	Rtx-Amine 49	MEA 1	kali5	MEA in tolue
240	Rtx-Amine 50	MEA 1	kali5	Tolue
241	Rtx-Amine 51	MEA 1	kali5	Oxazol MEA in Tolue
242	Rtx-Amine 52	MEA 1	kali5	Tolue
243	Rtx-Amine 53	MEA 1	kali5	HEEDA MEA in Tolue
244	Rtx-Amine 54	MEA 1	kali5	Tolue
245	Rtx-Amine 55	MEA 1	kali5	HEIA MEA in Tolue
246	Rtx-Amine 56	MEA 1	kali5	Tolue

	File Name	MS Method	GC Method	Sample ID
247	Rtx-Amine 57	MEA 1	kali6	MTBE
248	Rtx-Amine 58	MEA 1	kali6	MEA in MTBE
249	Rtx-Amine 59	MEA 1	kali6	MTBE
250	Rtx-Amine 60	MEA 1	kali6	Oxazol MEA in MTBE
251	Rtx-Amine 61	MEA 1	kali6	MTBE
252	Rtx-Amine 62	MEA 1	kali6	HEEDA MEA in MTBE
253	Rtx-Amine 63	MEA 1	kali6	MTBE
254	Rtx-Amine 64	MEA 1	kali6	HEIA MEA in MTBE
255	Rtx-Amine 65	MEA 1	kali6	MTBE
256	Rtx-Amine 66	MEA 1	kali6	DCM
257	Rtx-Amine 67	MEA 1	kali6	MEA in DCM
258	Rtx-Amine 68	MEA 1	kali6	DCM
259	Rtx-Amine 69	MEA 1	kali6	Oxazol MEA in DCM
260	Rtx-Amine 70	MEA 1	kali6	DCM
261	Rtx-Amine 71	MEA 1	kali6	HEEDA MEA in DCM
262	Rtx-Amine 72	MEA 1	kali6	DCM
263	Rtx-Amine 73	MEA 1	kali6	HEIA MEA in DCM
264	Rtx-Amine 74	MEA 1	kali6	DCM
265	Rtx-Amine 75	MEA 1	kali6	Toluene
266	Rtx-Amine 76	MEA 1	kali6	MEA in tolue
267	Rtx-Amine 77	MEA 1	kali6	Tolue
268	Rtx-Amine 78	MEA 1	kali6	Oxazol MEA in Tolue
269	Rtx-Amine 79	MEA 1	kali6	Tolue
270	Rtx-Amine 80	MEA 1	kali6	HEEDA MEA in Tolue
271	Rtx-Amine 81	MEA 1	kali6	Tolue
272	Rtx-Amine 82	MEA 1	kali6	HEIA MEA in Tolue
273	Rtx-Amine 83	MEA 1	kali6	Tolue
274	Rtx-Amine 84	MEA 1	kali3	MTBE
275	Rtx-Amine 85	MEA 1	kali3	MEA in MTBE
276	Rtx-Amine 86	MEA 1	kali3	MTBE
277	Rtx-Amine 87	MEA 1	kali3	Oxazol MEA in MTBE
278	Rtx-Amine 88	MEA 1	kali3	MTBE
279	Rtx-Amine 89	MEA 1	kali3	HEEDA MEA in MTBE
280	Rtx-Amine 90	MEA 1	kali3	MTBE
281	Rtx-Amine 91	MEA 1	kali3	HEIA MEA in MTBE
282	Rtx-Amine 92	MEA 1	kali3	MTBE
283	Rtx-Amine 93	MEA 1	kali3	DCM
284	Rtx-Amine 94	MEA 1	kali3	MEA in DCM
285	Rtx-Amine 95	MEA 1	kali3	DCM
286	Rtx-Amine 96	MEA 1	kali3	Oxazol MEA in DCM
287	Rtx-Amine 97	MEA 1	kali3	DCM

	File Name	MS Method	GC Method	Sample ID
288	Rtx-Amine 98	MEA 1	kali3	HEEDA MEA in DCM
289	Rtx-Amine 99	MEA 1	kali3	DCM
290	Rtx-Amine 100	MEA 1	kali3	HEIA MEA in DCM
291	Rtx-Amine 101	MEA 1	kali3	DCM
292	Rtx-Amine 102	MEA 1	kali3	Toluene
293	Rtx-Amine 103	MEA 1	kali3	MEA in tolue
294	Rtx-Amine 104	MEA 1	kali3	Tolue
295	Rtx-Amine 105	MEA 1	kali3	Oxazol MEA in Tolue
296	Rtx-Amine 106	MEA 1	kali3	Tolue
297	Rtx-Amine 107	MEA 1	kali3	HEEDA MEA in Tolue
298	Rtx-Amine 108	MEA 1	kali3	Tolue
299	Rtx-Amine 109	MEA 1	kali3	HEIA MEA in Tolue
300	Rtx-Amine 110	MEA 1	kali3	Tolue
301	Rtx-Amine 111	MEA 1	kali4	MTBE
302	Rtx-Amine 112	MEA 1	kali4	MEA in MTBE
303	Rtx-Amine 113	MEA 1	kali4	MTBE
304	Rtx-Amine 114	MEA 1	kali4	Oxazol MEA in MTBE
305	Rtx-Amine 115	MEA 1	kali4	MTBE
306	Rtx-Amine 116	MEA 1	kali4	HEEDA MEA in MTBE
307	Rtx-Amine 117	MEA 1	kali4	MTBE
308	Rtx-Amine 118	MEA 1	kali4	HEIA MEA in MTBE
309	Rtx-Amine 119	MEA 1	kali4	MTBE
310	Rtx-Amine 120	MEA 1	kali4	DCM
311	Rtx-Amine 121	MEA 1	kali4	MEA in DCM
312	Rtx-Amine 122	MEA 1	kali4	DCM
313	Rtx-Amine 123	MEA 1	kali4	Oxazol MEA in DCM
314	Rtx-Amine 124	MEA 1	kali4	DCM
315	Rtx-Amine 125	MEA 1	kali4	HEEDA MEA in DCM
316	Rtx-Amine 126	MEA 1	kali4	DCM
317	Rtx-Amine 127	MEA 1	kali4	HEIA MEA in DCM
318	Rtx-Amine 128	MEA 1	kali4	DCM
319	Rtx-Amine 129	MEA 1	kali4	Toluene
320	Rtx-Amine 130	MEA 1	kali4	MEA in tolue
321	Rtx-Amine 131	MEA 1	kali4	Tolue
322	Rtx-Amine 132	MEA 1	kali4	Oxazol MEA in Tolue
323	Rtx-Amine 133	MEA 1	kali4	Tolue
324	Rtx-Amine 134	MEA 1	kali4	HEEDA MEA in Tolue
325	Rtx-Amine 135	MEA 1	kali4	Tolue
326	Rtx-Amine 136	MEA 1	kali4	HEIA MEA in Tolue
327	Rtx-Amine 137	MEA 1	kali4	Tolue
328	Rtx-Amine 138	MEA 1	MEA 1	MTBE

	File Name	MS Method	GC Method	Sample ID
329	Rtx-Amine 139	MEA 1	MEA 1	MEA in MTBE
330	Rtx-Amine 140	MEA 1	MEA 1	MTBE
331	Rtx-Amine 141	MEA 1	MEA 1	Oxazol MEA in MTBE
332	Rtx-Amine 142	MEA 1	MEA 1	MTBE
333	Rtx-Amine 143	MEA 1	MEA 1	HEEDA MEA in MTBE
334	Rtx-Amine 144	MEA 1	MEA 1	MTBE
335	Rtx-Amine 145	MEA 1	MEA 1	HEIA MEA in MTBE
336	Rtx-Amine 146	MEA 1	MEA 1	MTBE
337	Rtx-Amine 147	MEA 1	MEA 1	DCM
338	Rtx-Amine 148	MEA 1	MEA 1	MEA in DCM
339	Rtx-Amine 149	MEA 1	MEA 1	DCM
340	Rtx-Amine 150	MEA 1	MEA 1	Oxazol MEA in DCM
341	Rtx-Amine 151	MEA 1	MEA 1	DCM
342	Rtx-Amine 152	MEA 1	MEA 1	HEEDA MEA in DCM
343	Rtx-Amine 153	MEA 1	MEA 1	DCM
344	Rtx-Amine 154	MEA 1	MEA 1	HEIA MEA in DCM
345	Rtx-Amine 155	MEA 1	MEA 1	DCM
346	Rtx-Amine 156	MEA 1	MEA 1	Toluene
347	Rtx-Amine 157	MEA 1	MEA 1	MEA in tolue
348	Rtx-Amine 158	MEA 1	MEA 1	Tolue
349	Rtx-Amine 159	MEA 1	MEA 1	Oxazol MEA in Tolue
350	Rtx-Amine 160	MEA 1	MEA 1	Tolue
351	Rtx-Amine 161	MEA 1	MEA 1	HEEDA MEA in Tolue
352	Rtx-Amine 162	MEA 1	MEA 1	Tolue
353	Rtx-Amine 163	MEA 1	MEA 1	HEIA MEA in Tolue
354	Rtx-Amine 164	MEA 1	MEA 1	Tolue
355	Rtx-Amine 165	MEA 1	kz1	MTBE
356	Rtx-Amine 166	MEA 1	kz1	MEA in MTBE
357	Rtx-Amine 167	MEA 1	kz1	MTBE
358	Rtx-Amine 168	MEA 1	kz1	Oxazol MEA in MTBE
359	Rtx-Amine 169	MEA 1	kz1	MTBE
360	Rtx-Amine 170	MEA 1	kz1	HEEDA MEA in MTBE
361	Rtx-Amine 171	MEA 1	kz1	MTBE
362	Rtx-Amine 172	MEA 1	kz1	HEIA MEA in MTBE
363	Rtx-Amine 173	MEA 1	kz1	MTBE
364	Rtx-Amine 174	MEA 1	kz1	DCM
365	Rtx-Amine 175	MEA 1	kz1	MEA in DCM
366	Rtx-Amine 176	MEA 1	kz1	DCM
367	Rtx-Amine 177	MEA 1	kz1	Oxazol MEA in DCM
368	Rtx-Amine 178	MEA 1	kz1	DCM
369	Rtx-Amine 179	MEA 1	kz1	HEEDA MEA in DCM

	File Name	MS Method	GC Method	Sample ID
370	Rtx-Amine 180	MEA 1	kz1	DCM
371	Rtx-Amine 181	MEA 1	kz1	HEIA MEA in DCM
372	Rtx-Amine 182	MEA 1	kz1	DCM
373	Rtx-Amine 183	MEA 1	kz1	Toluene
374	Rtx-Amine 184	MEA 1	kz1	MEA in tolue
375	Rtx-Amine 185	MEA 1	kz1	Tolue
376	Rtx-Amine 186	MEA 1	kz1	Oxazol MEA in Tolue
377	Rtx-Amine 187	MEA 1	kz1	Tolue
378	Rtx-Amine 188	MEA 1	kz1	HEEDA MEA in Tolue
379	Rtx-Amine 189	MEA 1	kz1	Tolue
380	Rtx-Amine 190	MEA 1	kz1	HEIA MEA in Tolue
381	Rtx-Amine 191	MEA 1	kz1	Tolue
382	Rtx-Amine 192	MEA 1	kz1	DCM
383	Rtx-Amine 193	MEA 1	kz1	DCM
384	Rtx-Amine 194	MEA 1	kz1	MEA in DCM
385	Rtx-Amine 195	MEA 1	kz1	MEA in DCM
386	Rtx-Amine 196	MEA 1	kz1	HEEDA in DCM
387	Rtx-Amine 197	MEA 1	kz1	HEEDA in DCM
388	Rtx-Amine 198	MEA 1	kz1	Acetone
389	Rtx-Amine 199	MEA 1	kz1	Acetone
390	Rtx-Amine 200	MEA 1	kz1	MEA in Acetone
391	Rtx-Amine 201	MEA 1	kz1	MEA in Acetone
392	Rtx-Amine 202	MEA 1	kz1	HEEDA in Acetone
393	Rtx-Amine 203	MEA 1	kz1	HEEDA in Acetone
394	Rtx-Amine 204	MEA 1	kz1	pure MEA
395	Rtx-Amine 205	MEA 1	kz1	pure HEEDA
396	Rtx-Amine 206	MEA 2	kz1	pure MEA
397	Rtx-Amine 207	MEA 2	kz1	pure HEEDA
398	Rtx-Amine 208	MEA 2	kz1	MEA in DCM : 1drop in 2ml
399	Rtx-Amine 209	MEA 2	kz1	HEEDA in DCM : 1drop in 2ml
400	Rtx-Amine 210	MEA 3	kz1	MEA in DCM : 1drop in 10ml
401	Rtx-Amine 211	MEA 3	kz1	HEEDA in DCM 1 drop in 10ml
402	Rtx-Amine 212	MEA 3	kz1	MEA in DCM : 1drop in 10ml
403	Rtx-Amine 213	MEA 3	kz1	HEEDA in DCM 1 drop in 10ml
404	Rtx-Amine 214	MEA 4	kz1	MEA in DCM : 1drop in 10ml
405	Rtx-Amine 215	MEA 4	kz1	HEEDA in DCM 1 drop in 10ml
406	Rtx-Amine 216	MEA 4	kz1	MEA in DCM : 1drop in 10ml
407	Rtx-Amine 217	MEA 4	kz1	MEA in DCM : 1drop in 10ml
408	Rtx-Amine 218	MEA 4	kz1	HEEDA in DCM 1 drop in 10ml
409	Rtx-Amine 219	MEA 4	kz2	MEA in DCM : 1drop in 10ml
410	Rtx-Amine 220	MEA 4	kz2	HEEDA in DCM 1 drop in 10ml

	File Name	MS Method	GC Method	Sample ID
411	Rtx-Amine 221	MEA 4	kz2	MEA + DCM : Kali
412	Rtx-Amine 222	MEA 4	kz2	MEA + HEEDA + DCM : Kali
413	Rtx-Amine 223	MEA 4	kz2	MEA + HEEDA + TOLUENE : Kali
414	Rtx-Amine 224	MEA 4	kz2	MEA + HEEDA + MTBE : Kali
415	Rtx-Amine 225	MEA 4	kz2	mtbe
416	Rtx-Amine 226	MEA 4	kz2	kz1 : 1 drop each MEA + HEEDA in 100ml MTBE
417	Rtx-Amine 227	MEA 4	kz2	kz1 : 1 drop each MEA + HEEDA in 101ml MTBE
418	Rtx-Amine 228	MEA 4	kz2	kz1 : 1 drop each MEA + HEEDA in 102ml MTBE
419	Rtx-Amine 229	MEA 4	kz2	MEA in DCM Standard - no.8
420	Rtx-Amine 230	MEA 4	kz2	MEA in DCM Standard - no 7
421	Rtx-Amine 231	MEA 4	kz2	MEA in DCM Standard - no 6
422	Rtx-Amine 232	MEA 4	kz2	MEA in DCM Standard : no 5
423	Rtx-Amine 233	MEA 4	kz2	MEA in DCM Standard : no 4
424	Rtx-Amine 234	MEA 4	kz2	MEA in DCM Standard : no 3
425	Rtx-Amine 235	MEA 4	kz2	MEA in DCM Standard : no 2
426	Rtx-Amine 236	MEA 4	kz2	MEA in DCM Standard : no 1
427	Rtx-Amine 237	MEA 4	kz2	MEA in DCM std 13
428	Rtx-Amine 238	MEA 4	kz2	MEA in DCM std 12
429	Rtx-Amine 239	MEA 4	kz2	MEA in DCM std 11
430	Rtx-Amine 240	MEA 4	kz2	MEA in DCM std 10
431	Rtx-Amine 241	MEA 4	kz2	MEA in DCM std 9
432	Rtx-Amine 242	MEA 4	kz2	std 21
433	Rtx-Amine 243	MEA 4	kz2	std 20
434	Rtx-Amine 244	MEA 4	kz2	std 19
435	Rtx-Amine 245	MEA 4	kz2	std 18
436	Rtx-Amine 246	MEA 4	kz2	std 17
437	Rtx-Amine 247	MEA 4	kz2	std 16
438	Rtx-Amine 248	MEA 4	kz2	std 21
439	Rtx-Amine 249	MEA 4	kz2	std 20
440	Rtx-Amine 250	MEA 4	kz2	std 19
441	Rtx-Amine 251	MEA 4	kz2	std 18
442	Rtx-Amine 252	MEA 4	kz2	std 17
443	Rtx-Amine 253	MEA 4	kz2	std 16
444	Rtx-Amine 254	MEA 4	kz2	std 21
445	Rtx-Amine 255	MEA 4	kz2	std 20
446	Rtx-Amine 256	MEA 4	kz2	std 19
447	Rtx-Amine 257	MEA 4	kz2	std 18
448	Rtx-Amine 258	MEA 4	kz2	std 17
449	Rtx-Amine 259	MEA 4	kz2	std 16
450	Rtx-Amine 260	MEA 4	kz3	std 28
451	Rtx-Amine 261	MEA 4	kz3	std 27

	File Name	MS Method	GC Method	Sample ID
452	Rtx-Amine 262	MEA 4	kz3	std 26
453	Rtx-Amine 263	MEA 4	kz3	std 25
454	Rtx-Amine 264	MEA 4	kz3	std 24
455	Rtx-Amine 265	MEA 4	kz3	std 23
456	Rtx-Amine 266	MEA 4	kz3	std 35
457	Rtx-Amine 267	MEA 4	kz3	std 34
458	Rtx-Amine 268	MEA 4	kz3	std 33
459	Rtx-Amine 269	MEA 4	kz3	std 32
460	Rtx-Amine 270	MEA 4	kz3	std 31
461	Rtx-Amine 271	MEA 4	kz3	std 30
462	Rtx-Amine 272	MEA 4	kz3	std 29
463	Rtx-Amine 273	MEA 4	kz3	std 42
464	Rtx-Amine 274	MEA 4	kz3	std 41
465	Rtx-Amine 275	MEA 4	kz3	std 40
466	Rtx-Amine 276	MEA 4	kz3	std 39
467	Rtx-Amine 277	MEA 4	kz3	std 38
468	Rtx-Amine 278	MEA 4	kz3	std 37
469	Rtx-Amine 279	MEA 4	kz3	std 36
470	Rtx-Amine 280	MEA 4	kz3	MTBE
471	Rtx-Amine 281	MEA 4	kz3	MEA extract in MTBE (0.06%)
472	Rtx-Amine 282	MEA 4	kz3	HEEDA extract in MTBE (0.06%)
473	Rtx-Amine 283	MEA 4	kz4	MEA extract in MTBE (0.06%)
474	Rtx-Amine 284	MEA 4	kz4	HEEDA extract in MTBE (0.06%)
475	Rtx-Amine 285	MEA 1	kali4	std 33
476	Rtx-Amine 286	MEA 4	kz3	DCM
477	Rtx-Amine 287	MEA 4	kz3	MEA in DCM
478	Rtx-Amine 288	MEA 4	kz3	HEEDA in DCM
479	Rtx-Amine 289	MEA 4	kz3	std 33
480	Rtx-Amine 290	MEA 4	kz3	MEA in DCM
481	Rtx-Amine 291	MEA 4	kz3	MEA in MTBE
482	Rtx-Amine 292	MEA 4	kz3	HEEDA in DCM
483	Rtx-Amine 293	MEA 4	kz3	HEEDA in MTBE
484	Rtx-Amine 294	MEA 4	kz3	MEA in MTBE - 2nd pre
485	Rtx-Amine 295	MEA 4	kz3	HEEDA in MTBE - 2nd prep
486	Rtx-Amine 296	MEA 4	kz3	MTBE
487	Rtx-Amine 297	MEA 4	kz3	HEEDA in MTBE - 3rd
488	Rtx-Amine 298	MEA 4	kz3	MTBE
489	Rtx-Amine 299	MEA 4	kz3	MEA in MTBE - 3rd
490	Rtx-Amine 300	MEA 4	kz3	HEEDA in MTBE - 4th
491	Rtx-Amine 301	MEA 4	kz3	diethylether
492	Rtx-Amine 302	MEA 4	kz3	MEA in diethylether 1

	File Name	MS Method	GC Method	Sample ID
493	Rtx-Amine 303	MEA 4	kz3	HEEDA in diethylether 1
494	Rtx-Amine 304	MEA 4	kz3	ETHER
495	Rtx-Amine 305	MEA 4	kz3	std 49 ---- MEA
496	Rtx-Amine 306	MEA 4	kz3	std 48
497	Rtx-Amine 307	MEA 4	kz3	std 47
498	Rtx-Amine 308	MEA 4	kz3	std 46
499	Rtx-Amine 309	MEA 4	kz3	std 45
500	Rtx-Amine 310	MEA 4	kz3	std 44
501	Rtx-Amine 311	MEA 4	kz3	std 43
502	Rtx-Amine 312	MEA 4	kz3	diethylether
503	Rtx-Amine 313	MEA 4	kz3	MEA in diethylether
504	Rtx-Amine 314	MEA 4	kz3	HEEDA in diethylether
505	Rtx-Amine 315	MEA 4	kz3	ETHER
506	Rtx-Amine 316	MEA 4	kz3	std 56 ---- HEEDA
507	Rtx-Amine 317	MEA 4	kz3	std 55
508	Rtx-Amine 318	MEA 4	kz3	std 54
509	Rtx-Amine 319	MEA 4	kz3	std 53
510	Rtx-Amine 320	MEA 4	kz3	std 52
511	Rtx-Amine 321	MEA 4	kz3	std 51
512	Rtx-Amine 322	MEA 4	kz3	std 50
513	Rtx-Amine 323	MEA 4	kz3	sample #57 - HEIA in ETHER
514	Rtx-Amine 324	MEA 4	kz3	sample #58 - OXAZ in ETHER
515	Rtx-Amine 325	MEA 4	kz3	sample #59 - HEIA in DCM
516	Rtx-Amine 326	MEA 4	kz3	sample #60 - HEIA neat - from the bottle
517	Rtx-Amine 327	MEA 4	kz3	#61 - HEIA (neat) + ETHER
518	Rtx-Amine 328	MEA 4	kz3	#62 - HEIA (neat) + MTBE
519	Rtx-Amine 329	MEA 4	kz3	#63 - HEIA - 10um + 2ml ETHER
520	Rtx-Amine 330	MEA 4	kz3	Ether
521	Rtx-Amine 331	MEA 4	kz3	0.06% Oxazol in ether 1st extraction
522	Rtx-Amine 332	MEA 4	kz3	0.06% HEIA in ether 1st extraction
523	Rtx-Amine 333	MEA 4	kz3	Ether
524	Rtx-Amine 334	MEA 4	kz3	0.06% Oxazol in ether 2 extraction
525	Rtx-Amine 335	MEA 4	kz3	0.06% HEIA in ether 2 extraction
526	Rtx-Amine 336	MEA 4	kz3	Ether
527	Rtx-Amine 337	MEA 4	kz3	0.06% Oxazol in ether 2nd extraction same sample
528	Rtx-Amine 338	MEA 4	kz3	0.06% HEIA in ether 2nd extraction same sample
529	Rtx-Amine 339	MEA 4	kz3	ether
530	Rtx-Amine 340	MEA 4	kz3	std 70
531	Rtx-Amine 341	MEA 4	kz3	std 69
532	Rtx-Amine 342	MEA 4	kz3	std 68
533	Rtx-Amine 343	MEA 4	kz3	std 67

	File Name	MS Method	GC Method	Sample ID
534	Rtx-Amine 344	MEA 4	kz3	std 66
535	Rtx-Amine 345	MEA 4	kz3	std 65
536	Rtx-Amine 346	MEA 4	kz3	std 64
537	Rtx-Amine 347	MEA 4	kz3	#63 repeat - see above
538	Rtx-Amine 348	MEA 4	kz3	0.06% HEIA in ether 1st extraction - repeat
539	Rtx-Amine 349	MEA 4	kz3	#63 repeat - see above - after shaking vial
540	Rtx-Amine 350	MEA 4	kz3	std 70 - after shaking
541	Rtx-Amine 351	MEA 4	kz3	std 69 - after shaking
542	Rtx-Amine 352	MEA 4	kz3	std 68 - after shaking
543	Rtx-Amine 353	MEA 4	kz3	std 67 - after shaking
544	Rtx-Amine 354	MEA 4	kz3	ether
545	Rtx-Amine 355	MEA 4	kz3	std 77 - oxozolidone
546	Rtx-Amine 356	MEA 4	kz3	std 76
547	Rtx-Amine 357	MEA 4	kz3	std 75
548	Rtx-Amine 358	MEA 4	kz3	std 74
549	Rtx-Amine 359	MEA 4	kz3	std 73
550	Rtx-Amine 360	MEA 4	kz3	std 72
551	Rtx-Amine 361	MEA 4	kz3	std 71
552	Rtx-Amine 362	MEA 4	kz3	ether
553	Rtx-Amine 363	MEA 4	kz3	std 84 - HEIA - repeat
554	Rtx-Amine 364	MEA 4	kz3	std 83
555	Rtx-Amine 365	MEA 4	kz3	std 82
556	Rtx-Amine 366	MEA 4	kz3	std 81
557	Rtx-Amine 367	MEA 4	kz3	std 80
558	Rtx-Amine 368	MEA 4	kz3	std 79
559	Rtx-Amine 369	MEA 4	kz3	std 78
560	Rtx-Amine 370	MEA 4	kz3	Ether
561	Rtx-Amine 371	MEA 4	kz3	Degraded sample 8 weeks extr 1 bottle 1 50s/10e
562	Rtx-Amine 372	MEA 4	kz3	Degraded sample 8 weeks extr 1 bottle 2 50s/10e
563	Rtx-Amine 373	MEA 4	kz3	Ether
564	Rtx-Amine 374	MEA 4	kz3	Degraded sample 8 weeks extr 2 bottle 1 50s/10e
565	Rtx-Amine 375	MEA 4	kz3	Degraded sample 8 weeks extr 2 bottle 2 50s/10e
566	Rtx-Amine 376	MEA 4	kz3	Ether
567	Rtx-Amine 377	MEA 4	kz3	Degraded sample 2 weeks extr 1 bottle 1 50s/10e
568	Rtx-Amine 378	MEA 4	kz3	Degraded sample 3 weeks extr 1 bottle 2 50s/10e
569	Rtx-Amine 379	MEA 4	kz3	DCM
570	Rtx-Amine 380	MEA 4	kz3	DCM - repeat
571	Rtx-Amine 381	MEA 4	kz3	DCM - repeat1
572	Rtx-Amine 382	MEA 4	kz3	DCM - repeat2
573	Rtx-Amine 383	MEA 4	kz3	DCM - repeat3
574	Rtx-Amine 384	MEA 4	kz3	DCM - repeat4

	File Name	MS Method	GC Method	Sample ID
575	Rtx-Amine 385	MEA 4	kz3	Ether
576	Rtx-Amine 386	MEA 4	kz3	Degraded 2 weeks lean loading 10s/50e
577	Rtx-Amine 387	MEA 4	kz3	Ether
578	Rtx-Amine 388	MEA 4	kz3	Degraded 3 weeks lean loading 10s/50e
579	Rtx-Amine 389	MEA 4	kz3	Ether
580	Rtx-Amine 390	MEA 4	kz3	Degraded 8 weeks lean loading 10s/50e
581	Rtx-Amine 391	MEA 4	kz3	Ether
582	Rtx-Amine 392	MEA 4	kz3	Ether
583	Rtx-Amine 393	MEA 4	kz3	Ether1
584	Rtx-Amine 393	MEA 4	kz3	std 91
585	Rtx-Amine 394	MEA 4	kz3	std 90
586	Rtx-Amine 395	MEA 4	kz3	std 89
587	Rtx-Amine 396	MEA 4	kz3	std 88
588	Rtx-Amine 397	MEA 4	kz3	std 87
589	Rtx-Amine 398	MEA 4	kz3	std 86
590	Rtx-Amine 399	MEA 4	kz3	std 85
591	Rtx-Amine 400	MEA 4	kz3	Ether
592	Rtx-Amine 401	MEA 4	kz3	Degraded 2 weeks lean loading 25/25
593	Rtx-Amine 402	MEA 4	kz3	Ether
594	Rtx-Amine 403	MEA 4	kz3	Degraded 3 weeks lean loading 25/25
595	Rtx-Amine 404	MEA 4	kz3	Ether
596	Rtx-Amine 405	MEA 4	kz3	Degraded 8 weeks lean loading 25/25
597	Rtx-Amine 406	MEA 4	kz3	Ether
598	Rtx-Amine 407	MEA 4	kz3	Ether
599	Rtx-Amine 408	MEA 4	kz3	Degraded 2 weeks lean loading 25/25 2days
600	Rtx-Amine 409	MEA 4	kz3	Ether
601	Rtx-Amine 410	MEA 4	kz3	Degraded 3 weeks lean loading 25/25 2days
602	Rtx-Amine 411	MEA 4	kz3	Ether
603	Rtx-Amine 412	MEA 4	kz3	Degraded 8 weeks lean loading 25/25 2days
604	Rtx-Amine 413	MEA 4	kz3	Ether
605	Rtx-Amine 414	MEA 4	kz3	Ether
606	Rtx-Amine 415	MEA 4	kz3	Degraded 2 weeks lean loading 25/25 5days oe
607	Rtx-Amine 416	MEA 4	kz3	Ether
608	Rtx-Amine 417	MEA 4	kz3	Degraded 3 weeks lean loading 25/25 5days oe
609	Rtx-Amine 418	MEA 4	kz3	Ether
610	Rtx-Amine 419	MEA 4	kz3	Degraded 8 weeks lean loading 25/25 5days oe
611	Rtx-Amine 420	MEA 4	kz3	Ether
612	Rtx-Amine 421	MEA 4	kz3	Degraded 2 weeks lean loading 25/25 5days, 2e+1s
613	Rtx-Amine 422	MEA 4	kz3	Ether
614	Rtx-Amine 423	MEA 4	kz3	Degraded 3 weeks lean loading 25/25 5days, 2e+1s
615	Rtx-Amine 424	MEA 4	kz3	Ether

	File Name	MS Method	GC Method	Sample ID
616	Rtx-Amine 425	MEA 4	kz3	Degraded 8 weeks lean loading 25/25 5days, 2e+1s
617	Rtx-Amine 426	MEA 4	kz3	Ether
618	Rtx-Amine 427	MEA 4	kz3	Ether
619	Rtx-Amine 428	MEA 4	kz3	Degraded 2 weeks lean 25/25 5days,2.5e+0.5s
620	Rtx-Amine 429	MEA 4	kz3	Ether
621	Rtx-Amine 430	MEA 4	kz3	Degraded 3 weeks lean 25/25 5days, 2.5e+0.5s
622	Rtx-Amine 431	MEA 4	kz3	Ether
623	Rtx-Amine 432	MEA 4	kz3	Degraded 8 weeks lean 25/25 5days, 2.5e+0.5s
624	Rtx-Amine 433	MEA 4	kz3	Degraded 8 weeks lean 25/25 5days, 2.5e+0.6s
625	Rtx-Amine 433	MEA 4	kz3	std 91
626	Rtx-Amine 434	MEA 4	kz3	std 92
627	Rtx-Amine 435	MEA 4	kz3	ether
628	Rtx-Amine 436	MEA 4	kz3	ether
629	Rtx-Amine 437	MEA 4	kz3	std heeda
630	Rtx-Amine 438	MEA 4	kz3	oxazolidone
631	Rtx-Amine 439	MEA 4	kz3	oxazolidone
632	Rtx-Amine 440	MEA 4	kz3	oxazolidone1
633	Rtx-Amine 441	MEA 4	kz3	oxazolidone2
634	Rtx-Amine 442	MEA 4	kz3	Ether
635	Rtx-Amine 443	MEA 4	kz3	Std p.e.
636	Rtx-Amine 444	MEA 4	kz3	ether
637	Rtx-Amine 445	MEA 4	kz3	std 2e +1 s
638	Rtx-Amine 446	MEA 4	kz3	Ether
639	Rtx-Amine 447	MEA 4	kz3	Std p.e.
640	Rtx-Amine 448	MEA 4	kz3	ether
641	Rtx-Amine 449	MEA 4	kz3	std 2e +1 s
642	Rtx-Amine 450	MEA 4	kz3	Ether
643	Rtx-Amine 451	MEA 4	kz3	Std MEA HEIA p.e.
644	Rtx-Amine 452	MEA 4	kz3	Std MEA HEIA p.e.1
645	Rtx-Amine 452	MEA 4	kz3	ether
646	Rtx-Amine 453	MEA 4	kz3	std MEA HEIA 2e +1 s
647	Rtx-Amine 454	MEA 4	kz3	ether
648	Rtx-Amine 455	MEA 4	kz3	std MEA HEIA 2e +0.5 s +0.5 b
649	Rtx-Amine 456	MEA 4	kz3	ether
650	Rtx-Amine 457	MEA 4	kz3	std MEA HEIA 2.5e + 0.5 s
651	Rtx-Amine 458	MEA 4	kz3	ether
652	Rtx-Amine 459	MEA 4	kz3	std MEA ether
653	Rtx-Amine 460	MEA 4	kz3	ether
654	Rtx-Amine 461	MEA 4	kz3	std MEA 0.5 + 2.5e
655	Rtx-Amine 462	MEA 4	kz3	oxazolidone in ether
656	Rtx-Amine 463	MEA 4	kz3	oxazolidone in ether

	File Name	MS Method	GC Method	Sample ID
657	Rtx-Amine 464	MEA 4	kz3	oxazolidone in ether1
658	Rtx-Amine 465	MEA 4	kz3	oxazolidone in ether2
659	Rtx-Amine 466	MEA 4	kz3	oxazolidone in ether3
660	Rtx-Amine 467	MEA 4	kz3	oxazolidone in ether4
661	Rtx-Amine 468	MEA 4	kz3	oxazolidone in ether5
662	Rtx-Amine 469	MEA 4	kz3	ether
663	Rtx-Amine 470	MEA 4	kz3	2 w Rich 1+2
664	Rtx-Amine 471	MEA 4	kz3	3 w Rich 1+2
665	Rtx-Amine 472	MEA 4	kz3	8 w Rich 1+2
666	Rtx-Amine 473	MEA 4	kz3	std mea heia heeda oxazol
667	Rtx-Amine 474	MEA 4	kz3	oxazolidone in ether
668	Rtx-Amine 475	MEA 4	kz3	oxazolidone in ether
669	Rtx-Amine 476	MEA 4	kz3	Ether
670	Rtx-Amine 477	MEA 4	kz3	HEIA 1.25% ether
671	Rtx-Amine 478	MEA 4	kz3	HEIA 2.5% ether
672	Rtx-Amine 479	MEA 4	kz3	HEIA 5% ether
673	Rtx-Amine 480	MEA 4	kz3	HEIA 10% ether
674	Rtx-Amine 481	MEA 4	kz3	Ether
675	Rtx-Amine 482	MEA 4	kz3	HEIA 1.25% ether
676	Rtx-Amine 483	MEA 4	kz3	HEIA 2.5% ether
677	Rtx-Amine 484	MEA 4	kz3	HEIA 5% ether
678	Rtx-Amine 485	MEA 4	kz3	HEIA 10% ether
679	Rtx-Amine 486	MEA 4	kz3	ether
680	Rtx-Amine 487	MEA 4	kz3	HEIA 1.25% ether
681	Rtx-Amine 488	MEA 4	kz3	ether2
682	Rtx-Amine 489	MEA 4	kz3	HEIA 2.5% ether
683	Rtx-Amine 490	MEA 4	kz3	ether4
684	Rtx-Amine 491	MEA 4	kz3	HEIA 5% ether
685	Rtx-Amine 492	MEA 4	kz3	ether6
686	Rtx-Amine 493	MEA 4	kz3	HEIA 10% ether
687	Rtx-Amine 494	MEA 4	kz3	ether8
688	Rtx-Amine 495	MEA 4	kz3	ether
689	Rtx-Amine 496	MEA 4	kz3	HEIA 1.25% ether
690	Rtx-Amine 497	MEA 4	kz3	ether2
691	Rtx-Amine 498	MEA 4	kz3	HEIA 2.5% ether
692	Rtx-Amine 499	MEA 4	kz3	ether4
693	Rtx-Amine 500	MEA 4	kz3	HEIA 5% ether
694	Rtx-Amine 501	MEA 4	kz3	ether6
695	Rtx-Amine 502	MEA 4	kz3	HEIA 10% ether
696	Rtx-Amine 503	MEA 4	kz3	ether8
697	Rtx-Amine 504	MEA 4	kz3	ether1

	File Name	MS Method	GC Method	Sample ID
698	Rtx-Amine 505	MEA 4	kz3	ether1
699	Rtx-Amine 506	MEA 4	kz3	ether1
700	Rtx-Amine 507	MEA 4	kz3	HEIA 10%
701	Rtx-Amine 508	MEA 4	kz3	ether 1
702	Rtx-Amine 509	MEA 4	kz3	ether1
703	Rtx-Amine 510	MEA 4	kz3	ether1
704	Rtx-Amine 511	MEA 4	kz3	ether1
705	Rtx-Amine 512	MEA 4	kz3	ether1
706	Rtx-Amine 513	MEA 4	kz3	ether1
707	Rtx-Amine 514	MEA 4	kz3	HEIA 1.25%
708	Rtx-Amine 515	MEA 4	kz3	ether2
709	Rtx-Amine 516	MEA 4	kz3	ether2
710	Rtx-Amine 517	MEA 4	kz3	ether2
711	Rtx-Amine 518	MEA 4	kz3	ether2
712	Rtx-Amine 519	MEA 4	kz3	HEIA 2.5 %
713	Rtx-Amine 520	MEA 4	kz3	ether2
714	Rtx-Amine 521	MEA 4	kz3	ether2
715	Rtx-Amine 522	MEA 4	kz3	ether2
716	Rtx-Amine 523	MEA 4	kz3	ether2
717	Rtx-Amine 524	MEA 4	kz3	HEIA 5%
718	Rtx-Amine 525	MEA 4	kz3	ether2
719	Rtx-Amine 526	MEA 4	kz3	ether2
720	Rtx-Amine 527	MEA 4	kz3	ether2
721	Rtx-Amine 528	MEA 4	kz3	ether2
722	Rtx-Amine 529	MEA 4	kz3	ether1
723	Rtx-Amine 530	MEA 4	kz3	ether1
724	Rtx-Amine 531	MEA 4	kz3	ether1
725	Rtx-Amine 532	MEA 4	kz3	HEIA 10%
726	Rtx-Amine 533	MEA 4	kz3	ether 1
727	Rtx-Amine 534	MEA 4	kz3	ether1
728	Rtx-Amine 535	MEA 4	kz3	ether1
729	Rtx-Amine 536	MEA 4	kz3	ether1
730	Rtx-Amine 537	MEA 4	kz3	ether1
731	Rtx-Amine 538	MEA 4	kz3	ether1
732	Rtx-Amine 539	MEA 4	kz3	HEIA 1.25%
733	Rtx-Amine 540	MEA 4	kz3	ether2
734	Rtx-Amine 541	MEA 4	kz3	ether2
735	Rtx-Amine 542	MEA 4	kz3	ether2
736	Rtx-Amine 543	MEA 4	kz3	ether2
737	Rtx-Amine 544	MEA 4	kz3	HEIA 2.5 %
738	Rtx-Amine 545	MEA 4	kz3	ether2

	File Name	MS Method	GC Method	Sample ID
739	Rtx-Amine 546	MEA 4	kz3	ether2
740	Rtx-Amine 547	MEA 4	kz3	ether2
741	Rtx-Amine 548	MEA 4	kz3	ether2
742	Rtx-Amine 549	MEA 4	kz3	HEIA 5%
743	Rtx-Amine 550	MEA 4	kz3	ether2
744	Rtx-Amine 551	MEA 4	kz3	ether2
745	Rtx-Amine 552	MEA 4	kz3	ether2
746	Rtx-Amine 553	MEA 4	kz3	ether2
747	Rtx-Amine 554	MEA 4	kz3	ether7
748	Rtx-Amine 555	MEA 4	kz3	ether7
749	Rtx-Amine 556	MEA 4	kz3	8weeks rich 1/100
750	Rtx-Amine 557	MEA 4	kz3	ether7
751	Rtx-Amine 558	MEA 4	kz3	ether7
752	Rtx-Amine 559	MEA 4	kz3	ether7
753	Rtx-Amine 560	MEA 4	kz3	ether7
754	Rtx-Amine 561	MEA 4	kz3	ether7
755	Rtx-Amine 562	MEA 4	kz3	8 weeks rich
756	Rtx-Amine 563	MEA 4	kz3	ether8
757	Rtx-Amine 564	MEA 4	kz3	ether8
758	Rtx-Amine 565	MEA 4	kz3	ether8
759	Rtx-Amine 566	MEA 4	kz3	ether8
760	Rtx-Amine 567	MEA 4	kz3	ether8
761	Rtx-Amine 568	MEA 4	kz3	ether8
762	Rtx-Amine 569	MEA 4	kz3	ether7
763	Rtx-Amine 570	MEA 4	kz3	ether7
764	Rtx-Amine 571	MEA 4	kz3	8weeks rich 1/100
765	Rtx-Amine 572	MEA 4	kz3	ether7
766	Rtx-Amine 573	MEA 4	kz3	ether7
767	Rtx-Amine 574	MEA 4	kz3	ether7
768	Rtx-Amine 575	MEA 4	kz3	ether7
769	Rtx-Amine 576	MEA 4	kz3	ether7
770	Rtx-Amine 577	MEA 4	kz3	8 weeks rich
771	Rtx-Amine 578	MEA 4	kz3	ether8
772	Rtx-Amine 579	MEA 4	kz3	ether8
773	Rtx-Amine 580	MEA 4	kz3	ether8
774	Rtx-Amine 581	MEA 4	kz3	ether8
775	Rtx-Amine 582	MEA 4	kz3	ether8
776	Rtx-Amine 583	MEA 4	kz3	ether8
777	Rtx-Amine 584	MEA 4	kz3	8 weeks rich
778	Rtx-Amine 585	MEA 4	kz3	ether10
779	Rtx-Amine 586	MEA 4	kz3	dcm

	File Name	MS Method	GC Method	Sample ID
780	Rtx-Amine 587	MEA 4	kz3	ether 12
781	Rtx-Amine 588	MEA 4	kz3	ether 12
782	Rtx-Amine 589	MEA 4	kz3	ether 12
783	Rtx-Amine 590	MEA 4	kz3	ether 12
784	Rtx-Amine 591	MEA 4	kz3	ether 12
785	Rtx-Amine 592	MEA 4	kz3	ether 13
786	Rtx-Amine 593	MEA 4	kz3	ether 13
787	Rtx-Amine 594	MEA 4	kz3	ether 13
788	Rtx-Amine 595	MEA 4	kz3	ether 13
789	Rtx-Amine 596	MEA 4	kz3	ether 13
790	Rtx-Amine 597	MEA 4	kz3	ether 14
791	Rtx-Amine 598	MEA 4	kz3	piperazine 0.1% 1
792	Rtx-Amine 599	MEA 4	kz3	ether 16
793	Rtx-Amine 600	MEA 4	kz3	ether 17
794	Rtx-Amine 601	MEA 4	kz3	ether 18
795	Rtx-Amine 602	MEA 4	kz3	ether 19
796	Rtx-Amine 603	MEA 4	kz3	ether 20
797	Rtx-Amine 604	MEA 4	kz3	ether 21
798	Rtx-Amine 605	MEA 4	kz3	piperazine 0.5% 1
799	Rtx-Amine 606	MEA 4	kz3	ether 23
800	Rtx-Amine 607	MEA 4	kz3	ether 24
801	Rtx-Amine 608	MEA 4	kz3	ether 25
802	Rtx-Amine 609	MEA 4	kz3	ether 26
803	Rtx-Amine 610	MEA 4	kz3	ether 27
804	Rtx-Amine 611	MEA 4	kz3	piperazine 0.1% 2
805	Rtx-Amine 612	MEA 4	kz3	ether
806	Rtx-Amine 613	MEA 4	kz3	ether 30
807	Rtx-Amine 614	MEA 4	kz3	ether 31
808	Rtx-Amine 615	MEA 4	kz3	ether 32
809	Rtx-Amine 616	MEA 4	kz3	piperazine 0.5% 2
810	Rtx-Amine 617	MEA 4	kz3	oxazolidone in ether
811	Rtx-Amine 618	MEA 4	kz3	oxazolidone in ether
812	Rtx-Amine 619	MEA 4	kz3	ether
813	Rtx-Amine 620	MEA 4	kz3	MEA 1 calibration extr
814	Rtx-Amine 621	MEA 4	kz3	ether
815	Rtx-Amine 622	MEA 4	kz3	ehter
816	Rtx-Amine 623	MEA 4	kz3	MEA 2 calibration extr
817	Rtx-Amine 624	MEA 4	kz3	ether
818	Rtx-Amine 625	MEA 4	kz3	ehter
819	Rtx-Amine 626	MEA 4	kz3	ether
820	Rtx-Amine 627	MEA 4	kz3	MEA 3 calibration extr

	File Name	MS Method	GC Method	Sample ID
821	Rtx-Amine 628	MEA 4	kz3	ether
822	Rtx-Amine 629	MEA 4	kz3	ehter
823	Rtx-Amine 630	MEA 4	kz3	ether
824	Rtx-Amine 631	MEA 4	kz3	ehter
825	Rtx-Amine 632	MEA 4	kz3	MEA 4 calibration extr
826	Rtx-Amine 633	MEA 4	kz3	ehter
827	Rtx-Amine 634	MEA 4	kz3	ether
828	Rtx-Amine 635	MEA 4	kz3	ehter
829	Rtx-Amine 636	MEA 4	kz3	ether
830	Rtx-Amine 637	MEA 4	kz3	ether
831	Rtx-Amine 638	MEA 4	kz3	ether
832	Rtx-Amine 639	MEA 4	kz3	ehter
833	Rtx-Amine 640	MEA 4	kz3	MEA 1 calibration extr
834	Rtx-Amine 641	MEA 4	kz3	ether
835	Rtx-Amine 642	MEA 4	kz3	ehter
836	Rtx-Amine 643	MEA 4	kz3	MEA 2 calibration extr
837	Rtx-Amine 644	MEA 4	kz3	ether
838	Rtx-Amine 645	MEA 4	kz3	ehter
839	Rtx-Amine 646	MEA 4	kz3	ether
840	Rtx-Amine 647	MEA 4	kz3	MEA 3 calibration extr
841	Rtx-Amine 648	MEA 4	kz3	ether
842	Rtx-Amine 649	MEA 4	kz3	ehter
843	Rtx-Amine 650	MEA 4	kz3	ether
844	Rtx-Amine 651	MEA 4	kz3	ehter
845	Rtx-Amine 652	MEA 4	kz3	MEA 4 calibration extr
846	Rtx-Amine 653	MEA 4	kz3	ehter
847	Rtx-Amine 654	MEA 4	kz3	ether
848	Rtx-Amine 655	MEA 4	kz3	ehter

Appendix 1.6: GC Conditions – Final Set Up

GC conditions for the new system set up

Method: Kali

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\Kali.mth
   Printed by                          : Mathew     on:  26/07/2011  16:18:00
   Created by                          : Mathew     on:  15/07/2008  09:47:29
   Edited by                           : Mathew     on:  07/10/2008  14:25:49
   Number of Times Edited              : 3
   Number of Times Calibrated          : 0
   Description:  MEA analysis

Instrument Conditions


Instrument Control Method
   Instrument Name        : inst1
   Instrument Type        : PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time          : 0.00 min
   Run Time            : 38.57 min
   Sampling Rate       : 1.5625 pts/s

                     Channel A     Channel B
   ________________  ___________   ___________

   Signal Source     DetA          DetB
   Analog Output     INT           INT
   Attenuation       0             0
   Offset            5.0 mV        5.0 mV

Autosampler Method
   Syringe Capacity                      : 5.0 µL                Injection Volume              : 1.0 µL
   Injection Speed                       : Normal                Sample Pumps                  : 6
   Viscosity Delay                       : 0                     Wash/Waste Vial Set           : 1
   Pre-injection Solvent Washes          : 2                     Pre-injection Sample Washes   : 4
   Post-injection Solvent Washes (A)     : 4

Carriers Parameters
26/07/2011 16:18:00 Method: C:\TurboMass\Kali.PRO\ACQUDB\Kali.mth

   Carrier A control              : PFlow - He
   Column A length                : 30.00 m                      Diameter       : 250 µm
   Vacuum Compensation            : ON
   Split Flow                     : 200.0 mL/min
   Initial Setpoint               : 1.00 ML/MIN                  Initial Hold   : 999.00 min



   Auxiliary Pneumatics
      Number        Type          Setpoint
      _________   ______________  __________

      1           Press - PSIG    0.0 PSIG

Valve configuration and settings
   Valve 1    : SPLIT On                                         Valve 2    : NONE
   Valve 3    : VALVE Off                                        Valve 4    : NONE
   Valve 5    : NONE                                             Valve 6    : NONE

Detector Parameters
                     Detector A    Detector B
   ________________  ___________   ___________

   Detector          NONE          NONE
   Range             1             1
   Time Constant     200           200
   Autozero          ON            ON
   Polarity          ___________   ___________

Heated Zones
   Injector A:  PSSI
      Initial Setpoint       : 250°C                              Initial Hold     : 999.00 min

   Injector B:  NONE
      Setpoint     : OFF
```

```
26/07/2011 16:18:00 Method: C:\TurboMass\Kali.PRO\ACQUDB\Kali.mth

  Detector A              : 0°C
  Detector B              : 0°C
  Auxiliary (NONE)        : 0°C

Oven Program
  Cryogenics    : Off                                                         Total Run Time        : 38.57 min
  Initial Temp  : 40°C                                                        Maximum Temp          : 350°C
  Initial Hold  : 5.00 min                                                    Equilibration Time    : 0.5 min
     Ramp 1    : 7.0 0/min to 240°, hold for 5.00 min

Timed Events
  SPL1 set to 0 at -1.00 min
  SPL1 set to 50 at 1.00 min
```

Method: Kali1

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kali1.mth
   Printed by                          : Mathew     on:  26/07/2011  16:21:10
   Created by                          : Mathew     on:  07/10/2008  16:25:10
   Edited by                           : Mathew     on:  07/10/2008  16:26:50
   Number of Times Edited              : 1
   Number of Times Calibrated          : 0
   Description:  kali1

Instrument Conditions


Instrument Control Method
   Instrument Name        : inst1
   Instrument Type        : PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time          :  0.00 min
   Run Time            :  38.57 min
   Sampling Rate       :  1.5625 pts/s

                       Channel A      Channel B
   _________________   ____________   ____________

   Signal Source       DetA           DetB
   Analog Output       INT            INT
   Attenuation         0              0
   Offset              5.0 mV         5.0 mV

Autosampler Method
   Syringe Capacity                     : 5.0 µL          Injection Volume              : 1.0 µL
   Injection Speed                      : Normal          Sample Pumps                  : 6
   Viscosity Delay                      : 0               Wash/Waste Vial Set           : 1
   Pre-injection Solvent Washes         : 2               Pre-injection Sample Washes   : 4
   Post-injection Solvent Washes (A)    : 4

Carriers Parameters




26/07/2011 16:21:10 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali1.mth

   Carrier A control              : PFlow - He
   Column A length                : 30.00 m                  Diameter       : 250 µm
   Vacuum Compensation            : ON
   Split Flow                     : 20.0 mL/min
   Initial Setpoint               : 1.00 ML/MIN              Initial Hold   : 999.00 min



   Auxiliary Pneumatics
      Number       Type            Setpoint
      _________    _____________   __________

      1            Press - PSIG    0.0 PSIG

Valve configuration and settings
   Valve 1    : SPLIT On                                     Valve 2    : NONE
   Valve 3    : VALVE Off                                    Valve 4    : NONE
   Valve 5    : NONE                                         Valve 6    : NONE

Detector Parameters
                       Detector A     Detector B
   _________________   ____________   ____________

   Detector            NONE           NONE
   Range               1              1
   Time Constant       200            200
   Autozero            ON             ON
   Polarity            ____________   ____________

Heated Zones
   Injector A:  PSSI
      Initial Setpoint       : 250°C                          Initial Hold    : 999.00 min

   Injector B:  NONE
      Setpoint     : OFF
```

```
26/07/2011 16:21:10 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali1.mth

  Detector A              :  0°C
  Detector B              :  0°C
  Auxiliary (NONE)        :  0°C

Oven Program
  Cryogenics      :  Off                                          Total Run Time        :  38.57 min
  Initial Temp    :  40°C                                         Maximum Temp          :  350°C
  Initial Hold    :  5.00 min                                     Equilibration Time    :  0.5 min
     Ramp 1     :  7.0 0/min to 240°, hold for 5.00 min

Timed Events
  SPL1 set to 0 at -1.00 min
  SPL1 set to 20 at 1.00 min
```

Method: Kali2

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kali2.mth
  Printed by                        : Mathew     on: 26/07/2011  16:20:37
  Created by                        : Mathew     on: 08/10/2008  14:11:07
  Edited by                         : Mathew     on: 08/10/2008  15:48:11
  Number of Times Edited            : 1
  Number of Times Calibrated        : 0
  Description:  kali2

Instrument Conditions


Instrument Control Method
  Instrument Name        : inst1
  Instrument Type        : PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time          : 0.00 min
  Run Time            : 20.00 min
  Sampling Rate       : 1.5625 pts/s

                    Channel A     Channel B
  ________________  ___________   ___________

  Signal Source     DetA          DetB
  Analog Output     INT           INT
  Attenuation       0             0
  Offset            5.0 mV        5.0 mV

Autosampler Method
  Syringe Capacity                      : 5.0 µL              Injection Volume               : 1.0 µL
  Injection Speed                       : Normal              Sample Pumps                   : 6
  Viscosity Delay                       : 0                   Wash/Waste Vial Set            : 1
  Pre-injection Solvent Washes          : 2                   Pre-injection Sample Washes    : 4
  Post-injection Solvent Washes (A)     : 4

Carriers Parameters
26/07/2011 16:20:37 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali2.mth

  Carrier A control            : PFlow - He
  Column A length              : 30.00 m                      Diameter      : 250 µm
  Vacuum Compensation          : ON
  Split Flow                   : 73.0 mL/min
  Initial Setpoint             : 1.00 ML/MIN                  Initial Hold  : 999.00 min



  Auxiliary Pneumatics
    Number       Type           Setpoint
    _________    ____________   __________

    1            Press - PSIG   0.0 PSIG

Valve configuration and settings
  Valve 1   : SPLIT On                                        Valve 2   : NONE
  Valve 3   : VALVE Off                                       Valve 4   : NONE
  Valve 5   : NONE                                            Valve 6   : NONE

Detector Parameters
                    Detector A    Detector B
  ________________  ___________   ___________

  Detector          NONE          NONE
  Range             1             1
  Time Constant     200           200
  Autozero          ON            ON
  Polarity          ___________   ___________

Heated Zones
  Injector A:  PSSI
    Initial Setpoint      : 250°C                              Initial Hold     : 999.00 min

  Injector B:  NONE
    Setpoint     : OFF
```

```
26/07/2011 16:20:37 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali2.mth

  Detector A           : 0°C
  Detector B           : 0°C
  Auxiliary (NONE)     : 0°C

Oven Program
  Cryogenics     : Off                                        Total Run Time      : 20.00 min
  Initial Temp   : 100°C                                      Maximum Temp        : 350°C
  Initial Hold   : 1.00 min                                   Equilibration Time  : 0.5 min
     Ramp 1    : 10.0 0/min to 240°, hold for 5.00 min

Timed Events
  SPL1 set to 0 at -1.00 min
  SPL1 set to 73 at 1.00 min
```

Method: Kali3

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kali3.mth
  Printed by                         : Mathew      on:  26/07/2011  16:20:10
  Created by                         : Mathew      on:  08/10/2008  16:29:27
  Edited by                          : Mathew      on:  08/10/2008  16:29:27
  Number of Times Edited             : 0
  Number of Times Calibrated         : 0
  Description:  kali3

Instrument Conditions


Instrument Control Method
  Instrument Name        : inst1
  Instrument Type        : PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time          :  0.00 min
  Run Time            :  34.00 min
  Sampling Rate       :  1.5625 pts/s

                      Channel A       Channel B
  ________________    ____________    ____________

  Signal Source       DetA            DetB
  Analog Output       INT             INT
  Attenuation         0               0
  Offset              5.0 mV          5.0 mV

Autosampler Method
  Syringe Capacity                    : 5.0 µL                  Injection Volume                  : 1.0 µL
  Injection Speed                     : Normal                  Sample Pumps                      : 6
  Viscosity Delay                     : 0                       Wash/Waste Vial Set               : 1
  Pre-injection Solvent Washes        : 2                       Pre-injection Sample Washes       : 4
  Post-injection Solvent Washes (A)   : 4

Carriers Parameters



26/07/2011 16:20:10 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali3.mth

  Carrier A control             : PFlow - He
  Column A length               : 30.00 m                       Diameter       : 250 µm
  Vacuum Compensation           : ON
  Split Flow                    : 10.3 mL/min
  Initial Setpoint              : 1.00 ML/MIN                   Initial Hold   : 999.00 min



  Auxiliary Pneumatics
    Number       Type            Setpoint
    _________    _____________   __________

    1            Press - PSIG    0.0 PSIG

Valve configuration and settings
  Valve 1   : SPLIT On                                          Valve 2   : NONE
  Valve 3   : VALVE Off                                         Valve 4   : NONE
  Valve 5   : NONE                                              Valve 6   : NONE

Detector Parameters
                      Detector A      Detector B
  ________________    ____________    ____________

  Detector            NONE            NONE
  Range               1               1
  Time Constant       200             200
  Autozero            ON              ON
  Polarity            ____________    ____________

Heated Zones
  Injector A:  PSSI
    Initial Setpoint     : 250°C                                 Initial Hold     : 999.00 min

  Injector B:  NONE
    Setpoint     : OFF
```

```
  Detector A            :  0°C
  Detector B            :  0°C
  Auxiliary (NONE)      :  0°C

Oven Program
  Cryogenics      :  Off                                         Total Run Time        :  34.00 min
  Initial Temp    :  100°C                                       Maximum Temp          :  350°C
  Initial Hold    :  10.00 min                                   Equilibration Time    :  0.5 min
     Ramp 1    :  10.0 0/min to 240°, hold for 10.00 min

Timed Events
  SPL1 set to 20 at 1.00 min
```

Method: Kali4

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kali4.mth
   Printed by                      : Mathew     on: 26/07/2011  16:19:33
   Created by                      : Mathew     on: 08/10/2008  16:42:19
   Edited by                       : Mathew     on: 08/10/2008  16:42:19
   Number of Times Edited          : 0
   Number of Times Calibrated      : 0
   Description:  kali4
```

```
Instrument Conditions


Instrument Control Method
   Instrument Name       : inst1
   Instrument Type       : PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time        : 0.00 min
   Run Time          : 75.00 min
   Sampling Rate     : 1.5625 pts/s

                      Channel A     Channel B
   ________________  ___________   ___________

   Signal Source      DetA          DetB
   Analog Output      INT           INT
   Attenuation        0             0
   Offset             5.0 mV        5.0 mV

Autosampler Method
   Syringe Capacity                    : 5.0 µL          Injection Volume               : 1.0 µL
   Injection Speed                     : Normal          Sample Pumps                   : 6
   Viscosity Delay                     : 0               Wash/Waste Vial Set            : 1
   Pre-injection Solvent Washes        : 2               Pre-injection Sample Washes    : 4
   Post-injection Solvent Washes (A)   : 4

Carriers Parameters
26/07/2011 16:19:33 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali4.mth

   Carrier A control          : PFlow - He
   Column A length            : 30.00 m                  Diameter       : 250 µm
   Vacuum Compensation        : ON
   Split Flow                 : 30.0 mL/min
   Initial Setpoint           : 1.00 ML/MIN              Initial Hold   : 999.00 min



   Auxiliary Pneumatics
     Number       Type          Setpoint
     ________   ____________   _________

     1          Press - PSIG    0.0 PSIG

Valve configuration and settings
   Valve 1    : SPLIT On                                 Valve 2    : NONE
   Valve 3    : VALVE Off                                Valve 4    : NONE
   Valve 5    : NONE                                     Valve 6    : NONE

Detector Parameters
                      Detector A    Detector B
   ________________  ___________   ___________

   Detector           NONE          NONE
   Range              1             1
   Time Constant      200           200
   Autozero           ON            ON
   Polarity          ___________   ___________

Heated Zones
   Injector A:  PSSI
     Initial Setpoint      : 250°C                        Initial Hold    : 999.00 min

   Injector B:  NONE
     Setpoint     : OFF
```

```
   Detector A             :  0°C
   Detector B             :  0°C
   Auxiliary (NONE)       :  0°C

Oven Program
   Cryogenics      :  Off                                                        Total Run Time        :  75.00 min
   Initial Temp    :  100°C                                                      Maximum Temp          :  350°C
   Initial Hold    :  10.00 min                                                  Equilibration Time    :  0.5 min
      Ramp 1    :  7.0 0/min to 240°, hold for 45.00 min

Timed Events
   SPL1 set to 20 at 1.00 min
```

Method: Kali5

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kali5.mth
  Printed by                       : Mathew     on: 26/07/2011  16:18:58
  Created by                       : Mathew     on: 10/10/2008  14:32:17
  Edited by                        : Mathew     on: 10/10/2008  14:32:17
  Number of Times Edited           : 0
  Number of Times Calibrated       : 0
  Description: kali5

Instrument Conditions


Instrument Control Method
  Instrument Name       : inst1
  Instrument Type       : PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time         : 0.00 min
  Run Time           : 17.00 min
  Sampling Rate      : 1.5625 pts/s

                     Channel A      Channel B
  ________________   ____________   ____________

  Signal Source      DetA           DetB
  Analog Output      INT            INT
  Attenuation        0              0
  Offset             5.0 mV         5.0 mV

Autosampler Method
  Syringe Capacity                       : 5.0 µL        Injection Volume               : 1.0 µL
  Injection Speed                        : Normal        Sample Pumps                   : 6
  Viscosity Delay                        : 0             Wash/Waste Vial Set            : 1
  Pre-injection Solvent Washes           : 0             Pre-injection Sample Washes    : 2
  Post-injection Solvent Washes (A)      : 2

Carriers Parameters
26/07/2011 16:18:58 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali5.mth

  Carrier A control          : PFlow - He
  Column A length            : 30.00 m                      Diameter      : 250 µm
  Vacuum Compensation        : ON
  Split Flow                 : 58.0 mL/min
  Initial Setpoint           : 1.00 ML/MIN                  Initial Hold  : 999.00 min



  Auxiliary Pneumatics
    Number      Type            Setpoint
    _________   _____________   __________

    1           Press - PSIG    0.0 PSIG

Valve configuration and settings
  Valve 1   : SPLIT On                                      Valve 2   : NONE
  Valve 3   : VALVE Off                                     Valve 4   : NONE
  Valve 5   : NONE                                          Valve 6   : NONE

Detector Parameters
                     Detector A     Detector B
  ________________   ____________   ____________

  Detector           NONE           NONE
  Range              1              1
  Time Constant      200            200
  Autozero           ON             ON
  Polarity           ____________   ____________

Heated Zones
  Injector A: PSSI
    Initial Setpoint     : 250°C                            Initial Hold     : 999.00 min

  Injector B: NONE
    Setpoint     : OFF
```

```
26/07/2011 16:18:58 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali5.mth

   Detector A              :  0°C
   Detector B              :  0°C
   Auxiliary (NONE)        :  0°C

Oven Program
   Cryogenics      :  Off                                              Total Run Time          :  17.00 min
   Initial Temp    :  50°C                                             Maximum Temp            :  350°C
   Initial Hold    :  2.00 min                                         Equilibration Time      :  2.0 min
      Ramp 1     :  10.0 0/min to 180°, hold for 2.00 min

Timed Events
   There are no timed events in the method
```

Method: Kali6

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kali6.mth
  Printed by                     : Mathew      on:  26/07/2011  16:18:32
  Created by                     : Mathew      on:  10/10/2008  14:58:58
  Edited by                      : Mathew      on:  10/10/2008  14:58:58
  Number of Times Edited         : 0
  Number of Times Calibrated     : 0
  Description:  kali6

Instrument Conditions


Instrument Control Method
  Instrument Name      : inst1
  Instrument Type      : PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time         : 0.00 min
  Run Time           : 17.83 min
  Sampling Rate      : 1.5625 pts/s

                       Channel A     Channel B
  ________________   ___________   ___________

  Signal Source        DetA          DetB
  Analog Output        INT           INT
  Attenuation          0             0
  Offset               5.0 mV        5.0 mV

Autosampler Method
  Syringe Capacity                      : 5.0 µL              Injection Volume                   : 1.0 µL
  Injection Speed                       : Normal              Sample Pumps                       : 6
  Viscosity Delay                       : 0                   Wash/Waste Vial Set                : 1
  Pre-injection Solvent Washes          : 0                   Pre-injection Sample Washes        : 2
  Post-injection Solvent Washes (A)     : 2

Carriers Parameters
26/07/2011 16:18:32 Method: C:\TurboMass\Kali.PRO\ACQUDB\kali6.mth

  Carrier A control               : PFlow - He
  Column A length                 : 30.00 m                        Diameter        : 250 µm
  Vacuum Compensation             : ON
  Split Flow                      : 10.0 mL/min
  Initial Setpoint                : 1.00 ML/MIN                    Initial Hold    : 999.00 min



  Auxiliary Pneumatics
    Number       Type            Setpoint
    ________   ______________   __________

    1          Press - PSIG     0.0 PSIG

Valve configuration and settings
  Valve 1    : SPLIT On                                            Valve 2    : NONE
  Valve 3    : VALVE Off                                           Valve 4    : NONE
  Valve 5    : NONE                                                Valve 6    : NONE

Detector Parameters
                       Detector A     Detector B
  ________________   ____________   ____________

  Detector             NONE           NONE
  Range                1              1
  Time Constant        200            200
  Autozero             ON             ON
  Polarity           ____________   ____________

Heated Zones
  Injector A:  PSSI
    Initial Setpoint     : 250°C                                    Initial Hold     : 999.00 min

  Injector B:  NONE
    Setpoint     : OFF
```

Detector A : 0°C
Detector B : 0°C
Auxiliary (NONE) : 0°C

Oven Program

Cryogenics : Off
Initial Temp : 50°C
Initial Hold : 0.50 min
Ramp 1 : 15.0 0/min to 280°, hold for 2.00 min

Total Run Time : 17.83 min
Maximum Temp : 350°C
Equilibration Time : 2.0 min

Timed Events

There are no timed events in the method

Method: KZ1

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kz1.mth
  Printed by                          : Mathew     on:  26/07/2011  16:17:24
  Created by                          : Mathew     on:  15/04/2010  10:40:18
  Edited by                           : Mathew     on:  11/05/2010  16:43:06
  Number of Times Edited              : 6
  Number of Times Calibrated          : 0
  Description:  kz2

Instrument Conditions


Instrument Control Method
  Instrument Name        :  inst1
  Instrument Type        :  PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time          :  0.00 min
  Run Time            :  14.50 min
  Sampling Rate       :  1.5625 pts/s

                       Channel A      Channel B
  _______________     ___________    ___________

  Signal Source        DetA           DetB
  Analog Output        INT            INT
  Attenuation          0              0
  Offset               5.0 mV         5.0 mV

Autosampler Method
  Syringe Capacity                    : 5.0 µL                    Injection Volume                  : 1.0 µL
  Injection Speed                     : Normal                    Sample Pumps                      : 6
  Viscosity Delay                     : 0                         Wash/Waste Vial Set               : 1
  Pre-injection Solvent Washes        : 2                         Pre-injection Sample Washes       : 4
  Post-injection Solvent Washes (A)   : 4

Carriers Parameters
26/07/2011 16:17:24 Method: C:\TurboMass\Kali.PRO\ACQUDB\kz1.mth

  Carrier A control            : PFlow - He
  Column A length              : 30.00 m                          Diameter       : 250 µm
  Vacuum Compensation          : ON
  Split Flow                   : 100.0 mL/min
  Initial Setpoint             : 1.00 ML/MIN                      Initial Hold   : 999.00 min



  Auxiliary Pneumatics
    Number         Type           Setpoint
    _________    ______________   __________

    1            Press - PSIG     0.0 PSIG

Valve configuration and settings
  Valve 1    :  SPLIT On                                          Valve 2    :  NONE
  Valve 3    :  VALVE Off                                         Valve 4    :  NONE
  Valve 5    :  NONE                                              Valve 6    :  NONE

Detector Parameters
                       Detector A     Detector B
  _______________     ___________    ___________

  Detector             NONE           NONE
  Range                1              1
  Time Constant        200            200
  Autozero             ON             ON
  Polarity             ___________    ___________

Heated Zones
  Injector A:  PSSI
    Initial Setpoint     :  250°C                                  Initial Hold     :  999.00 min

  Injector B:  NONE
    Setpoint     :  OFF
```

```
26/07/2011 16:17:24 Method: C:\TurboMass\Kali.PRO\ACQUDB\kz1.mth

   Detector A             :  0°C
   Detector B             :  0°C
   Auxiliary (NONE)       :  0°C

Oven Program
   Cryogenics      :  Off                                                                   Total Run Time        :  14.50 min
   Initial Temp    :  50°C                                                                  Maximum Temp          :  350°C
   Initial Hold    :  0.50 min                                                              Equilibration Time    :  0.5 min
      Ramp 1     :  20.0 0/min to 320°, hold for 0.50 min

Timed Events
   SPL1 set to 0 at -1.00 min
   SPL1 set to 20 at 1.00 min
```

Method: KZ2

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kz2.mth
  Printed by                    : Mathew    on: 26/07/2011  16:16:52
  Created by                    : Mathew    on: 14/05/2010  12:13:16
  Edited by                     : Mathew    on: 14/05/2010  12:13:16
  Number of Times Edited        : 0
  Number of Times Calibrated    : 0
  Description: kz2

Instrument Conditions


Instrument Control Method
  Instrument Name      : inst1
  Instrument Type      : PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time         : 0.00 min
  Run Time           : 16.33 min
  Sampling Rate      : 1.5625 pts/s

                     Channel A     Channel B
  _______________    ___________   ___________

  Signal Source      DetA          DetB
  Analog Output      INT           INT
  Attenuation        0             0
  Offset             5.0 mV        5.0 mV

Autosampler Method
  Syringe Capacity                  : 5.0 µL          Injection Volume              : 1.0 µL
  Injection Speed                   : Normal          Sample Pumps                  : 6
  Viscosity Delay                   : 0               Wash/Waste Vial Set           : 1
  Pre-injection Solvent Washes      : 2               Pre-injection Sample Washes   : 4
  Post-injection Solvent Washes (A) : 4

Carriers Parameters
26/07/2011 16:16:52 Method: C:\TurboMass\Kali.PRO\ACQUDB\kz2.mth

  Carrier A control          : PFlow - He
  Column A length            : 30.00 m              Diameter      : 250 µm
  Vacuum Compensation        : ON
  Split Flow                 : 50.0 mL/min
  Initial Setpoint           : 1.00 ML/MIN          Initial Hold  : 999.00 min



  Auxiliary Pneumatics
    Number       Type           Setpoint
    ________     ____________   _________

    1            Press - PSIG   0.0 PSIG

Valve configuration and settings
  Valve 1   : SPLIT On                               Valve 2   : NONE
  Valve 3   : VALVE Off                              Valve 4   : NONE
  Valve 5   : NONE                                   Valve 6   : NONE

Detector Parameters
                     Detector A    Detector B
  _______________    ___________   ___________

  Detector           NONE          NONE
  Range              1             1
  Time Constant      200           200
  Autozero           ON            ON
  Polarity           ___________   ___________

Heated Zones
  Injector A:  PSSI
    Initial Setpoint    : 300°C                       Initial Hold    : 999.00 min

  Injector B:  NONE
    Setpoint    : OFF
```

```
26/07/2011 16:16:52 Method: C:\TurboMass\Kali.PRO\ACQUDB\kz2.mth

  Detector A          : 0°C
  Detector B          : 0°C
  Auxiliary (NONE)    : 0°C

Oven Program
  Cryogenics     : Off                                             Total Run Time       : 16.33 min
  Initial Temp   : 50°C                                            Maximum Temp         : 350°C
  Initial Hold   : 0.50 min                                        Equilibration Time   : 2.0 min
     Ramp 1    : 15.0 0/min to 280°, hold for 0.50 min

Timed Events
  SPL1 set to 0 at -1.00 min
  SPL1 set to 20 at 1.00 min
```

Method: KZ3

```
Turbochrom Method File C:\TURBOMASS\KALI.PRO\ACQUDB\kz3.mth
   Printed by                        : Mathew     on:  26/07/2011  16:12:18
   Created by                        : Mathew     on:  14/05/2010  14:47:57
   Edited by                         : Mathew     on:  22/02/2011  15:14:59
   Number of Times Edited            : 6
   Number of Times Calibrated        : 0
   Description:  kz3_2

Instrument Conditions


Instrument Control Method
   Instrument Name       :  inst1
   Instrument Type       :  PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time         :  0.00 min
   Run Time           :  14.50 min
   Sampling Rate      :  1.5625 pts/s

                    Channel A    Channel B
   ______________   __________   __________

   Signal Source    DetA         DetB
   Analog Output    INT          INT
   Attenuation      0            0
   Offset           5.0 mV       5.0 mV

Autosampler Method
   Syringe Capacity                     :  5.0 µL           Injection Volume              :  1.0 µL
   Injection Speed                      :  Normal           Sample Pumps                  :  6
   Viscosity Delay                      :  0                Wash/Waste Vial Set           :  1
   Pre-injection Solvent Washes         :  2                Pre-injection Sample Washes   :  4
   Post-injection Solvent Washes (A)    :  4

Carriers Parameters
26/07/2011 16:12:18 Method: C:\TURBOMASS\KALI.PRO\ACQUDB\kz3.mth

   Carrier A control          :  PFlow - He
   Column A length            :  30.00 m                    Diameter       :  250 µm
   Vacuum Compensation        :  ON
   Split Flow                 :  100.0 mL/min
   Initial Setpoint           :  1.00 ML/MIN                Initial Hold   :  999.00 min



   Auxiliary Pneumatics
      Number        Type          Setpoint
      _______    ____________    _________

      1          Press - PSIG    0.0 PSIG

Valve configuration and settings
   Valve 1    :  SPLIT On                                   Valve 2   :  NONE
   Valve 3    :  VALVE Off                                  Valve 4   :  NONE
   Valve 5    :  NONE                                       Valve 6   :  NONE

Detector Parameters
                    Detector A   Detector B
   ______________   __________   __________

   Detector         NONE         NONE
   Range            1            1
   Time Constant    200          200
   Autozero         ON           ON
   Polarity         __________   __________

Heated Zones
   Injector A:  PSSI
      Initial Setpoint      :  250°C                         Initial Hold     :  999.00 min

   Injector B:  NONE
      Setpoint    :  OFF
```

```
26/07/2011 16:12:18 Method: C:\TURBOMASS\KALI.PRO\ACQUDB\kz3.mth

   Detector A             :  0°C
   Detector B             :  0°C
   Auxiliary (NONE)       :  0°C

Oven Program
   Cryogenics     :  Off                                                   Total Run Time        :  14.50 min
   Initial Temp   :  50°C                                                  Maximum Temp          :  350°C
   Initial Hold   :  0.50 min                                              Equilibration Time    :  2.0 min
      Ramp 1    :  20.0 0/min to 320°, hold for 0.50 min

Timed Events
   SPL1 set to 0 at -1.00 min
   SPL1 set to 20 at 1.00 min
```

Method: KZ4

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\kz4.mth
  Printed by                    : Mathew    on: 26/07/2011  16:16:12
  Created by                    : Mathew    on: 20/05/2010  13:47:02
  Edited by                     : Mathew    on: 20/05/2010  13:47:02
  Number of Times Edited        : 0
  Number of Times Calibrated    : 0
  Description: kz4

Instrument Conditions


Instrument Control Method
  Instrument Name     : inst1
  Instrument Type     : PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time        : 0.00 min
  Run Time          : 16.33 min
  Sampling Rate     : 1.5625 pts/s

                    Channel A     Channel B
  ________________  ____________  ____________

  Signal Source     DetA          DetB
  Analog Output     INT           INT
  Attenuation       0             0
  Offset            5.0 mV        5.0 mV

Autosampler Method
  Syringe Capacity                  : 5.0 µL       Injection Volume               : 1.0 µL
  Injection Speed                   : Normal       Sample Pumps                   : 6
  Viscosity Delay                   : 0            Wash/Waste Vial Set            : 1
  Pre-injection Solvent Washes      : 2            Pre-injection Sample Washes    : 4
  Post-injection Solvent Washes (A) : 4

Carriers Parameters
26/07/2011 16:16:12 Method: C:\TurboMass\Kali.PRO\ACQUDB\kz4.mth

  Carrier A control          : PFlow - He
  Column A length            : 30.00 m              Diameter      : 250 µm
  Vacuum Compensation        : ON
  Split Flow                 : 10.0 mL/min
  Initial Setpoint           : 1.00 ML/MIN          Initial Hold  : 999.00 min



  Auxiliary Pneumatics
    Number      Type          Setpoint
    ________    __________    ________

    1           Press - PSIG  0.0 PSIG

Valve configuration and settings
  Valve 1   : SPLIT On                              Valve 2   : NONE
  Valve 3   : VALVE Off                             Valve 4   : NONE
  Valve 5   : NONE                                  Valve 6   : NONE

Detector Parameters
                    Detector A    Detector B
  ________________  ____________  ____________

  Detector          NONE          NONE
  Range             1             1
  Time Constant     200           200
  Autozero          ON            ON
  Polarity          ____________  ____________

Heated Zones
  Injector A:  PSSI
    Initial Setpoint     : 300°C                          Initial Hold     : 999.00 min

  Injector B:  NONE
    Setpoint     : OFF
```

```
26/07/2011 16:16:12 Method: C:\TurboMass\Kali.PRO\ACQUDB\kz4.mth

  Detector A              :  0°C
  Detector B              :  0°C
  Auxiliary (NONE)        :  0°C

Oven Program
  Cryogenics      :  Off                                              Total Run Time          :  16.33 min
  Initial Temp    :  50°C                                             Maximum Temp            :  350°C
  Initial Hold    :  0.50 min                                         Equilibration Time      :  2.0 min
     Ramp 1    :  15.0 0/min to 280°, hold for 0.50 min

Timed Events
  SPL1 set to 0 at -1.00 min
  SPL1 set to 20 at 1.00 min
```

Method: MEA1.100

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\MEA 1.100.mth
   Printed by                        : Mathew    on: 26/07/2011  16:15:34
   Created by                        : Mathew    on: 26/02/2009  15:21:41
   Edited by                         : Mathew    on: 26/02/2009  15:21:41
   Number of Times Edited            : 0
   Number of Times Calibrated        : 0
   Description:  MEA 1.100

Instrument Conditions


Instrument Control Method
   Instrument Name       : inst1
   Instrument Type       : PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time         : 0.00 min
   Run Time           : 38.57 min
   Sampling Rate      : 1.5625 pts/s

                      Channel A     Channel B
   _______________    __________    __________

   Signal Source      DetA          DetB
   Analog Output      INT           INT
   Attenuation        0             0
   Offset             5.0 mV        5.0 mV

Autosampler Method
   Syringe Capacity                  : 5.0 µL        Injection Volume              : 1.0 µL
   Injection Speed                   : Normal        Sample Pumps                  : 6
   Viscosity Delay                   : 0             Wash/Waste Vial Set           : 1
   Pre-injection Solvent Washes      : 0             Pre-injection Sample Washes   : 2
   Post-injection Solvent Washes (A) : 2

Carriers Parameters


26/07/2011 16:15:34 Method: C:\TurboMass\Kali.PRO\ACQUDB\MEA 1.100.mth

   Carrier A control        : PFlow - He
   Column A length          : 30.00 m                Diameter       : 250 µm
   Vacuum Compensation      : ON
   Split Flow               : 100.0 mL/min
   Initial Setpoint         : 1.00 ML/MIN            Initial Hold   : 999.00 min



   Auxiliary Pneumatics
      Number     Type          Setpoint
      ________   ___________   _________

      1          Press - PSIG  0.0 PSIG

Valve configuration and settings
   Valve 1   : SPLIT On                              Valve 2   : NONE
   Valve 3   : VALVE Off                             Valve 4   : NONE
   Valve 5   : NONE                                  Valve 6   : NONE

Detector Parameters
                      Detector A    Detector B
   _______________    __________    __________

   Detector           NONE          NONE
   Range              1             1
   Time Constant      200           200
   Autozero           ON            ON
   Polarity           __________    __________

Heated Zones
   Injector A:  PSSI
      Initial Setpoint     : 250°C                    Initial Hold    : 999.00 min

   Injector B:  NONE
      Setpoint    : OFF
```

```
26/07/2011 16:15:34 Method: C:\TurboMass\Kali.PRO\ACQUDB\MEA 1.100.mth

  Detector A          :  0°C
  Detector B          :  0°C
  Auxiliary (NONE)    :  0°C

Oven Program
  Cryogenics    :  Off                                              Total Run Time      :  38.57 min
  Initial Temp  :  40°C                                             Maximum Temp        :  350°C
  Initial Hold  :  5.00 min                                         Equilibration Time  :  2.0 min
     Ramp 1   :  7.0 0/min to 240°, hold for 5.00 min

Timed Events
  There are no timed events in the method
```

Method: MEA1

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\MEA 1.mth
   Printed by                     : Mathew     on: 26/07/2011  16:14:59
   Created by                     : Mathew     on: 07/10/2008  09:40:55
   Edited by                      : Mathew     on: 07/10/2008  09:56:47
   Number of Times Edited         : 2
   Number of Times Calibrated     : 0
   Description:

Instrument Conditions


Instrument Control Method
   Instrument Name       :  inst1
   Instrument Type       :  PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time          :  0.00 min
   Run Time            :  38.57 min
   Sampling Rate       :  1.5625 pts/s

                       Channel A      Channel B
   ____________       ___________    ___________

   Signal Source       DetA           DetB
   Analog Output       INT            INT
   Attenuation         0              0
   Offset              5.0 mV         5.0 mV

Autosampler Method
   Syringe Capacity                     : 5.0 µL          Injection Volume              : 1.0 µL
   Injection Speed                      : Normal          Sample Pumps                  : 6
   Viscosity Delay                      : 0               Wash/Waste Vial Set           : 1
   Pre-injection Solvent Washes         : 0               Pre-injection Sample Washes   : 2
   Post-injection Solvent Washes (A)    : 2

Carriers Parameters
26/07/2011 16:14:59 Method: C:\TurboMass\Kali.PRO\ACQUDB\MEA 1.mth

   Carrier A control              : PFlow - He
   Column A length                : 30.00 m                 Diameter      : 250 µm
   Vacuum Compensation            : ON
   Split Flow                     : 20.0 mL/min
   Initial Setpoint               : 1.00 ML/MIN             Initial Hold  : 999.00 min



   Auxiliary Pneumatics
      Number      Type          Setpoint
      ________    __________    ________

      1           Press - PSIG  0.0 PSIG

Valve configuration and settings
   Valve 1   : SPLIT On                                     Valve 2   : NONE
   Valve 3   : VALVE Off                                    Valve 4   : NONE
   Valve 5   : NONE                                         Valve 6   : NONE

Detector Parameters
                       Detector A     Detector B
   ____________       ___________    ___________

   Detector            NONE           NONE
   Range               1              1
   Time Constant       200            200
   Autozero            ON             ON
   Polarity            ___________    ___________

Heated Zones
   Injector A:  PSSI
      Initial Setpoint     : 250°C                           Initial Hold     : 999.00 min

   Injector B:  NONE
      Setpoint    : OFF
```

26/07/2011 16:14:59 Method: C:\TurboMass\Kali.PRO\ACQUDB\MEA 1.mth

Detector A : 0°C
Detector B : 0°C
Auxiliary (NONE) : 0°C

Oven Program

Cryogenics : Off
Initial Temp : 40°C
Initial Hold : 5.00 min
Ramp 1 : 7.0 0/min to 240°, hold for 5.00 min

Total Run Time : 38.57 min
Maximum Temp : 350°C
Equilibration Time : 2.0 min

Timed Events

There are no timed events in the method

Method: MEA2

```
________________________________________________________________________________
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\MEA 2.mth
   Printed by                    : Mathew    on: 26/07/2011  16:14:17
   Created by                    : Mathew    on: 10/10/2008  09:18:52
   Edited by                     : Mathew    on: 10/10/2008  09:18:52
   Number of Times Edited        : 0
   Number of Times Calibrated    : 0
   Description:  MEA 2
________________________________________________________________________________
Instrument Conditions


Instrument Control Method
   Instrument Name      : inst1
   Instrument Type      : PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time        : 0.00 min
   Run Time          : 38.57 min
   Sampling Rate     : 1.5625 pts/s

                     Channel A     Channel B
   ______________    _________     _________

   Signal Source     DetA          DetB
   Analog Output     INT           INT
   Attenuation       0             0
   Offset            5.0 mV        5.0 mV

Autosampler Method
   Syringe Capacity                     : 5.0 µL       Injection Volume               : 1.0 µL
   Injection Speed                      : Normal       Sample Pumps                   : 6
   Viscosity Delay                      : 0            Wash/Waste Vial Set            : 1
   Pre-injection Solvent Washes         : 0            Pre-injection Sample Washes    : 2
   Post-injection Solvent Washes (A)    : 2

Carriers Parameters
26/07/2011 16:14:17 Method: C:\TurboMass\Kali.PRO\ACQUDB\MEA 2.mth

   Carrier A control           : PFlow - He
   Column A length             : 30.00 m             Diameter      : 250 µm
   Vacuum Compensation         : ON
   Split Flow                  : 60.0 mL/min
   Initial Setpoint            : 1.00 ML/MIN         Initial Hold  : 999.00 min



   Auxiliary Pneumatics
      Number       Type          Setpoint
      ________     ___________   _________

      1            Press - PSIG  0.0 PSIG

Valve configuration and settings
   Valve 1   : SPLIT On                              Valve 2   : NONE
   Valve 3   : VALVE Off                             Valve 4   : NONE
   Valve 5   : NONE                                  Valve 6   : NONE

Detector Parameters
                     Detector A    Detector B
   ______________    __________    __________

   Detector          NONE          NONE
   Range             1             1
   Time Constant     200           200
   Autozero          ON            ON
   Polarity          __________    __________

Heated Zones
   Injector A:  PSSI
      Initial Setpoint     : 250°C                    Initial Hold     : 999.00 min

   Injector B:  NONE
      Setpoint    : OFF
```

```
26/07/2011 16:14:17 Method: C:\TurboMass\Kali.PRO\ACQUDB\MEA 2.mth

   Detector A            :  0°C
   Detector B            :  0°C
   Auxiliary (NONE)      :  0°C

Oven Program
   Cryogenics      :  Off                                        Total Run Time        :  38.57 min
   Initial Temp    :  40°C                                       Maximum Temp          :  350°C
   Initial Hold    :  5.00 min                                   Equilibration Time    :  2.0 min
      Ramp 1     :  7.0 0/min to 240°, hold for 5.00 min

Timed Events
   There are no timed events in the method
```

Method: MEA3

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\MEA 3.mth
   Printed by                      : Mathew    on: 26/07/2011  16:13:44
   Created by                      : Mathew    on: 10/10/2008  09:43:02
   Edited by                       : Mathew    on: 10/10/2008  09:43:02
   Number of Times Edited          : 0
   Number of Times Calibrated      : 0
   Description:  MEA 3
```

```
Instrument Conditions


Instrument Control Method
   Instrument Name      : inst1
   Instrument Type      : PE AutoSystem GC with built-in Autosampler

Channel Parameters
   Data will be collected from channel B
   Delay Time        : 0.00 min
   Run Time          : 38.57 min
   Sampling Rate     : 1.5625 pts/s

                     Channel A      Channel B
   ______________    ___________    ___________

   Signal Source     DetA           DetB
   Analog Output     INT            INT
   Attenuation       0              0
   Offset            5.0 mV         5.0 mV

Autosampler Method
   Syringe Capacity                      : 5.0 µL      Injection Volume                 : 1.0 µL
   Injection Speed                       : Normal      Sample Pumps                     : 6
   Viscosity Delay                       : 0           Wash/Waste Vial Set              : 1
   Pre-injection Solvent Washes          : 0           Pre-injection Sample Washes      : 2
   Post-injection Solvent Washes (A)     : 2

Carriers Parameters
26/07/2011 16:13:44 Method: C:\TurboMass\Kali.PRO\ACQUDB\MEA 3.mth

   Carrier A control          : PFlow - He
   Column A length            : 30.00 m                   Diameter       : 250 µm
   Vacuum Compensation        : ON
   Split Flow                 : 30.0 mL/min
   Initial Setpoint           : 1.00 ML/MIN               Initial Hold   : 999.00 min



   Auxiliary Pneumatics
      Number       Type           Setpoint
      ________     ____________   __________

      1            Press - PSIG   0.0 PSIG

Valve configuration and settings
   Valve 1    : SPLIT On                                  Valve 2    : NONE
   Valve 3    : VALVE Off                                 Valve 4    : NONE
   Valve 5    : NONE                                      Valve 6    : NONE

Detector Parameters
                     Detector A     Detector B
   ______________    ___________    ___________

   Detector          NONE           NONE
   Range             1              1
   Time Constant     200            200
   Autozero          ON             ON
   Polarity          ___________    ___________

Heated Zones
   Injector A:  PSSI
      Initial Setpoint     : 250°C                         Initial Hold     : 999.00 min

   Injector B:  NONE
      Setpoint     : OFF
```

```
  Detector A              : 0°C
  Detector B              : 0°C
  Auxiliary (NONE)        : 0°C

Oven Program
  Cryogenics     : Off                                              Total Run Time      : 38.57 min
  Initial Temp   : 40°C                                             Maximum Temp        : 350°C
  Initial Hold   : 5.00 min                                         Equilibration Time  : 2.0 min
     Ramp 1    : 7.0 0/min to 240°, hold for 5.00 min

Timed Events
  There are no timed events in the method
```

Method: VOCs

```
Turbochrom Method File C:\TurboMass\Kali.PRO\ACQUDB\VOCs.mth
  Printed by                       : Mathew     on: 26/07/2011  16:13:14
  Created by                       : Mathew     on: 07/09/2007  09:04:03
  Edited by                        : Mathew     on: 17/11/2009  14:24:19
  Number of Times Edited           : 9
  Number of Times Calibrated       : 0
  Description:  VOCs

Instrument Conditions


Instrument Control Method
  Instrument Name       : inst1
  Instrument Type       : PE AutoSystem GC with built-in Autosampler

Channel Parameters
  Data will be collected from channel B
  Delay Time         : 0.00 min
  Run Time           : 35.57 min
  Sampling Rate      : 1.5625 pts/s

                    Channel A    Channel B
  ________________  ___________  ___________

  Signal Source     DetA         DetB
  Analog Output     INT          INT
  Attenuation       0            0
  Offset            5.0 mV       5.0 mV

Autosampler Method
  Syringe Capacity                   : 5.0 µL        Injection Volume              : 1.0 µL
  Injection Speed                    : Normal        Sample Pumps                  : 6
  Viscosity Delay                    : 0             Wash/Waste Vial Set           : 1
  Pre-injection Solvent Washes       : 2             Pre-injection Sample Washes   : 4
  Post-injection Solvent Washes (A)  : 3

Carriers Parameters
26/07/2011 16:13:14 Method: C:\TurboMass\Kali.PRO\ACQUDB\VOCs.mth

  Carrier A control          : PFlow - He
  Column A length            : 30.00 m               Diameter      : 250 µm
  Vacuum Compensation        : ON
  Split Flow                 : 30.0 mL/min
  Initial Setpoint           : 1.00 ML/MIN           Initial Hold  : 999.00 min



  Auxiliary Pneumatics
    Number       Type           Setpoint
    _________    ____________   _________

    1            Press - PSIG   0.0 PSIG

Valve configuration and settings
  Valve 1   : SPLIT On                               Valve 2   : NONE
  Valve 3   : VALVE Off                              Valve 4   : NONE
  Valve 5   : NONE                                   Valve 6   : NONE

Detector Parameters
                    Detector A    Detector B
  ________________  ___________   ___________

  Detector          NONE          NONE
  Range             1             1
  Time Constant     200           200
  Autozero          ON            ON
  Polarity          ___________   ___________

Heated Zones
  Injector A:  PSSI
    Initial Setpoint     : 250°C                      Initial Hold     : 999.00 min

  Injector B:  NONE
    Setpoint     : OFF
```

26/07/2011 16:13:14 Method: C:\TurboMass\Kali.PRO\ACQUDB\VOCs.mth

Detector A : 0°C
Detector B : 0°C
Auxiliary (NONE) : 0°C

Oven Program

Cryogenics : Off
Initial Temp : 40°C
Initial Hold : 2.00 min
Ramp 1 : 7.0 0/min to 240°, hold for 5.00 min

Total Run Time : 35.57 min
Maximum Temp : 350°C
Equilibration Time : 0.5 min

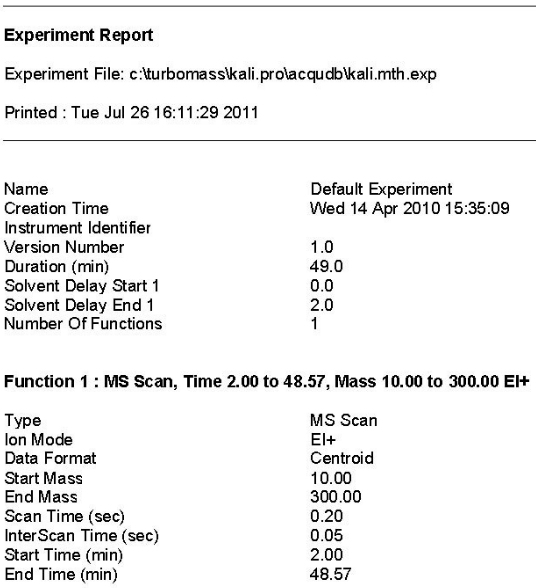
Timed Events

SPL1 set to 20 at 1.00 min

Appendix 1.7: MS Conditions – Final Set Up

MS conditions new set up

Method: Kali



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\kali.mth.exp

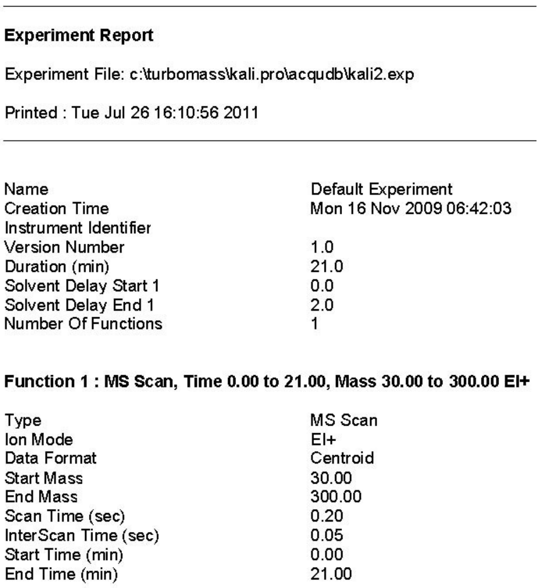
Printed : Tue Jul 26 16:11:29 2011

Name	Default Experiment
Creation Time	Wed 14 Apr 2010 15:35:09
Instrument Identifier	
Version Number	1.0
Duration (min)	49.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 2.00 to 48.57, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	2.00
End Time (min)	48.57

Method: Kali2



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\kali2.exp

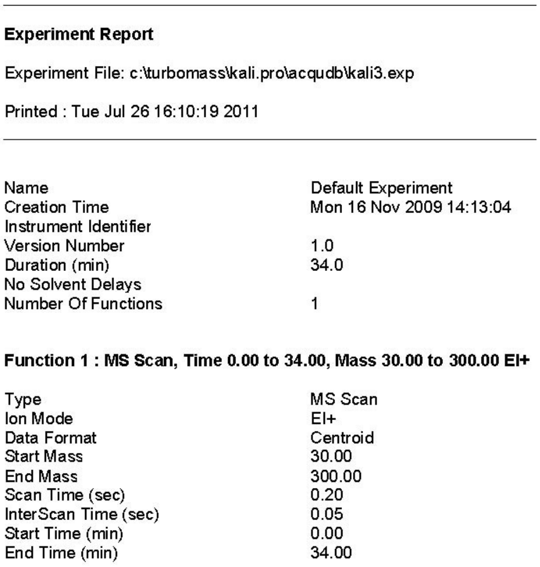
Printed : Tue Jul 26 16:10:56 2011

Name	Default Experiment
Creation Time	Mon 16 Nov 2009 06:42:03
Instrument Identifier	
Version Number	1.0
Duration (min)	21.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 0.00 to 21.00, Mass 30.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	30.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.00
End Time (min)	21.00

Method: Kali3



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\kali3.exp

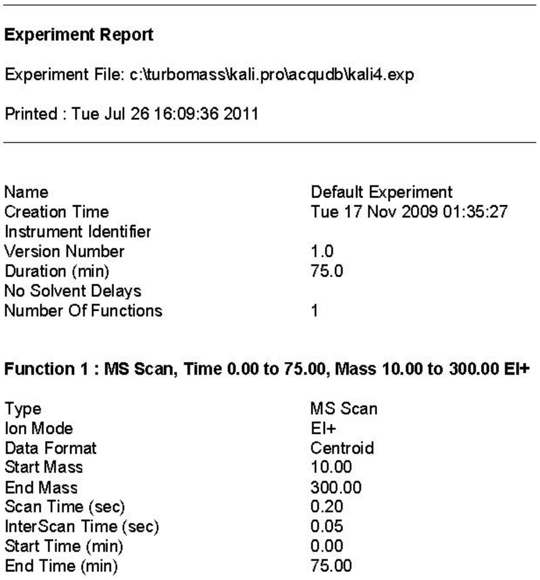
Printed : Tue Jul 26 16:10:19 2011

Name	Default Experiment
Creation Time	Mon 16 Nov 2009 14:13:04
Instrument Identifier	
Version Number	1.0
Duration (min)	34.0
No Solvent Delays	
Number Of Functions	1

Function 1 : MS Scan, Time 0.00 to 34.00, Mass 30.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	30.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.00
End Time (min)	34.00

Method: Kali4



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\kali4.exp

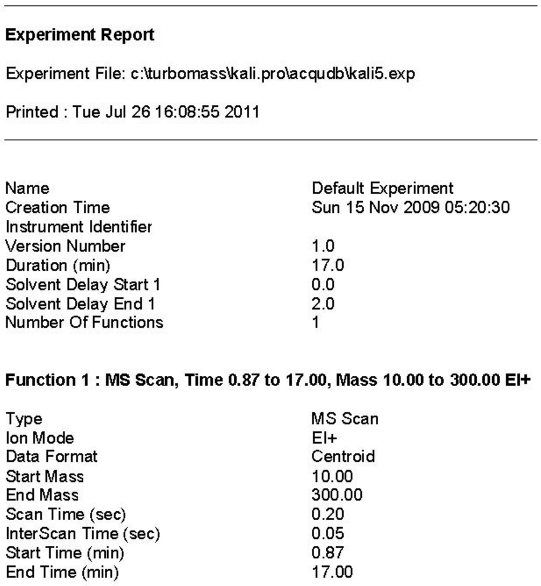
Printed : Tue Jul 26 16:09:36 2011

Name	Default Experiment
Creation Time	Tue 17 Nov 2009 01:35:27
Instrument Identifier	
Version Number	1.0
Duration (min)	75.0
No Solvent Delays	
Number Of Functions	1

Function 1 : MS Scan, Time 0.00 to 75.00, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.00
End Time (min)	75.00

Method: Kali5



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\kali5.exp

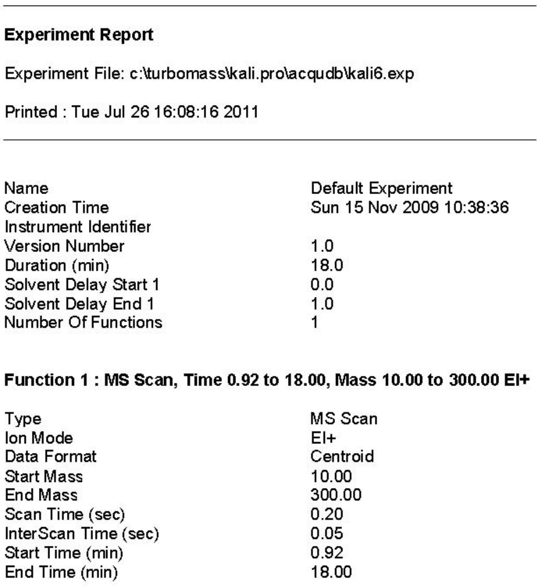
Printed : Tue Jul 26 16:08:55 2011

Name	Default Experiment
Creation Time	Sun 15 Nov 2009 05:20:30
Instrument Identifier	
Version Number	1.0
Duration (min)	17.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 0.87 to 17.00, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.87
End Time (min)	17.00

Method: Kali6



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\kali6.exp

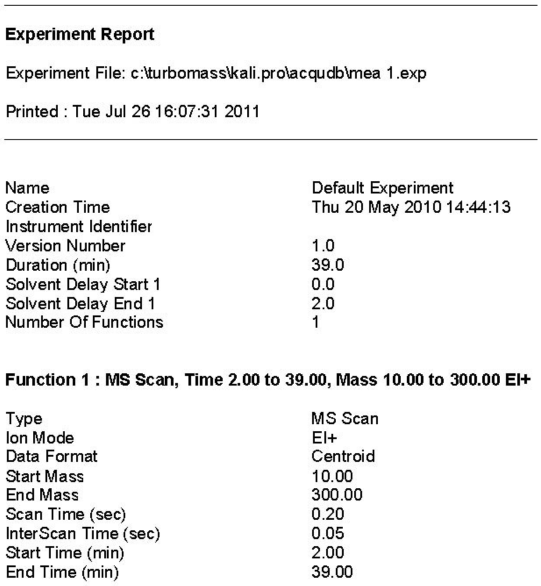
Printed : Tue Jul 26 16:08:16 2011

Name	Default Experiment
Creation Time	Sun 15 Nov 2009 10:38:36
Instrument Identifier	
Version Number	1.0
Duration (min)	18.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	1.0
Number Of Functions	1

Function 1 : MS Scan, Time 0.92 to 18.00, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.92
End Time (min)	18.00

Method: MEA1



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\mea 1.exp

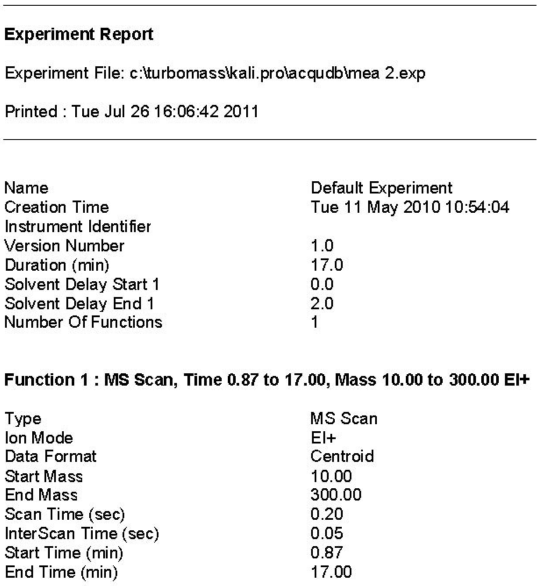
Printed : Tue Jul 26 16:07:31 2011

Name	Default Experiment
Creation Time	Thu 20 May 2010 14:44:13
Instrument Identifier	
Version Number	1.0
Duration (min)	39.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 2.00 to 39.00, Mass 10.00 to 300.00 EI+

Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	2.00
End Time (min)	39.00

Method: MEA2



Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\mea 2.exp

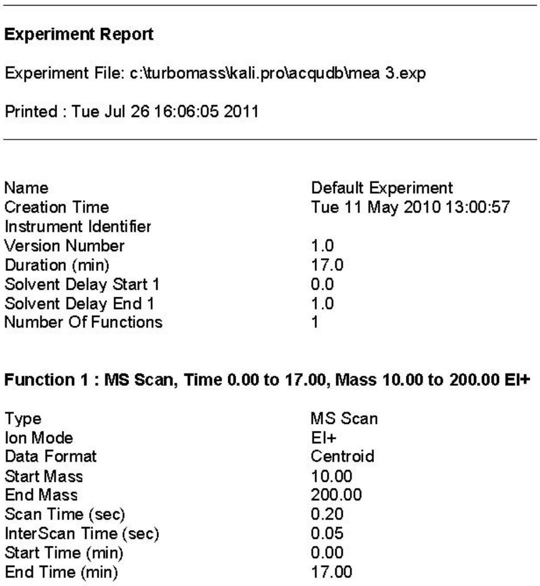
Printed : Tue Jul 26 16:06:42 2011

Name	Default Experiment
Creation Time	Tue 11 May 2010 10:54:04
Instrument Identifier	
Version Number	1.0
Duration (min)	17.0
Solvent Delay Start 1	0.0
Solvent Delay End 1	2.0
Number Of Functions	1

Function 1 : MS Scan, Time 0.87 to 17.00, Mass 10.00 to 300.00 EI+

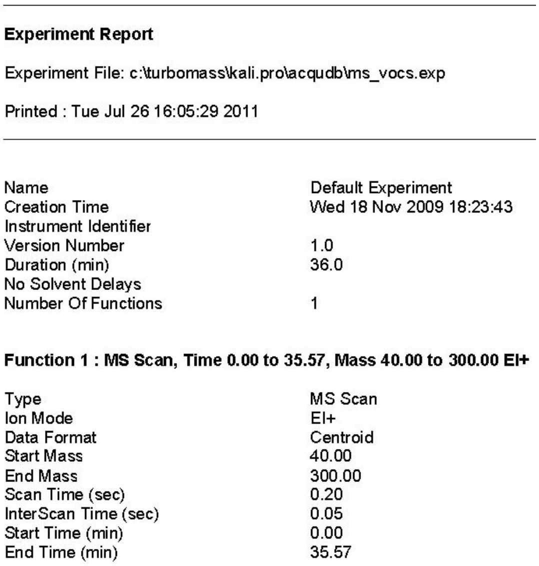
Type	MS Scan
Ion Mode	EI+
Data Format	Centroid
Start Mass	10.00
End Mass	300.00
Scan Time (sec)	0.20
InterScan Time (sec)	0.05
Start Time (min)	0.87
End Time (min)	17.00

Method: MEA3



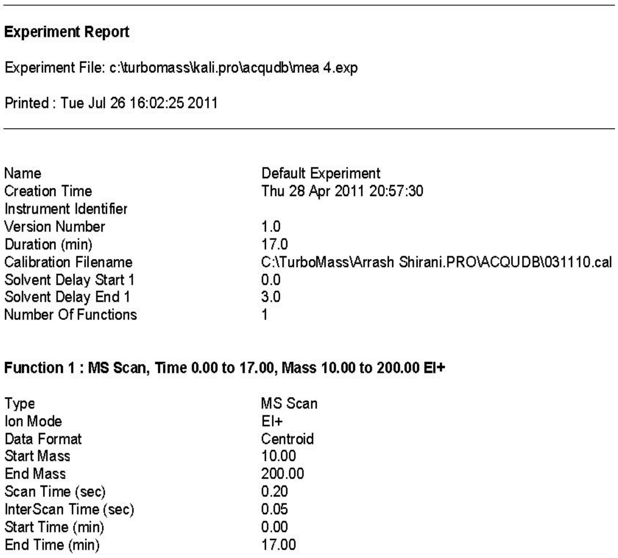
```
Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\mea 3.exp

Printed : Tue Jul 26 16:06:05 2011

Name                          Default Experiment
Creation Time                 Tue 11 May 2010 13:00:57
Instrument Identifier
Version Number                1.0
Duration (min)                17.0
Solvent Delay Start 1         0.0
Solvent Delay End 1           1.0
Number Of Functions           1

Function 1 : MS Scan, Time 0.00 to 17.00, Mass 10.00 to 200.00 EI+

Type                          MS Scan
Ion Mode                      EI+
Data Format                   Centroid
Start Mass                    10.00
End Mass                      200.00
Scan Time (sec)               0.20
InterScan Time (sec)          0.05
Start Time (min)              0.00
End Time (min)                17.00
```

Method: MS_VOCs



```
Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\ms_vocs.exp

Printed : Tue Jul 26 16:05:29 2011

Name                          Default Experiment
Creation Time                 Wed 18 Nov 2009 18:23:43
Instrument Identifier
Version Number                1.0
Duration (min)                36.0
No Solvent Delays
Number Of Functions           1

Function 1 : MS Scan, Time 0.00 to 35.57, Mass 40.00 to 300.00 EI+

Type                          MS Scan
Ion Mode                      EI+
Data Format                   Centroid
Start Mass                    40.00
End Mass                      300.00
Scan Time (sec)               0.20
InterScan Time (sec)          0.05
Start Time (min)              0.00
End Time (min)                35.57
```

Method: MEA4



```
Experiment Report

Experiment File: c:\turbomass\kali.pro\acqudb\mea 4.exp

Printed : Tue Jul 26 16:02:25 2011

Name                          Default Experiment
Creation Time                 Thu 28 Apr 2011 20:57:30
Instrument Identifier
Version Number                1.0
Duration (min)                17.0
Calibration Filename          C:\TurboMass\Arrash Shirani.PRO\ACQUDB\031110.cal
Solvent Delay Start 1         0.0
Solvent Delay End 1           3.0
Number Of Functions           1

Function 1 : MS Scan, Time 0.00 to 17.00, Mass 10.00 to 200.00 EI+

Type                          MS Scan
Ion Mode                      EI+
Data Format                   Centroid
Start Mass                    10.00
End Mass                      200.00
Scan Time (sec)               0.20
InterScan Time (sec)          0.05
Start Time (min)              0.00
End Time (min)                17.00
```

Appendix 1.8: GC-MS Calibration Curves – Pure Analyte in Diethyl Ether

Raw data – Calibration Curves GC-MS for HEEDA, 2-Oxazolidone, MEA and HEIA produced by adding pure chemicals into diethyl ether

MEA		HEEDA		HEIA		2-Oxazolidone	
Concentration % v/v	GC-MS response	Concentration % v/v	GC-MS response	Concentration % v/v	GC-MS response	Concentration w/v %	GC-MS response
0.625	989277376	1.19	6201298432	1.25	6727352832	2.857	216254992
1.25	1353606144	0.6	3155166464	2.5	12259343360	1.4285	97231120
2.5	1861499008	0.3	1402861952	5	17425025024	0.71425	50049128
5	3399958272	0.15	657810944	10	23485288448	0.357125	12910669
		0.074	205217984			0.1785625	4722824
						0.08928125	1603088
						0.044640625	494287

One extraction using diethyl ether was performed for 2-Oxazolidone and HEEDA and the measured GC-MS response was used to calculate the partition coefficient by dividing the measured value with the value calculated from the calibration curve.

2-Oxazolidone

Concentration	Calibration	Measured	Coefficient (%)
2 % w/v	152000000	174829072	101.5019126

HEEDA

Concentration	Calibration	Measured	Coefficient (%)
1 % v/v	4800000000	867376128	19.700336

Appendix 1.9: GC-MS Calibration Curves – MEA and HEIA

Raw data calibration curves for MEA and HEIA performed after extracting the organics from all samples using diethyl ether.

MEA		HEIA	
concentrations (% v/v)	GC-MS response	Concentration (% v/v)	GC-MS response
4.76	1296848000	0.625	3056281321
2.38	534595360	1.25	7284248064
1.19	268528640	2.5	12379062272
0.6	135665680	5	21206726656
0.03	63556244	10	27449561088
0.15	26870438		
0.074	10658771		

APPENDIX 2: RESULTS-DISCUSSION

Appendix 2.1: MicroGC Data – Full Loading Experiment

Raw data for the full loading experiment

CO2 Time minutes	Area (GC)	Calibr Gas 15% Area Calibration (GC)	CO2 at outlet w/v
		Day 1	
15	24.1	2134.3	0.169376376
30	18.3	2134.3	0.128613597
45	77.1	2134.3	0.541863843
60	16.4	2134.3	0.115260273
75	14.3	2134.3	0.100501335
90	15.6	2134.3	0.10963782
105	15.5	2134.3	0.108935014
120	15.4	2134.3	0.108232207
135	13.4	2134.3	0.094176076
150	14.6	2134.3	0.102609755
165	15.9	2134.3	0.11174624
180	16.7	2134.3	0.117368692
195	17.8	2134.3	0.125099564
210	16.3	2134.3	0.114557466
225	12	2134.3	0.084336785
240	11.2	2134.3	0.078714333
255	11.6	2134.3	0.081525559
270	11.3	2134.3	0.079417139
285	11.9	2134.3	0.083633978
300	11	2134.3	0.077308719
		Day 2	
315	35.8	2107.6	0.254792181
330	33.9	2107.6	0.241269691
345	27.8	2107.6	0.197855381
360	25.8	2107.6	0.18362118
375	26.6	2107.6	0.189314861
390	27.4	2107.6	0.195008541
405	37.5	2107.6	0.266891251
420	39.6	2107.6	0.281837161
435	42.8	2107.6	0.304611881
450	43.3	2107.6	0.308170431
465	38.7	2107.6	0.275431771
480	36.7	2107.6	0.261197571
495	63.2	2107.6	0.449800721
510	70	2107.6	0.498197001
525	57.3	2107.6	0.407809831
540	79.8	2107.6	0.567944582
555	89.2	2107.6	0.634845322
570	93	2107.6	0.661890302
		Day 3	
585	136	2054	0.993184031
600	148.9	2054	1.087390458
615	162.6	2054	1.187439143
630	259.7	2054	1.89654333
645	388.4	2054	2.836416748

660	490.3	2054	3.580574489
675	526.9	2054	3.847857838
690	593.05	2054	4.33093963
705	548.8	2054	4.007789679
720	584.5	2054	4.268500487
735	850.6	2054	6.211781889
750	683.3	2054	4.990019474
765	589.5	2054	4.305014606
780	658.5	2054	4.808909445
795	782.9	2054	5.717380721
810	1028	2054	7.507302824
825	1159.9	2054	8.470545278
840	1172.5	2054	8.562560857
855	1202.1	2054	8.77872444
		Day 4	
870	700.5	2335.1	4.499807289
885	747.2	2335.1	4.799794441
900	1349	2335.1	8.665581774
915	976.1	2335.1	6.270181149
930	1486.5	2335.1	9.548841591
945	1583.7	2335.1	10.17322599
960	1376.6	2335.1	8.842876108
975	1285.2	2335.1	8.255749218
990	1315.4	2335.1	8.449745193
1005	1048	2335.1	6.732045737
1020	1087.3	2335.1	6.984497452
1035	1153	2335.1	7.406535052
1050	1403.2	2335.1	9.013746735
1065	1216.9	2335.1	7.817009978
1080	1097.1	2335.1	7.047449788
1095	997.7	2335.1	6.408933236
1110	1209.4	2335.1	7.76883217
1125	1035.2	2335.1	6.649822277
1140	1427.6	2335.1	9.170485204
1155	1427.7	2335.1	9.171127575
1170	1370.7	2335.1	8.804976232
1185	1517.3	2335.1	9.746691791
1200	1567.7	2335.1	10.07044666
1215	1445.1	2335.1	9.28290009
1230	1306.7	2335.1	8.393858935
1245	1126.8	2335.1	7.238233909
		Day 5	
1260	871.1	2055	6.358394161
1275	1244.7	2055	9.08540146
1290	1108.2	2055	8.089051095
1305	1627.1	2055	11.87664234
1320	1588.1	2055	11.5919708
1335	1479.1	2055	10.79635036
1350	1504.1	2055	10.97883212
1365	1405.9	2055	10.2620438
1380	1833.4	2055	13.38248175
1395	1569.4	2055	11.45547445
1410	1310.8	2055	9.567883212
1425	1186.3	2055	8.659124088

1440	1718.1	2055	12.54087591
1455	1372.4	2055	10.01751825
1470	1544.9	2055	11.27664234
1485	1322.7	2055	9.654744526
1500	1647.7	2055	12.0270073
1515	1644.2	2055	12.00145985
1530	1607.9	2055	11.73649635
1545	1488	2055	10.86131387
1560	1414.3	2055	10.32335766
1575	1357.9	2055	9.911678832
1590	1232.4	2055	8.995620438
1605	1139.4	2055	8.316788321
1620	1100.5	2055	8.032846715
1635	1057.4	2055	7.718248175
1650	982.3	2055	7.170072993
		Day 6	
1665	1064.8	2040.4	7.827876887
1680	1730.7	2040.4	12.72324054
1695	1421.7	2040.4	10.45162713
1710	1461.9	2040.4	10.74715742
1725	1293.7	2040.4	9.51063517
1740	1271.4	2040.4	9.346696726
1755	1256.2	2040.4	9.234953931
1770	1686.9	2040.4	12.40124485
1785	1517.1	2040.4	11.1529602
1800	1161	2040.4	8.535091159
1815	1012	2040.4	7.439717702
1830	1196.4	2040.4	8.795334248
1845	1157.7	2040.4	8.51083121
1860	1175.9	2040.4	8.644628504
1875	1480.8	2040.4	10.88610076
1890	1390.2	2040.4	10.22005489
		Day 7	
1905	973.8	2049.5	7.127104172
1920	1297.9	2049.5	9.499146133
1935	1499	2049.5	10.97096853
1950	1710.2	2049.5	12.51671139
1965	1435.7	2049.5	10.5076848
1980	1375.6	2049.5	10.06782142
1995	1230.4	2049.5	9.005123201
2010	1296.9	2049.5	9.491827275
2025	1370.4	2049.5	10.02976336
2040	1273.8	2049.5	9.322761649
2055	1107.4	2049.5	8.104903635
2070	998.6	2049.5	7.308611857
2085	801.26	2049.5	5.864308368
2100	633.1	2049.5	4.633569163

Appendix 2.2: MicroGC Data – 14 Full Cycles Experiment - Absorption

Raw microGC data from the 14 full cycles experiment, absorption

	Absorption							
		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Time	Time (min)	1rst absorption	1rst absorption	1rst absorption	1rst absorption	1rst absorption	1rst absorption	1rst absorption
09:10:00	10	8	10.476	10.629	12.34	7.92	10.32	13.8
09:20:00	20	6.89	8.464	8.4035	10.28	5.8	8.35	11
09:30:00	30	3.56	6.45	6.6975	8.35	4.3	6.24	9.8
09:40:00	40	1.8	2.516	2.574	3	1.88	2.4	3.5
09:50:00	50	0.8	1.6	1.316666667	1.86	1	1.82	0.82
10:00:00	60	0.12	0.8	0.18	0.22	0.92	0.86	0.88
10:10:00	70	0.18	0.2	0.16	0.27	0.38	0.2	0.11
10:20:00	80	0.2	0.14	0.13	0.1	0.15	0.11	0.09
10:30:00	90	0.1	0.1	0.11	0.09	0.12	0.09	0.03
10:40:00	100	0.08	0.11	0.1	0.06	0.08	0.03	0.06
10:50:00	110	0.04	0.14	0.09	0.12	0.04	0	0.08
11:00:00	120	0.01	0.09	0.12	0.04	0.02	0.14	0
Time	Time (min)	2nd absorption	2nd absorption	2nd absorption	2nd absorption	2nd absorption	2nd absorption	2nd absorption
13:20:00	10	0.66	3.32	4.8	0.24	0.86	1.4	2.36
13:30:00	20	0.27	2.8	4	0.19	0.54	0.13	3.02
13:40:00	30	0.17	1.94	1.6	0.16	0.32	0.12	1.53
13:50:00	40	0.13	0.79	0.93	0.13	0.2	0.1	0.9
14:00:00	50	0.09	0.45	0.67	0.11	0.16	0.11	0.4
14:10:00	60	0.08	0.36	0.54	0.1	0.13	0.11	0.11
14:20:00	70	0.07	0.24	0.13	0.09	0.11	0.1	0.09
14:30:00	80	0.06	0.12	0.27	0.08	0.08	0.11	0.03
14:40:00	90	0.06	0.08	0.33	0.07	0.06	0.12	0.03
14:50:00	100	0.06	0.11	0.27	0.07	0.07	0.12	0.03
15:00:00	110	0.05	0.09	0.08	0.14	0.09	0.09	0
15:10:00	120	0	0.03	0.04	0.11	0.06	0.08	0

Appendix 2.3: MicroGC Data – 14 Full Cycles Experiment - Stripping

Raw microGC data from the 14 full cycles experiment, stripping

				Stripping 1				
		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Time	Time (min)	1rst stripping	1rst stripping	1rst stripping	1rst stripping	1rst stripping	1rst stripping	1rst stripping
11:20:00	10	0.54	0.07	0.09	0.27	0.8	0.12	0.06
11:30:00	20	1.06	0.14	0.06	0.12	2.62	0.89	0.3
11:40:00	30	4.76	2.02	2.62	2.46	3.87	2.46	3.28
11:50:00	40	7.86	6.64	6.22	7.66	7.93	6.87	7.21
12:00:00	50	7.88	10.32	7.62	7.97	8.31	7.56	7.93
12:10:00	60	7.92	12.34	7.9	7.99	8.39	7.92	9.27
				Stripping 2				
Time	Time (min)	2nd stripping	2nd stripping	2nd stripping	2nd stripping	2nd stripping	2nd stripping	2nd stripping
15:30:00	10	0.12	0.21	0.54	0.14	0.61	0.25	0.12
15:40:00	20	0.14	1.24	0.92	1.26	2.37	0.32	1.12
15:50:00	30	2.25	3.52	3.26	2.46	4.01	6.87	3.01
16:00:00	40	7.01	7.89	7.9	7.35	7.62	7.32	7.06
16:10:00	50	8.05	9.98	8.01	7.96	8.15	8.26	7.95
16:20:00	60	9.01	8.12	8.86	8.41	9.05	9.37	8.24

Appendix 2.4: Raw Data CO_2 Solubility Experiment

Raw data and calculations CO_2 solubility

	TOC response	Loading	time to equilibrium	pressure kPa
25/02/2010	23.26	0.039162245	3	240.7
02/03/2010	133.78	0.225241837	5	275.08
03/03/2010	245.7	0.413678571	8	618.93
04/03/2010	264.88	0.445971429	10	861.85
05/03/2010	209	0.351887755	7	584.54
09/03/2010	167.9	0.282688776	6	550.16

100 °C mole MEA in 400ml 30% w/v	1.965		400 ml 30% w/v MEA				Raoults law	
Loading	mole CO_2	mole CO_2 /mole MEA	moles of MEA	moles of water	moles of CO2	total number of moles in solution	X_{mea}	X_{water}
25/02/2010	0.0775	0.0392	1.965	15.63	0.075	17.66803119	0.111197253	0.88441806
02/03/2010	0.446	0.225	1.965	15.63	0.446	18.03612444	0.108927866	0.866368267
03/03/2010	0.818	0.414	1.965	15.63	0.818	18.40888048	0.106722217	0.848825429
04/03/2010	0.882	0.446	1.965	15.63	0.882	18.47276058	0.106353164	0.845890131
05/03/2010	0.696	0.352	1.965	15.63	0.696	18.28664901	0.107435569	0.854499141
09/03/2010	0.559	0.283	1.965	15.63	0.559	18.14976308	0.108245851	0.860943793

Partial Pressure H_2O steam tables 100 °C		Partial Pressure MEA 104.44 °C		P_{CO_2}
steam tables 100 °C kPa	Raoult's law	tables kPa	Raoult's law	kPa
101.35	89.63577039	0.00801	0.000891	60.06422961
101.35	87.80642382	0.00801	0.000873	96.27357618
101.35	86.02845722	0.00801	0.000855	441.9015428
101.35	85.73096479	0.00801	0.000852	685.1190352

101.35	86.60348795	0.00801	0.000861	406.936512
101.35	87.25665344	0.00801	0.000867	371.9033466

Appendix 2.5: Pressure Changes During Thermal Degradation – Lean Samples

Pressure changes during thermal degradation experiment – Lean initial molar loading

Time (hours)	Total Pressure (psi)	Total Pressure (kPa)
0	0	0
8	400	2757,902917
24	440	3033,693209
32	400	2757,902917
48	360	2482,112626
56	340	2344,21748
72	320	2206,322334
80	300	2068,427188
96	290	1999,479615
104	285	1965,005829
120	280	1930,532042
128	250	1723,689323
144	270	1861,584469
152	260	1792,636896
168	250	1723,689323
176	240	1654,74175
192	230	1585,794177
200	230	1585,794177
216	220	1516,846604
224	210	1447,899032
240	210	1447,899032
248	200	1378,951459
264	195	1344,477672
272	190	1310,003886
288	180	1241,056313
296	180	1241,056313
312	180	1241,056313
320	180	1241,056313
336	180	1241,056313
344	180	1241,056313
360	180	1241,056313
368	180	1241,056313
384	180	1241,056313
392	170	1172,10874
408	170	1172,10874
416	170	1172,10874
432	170	1172,10874
440	150	1034,213594
456	160	1103,161167
464	150	1034,213594
480	140	965,266021
488	140	965,266021
504	140	965,266021
512	140	965,266021
528	140	965,266021
536	140	965,266021
552	140	965,266021
560	140	965,266021
576	140	965,266021
584	140	965,266021

600	140	965,266021
Time (hours)	Total Pressure (psi)	Total Pressure (kPa)
608	140	965,266021
624	140	965,266021
632	140	965,266021
648	140	965,266021
656	140	965,266021
672	140	965,266021
680	140	965,266021
696	140	965,266021
704	140	965,266021
720	140	965,266021
728	140	965,266021
744	140	965,266021
752	140	965,266021
768	140	965,266021
776	140	965,266021
792	140	965,266021
800	140	965,266021
816	140	965,266021
824	140	965,266021
840	140	965,266021
848	140	965,266021
864	140	965,266021
872	140	965,266021
888	140	965,266021
896	140	965,266021
912	140	965,266021
920	140	965,266021
936	140	965,266021
944	140	965,266021
960	140	965,266021
968	140	965,266021
984	140	965,266021
992	140	965,266021
1008	140	965,266021
1016	140	965,266021
1032	140	965,266021
1040	140	965,266021
1056	140	965,266021
1064	140	965,266021
1080	140	965,266021
1088	140	965,266021
1104	140	965,266021
1112	140	965,266021
1128	140	965,266021
1136	140	965,266021
1152	140	965,266021
1160	140	965,266021
1176	140	965,266021
1184	140	965,266021
1200	140	965,266021
1208	140	965,266021

Appendix 2.6: MicroGC Raw Data – 1st Stripping Lean Samples

1st Stripping raw data and calculations – Lean initial molar loading

2 weeks

Date	Time	Run number	microGC Area	CO_2 Concentration % v/v	Flow	Flow Corrected	CO_2 Volume = Corrected flow*Concentration*20 min	Cumulative CO_2 volume (ml)
19/7/2010		2	2083,8	9,75				
19/7/2010	09:20	3	100,9	0,472106248	400	391,3814055	36,9547214	36,9547214
19/7/2010	09:40	4	6213,1	29,07079614	300	271,8538858	1580,601779	1617,556501
19/7/2010	10:00	5	2707,8	12,66966599	300	283,6730439	718,8085437	2336,365044
19/7/2010	10:20	6	957,3	4,479160668	300	290,1833165	259,9555395	2596,320584
19/7/2010	10:40	7	566,2	2,649222574	200	194,4667463	103,0371388	2699,357723
19/7/2010	11:00	8	526	2,461128707	200	194,5715858	95,77314306	2795,130866
19/7/2010	11:20	9	426,1	1,993701411	200	194,8328558	77,68770789	2872,818573
19/7/2010	11:40	10	384,8	1,800460697	200	194,9411762	70,1967852	2943,015359
19/7/2010	12:00	11	313,1	1,464979845	200	195,1296588	57,17220344	3000,187562
19/7/2010	12:20	12	300	1,403685574	200	195,1641547	54,78982173	3054,977384
19/7/2010	12:40	-	300	1,403685574	200	195,1641547	54,78982173	3109,767206
19/7/2010	13:00	-	300	1,403685574	200	195,1641547	54,78982173	3164,557027
19/7/2010	13:20	-	300	1,403685574	200	195,1641547	54,78982173	3219,346849
19/7/2010	13:40	-	300	1,403685574	200	195,1641547	54,78982173	3274,136671
19/7/2010	14:00	13	231,3	1,082241578	200	195,345361	42,28217434	3316,418845
19/7/2010	14:20	14	196,6	0,919881946	200	195,4370794	35,95580819	3352,374653
19/7/2010	14:40	15	184	0,860927152	200	195,4704154	33,65715762	3386,031811
19/7/2010	15:00	16	167,8	0,785128131	200	195,5133011	30,70059855	3416,732409
19/7/2010	15:20	17	143,6	0,671897495	200	195,5774176	26,28159539	3443,014005

3 Weeks

Date	Time	Run number	microGC	CO_2	Flow	Flow Corrected	CO_2 Volume =	Cumulative CO_2 volume
			Area	Concentration % v/v	(ml/min)	(ml/min)	Corrected flow*Concentration*20 min	(ml)
12/7/2010		2	2048	9,75				
12/7/2010	10:00	3	29,4	0,13996582	400	391,7589373	10,96657221	10,96657221
12/7/2010	10:20	4	5039	23,98937988	300	275,3565868	1321,126753	1332,093325
12/7/2010	10:40	5	1962,2	9,34152832	200	190,8434515	356,5539014	1688,647226
12/7/2010	11:00	6	886,3	4,219445801	250	241,9976245	204,2191721	1892,866398
12/7/2010	11:20	7	588,4	2,801220703	250	242,9776868	136,1268253	2028,993224
12/7/2010	11:40	8	445,3	2,119958496	250	243,4527253	103,2219347	2132,215158
12/7/2010	12:00	9	325,1	1,547717285	250	243,8539047	75,48338068	2207,698539
12/7/2010	12:20	10	288	1,37109375	250	243,9781308	66,90337805	2274,601917

8 Weeks

Date	Time	Run number	microGC Area	CO_2 Concentration % v/v	Flow (ml/min)	Flow Corrected (ml/min)	CO_2 Volume = Corrected flow*Concentration*20 min	Cumulative CO_2 volume (ml)
5/7/2010		2	2127,3	9,75				
5/7/2010	09:30	3	447,9	2,052848681	150	146,0998028	59,9841575	59,9841575
5/7/2010	09:50	4	198,2	0,90840502	200	195,4435677	35,50838362	95,49254111
5/7/2010	10:10	5	563,5	2,582675222	150	145,8778642	75,35102907	170,8435702
5/7/2010	10:30	6	537,7	2,464426738	200	194,569746	95,90057692	266,7441471
5/7/2010	10:50	7	500,8	2,295303906	150	145,9981153	67,02200887	333,766156
5/7/2010	11:10	8	505,1	2,315011987	150	145,9898589	67,59365467	401,3598106
5/7/2010	11:30	9	447,8	2,052390354	200	194,7999936	79,96112557	481,3209362
5/7/2010	11:50	10	359,1	1,645853899	200	195,0279708	64,19750924	545,5184455
5/7/2010	12:10	11	341,9	1,567021577	150	146,3042033	45,85236866	591,3708141
5/7/2010	12:30	12	312,2	1,430898322	200	195,1488373	55,84762877	647,2184429
5/7/2010	12:50	13	293,2	1,343816105	200	195,1978665	52,46200732	699,6804502
5/7/2010	13:10	14	222,2	1,01840361	200	195,3814082	39,7954263	739,4758765
5/7/2010	13:30	15	212,7	0,974862502	150	146,5545044	28,57409816	768,0499747
5/7/2010	13:50	16	121,5	0,556867861	150	146,7319631	16,34206287	784,3920375
5/7/2010	14:10	17	122,4	0,560992808	200	195,6402782	21,9505578	806,3425953
5/7/2010	14:30	18	112,9	0,517451699	200	195,6649738	20,24943464	826,59203
5/7/2010	14:50	19	96,9	0,444119306	150	146,7799407	13,03756108	839,6295911
5/7/2010	15:10	20	83,9	0,384536737	200	195,7404183	15,05387634	854,6834674
5/7/2010	15:30	21	73,4	0,336412354	200	195,7677559	13,17173831	867,8552057
5/7/2010	15:50	22	67,8	0,310746016	200	195,7823407	12,16771648	880,0229222

Appendix 2.7: MicroGC Raw Data – Absorption Lean Samples

Absorption raw data and calculations – Lean initial molar loading
Pure MEA

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume at outlet	CO_2 at inlet	Cumulative CO_2
			Area	Concentration (% v/v)	(ml/min)	(ml/min)	Cor. flow*concent*time	ml	Volume Absorbed (L)
20/6/2010		2	2149,4	9,75					
20/6/2010	10:20	3	7,6	0,034474737	0	0	0	2000	2
20/6/2010	10:40	4	0	0	0	0	0	2000	4
20/6/2010	11:00	5	5,7	0,025856053	0	0	0	2000	6
20/6/2010	11:20	6	0	0	0	0	0	2000	8
20/6/2010	11:40	7	0	0	0	0	0	2000	10
20/6/2010	12:00	8	0	0	0	0	0	2000	12
20/6/2010	12:20	9	0	0	0	0	0	2000	14
20/6/2010	12:40	10	0	0	0	0	0	2000	16
20/6/2010	13:00	11	0	0	0	0	0	2000	18
20/6/2010	13:20	12	0	0	0	0	0	2000	20
20/6/2010	13:40	13	0	0	0	0	0	2000	22
20/6/2010	14:00	14	0	0	10	12,83549765	0	2000	24
20/6/2010	14:20	15	0	0	10	12,83549765	0	2000	26
20/6/2010	14:40	16	1216,4	5,517772402	10	12,61217366	13,91822074	2000	27,98608178
20/6/2010	15:00	17	848,4	3,84846934	10	12,67850288	9,758565924	2000	29,97632321
20/6/2010	15:20	18	2788,6	12,64950684	10	12,34008173	31,21918964	2000	31,94510402
20/6/2010	15:40	19	3826,5	17,35757653	20	24,33963769	84,49542478	2000	33,8606086
20/6/2010	16:00	20	3156,4	14,31790267	20	24,55786245	70,32341687	2000	35,79028518
20/6/2010	16:20	21	2479	11,24511492	20	24,78454051	55,74100124	2000	37,73454418
20/6/2010	16:40	22	2094,1	9,499150926	20	24,91616944	47,3364908	2000	39,68720769
20/6/2010	17:00	23	807	3,660672746	20	25,37206117	18,57576257	2000	41,66863193
20/6/2010	17:20	24	3249,4	14,73976459	20	24,52722497	72,3051044	2000	43,59632682
20/6/2010	17:40	25	608,6	2,760700661	20	25,44458482	14,04897642	2000	45,58227785

20/6/2010	18:00	26	563,1	2,554305853	40	50,92260971	26,014384	2000	47,55626346
20/6/2010	18:20	27	527	2,390550851	30	38,21189117	18,2694938	2000	49,53799397
20/6/2010	18:40	28	570	2,585605285	30	38,18815075	19,74789688	2000	51,51824607

2 Weeks

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume at outlet	CO_2 at inlet	Cumulative CO_2
			Area	Concentration % v/v	(ml/min)	(ml/min)	Cor. flow*concent*time	ml	Volume Absorbed (L)
20/7/2010		2	2033,8	9,75					
20/7/2010	09:10	3	0	0	0	0	0	2000	2
20/7/2010	09:30	4	6,7	0,032119677	5	6,417081565	0,041222918	2000	3,999958777
20/7/2010	09:50	5	0	0	0	0	0	2000	5,999958777
20/7/2010	10:10	6	0	0	0	0	0	2000	7,999958777
20/7/2010	10:30	7	0	0	5	6,417748826	0	2000	9,999958777
20/7/2010	10:50	8	0	0	5	6,417748826	0	2000	11,99995878
20/7/2010	11:10	9	6,3	0,034516668	5	6,417031778	0,044298911	2000	13,99991448
20/7/2010	11:30	10	7,2	0,270859967	5	6,412128436	0,347357779	2000	15,99956712
20/7/2010	11:50	11	56,5	0,912774117	5	6,398867351	1,1681441	2000	17,99839898
20/7/2010	12:10	12	190,4	0,978451667	5	6,397515176	1,251931878	2000	19,99714704
20/7/2010	12:30	13	204,1	0,978451667	5	6,397515176	1,251931878	2000	21,99589511
20/7/2010	12:50	-	204,1	0,978451667	10	12,79503035	2,503863755	2000	23,99339125
20/7/2010	13:10	-	204,1	0,978451667	10	12,79503035	2,503863755	2000	25,99088739
20/7/2010	13:30	-	204,1	1,190345658	10	12,78631704	3,044027396	2000	27,98784336
20/7/2010	13:50	14	248,3	1,190345658	10	12,78631704	3,044027396	2000	29,98479933
20/7/2010	14:10	15	753,8	3,613703412	10	12,68791542	9,170072649	2000	31,97562926
20/7/2010	14:30	16	836,1	4,008248107	10	12,67210879	10,15859121	2000	33,96547067
20/7/2010	14:50	17	2243,7	10,75625676	10	12,41059265	26,69830422	2000	35,93877236
20/7/2010	15:10	18	5048,6	24,20289606	10	11,93437726	57,76929845	2000	37,88100306
20/7/2010	15:30	19	9987,6	47,88037172	10	11,21431762	107,3891392	2000	39,77361392
20/7/2010	15:50	20	12554,5	60,18604337	30	32,66425174	393,1864144	2000	41,38042751

20/7/2010	16:10	21	12897,9	61,83229669	20	21,69313004	268,2672106	2000	43,1121603
20/7/2010	16:30	22	13118,4	62,88936965	20	21,64030894	272,1890776	2000	44,83997122
20/7/2010	16:50	23	13964,5	66,94555758	20	21,44114761	287,0779163	2000	46,55289331
20/7/2010	17:10	24	14810,6	71,0017455	20	21,24738577	301,7202953	2000	48,25117301

3 Weeks

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume at outlet	CO_2 at inlet	Cumulative CO_2
			Area	Concentration % v/v	(ml/min)	(ml/min)	Cor. flow*concent*time	ml	Volume Absorbed (L)
15/7/2010		2	2061,6	9,75					
15/7/2010	09:10	3	9,2	0,043509895	5	6,416844992	0,055839251	2000	1,999944161
15/7/2010	09:30	4	0	0	5	6,417748826	0	2000	3,999944161
15/7/2010	09:50	5	0	0	5	6,417748826	0	2000	5,999944161
15/7/2010	10:10	6	0	0	5	6,417748826	0	2000	7,999944161
15/7/2010	10:30	7	0	0	5	6,417748826	0	2000	9,999944161
15/7/2010	10:50	8	0	0	5	6,417748826	0	2000	11,99994416
15/7/2010	11:10	9	0	0	5	6,417748826	0	2000	13,99994416
15/7/2010	11:30	10	0	0	5	6,417748826	0	2000	15,99994416
15/7/2010	11:50	11	0	0	5	6,417748826	0	2000	17,99994416
15/7/2010	12:10	12	0	0	5	6,417748826	0	2000	19,99994416
15/7/2010	12:30	13	0	0	10	12,83549765	0	2000	21,99994416
15/7/2010	12:50	-	1,8	0,008512806	10	12,83514392	0,021852617	2000	23,99992231
15/7/2010	13:10	-	2,2	0,01040454	10	12,83506531	0,026708591	2000	25,9998956
15/7/2010	13:30	-	1,8	0,008512806	10	12,83514392	0,021852617	2000	27,99987375
15/7/2010	13:50	14	1,8	0,008512806	10	12,83514392	0,021852617	2000	29,99985189
15/7/2010	14:10	15	1,8	0,008512806	20	25,67028784	0,043705234	2000	31,99980819
15/7/2010	14:30	16	5,7	0,026957218	30	38,50313278	0,207587466	2000	33,9996006
15/7/2010	14:50	17	7,2	0,034051222	40	51,33633156	0,349612968	2000	35,99925099
15/7/2010	15:10	18	0	0	40	51,34199061	0	2000	37,99925099
15/7/2010	15:30	19	1698,8	8,03419674	30	37,54236902	60,32455577	2000	39,93892643

15/7/2010	15:50	20	12770,2	60,39457218	40	43,53119354	525,809562	2000	41,41311687
15/7/2010	16:10	21	12048,7	56,98235594	40	43,8810695	500,0893442	2000	42,91302753
15/7/2010	16:30	22	14389	68,050422	40	42,77568825	582,1807274	2000	44,3308468
15/7/2010	16:50	23	14543,4	68,78063155	40	42,70566609	587,4645369	2000	45,74338226
15/7/2010	17:10	24	13720	64,88649593	40	43,08311673	559,1024956	2000	47,18427977

8 Weeks

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume at outlet	CO_2 at inlet	Cumulative CO_2
			Area	Concentration % v/v	(ml/min)	(ml/min)	Cor. flow*concent*time	ml	Volume Absorbed (L)
6/7/2010		2	2095,3	9,75					
6/7/2010	09:20	3	10,2	0,04746337	5	6,416762885	0,060912239	2000	1,999939088
6/7/2010	09:40	4	5,2	0,024197012	5	6,417246133	0,031055637	2000	3,999908032
6/7/2010	10:00	5	0	0	10	12,83549765	0	2000	5,999908032
6/7/2010	10:20	6	0	0	10	12,83549765	0	2000	7,999908032
6/7/2010	10:40	7	11,2	0,052116642	10	12,8333325	0,133766039	2000	9,999774266
6/7/2010	11:00	8	17,1	0,079570944	10	12,83219237	0,204213933	2000	11,99957005
6/7/2010	11:20	9	27	0,125638333	20	25,66055989	0,644789996	2000	13,99892526
6/7/2010	11:40	10	38,7	0,180081611	20	25,65604183	0,92403627	2000	15,99800123
6/7/2010	12:00	11	152,6	0,710089247	20	25,61218263	3,637387097	2000	17,99436384
6/7/2010	12:20	-	152,6	0,710089247	10	12,80609131	1,818693549	2000	19,99254515
6/7/2010	12:40	-	152,6	0,710089247	25	32,01522828	4,546733871	2000	21,98799841
6/7/2010	13:00	-	152,6	0,710089247	25	32,01522828	4,546733871	2000	23,98345168
6/7/2010	13:20	12	458,5	2,133525032	20	25,49549464	10,8790552	2000	25,97257262
6/7/2010	13:40	13	8303,8	38,63983678	25	28,69883047	221,783625	2000	27,750789
6/7/2010	14:00	14	14182	65,99269794	25	26,85929899	354,5035211	2000	29,39628548
6/7/2010	14:20	15	14255,7	66,33564406	25	26,83842969	356,0689039	2000	31,04021657
6/7/2010	14:40	16	14256	66,33704004	30	32,20601381	427,2903256	2000	32,61292625
6/7/2010	15:00	17	10440,2	48,58108624	30	33,58484446	326,317645	2000	34,2866086
6/7/2010	15:20	18	13148,3	61,18261108	30	32,58868032	398,7721107	2000	35,88783649

6/7/2010	15:40	19	13248,7	61,64979955	40	43,40457699	535,1766942	2000	37,3526598
6/7/2010	16:00	20	13349,1	62,11698802	40	43,35773239	538,6503487	2000	38,81400945
6/7/2010	16:20	21	13449,5	62,58417649	50	54,13879892	677,6464293	2000	40,13636302
6/7/2010	16:40	22	13549,9	63,05136496	50	54,08062051	681,9713882	2000	41,45439163
6/7/2010	17:00	23	13650,3	63,51855343	50	54,02262926	686,2878526	2000	42,76810378
6/7/2010	17:20	24	13750,7	63,9857419	50	53,96482416	690,5958621	2000	44,07750792
6/7/2010	17:40	25	13851,1	64,45293037	50	53,90720423	694,8954561	2000	45,38261246

Appendix 2.8: MicroGC Raw Data – Leak Investigation Absorption/Stripping Rig

Leak investigation – Water with low pH

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume at outlet	CO_2 at inlet
			Area	Concentration % v/v	(ml/min)	(ml/min)	Cor. flow*concent*time	ml
22/11/2010		2	2803,9	9,75				
22/11/2010	11:30	3	57,3	0,199249	30	38,4816776	1,150116868	3000
22/11/2010	12:00	4	64,3	0,22359	30	38,47864935	2,581036475	3000
22/11/2010	12:30	5	52,5	0,182558	50	64,13959089	3,512762911	3000
22/11/2010	13:00	6	518,3	1,802284	50	63,80626526	34,49910938	3000
22/11/2010	13:30	7	518,3	1,802284	50	63,80626526	34,49910938	3000
22/11/2010	14:00	8	284,6	0,989639	50	63,97284927	18,99301624	3000
22/11/2010	14:30	9	1593,2	5,540034	50	63,05648069	104,8005051	3000
22/11/2010	15:00	10	3629,4	12,62051	50	61,70576296	233,6274728	3000
22/11/2010	15:30	11	16228,2	56,43031	50	54,92308849	929,7980951	3000
22/11/2010	16:00	12	20147,4	70,05854	50	53,22993261	1118,763464	3000
22/11/2010	16:30	13	20318,6	70,65386	50	53,15949652	1126,777042	3000

Appendix 2.9: Inorganic Carbon Measurement – Absorption – Lean Samples

Absorption inorganic carbon measurement with TOC instrument – Lean initial molar loading

2 Weeks

Sample	Time (min)	TOC response (mg/L)	C Concentration after dilution (mg/L)	C Content in 330 ml (g)	atoms of C	gr of CO2	L of CO2	Cumulative CO_2 volume (L)
Initial	0	4,426605505	4426,605505	1,460779817	0,1217317	5,35741	2,709868	0
1	30	4,752803262	4752,803262	1,568425076	0,1307021	5,752199	2,909559	0,199691
2	60	9,635575943	9635,575943	3,179740061	0,2649783	11,6617	5,898683	3,188815
3	90	10,07390418	10073,90418	3,324388379	0,2770324	12,19219	6,167018	3,45715
4	120	10,51478084	10514,78084	3,469877676	0,2891565	12,72578	6,436913	3,727045
5	150	12,69622834	12696,22834	4,189755352	0,3491463	15,36593	7,772346	5,062478
6	210	12,89245668	12892,45668	4,254510703	0,3545426	15,60342	7,892472	5,182604
7	240	13,25942915	13259,42915	4,375611621	0,3646343	16,04756	8,117125	5,407257
8	270	13,56014271	13560,14271	4,474847095	0,3729039	16,4115	8,301215	5,591347
9	300	13,98063201	13980,63201	4,613608563	0,3844674	16,92041	8,558629	5,848761
10	330	14,23547401	14235,47401	4,697706422	0,3914755	17,22884	8,714637	6,004769

3 Weeks

Sample	Time (min)	TOC response (mg/L)	C Concentration after dilution (mg/L)	C Content in 310 ml (g)	atoms of C	gr of CO2	L of CO2	Cumulative CO_2 volume (L)
Initial	0	1,628464419	1628,464419	0,50482397	0,042068664	1,85144191	0,936490597	0
1	30	1,903370787	1903,370787	0,590044944	0,049170412	2,163989831	1,094582616	1,227499234
2	60	4,394506866	4394,506866	1,362297129	0,113524761	4,996224719	2,527174871	4,059734122
3	90	5,325842697	5325,842697	1,651011236	0,13758427	6,055083708	3,062763636	5,118593111
4	120	6,699126092	6699,126092	2,076729089	0,173060757	7,616403933	3,852505783	6,679913336
5	150	8,132334582	8132,334582	2,52102372	0,21008531	9,245854494	4,676709405	8,309363897
6	210	10,30212235	10302,12235	3,193657928	0,266138161	11,71274045	5,924501998	10,77624985
7	240	11,11860175	11118,60175	3,446766542	0,287230545	12,64101629	6,394039601	11,7045257
8	270	11,94257179	11942,57179	3,702197253	0,308516438	13,57780843	6,86788489	12,64131783
9	300	12,95131086	12951,31086	4,014906367	0,334575531	14,7246691	7,447986394	13,7881785
10	330	13,07365793	13073,65793	4,052833958	0,337736163	14,86376854	7,51834524	13,92727794
11	360	13,47565543	13475,65543	4,177453184	0,348121099	15,32080955	7,749524305	14,38431895

8 Weeks

Sample	Time (min)	TOC response (mg/L)	C Concentration after dilution (mg/L)	C Content in 310 ml (g)	atoms of C	gr of CO2	L of CO2	Cumulative CO_2 volume (L)
Initial	0	1,563232422	1563,232422	0,500234375	0,041686198	1,83460957	0,927976515	0
1	30	4,008789063	4008,789063	1,2828125	0,106901042	4,704714844	2,379724251	1,451747251
2	60	9,582519531	9582,519531	3,06640625	0,255533854	11,24604492	5,688439515	4,760462515
3	90	9,8046875	9804,6875	3,1375	0,261458333	11,50678125	5,820324355	4,892347355
4	120	9,685058594	9685,058594	3,09921875	0,258268229	11,36638477	5,749309441	4,821332441
5	150	9,379882813	9379,882813	3,0015625	0,250130208	11,00823047	5,568148947	4,640171947
6	210	8,930664063	8930,664063	2,8578125	0,238151042	10,48102734	5,3014807	4,3735037
7	240	9,8046875	9804,6875	3,1375	0,261458333	11,50678125	5,820324355	4,892347355

Appendix 2.10: MicroGC Raw Data – Stripping Lean Samples

Stripping raw data and calculations – Lean initial molar loading

2 Weeks

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume at outlet	Cumulative CO_2
			Area	Concentration % v/v	(ml/min)	(ml/min)	Cor. flow*concent*time	Volume (ml)
21/7/2010		2	2115,2	9,75				
21/7/2010	09:20	3	7228,4	33,31926059	400	358,7009954	2390,330388	2390,330388
21/7/2010	09:40	4	7828	36,08311271	350	311,7713563	2249,936198	4640,266586
21/7/2010	10:00	5	6571,4	30,29082356	250	225,8605141	1368,300196	6008,566782
21/7/2010	10:20	6	4269,7	19,68115308	250	232,0290137	913,3197077	6921,88649
21/7/2010	10:40	7	1823	8,403106089	250	239,1741741	401,9611918	7323,847681
21/7/2010	11:00	8	1238,2	5,70747447	250	240,9819678	275,0796858	7598,927367
21/7/2010	11:20	9	780,3	3,596787538	250	242,4264488	174,391286	7773,318653
21/7/2010	11:40	10	715,7	3,299014278	250	242,6323325	160,0895058	7933,408159
21/7/2010	12:00	11	785,3	3,619835004	150	145,4463212	105,298337	8038,706496
21/7/2010	12:20	12	565,1	2,604824603	150	145,8686081	75,99242783	8114,698924
21/7/2010	12:40	-	565,1	2,604824603	150	145,8686081	75,99242783	8190,691351
21/7/2010	13:00	-	565,1	2,604824603	200	194,4914775	101,3232371	8292,014589
21/7/2010	13:20	-	565,1	2,604824603	200	194,4914775	101,3232371	8393,337826
21/7/2010	13:40	13	283,8	1,308174168	200	195,2179443	51,07581437	8444,41364
21/7/2010	14:00	14	271,6	1,251938351	200	195,2496357	48,88810139	8493,301741
21/7/2010	14:20	15	249,3	1,149146653	200	195,3076033	44,88741571	8538,189157
21/7/2010	14:40	16	220,4	1,0159323	200	195,3828041	39,69914029	8577,888297
21/7/2010	15:00	17	215,4	0,992884834	150	146,5468676	29,10083244	8606,98913
21/7/2010	15:20	18	207,9	0,958313635	150	146,561518	28,0903802	8635,07951
21/7/2010	15:40	19	205,5	0,947250851	150	146,566207	27,76699287	8662,846503
21/7/2010	16:00	20	203,1	0,936188067	150	146,5708965	27,44358487	8690,290088

3 Weeks

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume released	Cumulative CO_2
			Area	Concentration % v/v	(ml/min)	(ml/min)	Cor. flow*concent*time	Volume (ml)
16/7/2010		2	2044,1	9,75				
16/7/2010	09:50	3	13076,1	62,37071327	400	335,7281987	4187,921443	4187,921443
16/7/2010	10:10	4	4516,7	21,54387016	300	277,091291	1193,923759	5381,845203
16/7/2010	10:30	5	2557,6	12,19930532	200	189,356745	462,0041491	5843,849352
16/7/2010	10:50	6	1437	6,854239029	250	240,2079078	329,2884833	6173,137835
16/7/2010	11:10	7	1077,5	5,139486816	250	241,3681379	248,1016724	6421,239507
16/7/2010	11:30	8	727,6	3,470524925	250	242,5136841	168,3299571	6589,569465
16/7/2010	11:50	9	494,2	2,357247688	250	243,2869494	114,6975198	6704,266984
16/7/2010	12:10	10	417,1	1,989494154	250	243,5440153	96,90587892	6801,172863
16/7/2010	12:30	11	357	1,70282765	250	243,7449661	83,01113357	6884,183997
16/7/2010	12:50	12	357	1,70282765	250	243,7449661	83,01113357	6967,19513
16/7/2010	13:10	-	357	1,70282765	250	243,7449661	83,01113357	7050,206264
16/7/2010	13:30	-	357	1,70282765	250	243,7449661	83,01113357	7133,217398
16/7/2010	13:50	-	229,6	1,095151901	200	195,3380734	42,78497246	7176,00237
16/7/2010	14:10	13	277	1,321241622	200	195,2105824	51,58406932	7227,586439
16/7/2010	14:30	14	248,2	1,183870652	200	195,2880155	46,23915005	7273,825589
16/7/2010	14:50	15	224,5	1,070825791	100	97,67590282	20,91877519	7294,744365
16/7/2010	15:10	16	210	1,001663324	100	97,6954321	19,57158625	7314,315951

8 Weeks

Date	Time	Run number	CO_2	CO_2	Flow	Corrected flow	CO_2 Volume released	Cumulative CO_2
			Area	Concentration % v/v	(ml/min)	(ml/min)	Cor. flow*concent*time	Volume (ml)
7/7/2010		2	2038,5	9,75				
7/7/2010	09:50	3	10931,5	52,28458425	200	171,5980332	1794,386365	1794,386365
7/7/2010	10:10	4	5720,4	27,3602649	150	136,5090072	746,9845197	2541,370884
7/7/2010	10:30	5	3595,4	17,19654157	150	140,1288491	481,9463157	3023,3172
7/7/2010	10:50	6	1410,8	6,747755703	100	96,11178779	129,7077728	3153,024973
7/7/2010	11:10	7	849,6	4,063576159	100	96,84190331	78,7048899	3231,729863
7/7/2010	11:30	8	699,9	3,347571744	100	97,0394894	64,96933055	3296,699193
7/7/2010	11:50	9	521,2	2,492862399	100	97,27694309	48,49960674	3345,1988
7/7/2010	12:10	10	427,3	2,043745401	100	97,4024166	39,8131482	3385,011948
7/7/2010	12:30	-	427,3	2,043745401	100	97,4024166	39,8131482	3424,825097
7/7/2010	12:50	-	427,3	2,043745401	100	97,4024166	39,8131482	3464,638245
7/7/2010	13:10	-	427,3	2,043745401	100	97,4024166	39,8131482	3504,451393
7/7/2010	13:30	-	427,3	2,043745401	100	97,4024166	39,8131482	3544,264541
7/7/2010	13:50	11	125,3	0,599300957	150	146,7139188	17,58515837	3561,849699
7/7/2010	14:10	12	153,6	0,734657837	150	146,656404	21,5484553	3583,398155
7/7/2010	14:30	13	113,7	0,543818985	150	146,7375133	15,9597291	3599,357884
7/7/2010	14:50	14	64,1	0,306585725	150	146,8385288	9,003719356	3608,361603
7/7/2010	15:10	15	33,5	0,160228109	150	146,900953	4,707532379	3613,069136
7/7/2010	15:30	16	42,1	0,201361295	150	146,8834009	5,915326365	3618,984462
7/7/2010	15:50	17	43,4	0,207579102	150	146,8807482	6,097874771	3625,082337
7/7/2010	16:10	18	82	0,392200147	150	146,8020496	11,51515709	3636,597494
7/7/2010	16:30	19	86,3	0,41276674	150	146,7932904	12,1182776	3648,715771
7/7/2010	16:50	20	0,53	0,002534952	150	146,9683012	0,074511523	3648,790283
7/7/2010	17:10	21	0,43	0,002056659	100	97,97900372	0,040301886	3648,830585
7/7/2010	17:30	22	0,31	0,001482708	100	97,97916725	0,029054897	3648,85964

Appendix 2.11: Pressure Changes Thermal Degradation Experiment – Rich Samples

Pressure changes during degradation experiment at 160 °C – Rich initial molar loading

Needle pressure gauge

Time (min)	Total Pressure (psi)	Total Pressure (kPa)
0	0	0
8	540	3723.168938
24	560	3861.064084
32	560	3861.064084
48	560	3861.064084
56	560	3861.064084
72	550	3792.116511
80	550	3792.116511
96	550	3792.116511
104	550	3792.116511
120	540	3723.168938
128	530	3654.221365
144	530	3654.221365
152	530	3654.221365
168	520	3585.273792
176	520	3585.273792
192	510	3516.32622
200	510	3516.32622
216	500	3447.378647
224	500	3447.378647
240	490	3378.431074
248	490	3378.431074
264	490	3378.431074
272	490	3378.431074
288	490	3378.431074
296	490	3378.431074
312	490	3378.431074
320	490	3378.431074
336	490	3378.431074
344	490	3378.431074
360	490	3378.431074
368	490	3378.431074
384	485	3343.957287
392	485	3343.957287
408	485	3343.957287

Digital pressure gauge

Time (min)	Pressure (psi)	Pressure (kPa)
0	5.741961254	39.58942923
15	9.237068105	63.68734268
30	18.47413621	127.3746854
45	57.66926303	397.6155719
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75	194.4777312	1340.876755
90	257.8889555	1778.081757
105	311.5638107	2148.156856
120	354.7533453	2445.938215
135	386.9582584	2667.983275
150	412.9219093	2846.996346
165	432.644298	2982.977429
180	447.6233273	3086.254201
195	458.8575994	3163.71178
210	467.5953665	3223.956563
225	474.0862792	3268.709831
240	477.5813861	3292.807745
255	481.3261434	3318.626938
270	484.5715998	3341.003572
285	487.0681047	3358.216367
300	488.8156581	3370.265324
315	490.5632115	3382.31428
330	492.3107649	3394.363237
345	493.8086679	3404.690914
360	494.5576193	3409.854753
375	495.3065708	3415.018591
390	495.8058718	3418.46115
405	496.3051728	3421.90371
420	497.0541242	3427.067548
435	497.0541242	3427.067548
450	497.3037747	3428.788828
465	497.5534252	3430.510107
480	497.8030757	3432.231387
495	498.3023767	3435.673946
510	498.3023767	3435.673946
525	498.5520272	3437.395225
540	498.5520272	3437.395225
555	498.8016777	3439.116505
570	499.0513281	3440.837784
585	499.0513281	3440.837784
600	499.3009786	3442.559064
615	499.5506291	3444.280343
630	499.8002796	3446.001623
645	499.8002796	3446.001623
660	499.8002796	3446.001623
675	500.0499301	3447.722902
690	500.2995806	3449.444182
705	500.2995806	3449.444182
720	500.5492311	3451.165462
735	500.7988816	3452.886741
750	500.7988816	3452.886741
765	501.0485321	3454.608021
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825	501.7974835	3459.771859
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855	502.047134	3461.493139
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37125	475.3345317	3277.316229
37140	475.3345317	3277.316229
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37440	366.2372678	2525.117073
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37470	395.9456761	2729.949338
37485	409.4268025	2822.898432
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37560	444.377871	3063.877567
37575	448.3722788	3091.418039
37590	452.1170361	3117.237232
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37620	459.3569003	3167.154339
37635	463.3513082	3194.694811
37650	466.347114	3215.350166
37665	469.0932694	3234.284241
37680	471.3401238	3249.775756
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37740	477.8310365	3294.529024

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37785	480.5771919	3313.463099
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37845	482.0750949	3323.790776
37860	482.5743958	3327.233335
37875	483.0736968	3330.675894
37890	483.0736968	3330.675894
37905	483.3233473	3332.397174
37920	483.5729978	3334.118453
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37950	483.5729978	3334.118453
37965	484.0722988	3337.561012
37980	484.0722988	3337.561012
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38070	484.5715998	3341.003572
38085	484.3219493	3339.282292
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38115	484.5715998	3341.003572
38130	484.8212502	3342.724851
38145	484.5715998	3341.003572
38160	484.3219493	3339.282292
38175	484.5715998	3341.003572
38190	484.5715998	3341.003572
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38235	484.8212502	3342.724851
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38325	484.5715998	3341.003572
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51885	477.5813861	3292.807745
51900	477.8310365	3294.529024
51915	477.8310365	3294.529024
51930	477.8310365	3294.529024
51945	477.8310365	3294.529024
51960	477.3317356	3291.086465
51975	477.0820851	3289.365186
51990	476.8324346	3287.643906
52005	476.8324346	3287.643906
52020	477.0820851	3289.365186

52035	477.3317356	3291.086465
52050	477.0820851	3289.365186
52065	477.0820851	3289.365186
52080	476.8324346	3287.643906
52095	477.0820851	3289.365186
52110	477.3317356	3291.086465
52125	477.3317356	3291.086465
52140	477.3317356	3291.086465
52155	477.5813861	3292.807745
52170	477.3317356	3291.086465
52185	477.5813861	3292.807745
52200	477.3317356	3291.086465
52215	477.5813861	3292.807745
52230	477.5813861	3292.807745
52245	477.5813861	3292.807745
52260	477.5813861	3292.807745
52275	477.3317356	3291.086465
52290	477.5813861	3292.807745
52305	477.3317356	3291.086465
52320	477.3317356	3291.086465
52335	477.3317356	3291.086465
52350	477.0820851	3289.365186
52365	477.3317356	3291.086465
52380	477.3317356	3291.086465
52395	477.3317356	3291.086465
52410	477.0820851	3289.365186
52425	477.0820851	3289.365186
52440	477.0820851	3289.365186
52455	477.0820851	3289.365186
52470	477.0820851	3289.365186
52485	477.0820851	3289.365186
52500	477.0820851	3289.365186
52515	477.0820851	3289.365186
52530	477.0820851	3289.365186
52545	477.0820851	3289.365186
52560	477.0820851	3289.365186
52575	476.8324346	3287.643906
52590	477.0820851	3289.365186
52605	477.3317356	3291.086465
52620	477.5813861	3292.807745
52635	477.5813861	3292.807745
52650	477.5813861	3292.807745
52665	477.5813861	3292.807745
52680	477.3317356	3291.086465
52695	477.3317356	3291.086465
52710	477.3317356	3291.086465
52725	477.3317356	3291.086465
52740	477.3317356	3291.086465
52755	477.3317356	3291.086465
52770	477.3317356	3291.086465
52785	477.3317356	3291.086465
52800	477.3317356	3291.086465
52815	477.3317356	3291.086465
52830	477.0820851	3289.365186
52845	476.8324346	3287.643906
52860	477.0820851	3289.365186

52875	476.8324346	3287.643906
52890	476.8324346	3287.643906
52905	477.0820851	3289.365186
52920	476.8324346	3287.643906
52935	476.8324346	3287.643906
52950	477.0820851	3289.365186
52965	476.8324346	3287.643906
52980	476.8324346	3287.643906
52995	476.8324346	3287.643906
53010	476.8324346	3287.643906
53025	476.8324346	3287.643906
53040	476.8324346	3287.643906
53055	476.8324346	3287.643906
53070	476.8324346	3287.643906
53085	476.5827841	3285.922626
53100	476.8324346	3287.643906
53115	476.5827841	3285.922626
53130	476.5827841	3285.922626
53145	476.5827841	3285.922626
53160	476.5827841	3285.922626
53175	476.5827841	3285.922626
53190	476.8324346	3287.643906
53205	476.5827841	3285.922626
53220	477.0820851	3289.365186
53235	476.8324346	3287.643906
53250	476.5827841	3285.922626
53265	476.3331336	3284.201347

Appendix 2.12: MicroGC Raw Data – 1st Stripping – Rich Samples

1st Stripping raw data and calculations – Rich initial molar loading

2 weeks

Date	Time	Run number	microGC	CO_2	Flow	Flow Corrected	CO_2 Volume =	Cumulative CO_2 volume (ml)
			Area	Concentration % v/v			Corrected flow*Concentration*20 min	
08/12/2010		2	2764.2	9.75				
08/12/2010	10:50	3	1483.7	5.233367701	250	241.3041809	126.2833507	126.2834
08/12/2010	11:00	4	7189.4	25.35874756	300	274.3993532	695.8423929	822.1257
08/12/2010	11:10	5	14530.8	51.25363577	600	515.9816692	2644.593654	3466.719
08/12/2010	11:20	6	13586.6	47.92321467	500	433.2291308	2076.173264	5542.893
08/12/2010	11:30	7	10339.6	36.47026264	250	222.4868875	811.4155221	6354.308
08/12/2010	11:40	8	7628.5	26.90755915	250	227.7738512	612.8838373	6967.192
08/12/2010	11:50	9	6561.4	23.14364011	200	183.9685434	425.7701761	7392.962
08/12/2010	12:00	10	5515.2	19.45344042	200	185.7336022	361.3157563	7754.278
08/12/2010	12:10	11	2915.8	10.28472976	200	190.3489032	195.7687029	7950.047
08/12/2010	12:20	12	2103	7.417788148	200	191.8641908	142.3207921	8092.367
08/12/2010	12:30	13	1772.5	6.252034947	200	192.4907685	120.3459012	8212.713
08/12/2010	12:40	14	1599.3	5.641116779	200	192.8215906	108.772911	8321.486
08/12/2010	12:50	15	1425.3	5.027376818	200	193.1556641	97.10663079	8418.593
08/12/2010	13:00		1425.3	5.027376818	200	193.1556641	97.10663079	8515.7
08/12/2010	13:10		920	3.245061862	200	194.1357535	62.99825299	8578.698
08/12/2010	13:20		920	3.245061862	200	194.1357535	62.99825299	8641.696
08/12/2010	13:30		920	3.245061862	200	194.1357535	62.99825299	8704.694
08/12/2010	13:40		920	3.245061862	200	194.1357535	62.99825299	8767.693
08/12/2010	13:50		920	3.245061862	200	194.1357535	62.99825299	8830.691
08/12/2010	14:00	16	920.3	3.246120035	200	194.1351672	63.01860557	8893.709

08/12/2010	14:10	17	1057.4	3.729704797	200	193.8677739	72.30695665	8966.016
08/12/2010	14:20	18	809.6	2.855654439	200	194.3518804	55.50018099	9021.517
08/12/2010	14:30	19	647.9	2.285299544	200	194.6697427	44.48786742	9066.004
08/12/2010	14:40	20	406.8	1.434881702	200	195.1465955	28.0012279	9094.006
08/12/2010	14:50	21	120	0.423268939	200	195.7184243	8.284152973	9102.29
08/12/2010	15:00	22	120	0.423268939	200	195.7184243	8.284152973	9110.574

3 weeks

Date	Time	Run number	microGC	CO$_2$	Flow	Flow Corrected	CO$_2$ Volume =	Cumulative CO$_2$ volume (ml)
			Area	Concentration % v/v			Corrected flow*Concentration*20 min	
11/01/2011		2	3410.7	9.75				
11/01/2011	10:00	3	386.6	1.105154367	300	292.9986416	97.1426185	97.14262
11/01/2011	10:15	4	16836.8	48.13053039	300	259.8150133	3751.510318	3848.653
11/01/2011	10:30	5	6033.4	17.24738324	300	280.2200377	1449.918714	5298.572
11/01/2011	11:00	6	1806.6	5.164438385	300	289.6213614	448.7195028	5747.291
11/01/2011	11:30	7	880.3	2.516470226	300	291.811083	220.3001706	5967.591
11/01/2011	12:00	8	575.1	1.644010027	200	195.0290066	96.18889274	6063.78
11/01/2011	12:30	9	290.4	0.830152168	200	195.4878239	48.68539227	6112.466
11/01/2011	13:00	10	290.4	0.830152168	200	195.4878239	48.68539227	6161.151
11/01/2011	13:30	11	290.4	0.830152168	200	195.4878239	48.68539227	6209.836
11/01/2011	14:00	12	214.9	0.614324039	200	195.6100426	36.05038543	6245.887
11/01/2011	14:30	13	120.7	0.345039142	200	195.7628545	20.26375418	6266.151
11/01/2011	15:00	14	85.3	0.243842906	200	195.8203733	14.32482268	6280.475

8 weeks

Date	Time	Run number	microGC	CO_2	Flow	Flow Corrected	CO_2 Volume =	Cumulative CO_2 volume (ml)
			Area	Concentration % v/v			Corrected flow*Concentration*20 min	
14/01/2011		2	3823.9	9.75				
14/01/2011	10:30	3	247.9	0.632083736	300	293.3999655	55.63600395	0
14/01/2011	10:45	4	1512.3	3.855991265	250	242.2476586	280.2314567	55.636
14/01/2011	11:00	5	4530	11.5503805	250	237.1141077	821.6274499	335.8675
14/01/2011	11:30	6	2656.3	6.772908549	250	240.2625598	488.1829036	1157.495
14/01/2011	12:00	7	1353.9	3.452110411	250	242.5264147	251.1683883	1645.678
14/01/2011	12:30	8	1000	2.54975287	200	194.5221674	148.7950364	1896.846
14/01/2011	13:00	9	716.4	1.826642956	200	194.9264893	106.8183296	2045.641
14/01/2011	13:30	10	545.8	1.391655117	200	195.1709275	81.48318597	2152.46
14/01/2011	14:00	11	381.7	0.973240671	200	195.4069223	57.05338922	2233.943
14/01/2011	14:30	12	273	0.696082534	200	195.5637176	40.83854641	2290.996
14/01/2011	15:00	13	257.7	0.657071315	200	195.5858176	38.55414908	2331.835
14/01/2011	15:30	14	222.5	0.567320014	200	195.6366903	33.29658295	2370.389

Appendix 2.13: Inorganic Carbon Measurement – Absorption – Rich Samples

Absorption inorganic carbon measurement with TOC instrument – Rich initial molar loading

2 Weeks

Sample	Time (min)	TOC response (mg/L)	C Concentration after dilution (mg/L)	C Content in 396 ml (g)	atoms of C	gr of CO_2	L of CO_2	Cumulative CO_2 volume (ml)
		403.1						
Initial	0	12.36	3121.212121	1.236	0.102914238	4.52925562	2.290974011	0
2	30	16.93	4275.252525	1.693	0.140965862	6.203907577	3.138041263	847.0672517
3	60	17.88	4515.151515	1.788	0.148875937	6.552029975	3.314127453	1023.153442
4	90	23.38	5904.040404	2.338	0.194671107	8.567475437	4.333573817	2042.599806
5	120	42.09	10628.78788	4.209	0.350457952	15.42365445	7.801544995	5510.570983
6	150	45.16	11404.0404	4.516	0.376019983	16.54863947	8.37058142	6079.607409
	210	46.36	11707.07071	4.636	0.386011657	16.98837302	8.593006081	6302.03207
7	240	45.23	11421.71717	4.523	0.376602831	16.57429059	8.383556192	6092.582181
8	270	45.61	11517.67677	4.561	0.379766861	16.71353955	8.453990668	6163.016657
9	300	44.89	11335.85859	4.489	0.373771857	16.44969942	8.320535871	6029.56186
10	330	45.17	11406.56566	4.517	0.376103247	16.55230391	8.372434959	6081.460947
11	360	46.12	11646.46465	4.612	0.384013322	16.90042631	8.548521149	6257.547138

3 Weeks

Sample	Time (min)	TOC response (mg/L)	C Concentration after dilution (mg/L)	C Content in 396 ml (g)	atoms of C	gr of CO_2	L of CO_2	Cumulative CO_2 volume (ml)
		393.6						
Initial	0	6.117	1554.116	0.620092226	0.051631326	2.272295	1.149365	0
2	30	14.33	3640.752	1.452660061	0.12095421	5.323195	2.692562	1558.752
3	60	28.09	7136.687	2.84753811	0.237097261	10.43465	5.278022	4144.212
4	90	35.1	8917.683	3.558155488	0.296266069	13.03867	6.595179	5461.369
5	120	40	10162.6	4.054878049	0.33762515	14.85888	7.515874	6382.064
6	150	41.4	10518.29	4.19679878	0.34944203	15.37894	7.77893	6645.12
	210	40.87	10383.64	4.143071646	0.344968497	15.18206	7.679344	6545.534
7	240	40.21	10215.96	4.076166159	0.339397682	14.93689	7.555332	6421.522
8	270	38.96	9898.374	3.94945122	0.328846896	14.47255	7.320461	6186.651
9	300	39.42	10015.24	3.996082317	0.332729585	14.64343	7.406894	6273.084
10	330	41.36	10508.13	4.192743902	0.349104405	15.36408	7.771414	6637.604

8 Weeks

Sample	Time (min)	TOC response (mg/L)	C Concentration after dilution (mg/L)	C Content in 396 ml (g)	atoms of C	gr of CO_2	L of CO_2	Cumulative CO_2 volume (ml)
		456.3						
Initial	0	5.247	1308.478803	0.620092226	0.051631326	2.272295	1.149365	0
2	30	17.79	4436.408978	1.452660061	0.12095421	5.323195	2.692562	1558.752
3	60	27.63	6890.274314	2.84753811	0.237097261	10.43465	5.278022	4144.212
4	90	26.86	6698.254364	3.558155488	0.296266069	13.03867	6.595179	5461.369
5	120	27.45	6845.386534	4.054878049	0.33762515	14.85888	7.515874	6382.064
6	150	26.35	6571.072319	4.19679878	0.34944203	15.37894	7.77893	6645.12
	210	26.93	6715.710723	4.143071646	0.344968497	15.18206	7.679344	6545.534
7	240	27.01	6735.660848	4.076166159	0.339397682	14.93689	7.555332	6421.522
8	270	26	6483.790524	3.94945122	0.328846896	14.47255	7.320461	6186.651
9	300	27.6	6882.793017	3.996082317	0.332729585	14.64343	7.406894	6273.084
10	330	26.8	6683.291771	4.192743902	0.349104405	15.36408	7.771414	6637.604

Appendix 2.14: MicroGC Raw Data – Stripping – Rich Samples

Stripping microGC measurement – Rich initial molar loading

2 weeks

Date	Time	Run number	microGC	CO_2	Flow	Flow Corrected	CO_2 Volume =	Cumulative CO_2 volume (ml)
			Area	Concentration % v/v			Corrected flow*Concentration*20 min	
18/01/2011		2	3959	9.75				
18/01/2011	10:00	3	8088.3	19.91940515	250	231.8849011	1385.702788	0
18/01/2011	10:15	4	7455	18.35974994	300	279.3998444	1538.913383	1385.703
18/01/2011	10:30	5	7412.4	18.25483708	300	279.4768935	1530.541548	2924.616
18/01/2011	11:00	6	7315.9	18.01718237	300	279.6516656	1511.560518	4455.158
18/01/2011	11:30	7	4245.7	10.45606845	300	285.3892158	895.2147529	5966.718
18/01/2011	12:00	8	2694	6.634629957	250	240.3555653	478.4010702	6861.933
18/01/2011	12:30	9	1745.1	4.297733013	250	241.9438691	311.943046	7340.334
18/01/2011	13:00	10	934	2.300202071	250	243.3267719	167.9102234	7652.277
18/01/2011	13:30	11	568.8	1.400808285	250	243.9572181	102.5211877	7820.187
18/01/2011	14:00	12	511.3	1.259200556	200	195.2455422	73.75598859	7922.709
18/01/2011	14:30	13	471.2	1.160444557	200	195.3012295	67.99087461	7996.465
18/01/2011	15:00	14	288.2	0.709762566	200	195.5559696	41.63949206	8064.455
18/01/2011	15:30	15	101.3	0.249475878	200	195.8171703	14.65549813	8106.095

3 weeks

Date	Time	Run number	microGC	CO_2	Flow	Flow Corrected	CO_2 Volume =	Cumulative CO_2 volume (ml)
			Area	Concentration % v/v			Corrected flow*Concentration*20 min	
10/01/2011		2	4565.9	9.75				
10/01/2011	10:00	3	15339.2	32.75525088	300	269.3961243	2647.241292	0
10/01/2011	10:15	4	9894	21.12759806	300	277.3898485	1758.174368	2647.241
10/01/2011	10:30	5	6675.8	14.2554699	300	282.4624532	1207.9905	4405.416
10/01/2011	11:00	6	4466.7	9.538168817	200	190.7400291	545.7931792	5613.406
10/01/2011	11:30	7	2019.4	4.31221665	250	241.9339279	312.9814536	6159.199
10/01/2011	12:00	8	1674.2	3.575078298	250	242.4414411	260.0241404	6472.181
10/01/2011	12:30	9	1674.2	3.575078298	200	193.9531529	208.0193123	6732.205
10/01/2011	13:00	10	1674.2	3.575078298	200	193.9531529	208.0193123	6940.224
10/01/2011	13:30	11	1674.2	3.575078298	200	193.9531529	208.0193123	7148.244
10/01/2011	14:00	12	229	0.489005453	200	195.681113	28.70673942	7356.263
10/01/2011	14:30	13	169.9	0.362803609	200	195.7527626	21.30594265	7384.97
10/01/2011	15:00	14	140.9	0.300877155	200	195.7879495	17.67243634	7406.276
10/01/2011	15:30	15	123.1	0.262867124	200	195.8095563	15.44156846	7423.948

8 weeks

Date	Time	Run number	microGC	CO_2	Flow	Flow Corrected	CO_2 Volume =	Cumulative CO_2 volume (ml)
			Area	Concentration % v/v			Corrected flow*Concentration*20 min	
18/01/2011		2	3043.4	9.75				
18/01/2011	10:00	3	8788.2	28.1543504	250	227.0631091	1917.844301	0
18/01/2011	10:15	4	3160.6	10.12546823	300	285.6482084	867.6965575	1917.844
18/01/2011	10:30	5	2100	6.727672997	300	288.3515678	581.9805169	2785.541
18/01/2011	11:00	6	987.6	3.163928501	300	291.2710864	276.4682675	3367.521
18/01/2011	11:30	7	512.8	1.642833673	300	292.5445012	144.1805872	3643.99
18/01/2011	12:00	8	265.2	0.84960899	250	244.3460215	62.27957297	3788.17
18/01/2011	12:30	9	210.9	0.675650588	250	244.4691143	49.55271026	3850.45
18/01/2011	13:00	10	141.7	0.453957745	250	244.6262538	33.31499474	3900.003
18/01/2011	13:30	11	127.7	0.409106591	250	244.6580819	30.02737018	3933.318
18/01/2011	14:00	12	114.5	0.366818361	200	195.7504821	21.54146131	3963.345
18/01/2011	14:30	13	101.8	0.326131958	200	195.7735973	19.15440797	3984.886