

Copyright

by

Akinleye Olaolu Alawode

2005

**Oxidative Degradation of Piperazine in the
Absorption of Carbon Dioxide**

by

Akinleye Olaolu Alawode, B.S.

Thesis

**Presented to the Faculty of the Graduate School
of The University of Texas at Austin
in Partial Fulfilment
of the Requirements
for the Degree of**

Master of Science in Engineering

The University of Texas at Austin

May, 2005

**Oxidative Degradation of Piperazine in the
Absorption of Carbon Dioxide**

APPROVED BY

SUPERVISING COMMITTEE:

**(SUPERVISOR) _____
GARY ROCHELLE**

**_____
BRUCE ELDRIDGE**

Dedication

To Jesus Christ my Lord and Savior

Acknowledgments

To God Almighty for giving me this opportunity, and for being with me since the beginning of my program all the way to the end.

I would like to thank Dr. Gary Rochelle whose support and contributions to this work are immeasurable and without whom I would not even be here in the first place. He gave me the much needed encouragement at times when I hit road blocks in my research, finding a way to make me push forward and overcome the problems.

I am also grateful for the financial support from the Separations Research Program and the Texas Advanced Technology Program. I thank Dr. Mullins who gave me a chance to prove myself and provided me with the much needed guidance throughout the course of my stay in Austin. Thanks for being a friend.

I would also like to acknowledge my family for supporting me when I came over to the United States. Finally, to the most important person in my life, my wife who believed in me and was my major source of motivation throughout this program. Thanks for being there with me every step of the way. I love you very much.

May 2005

Austin, Texas

Oxidative Degradation of Piperazine in the Absorption of Carbon Dioxide

by

Akinleye Olaolu Alawode, M.S.E.

The University of Texas at Austin, 2005

SUPERVISOR: Gary T. Rochelle

Oxidative degradation of piperazine was quantified by using Gas and Ion Chromatography. The GC analysis involved the direct analysis of the piperazine using calibration standards, while the IC analysis was based on quantifying acetate, a degradation product which is an indication of piperazine loss. This study used an agitated reactor maintained at 55°C, with conditions similar to those in absorber/stripper configurations for CO₂ removal from flue gas.

The problems encountered with the apparatus by the previous investigator were eliminated and the effect of varying some process parameters such as catalyst concentration, duration and agitation on degradation was studied. The rate of acetate production ranged from 0.08 to 0.4mM/hr while actual piperazine loss ranged from 1mM/hr to 5mM/hr. The degradation rate was found to be dependent on agitation rate and catalyst concentration.

Table of Contents

CHAPTER 1 Introduction.....	1
1.1. Background.....	1
1.2. Importance of degradation.....	5
CHAPTER 2 Analytical Methods.....	11
2.1. Gas Chromatography.....	11
2.1.1. GC Method Development.....	13
2.2. Ion Chromatography.....	17
2.2.1. IC Method Development.....	18
2.3. Nuclear Magnetic Resonance.....	22
2.3.1. The NMR Method.....	23
CHAPTER 3 Oxidative Degradation.....	26
3.1. Experimental Apparatus.....	26
3.2. Experimental Procedure.....	30
CHAPTER 4 Results.....	33
4.1. Summary of Experimental Results.....	33
CHAPTER 5 Conclusions and Recommendations.....	40
5.1. Results.....	40
5.2. Apparatus and Sample Analysis.....	42

APPENDIX A Raw Results.....	44
APPENDIX B Procedure for Using the GC.....	46
APPENDIX C Ion Chromatograms.....	65
C.1. Analytical Information.....	65
C.2. Sample Preparation.....	65
C.3. Procedure for IC.....	66
APPENDIX D NMR Peaks and Positions.....	73
References.....	79
Vita.....	82

List of Tables

Table 4.1. Summary of Experimental Results.....	35
Table A.1. Peak Areas from GC.....	44
Table A.2. Concentration of PZ after Calibration.....	45
Table A.3. Concentration Values from IC.....	45
Table D.5. Position for Peaks in NMR Spectra.....	73

List of Figures

Figure 1.1. Schematics of a Typical Acid Gas Removal Process.....	4
Figure 2.1. A Typical Calibration Curve Showing Linear Response of the GC..	13
Figure 2.2. Chromatogram Showing Piperazine and Ethanol.....	16
Figure 2.3. Sample Chromatogram of Formate.....	20
Figure 2.4. Sample Chromatogram of Acetate.....	21
Figure 2.5. Sample Chromatogram of Glycolate.....	21
Figure 2.6. Calibration Curve of Ion Chromatograph.....	22
Figure 2.7. NMR Spectrum Showing Piperazine, Formate and Acetate.....	25
Figure 3.1a. Experimental Set-up.....	28
Figure 3.1b. Reactor Cover (Top View).....	29
Figure 4.1. Chromatogram for Experiment 1-4-2005.....	37
Figure 4.2. Chromatogram for 1-2-2005.....	37
Figure 4.3. Chromatogram for 12-20-2004.....	38
Figure 4.4. Chromatogram for 1-10-2005.....	38
Figure 4.5. Chromatogram for 12-22-2004.....	39
Figure B.1. Chromatogram for 6-13-2004, Initial.....	50
Figure B.2. Chromatogram for 6-13-2004, Final.....	51
Figure B.3. Chromatogram for 6-21-2004, Initial.....	52
Figure B.4. Chromatogram for 6-21-2004, Final.....	53

Figure B.5. Chromatogram for 6-30-2004, Initial.....	54
Figure B.6. Chromatogram for 6-30-2004, Final.....	55
Figure B.7. Chromatogram for 7-10-2004, Initial.....	56
Figure B.8. Chromatogram for 7-10-2004, Final.....	57
Figure B.9. Chromatogram for Calibration Sample1.....	58
Figure B.10. Chromatogram for Calibration Sample 2.....	59
Figure B.11. Chromatogram for Calibration Sample 3.....	60
Figure B.12. Chromatogram for Calibration Sample 4.....	61
Figure B.13. Calibration Curve for 6-21-2004.....	62
Figure B.14. Calibration Curve for 6-13-2004.....	63
Figure B.15. Calibration Curve for 6-30-2004.....	64
Figure C.1. Calibration Curve for 1-10-2005.....	68
Figure C.2. Calibration Curve for 12-20-2004.....	69
Figure C.3. Calibration Curve for 1-2-2005.....	70
Figure C.4. Calibration Curve for 1-4-2005.....	71
Figure C.5. Calibration Curve for 12-22-2004.....	72
Figure D.1. NMR Spectrum for experiment 1-10-2005.....	74
Figure D.2. NMR Spectrum for experiment 12-20-2004.....	75
Figure D.3. NMR Spectrum for experiment 1-4-2005.....	76
Figure D.4. NMR Spectrum for experiment 12-22-2004.....	77
Figure D.5. NMR Spectrum for experiment 1-2-2005.....	78

CHAPTER 1

Introduction

Greenhouse gas emissions have become important with a growing awareness of their impact on global climate change. In the United States alone, approximately fifteen thousand pounds of carbon equivalent greenhouse gases are emitted per person every year, eighty-two percent of which come from coal-fired power plants and automobiles. This is why significant research effort has been channeled towards technology for CO₂ capture and sequestration. This research is focused on investigating the oxidative degradation of a potential replacement solvent.

1.1. Background

Many processes have been developed for acid gas removal. The Absorption/stripping with amine solutions has extensive industrial applications (Figure 1.1). In this configuration, flue gas enters the absorber from the bottom while the amine solution flows down from the top. The amine contacts the gas

counter currently with the CO₂ transferring into the solution. After the loaded solution leaves the bottom of the absorber, it is heated in the heat exchanger and fed into the top of the stripper where it contacts steam produced in the reboiler at reduced pressure and high temperature. The energy supplied by the steam reverses the reaction of the gas with the amine, increasing the partial pressure of the gas and thereby stripping it from the solution. The lean solution is sent to the heat exchanger where the temperature is reduced before it is returned to the absorber. The flue gas can contain as much as 12 mole percent CO₂ and 5 mole percent O₂. The absorber usually operates at 40-60°C and 1 atm while the stripper is usually at 100-120°C and 1 to 2 atm.

One of the most common solvents used in this process is 15-30 wt-% monoethanolamine (MEA) solution, which has been considered the state-of-the-art solvent in spite of its shortcomings. This is probably because of the difficulty in finding a solvent that combines cheapness of raw materials with high rate and capacity for CO₂ absorption, as is the case with MEA. As the issue of greenhouse gases became more important, there has been the pressure to find more efficient and economical ways of removing greenhouse gases. Thus, the main focus of recent research has been finding other solvents that are as good as, or even better than MEA, without sharing its disadvantages.

One of the major problems of MEA is its high heat of CO₂ absorption; 18.9 kcal/gmol at 25°C and 23.6 kcal/gmol at 120°C (Austgen, 1989). This makes

the absorption process with MEA highly energy-intensive, driving up cost. MEA has a very high degradation rate and this also drives up the cost for raw materials because of the need for frequent replacement and disposal of the spent solvent. Finally, MEA has the highest corrosion rate of carbon steel when compared to all the other known amines and this has a direct effect on the equipment.

One of the solvents that is currently being tested as a possible replacement for MEA is potassium carbonate promoted with piperazine (Cullinane, 2005). On its own, potassium carbonate does not have the rate and capacity for CO₂ that MEA has, but this is greatly improved by the addition of piperazine (PZ), Cullinane (2002). In choosing piperazine as a promoter, it was also important to ensure that it would not drive up the heat of absorption of the mixture as most amines do. Apart from having rates and capacity comparable to or even better than that of MEA at certain concentrations, the heat of absorption for the potassium carbonate solvent is 6.3 kcal/gmol at 25°C and 3.0 kcal/gmol at 120°C. Piperazine is a secondary amine and because it is key to the properties of potassium, its kinetics and chemistry, of which little is currently known, has to be fully understood.

PZ is five times more expensive than MEA. Therefore it must have a lower rate of degradation than MEA if it is to be economically viable.. It is also important to have an understanding of the degradation by-products and their impact on the internals of the absorber-stripper system in terms of corrosion as

well as for reasons of disposal. In conclusion, if PZ-promoted potassium carbonate is to be economically viable industrially, the degradation process must be studied. Therefore this research is focused on understanding and quantifying the oxidative degradation of piperazine in aqueous potassium carbonate.

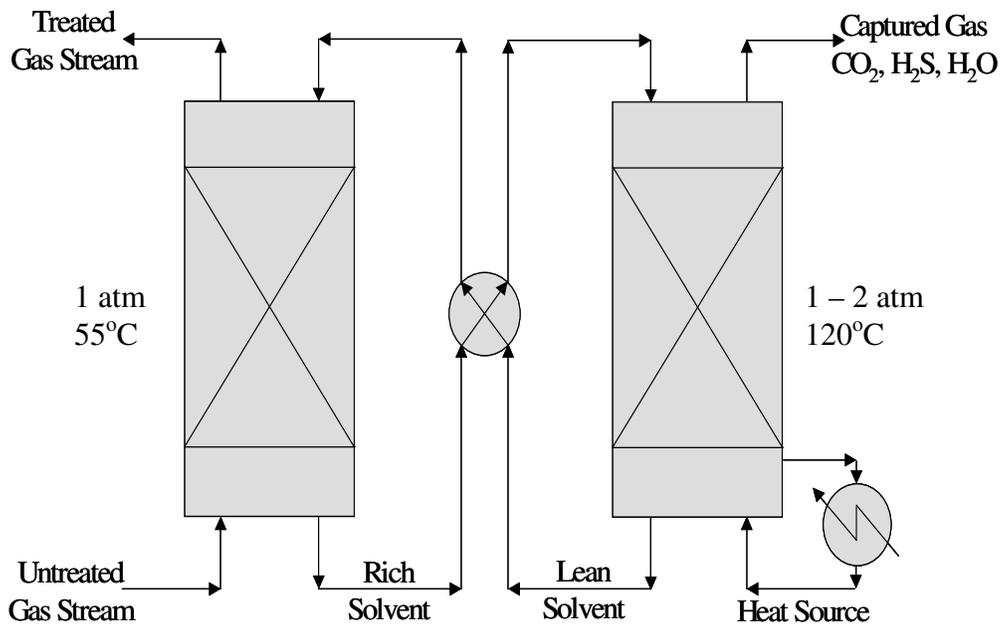


Figure 1.1 CO₂ Capture by Aqueous Absorption/Stripping

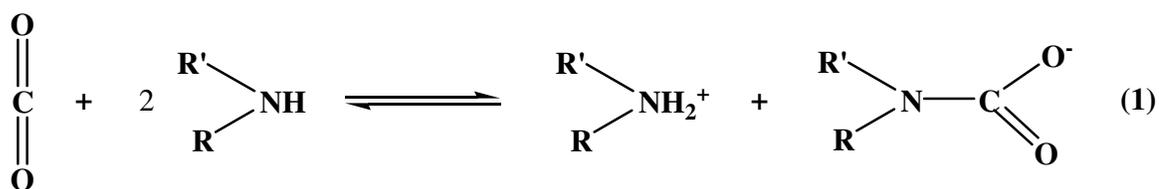
1.2. Importance of Degradation

A major factor in determining the economic viability of a solvent is the rate at which it degrades. Thus, apart from having absorption rates and capacity comparable to that of MEA, a solvent either has to be cheaper or have a lower rate of degradation before it can be considered as a possible replacement. Degradation is an irreversible process and the spent solvent must be replaced. Moreover, the waste must also be disposed of and the toxicity of the waste products is determined mainly by the kind of degradation products that are in it. Degradation products can also be responsible for a high degree of corrosion that occurs in the process equipment. Degradation products expected from MEA include ammonia, formate, acetate, formaldehyde, methyl amine and other carboxylic acids. According to data from IEA, the cost of CO₂ capture is about \$35/metric ton. MEA make-up comes to about \$4.86/metric ton of CO₂ (Kerr-McGee, 1992). This shows that although degradation is not critical, it is still an important factor to consider, contributing to about 5% of the total cost of CO₂ capture. This is lower than would be the case for a more expensive solvent because at \$0.67/lb, MEA is one of the cheapest solvents in use today.

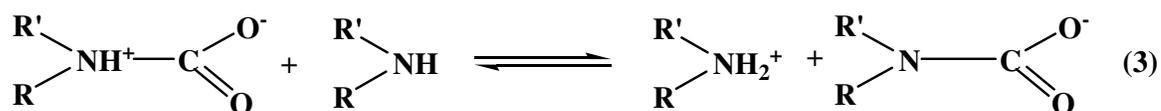
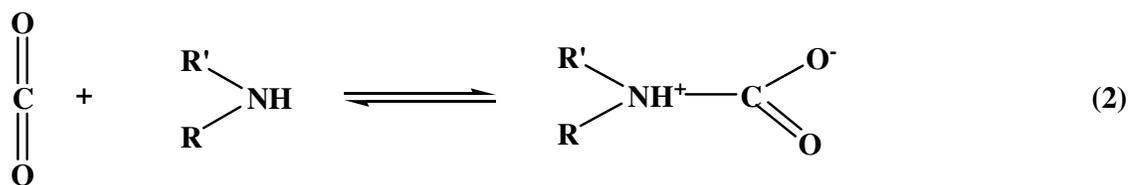
There are two types of degradation associated with the use of amines in stripper/absorber configurations for CO₂ capture – oxidative degradation and carbamate polymerization. Oxidative degradation requires dissolved oxygen or metals that can be reduced. Due to the high concentration of oxygen, oxidative

degradation is probably limited to the absorber. Carbamate polymerization involves amine carbamates bonding with the amino groups of free amines/amine compounds. This requires high temperatures and CO₂-loaded alkanolamines and is most likely to occur in the stripper. Piperazine is not an alkanolamine and should not be subject to carbamate polymerization. Therefore oxidative degradation will be most important for the piperazine-potassium carbonate..

The chemistry of the degradation process is very complex, as is evident in the complexity of the absorption reactions.



The absorption of CO₂ is believed to take place in two steps: the formation of a net-neutral charged intermediate (a zwitterion) and the extraction of a proton to yield a protonated amine and a carbamate (Equations 2 & 3).



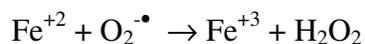
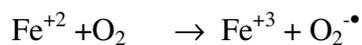
Over the years different researchers for degradation have proposed many mechanisms. Hull (1969) proposed a mechanism for tertiary amines from experimental work with oxidants such as chlorine dioxide and hexacyanoferrate. The free radical extracts an electron from the unprotonated nitrogen in the amine and a proton leaves the adjacent carbon to form an imine radical. The reaction can then have two different pathways. In the first half, the imine can hydrolyze to form an aldehyde or ketone and an amine. In the second half, the imine that has lost a constituent can be hydrolyzed to form either an aldehyde and a further fragmented amine or organic acids and more fragmented amines. In the case of piperazine, this mechanism would form ethylenediamine monoacetaldehyde in the pathway that uses two oxidizers atoms and ammonia or an amine that has an acetaldehyde group in the pathway that only needs one oxidizer. The aldehyde

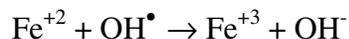
constituents can be readily oxidized to their carboxylate counterparts (Denisov, 1977; Sajus and Seree De Roch, 1980).

In industrial applications, there is an abundance of metals in solution. Amines are known to be highly corrosive and thus there is a supply of iron from the process equipment. Metals such as vanadium and copper are also added to amine solutions to act as corrosion inhibitors (Pearce et al, 1984, Faucher, 1989, Wolcott et al, 1986). It has been shown that these metals may also help to catalyze the degradation reaction by the pathway of free radicals (Ferris et al, 1968). Lee and Rochelle (1998) suggested that the ferrous ion reacts with peroxides in solution, producing free radicals that can initiate oxidation:



The ferrous ion can be regenerated by reacting with peroxide, making more free radicals available in solution and conserving the iron that can then react with dissolved oxygen to create ferric ion, hydrogen peroxide and hydroxyl and peroxy radicals.





These compounds can react with the amines themselves through autoxidation. In autoxidation, the oxygen, usually as peroxide, reacts with carbon adjacent to the nitrogen, with either the extraction of a hydrogen, or the loss of a proton. The radical carbon reacts with oxygen to produce more radicals and degradation products. It is expected that this reaction mechanism will be important in the study of degradation in piperazine.

Most of the work that has been done in the field of degradation has involved the more popular amines like Monoethanolamine, Diethanolamine (DEA), Diglycolamine (DGA) and Methyldiethanolamine (MDEA). Organic acids like formic, acetic and glycolic acid have been discovered as the degradation products of such amines. Rooney (1998) showed some of the degradation products of MEA to be formate, acetate and glycolate, and also went on to show that larger amine compounds such as DEA and MDEA and other secondary and tertiary amines have similar degradation products. The rates of oxidation for amines have been from 0.2mM/hr for MDEA to 7mM/hr for MEA and 10mM/hr for DEA (Kindrick, 1950).

Chi (2000) and Goff (2003) have both confirmed that metal ions, especially iron and copper, catalyze the degradation of MEA based on rate of ammonia evolution. Chi and Rochelle established the fact that only ferrous iron

catalyzes ammonia production in unloaded MEA and that the rates of degradation were two times faster in the loaded solutions in comparison to unloaded solutions. Goff also found out that the degradation rate is a strong function of mass transfer based on experiments conducted with 15 wt-% magnesium sulfate.

In the analysis of amines and their degradation products, different analytical tools have been employed. Rooney (1998) used ion chromatography to analyze for formate, acetate and glycolate. Dawodu and Meisen (1996) used gas chromatography to analyze degradation products of MDEA and blends of MDEA, DEA and MEA. Strazisar (2002) used gas chromatography with detection methods such as MS and FTIR.

For this study, attempts were made to investigate the degradation of PZ by quantifying and identifying possible degradation products in a laboratory environment. This also involved studying the effect of corrosion inhibitors and iron on the rate of degradation. A 2m PZ and 4m potassium bicarbonate solution was used in the experiments. The apparatus and conditions were chosen to simulate the conditions in an absorber. Reactor temperature was kept constant at 55°C and pure oxygen with 2% CO₂ flows into the reactor to cause degradation of the solution. Gas Chromatography, Ion Chromatography and Nuclear Magnetic Resonance Spectroscopy (NMR) were used to measure degradation of PZ and identify and quantify possible degradation products.

CHAPTER 2

Analytical Methods

2.1 Gas Chromatography (GC)

The Gas Chromatograph is a versatile analytical tool that is well suited to the analysis of piperazine. Due to the low level of degradation expected in the piperazine, there is a need for accuracy and reproducibility. The fact that the solutions to be analyzed contain a high concentration of potassium salt also impacts heavily on the method and the tool. The GC has a higher tolerance for the potassium bicarbonate than other methods for analyzing amines while maintaining a fairly high degree of sensitivity.

In GC, an important requirement is that the components be stable, have different molecular weights and/or boiling points. The closer the components are in terms of molecular weight, the more difficult the separation will be. The components also have to be able to interact with the column material (the stationary phase) and the mobile phase (the carrier gas), leading to differing

distribution of the sample components between the two phases. The choice of carrier gas depends solely on the type of detector being used, the most important characteristic being that it must be inert.

The components travel through the columns at rates determined by their affinity for the solid packing of the column. The GC separates components on the basis of boiling point, polarity or molecular weight. The boiling point is the method of choice here because a temperature program can be incorporated into the method development, thereby improving the separation efficiency. The components are measured by a detector, which converts the quantity into proportional peak areas. There are several kinds of detectors some of which are the Flame Ionization Detector (FID), Thermal Conductivity Detector (TCD) and Electron Capture Detector. The FID is preferred in this case because it is particularly suited to analysis of organic compounds, has a high degree of sensitivity and a wide linear response range (Fig. 2.1). It is also robust and very easy to use.

In the FID, the effluent from the column is mixed with hydrogen and air and ignited, producing ions and electrons, which conduct electricity through the flame. A large electric potential is applied at the burner tip and a collector electrode is located immediately above the flame. The resulting current is then measured and converted into peak areas by the associated software. Column

length, gas flow rates and temperature all play a vital role in ensuring a good separation.

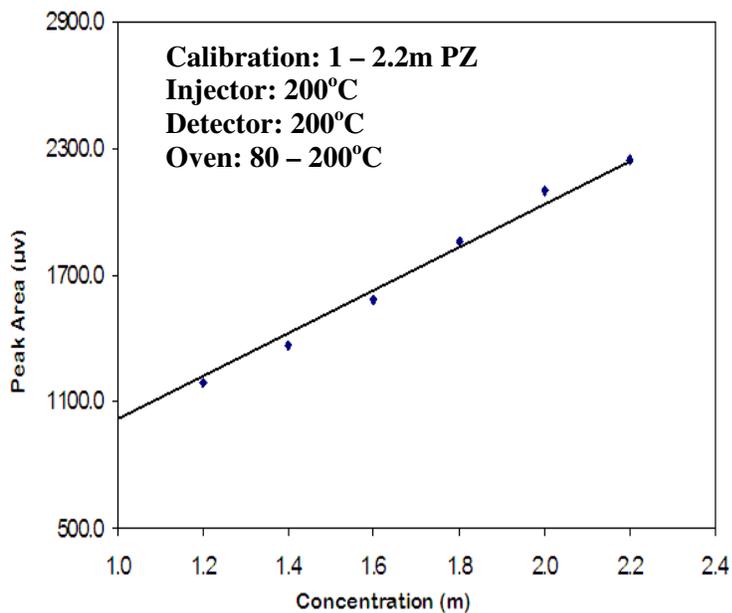


Figure 2.1 A typical calibration curve showing linear response of the GC

2.1.1. GC Method Development

The GC used for this study was an HP 5890 with an HP 7673 autosampler. The method was built round the more sensitive Flame Ionization Detector (FID), with a 30m HP-5 capillary column and a stationary/adsorbent part made of polyoxysiloxane. Due to the high concentration of potassium salts, samples were diluted a factor of 100 with 1-wt% ethanol, which also served as the internal

standard and helped in normalizing the injections. The GC operated with a split ratio of 20:1 to further reduce the load on the column, injector and detector. Injection volume of 1 μ L was made fairly reproducible by using the autosampler. Helium (99.999% purity) at a flow rate of 10mL/min was the carrier gas and transports the volatilized components through the column. Air (350mL/min) and hydrogen (45mL/min) were used in lighting the FID. All the gases were supplied by Matheson Trigas. The ratio of gas flows is important because excess helium or compressed air extinguishes the flame and makes detection impossible. All flow rates were controlled by the mass flow controller on the GC and were measured using a bubble flow meter.

The injector and detector temperatures were both at 200°C. The temperature of the injector was chosen to be at least 50°C more than the boiling point of the least volatile component expected in the matrix in order to ensure complete volatilization of the sample. The oven operated on a temperature program in order to improve the separation efficiency. The temperature started at 80°C and was held for 2 minutes. It is then raised to 120°C at 10°C/min, held for another 3 minutes and finally raised to 200°C at a ramp rate of 50°C/min. The middle ramp did an excellent job of eliminating the extreme tailing associated with the piperazine and the final ramp prepared the column for the subsequent injections by baking out the column. To improve the sensitivity of the analysis, certain maintenance procedures were necessary due to the high concentration of

salts. After every 50 injections the septum was changed, the column was trimmed, the injector liner and FID removed and cleaned. The GC was calibrated using piperazine/potassium solution in water. The ratio of PZ:K⁺ was 1:2 and the PZ concentrations ranged from 1.4m to 2.2m while the potassium concentration was from 2.8m to 4.4m. This was consistent with the concentration ratio used in all the experiments.

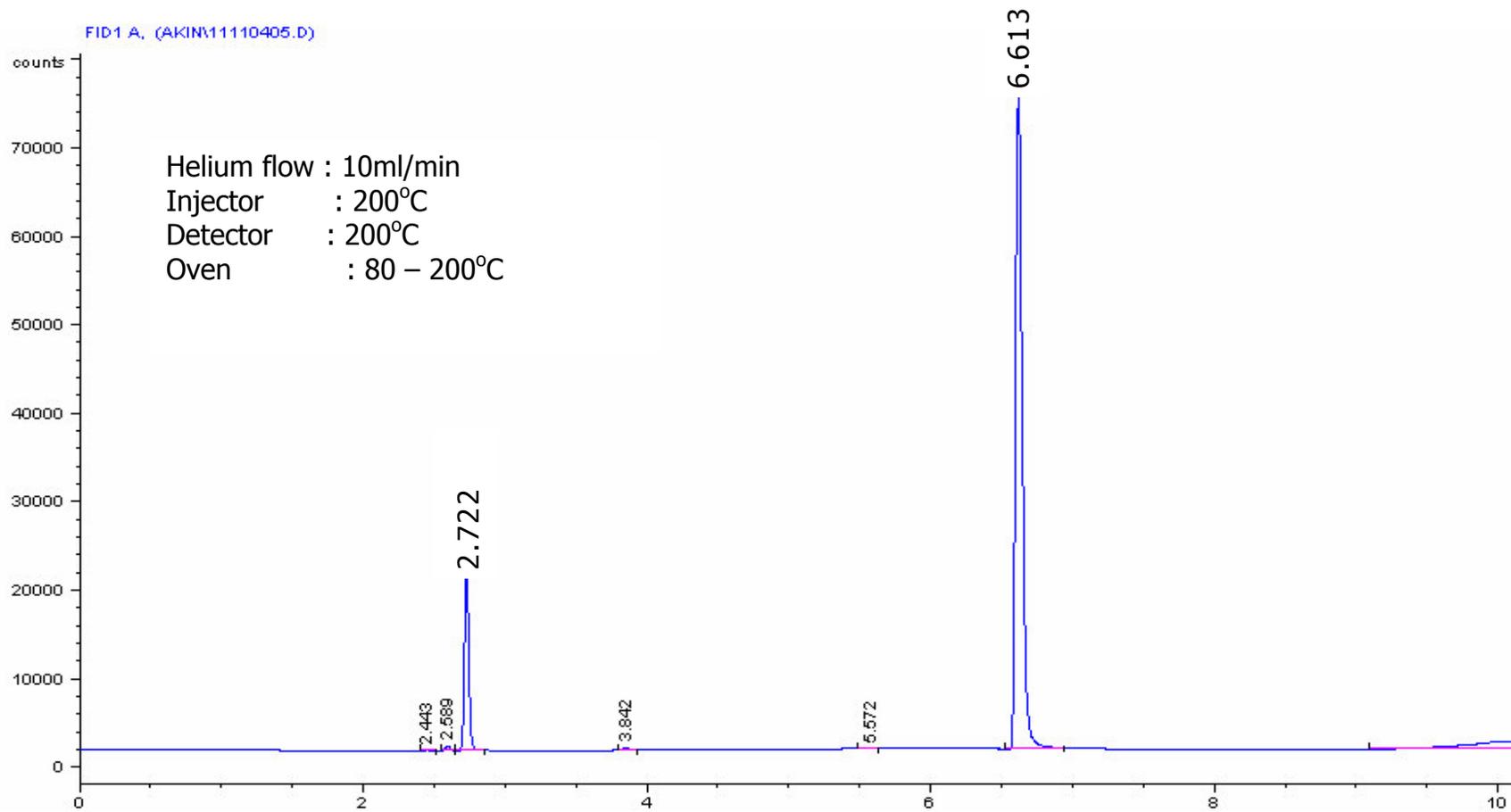


Figure 2.2 Chromatogram showing piperazine and ethanol

2.2 Ion Chromatography

With the dilution of the samples and the high split ratio it is almost impossible to use the Gas Chromatograph in identifying degradation products, which play an important part in quantifying piperazine losses. The IC is able to detect concentrations as low as parts per billion. The major advantage of this is that the samples can be diluted as much as a thousand without the system losing its sensitivity for the degradation products.

In principle the Ion Chromatograph has some similarities to the Gas Chromatograph although there are marked differences. For the GC, the analyte is transported by a carrier gas and separation is by difference in boiling point or molecular weight. In the IC, the analyte is transported by an eluent and gets attached to the stationary fixed material of the walls (the adsorbent) of the column. The success of the separation is based on the principle that different ions will adhere more strongly to the column than others and hence the least strongly attached ions elute first, followed by the next less strongly attached and so on. For anion chromatography, the eluent is usually $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ solution or NaOH/KOH solution over a range of concentrations, depending on the particular separation stage. The Ion Exchange Column is packed with positively charged adsorbent material and these sites act to attract the anions from both the analyte and the eluent. Depending on the size of the ion and the charge, some anions get

more tightly bound than others in solution, hence they elute much later and the separation is effected on this basis.

The solution coming out of the column passes through a suppressor column, which contains acidic protons to get rid of the carbonate, bicarbonate or hydroxide ions of the eluent, making it possible for the detector to measure the low concentrations of the anions of interest. The detector measures the electrical conductance of the solution and this is compared to a baseline of pure distilled deionized water. The conductance is proportional to the concentration of the ions dissolved in the solution and the results are presented in terms of peak areas.

2.2.1. IC Method Development

The Ion Chromatograph is a Dionex DX 600 with an AS 11-HC anion column, AG 11-HC guard column and an ULTRA II suppressor. The eluent is a relatively high concentration of potassium hydroxide that is a strong electrolyte. The actual concentration of the analyte anions of interest are present in the parts per million level or less and would not be noticeable if the eluent were allowed to pass through the column directly. This means it would be difficult if not impossible to measure the difference in the conductivity of the pure eluent itself and that of the anions of interest.

The eluent thus has to pass through the suppressor column before entering the conductivity detector to remove the hydroxide ions from the solution. This is what makes it possible to detect parts per billion concentrations of analytes in samples. The suppressor column is essentially an ion exchange column that is impregnated with acidic protons. As the eluent flows into the column, the hydroxide ions react with the acidic protons and are removed from the solution. The potassium ions that are left then get to fill up the vacant positions left in the column by the acidic protons. This way, the tiny anions are able to pass through to the conductivity detector and can then be measured.

6M Sulfuric acid was used in regenerating the suppressor. The IC uses an AS 40 automated sampler that holds 11 cassettes of six 5mL vials. Each sample is filtered through a 20- μ m filter in the vial cap, eliminating the pre-filtering step. In order to have an idea of the elution times of the target compounds, the IC was first calibrated with different concentrations of the ions that had the probability of being present in the experimental samples. 0.5 to 5 ppm solutions of formate, acetate and glycolate were prepared and loaded into the auto sampler. The elution times for each of the ions were noted and used as a basis for comparison when the actual samples were analyzed. Before going into the IC, the samples were diluted a factor of 1000 to avoid overloading the column and still be within the detection limit of the instrument.

All sample and eluent preparation was carried out using distilled de-ionized water to avoid contribution of ions in ordinary distilled water to the baseline found in the solutions. The samples tested in the IC were formate, acetate and glycolate. The chromatograms are shown in Figures 2.3 – 2.5. The calibration plot (Figure 2.6) shows the accuracy of the IC and the linearity of the concentration over the entire range.

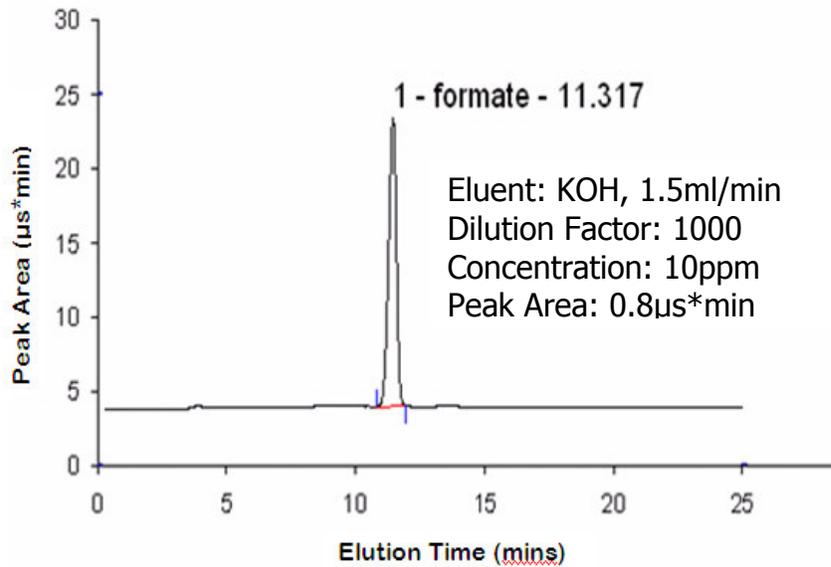


Figure 2.3 Sample Chromatogram of Formate

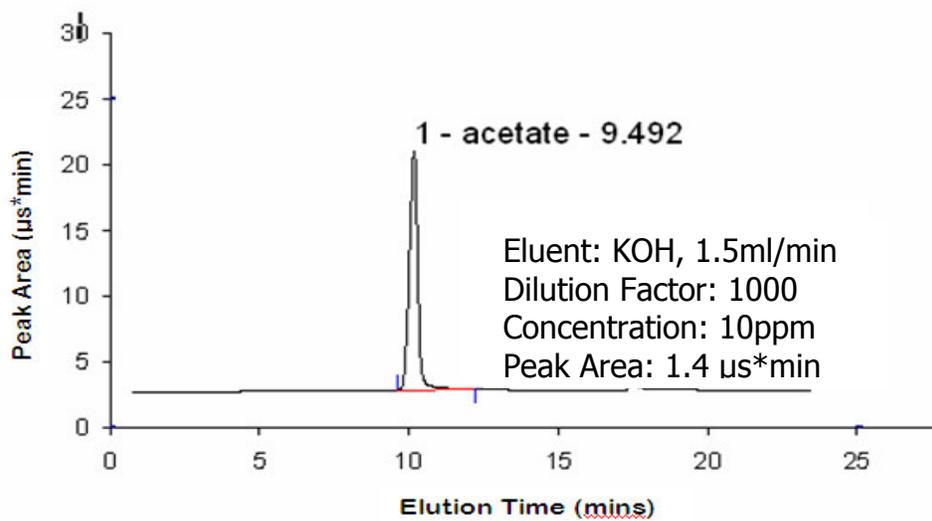


Figure 2.4 Sample Chromatogram of Acetate

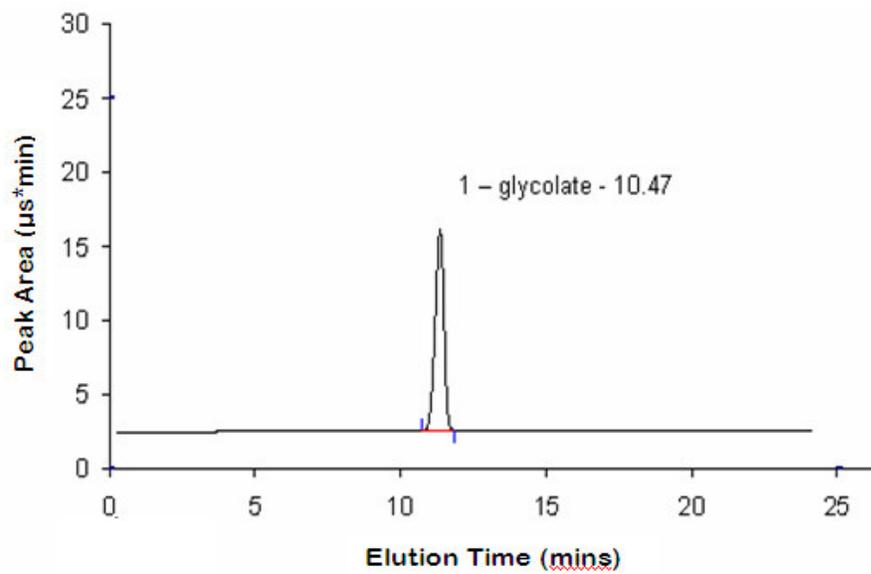


Figure 2.5 Sample Chromatogram of Glycolate

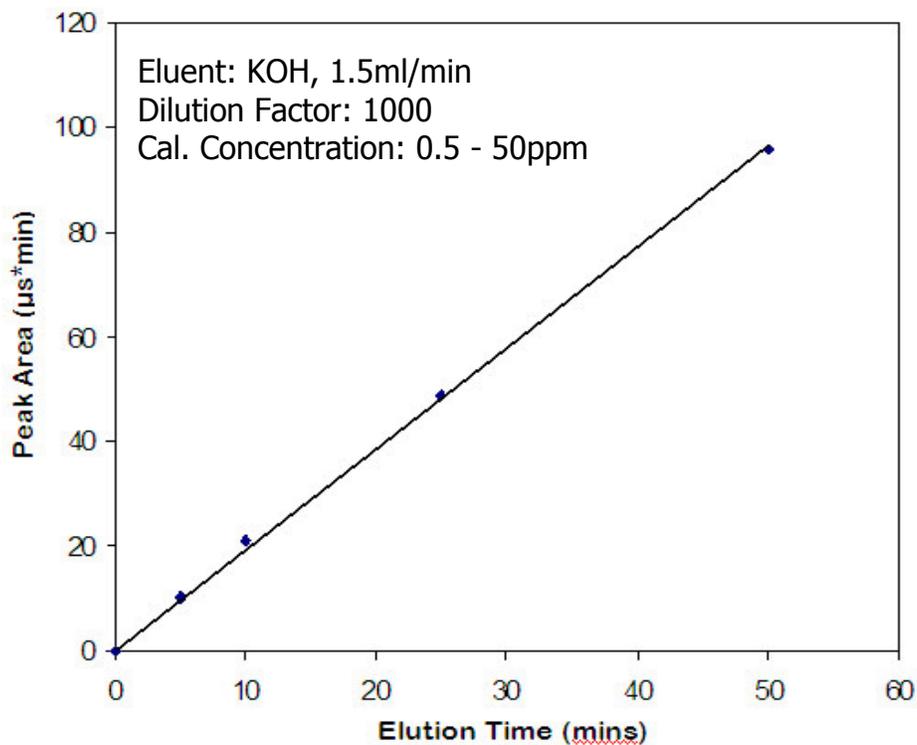


Figure 2.6 Calibration Curve for Ion Chromatograph, acetate

2.3. Nuclear Magnetic Resonance

NMR spectroscopy is a powerful tool that is very useful in identifying compounds and predicting /elucidating chemical structures. NMR is a phenomenon that occurs when the nuclei of certain atoms are immersed in a static, uniform magnetic field. A second rotating magnetic field is applied

perpendicular to the static field by beaming radio waves on the nucleus. The frequency of the radio wave is equal to the rate of rotation of the magnetic field. The frequency of the radio waves is changed in steps and its absorption by the nucleus is measured. When the frequency becomes equal to the rate of precession of the nucleus, the spin of the nucleus flips over and absorbs the energy of the radio waves. This gives the NMR spectrum when plotted.

The only drawback of the NMR technique is that this is only manifest in nuclei that have a property called “spin” and not all nuclei possess this property. This means the nuclei that do not have spin will not produce an NMR signal. There are different NMR methods/experiments that can be performed in trying to identify the structures of different compounds such as proton, carbon 13, 2-D and 3-D. Sometimes it takes a combination of different experiments before a structure can be confidently arrived at. The proton or ^1H experiment is the focus of analysis.

2.3.1. The NMR Method

The proton experiment was designed around the principle that in an NMR spectrum, different hydrogen atoms attached to carbon atoms behave differently. This is determined by the environment of each proton, the kind of bonds by which they are attached and the functional groups that are near them. This information

in turn affects the shape and position or chemical shift of the peaks in the spectra. The number of resonance signals or peaks corresponds to the number of equivalent groups of protons and the intensity of the signal corresponds to the number of protons contributing to it.

At the beginning, undegraded samples were first analyzed to create a baseline for comparison purposes. 1ml of the solution was acidified with 5ml 40% HCl to eliminate the carbamate peaks that might overlap the other peaks and prevent them from showing up. The acidified solution was then diluted with deuterium oxide in a 1:1 ratio to enhance and lock the signal. A drop of acetone was added directly to the final solution in each NMR tube to serve as a reference. After identifying extra peaks that showed up, different probable degradation products were added to the samples in turn to see if any of the extra peaks would be enhanced.

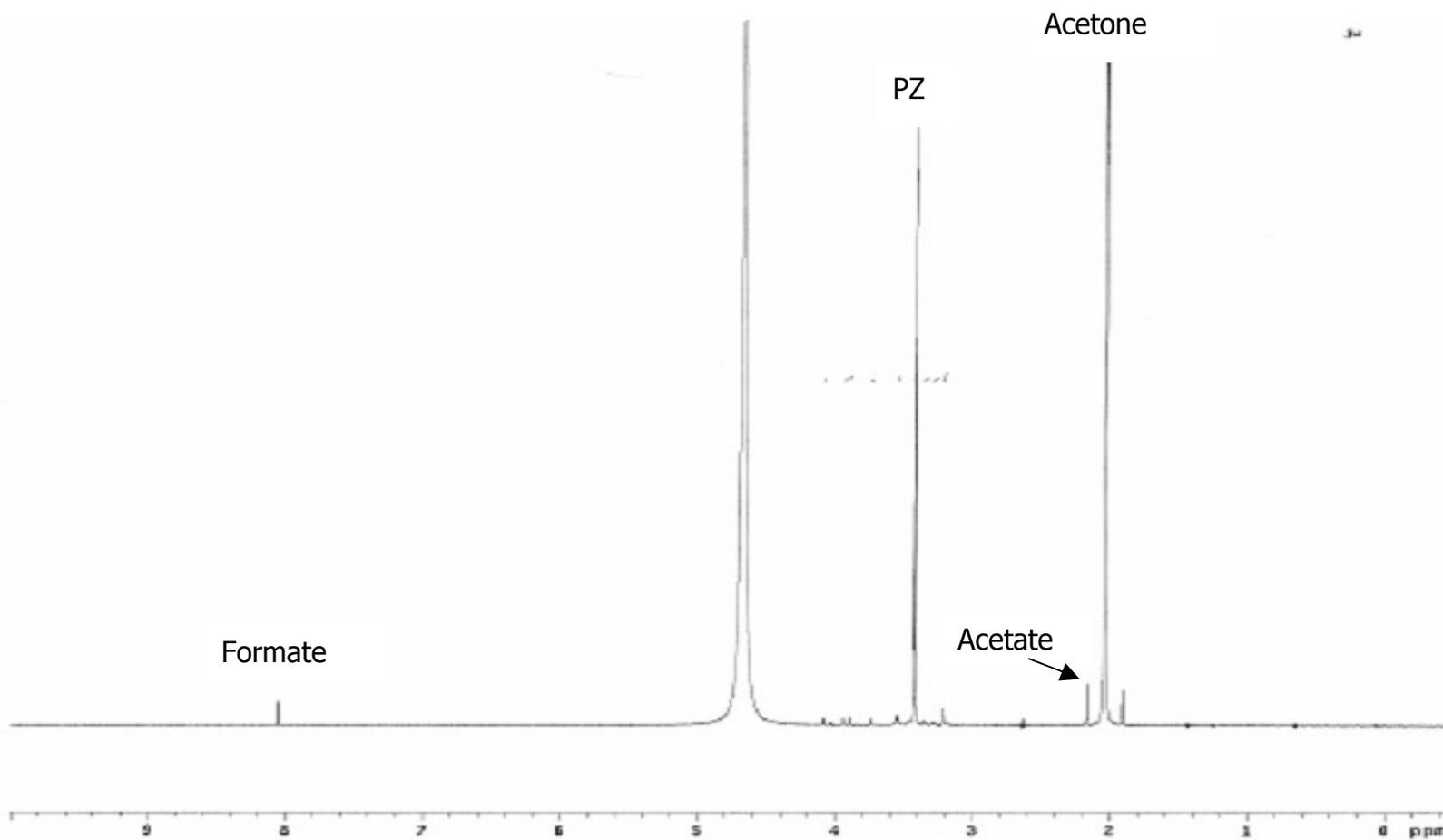


Figure 2.7 NMR spectrum showing Piperazine, Formate and Acetate

CHAPTER 3

Oxidative Degradation

3.1. Experimental Apparatus and Procedure

Initial experiments involving the oxidative degradation of PZ were conducted by Jones (2003), although he had some entrainment and evaporation problems with his set-up. This affected the accuracy of his results. In his experiments, air and CO₂ flowed into the reactor at a combined flow rate of 1.5 L/min. To achieve mass transfer, the gas flow was sparged into the solution at this high flow rate and this led to the problems encountered with evaporation and entrainment. The subsequent analytical methods thus had to be modified to account for these anomalies, introducing some degree of error into it.

The modified set-up consisted of a 500 ml jacketed reactor, five inches deep and three inches in diameter (Fig. 3.1a). Although the reactor is not pressurized, it was sealed tightly with a rubber cork into which three holes were

drilled (Fig. 3.1b). The agitator shaft passes through the central hole into the reactor. One of the holes was used for the gas inlet while the other was used to insert the thermometer. All the openings were made tight with rubber septa.

The temperature in the reactor was kept constant at 55°C by circulating water from a Lauda heating bath through the jacket. A 99.9 % purity pre-mix of O₂ with 2% CO₂ at 100 ml/min was used in the reactor, thereby creating more control over the gas flow. This significantly reduced the evaporation and completely eliminated the issue of entrainment. The gas was presaturated in an ace vacuum trap glass tube two inches in diameter and six inches tall, filled with water and immersed in the Lauda heating bath to keep the temperature near 55°C.

Mass transfer was achieved by using a variable speed agitator with 1-inch marine propellers. This made it easier to conduct experiments to investigate the effect of mass transfer on oxidative degradation by approximating the mass transfer as a function of the agitator speed. The gas flow rate was measured with a Fischer Model 520 precision rotameter and the temperature in the reactor monitored with a mercury thermometer.

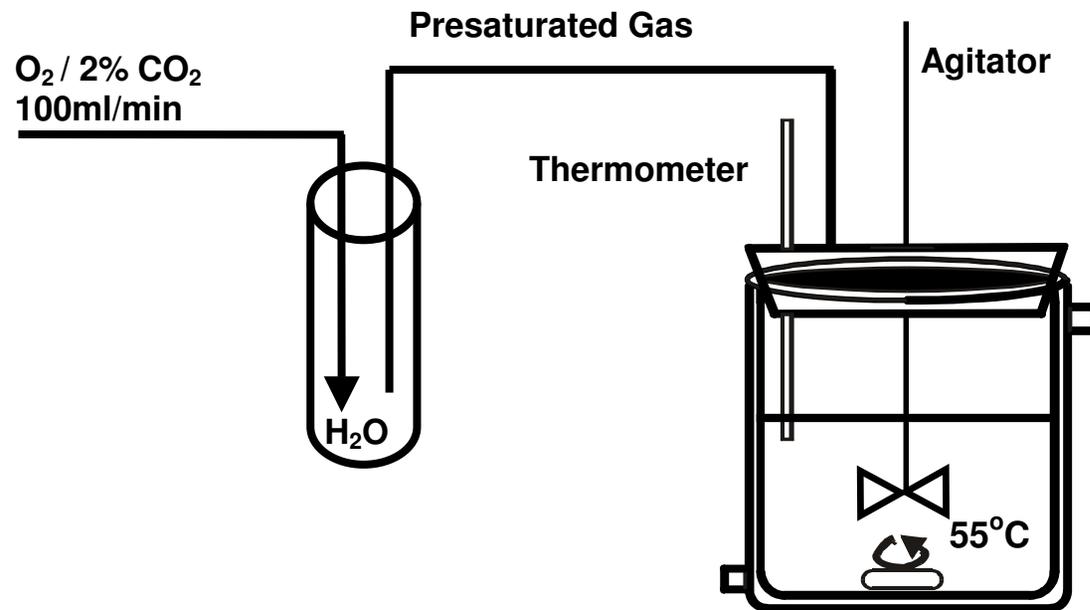


Figure 3.1a Experimental Set Up

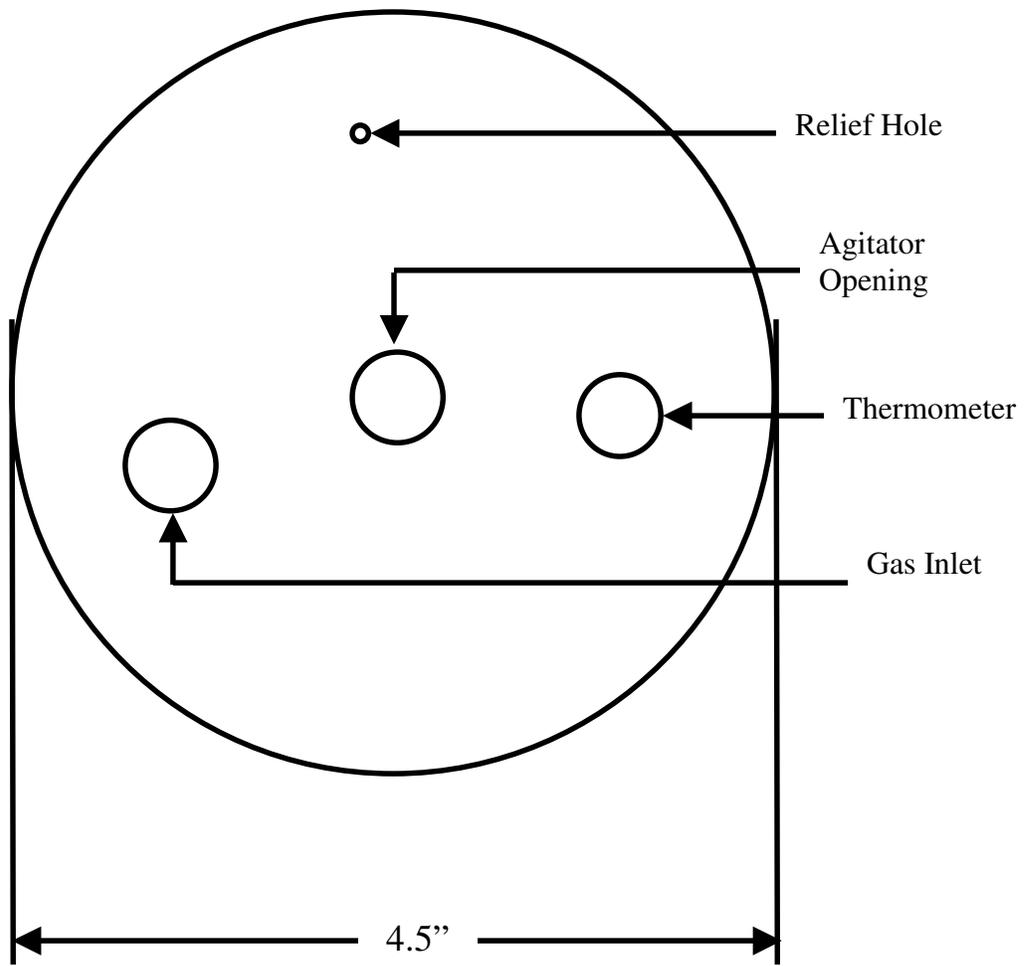


Figure 3.1b Reactor Cover (Top View)

3.2. Experimental Procedure

The test solution of 2m piperazine and 4m potassium was prepared from 99% purity anhydrous piperazine pellets from Acros Chemicals and potassium bicarbonate granules from Fisher Chemicals. A ratio of 1:2 for piperazine / potassium solution is known to be most effective for CO₂ absorption based on work that has been done by Cullinane (2002). Keeping in mind that the solution was being tested with the ultimate goal of being able to adapt it on an industrial scale for absorber-stripper systems, certain experiments were designed with this goal in mind. Amines are known to cause a lot of corrosion in absorbers and strippers and this ensures that iron, which is an important metal in oxidative degradation, is always readily available. Amine carbamates are notorious complexing agents and are expected to increase the corrosion rate. To reduce the corrosion rate, transition metals are sometimes added to solutions to act as inhibitors. Vanadium and copper salts have often been used for this purpose. Unfortunately, these inhibitors have also been known to act as catalysts in oxidative degradation. In order to investigate the effect of these metals, varying concentrations of iron and vanadium were added to the solutions for some of the experiments.

The first in the series of experiments had 2 molal piperazine and 4 molal potassium in the reactor with no metal added to serve as the control. The

subsequent experiments had the same composition of piperazine and potassium with different combinations of iron and vanadium. The iron used was in the form of Iron II sulfate granules, while the vanadium was a 96% purity Sodium Metavanadate salt, both from Acros Chemicals. Most of the experiments were conducted for 7 days. The samples were collected by inserting a needle into the reactor through the relief hole and drawing 4ml with a syringe. The samples were weighed and placed in glass bottles with rubber-sealed caps, which were then placed in the refrigerator.

The next experiment involved the same ratio of piperazine to potassium, 50 ppm iron and 5000 ppm vanadium for a period of 4 weeks. The intention was to provide a higher degree of confidence in the earlier experiments. The combination of iron and vanadium was chosen because it appeared to have given the highest piperazine loss in earlier experiments. Two samples were taken, one at the beginning of the experiment and one after four weeks. Samples were analyzed using the Gas Chromatograph and the Ion Chromatograph.

The last set of experiments was conducted to investigate the effect of varying different parameters on the rate of degradation. Based on results obtained by Goff with MEA, degradation in piperazine is also thought to be mass transfer controlled. One of the experiments varied the speed of the agitator while keeping other factors constant in order to check the effect mass transfer had on piperazine

degradation. Another set of experiments explored the effects of varying metal concentrations on the rate of degradation.

For each of these solutions the water loss was carefully monitored by weighing the solution at the beginning and end of each experiment. Samples were taken at 24-hr intervals, the weight was recorded for each and all were added together at the end of the experiment to get an idea of how much water was lost over the duration of the experiment. For this set of 7-day experiments, the ion chromatograph was the favored method of analysis. The method was designed around identifying and quantifying degradation products, which would be important indicators of piperazine losses. The change in method was necessary because the gas chromatograph was not able to give a conclusive analysis of the piperazine samples after seven days and the IC is more sensitive and able to detect parts per billion concentrations.

CHAPTER 4

Results

4.1. Summary of Experimental Results

The results for all the experiments are summarized in Table 4.1. As previously discussed, two methods were used to analyze the samples from the experiments. A correction was made for the water lost in the first three experiments and the 4-wk experiment. The water loss for the later set of experiments was negligible, less than 0.8 percent. The GC focused on identifying the direct loss of piperazine while the IC estimated the piperazine loss based on acetate production. The NMR was not used extensively for quantifying the degradation products due to the difficulty involved in identifying the numerous peaks present in the spectrum.

The initial analysis was done using the GC. From Table 4.1, it is not distinct which of the four solutions exhibited more degradation although the solution with the combination of the iron and vanadium had a slightly lower concentration of piperazine. This is probably due to the fact that the degradation did not occur long enough for the GC to show a clear difference in concentration and the difference was below the detection limit.

Table 4.1 Summary of Experimental Results

2.0m PZ,4.0 m K⁺,55°C, 100 ml/min of 2 % CO₂/98% O₂

Start Date	Agitation (rpm)	V (ppm)	Fe (ppm)	Time (hrs)	*PZ loss (mM/hr)	#Acetate (mM/hr)	PZ Loss (%)
6-13-2004	1260	5000	50	168	1.3	-	14.1
6-21-2004	“	0	“	“	1.2	-	13
6-30-2004	“	5000	0	“	0.7	-	7
7-10-2004	“	“	50	720	5	0.3	18
12-20-2004	“	“	“	168	-	0.4	6.3
12-22-2004	“	-	“	“	-	0.31	4.7
1-2-2005	630	“	“	“	-	0.13	1.35
1-4-2005	1260	500	5	“	-	0.37	5.4
1-10-2005	“	0	0	“	-	0.08	0.94

* Analysis with GC and final concentration corrected for water loss

Analysis with Ion Chromatograph

As previously stated, experiment 7-10-2004 was conducted to have a higher degree of confidence in the results for the first three experiments. After correction for water loss, the PZ concentration was found to be 1.64 m, corresponding to about 18% loss of the PZ. The analysis with the ion chromatograph was able to detect 12 ppm acetate in the sample.

Finally, for the last set of experiments, there was acetate in the samples tested after 7 days assuming that the rate of acetate production is representative of the rate of degradation of the piperazine. This is in agreement with what had been observed previously with the 4-week samples. The acetate concentration in the experiment with lower agitation is only a quarter of the one with the higher agitation rate. The solution with zero catalyst had the lowest concentration of acetate.

The chromatograms for the results of IC analysis are shown in Figures 4.1

– 4.5

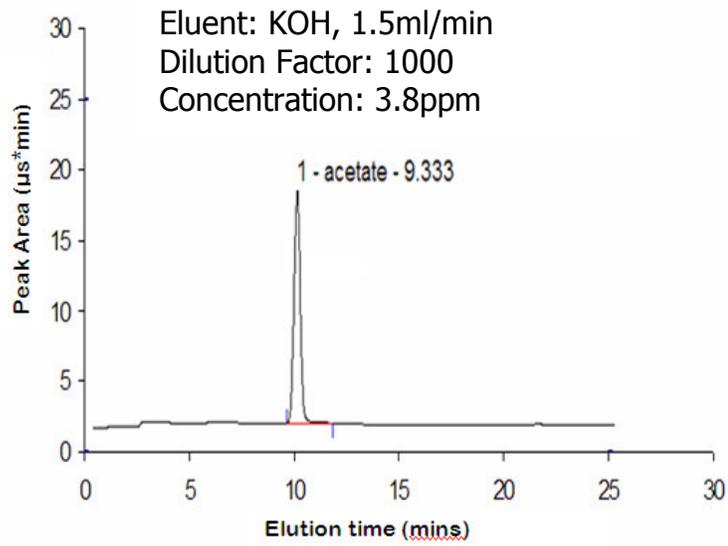


Figure 4.1 Chromatogram at the end of experiment 1-4-2005

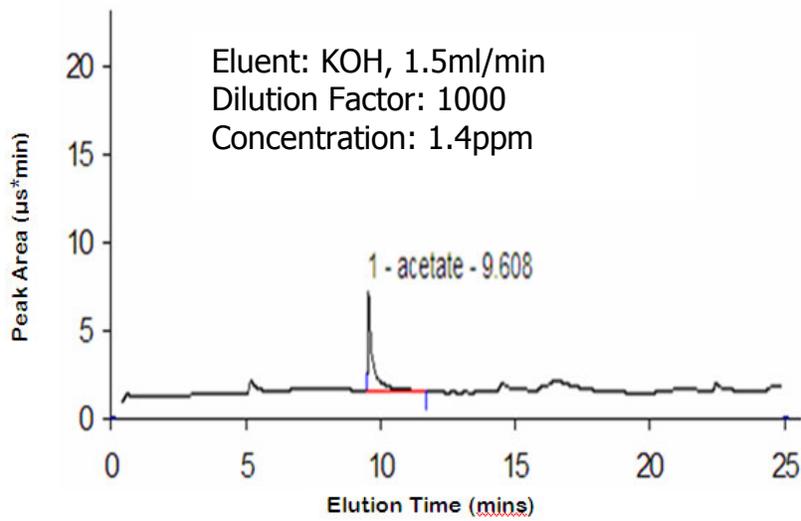


Figure 4.2 Chromatogram for 1-2-2005

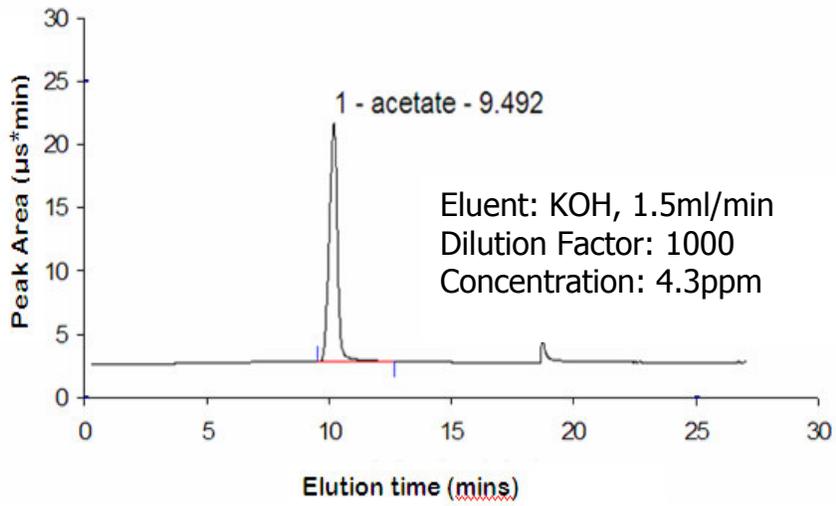


Figure 4.3 Chromatogram for 12-20-2004

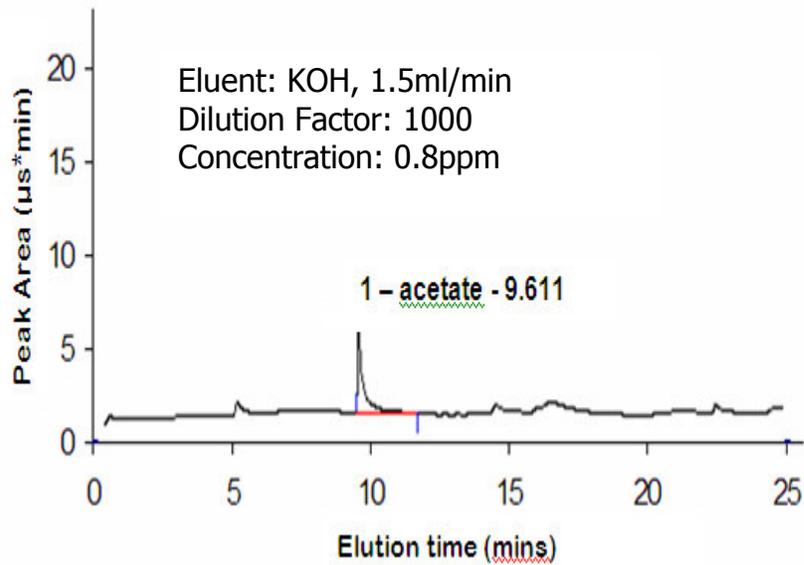


Figure 4.4 Chromatogram for 1-10-2005

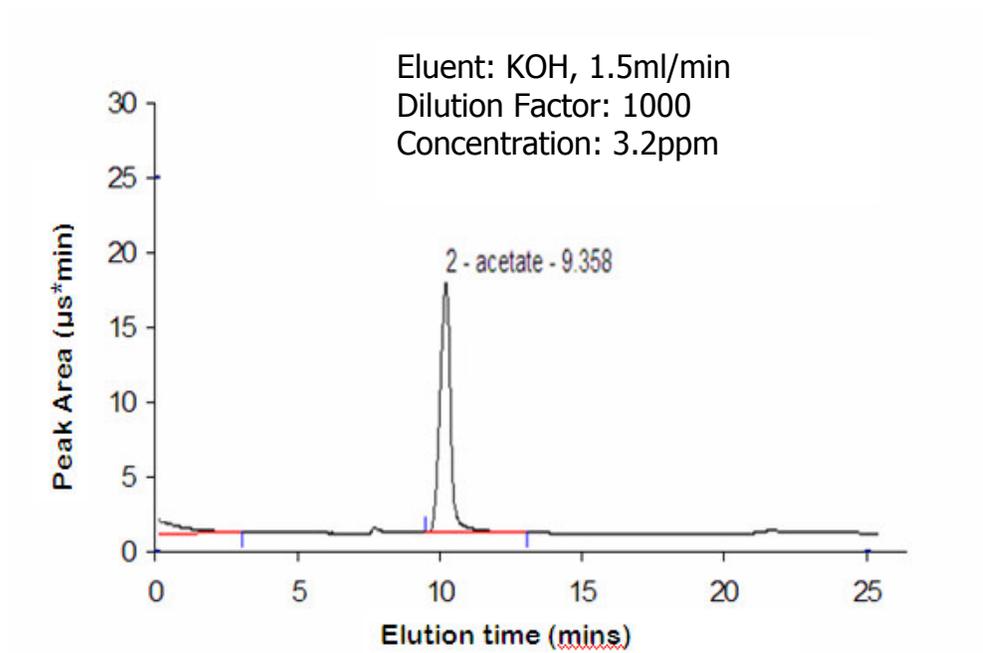


Figure 4.5 Chromatogram for 12-22-2004

The 4-week sample was analyzed with NMR and acetate was also identified. There were some other peaks showing up that may suggest more degradation products which have not been identified and were not picked up by anion chromatography. The presence of these other unknowns makes it difficult to use the NMR quantitatively but the positions of all the peaks are documented in Appendix I.

CHAPTER 5

Conclusions and Recommendations

5.1 Results

The rate of degradation of PZ observed here was about 1.3mm/hr, much lower than the 5mm/hr obtained by Goff for MEA. This could probably be explained by a number of factors. Piperazine degradation is limited by oxygen mass transfer when there is a significant amount of catalyst in solution. In this case, there was a high concentration of iron and vanadium in most of the experiments. Oxygen solubility in MEA is twice as much as that for a mixture of piperazine and potassium bicarbonate. This is because the presence of potassium and carbonate ions lowers the solubility significantly and thus mass transfer of oxygen to the solution is limited by the physical solubility of the oxygen. The estimate was based on solubility correlations by Tanaka (2000) and Tokunaga (1994).

Based on visual observation, agitation rate in the MEA experiments was clearly greater than that in the PZ experiments, which could also account for the lower rate of degradation due to the limitation in mass transfer. This is supported by the PZ experiments that showed that the degradation rate decreased significantly when the agitation rate was reduced by a factor of two.

There was a noticeable effect of varying metal concentration on the rate of degradation. The experiments showed a higher rate when both metals were present in solution, although a single catalyst at reduced concentration was still enough to contribute significantly to the rate. This would suggest that there was a minimum catalyst concentration that would still be effective. At low metal concentrations the kinetics become important, while at high metal concentration the degradation becomes oxygen mass transfer controlled. The results were in agreement with previous work done by Goff (2003) and Chi (2002).

Acetate was found to be an important product of PZ degradation, although it accounts for only 12% of the total piperazine loss based on experiment 7-10-2004. The ion chromatograph was not able to identify other degradation products, but the NMR analysis showed more degradation products in the spectra, especially after the samples were acidified. Acetate and formate were identified, but not the other peaks.

The gas chromatograph puts the piperazine loss at 18% of the original piperazine. The 6% difference between IC and GC values is expected to be from the yet unidentified peaks from the NMR analysis.

Experiments should be done to check effect of copper on the rate of degradation. The concentration of piperazine and potassium should be changed to see how it affects the rate. The flow rate of O₂ and CO₂ can also be varied to see how it affects degradation rate.

5.2. Apparatus and Sample Analysis

The changes made to the apparatus were quite efficient in solving the initial problems encountered with evaporation and entrainment, resulting in no loss of material and approximately 5g loss of water in the worst case. The methods used in investigating the effect of different variables on the rate of degradation were also more effective as a result of this.

The GC methods were improved with a more efficient temperature program and maintenance methods. In spite of the improved methods, the GC was still not well suited to quantifying piperazine loss over short periods, though quite effective over long durations. The temperature program did a good job of effecting excellent separation with thin peaks while eliminating the tailing effect that might bring errors into the analysis. It should however be noted that the separation is very poor when the initial temperature goes beyond 80°C. For even greater accuracy, the dilution of the piperazine/potassium solution can be increased. This will further reduce the salt effects and the likelihood of overloading the column thereby improving accuracy. Also, the more dilute the solution is, the easier it will be to identify piperazine loss between two different samples. This

will be particularly useful in the 7-day experiment, the downside being that it will be impossible to identify degradation products using the gas chromatograph.

The ion chromatography method is well developed and would only need minor fine tuning to make it perfect. It is however important to develop a method for cation chromatography because it is suspected that some of the degradation products appearing in the NMR might be identifiable using cation chromatography.

The NMR method has to be expanded and geared towards quantitative analysis. C-H correlation holds a lot of advantages which could be explored and modified to analyze the solutions being tested. Other NMR experiments such as 2D, C13 and Dept experiments will also be of great value in identifying the degradation products. A better reference other than acetone is also needed to ensure a more conclusive analysis.

Appendix A

Raw Results

The peak areas for the samples in the first three experiments are shown in Table A.1. These are based on GC analysis and they represent the raw values. The dates represent start dates for each of the experiments. The actual concentrations obtained from the peak areas after calibration are in Table A.2.

Table A.3 has the IC data showing the concentration of acetate in the last five experiments involving different catalyst concentrations and agitation rates.

Table A.1 Peak Areas from GC

Time (hrs)	Peak Area (μV)		
	PZ/K/Fe 6-21-2004	PZ/K/V 6-30-2004	PZ/K/Fe/V 6-13-2004
0	2021.3	2020.9	2001.0
24	2015.6	2018.1	1995.6
48	2016.3	2018.5	1992.5
72	1987.3	2009.6	1990.8
96	1952.6	2003.9	1943.5
120	1938.4	2000.5	1911.5
144	1932.13	1999.8	1904.6
168	1920.01	1998.79	1900.4

Table A.2 Concentration Values of PZ after Calibration

Time (hrs)	PZ/K/Fe (m) 6-21-2004	PZ/K/V (m) 6-30-2004	PZ/K/Fe/V (m) 6-13-2004
0	2.0	2.0	2.0
24	1.998	1.999	1.994
48	1.998	1.999	1.991
72	1.968	1.990	1.991
96	1.933	1.986	1.942
120	1.919	1.986	1.910
144	1.913	1.983	1.903
168	1.901	1.979	1.899

Table A.3 Concentration Values from IC

		1-10-2005	12-20-2004	1-2-2005	1-4-2005	12-22-2004
Acetate Conc. (ppm)	Initial	0	0	0	0	0
	Final	0.8	4.3	1.4	3.8	3.2

Appendix B

Procedure for using the GC

1. All the gases were opened and the gauges were checked to make sure they were at least 500psi.
2. The analytical column was connected and tightened at both ends, at the inlet and at the detector to prevent leaks.
3. The mass flow controller at the GC was opened to allow Helium to flow through the column.
4. The first step involved measuring the flow rate of the Helium by inserting the bubble flow meter into the detector opening.
5. The flow was calculated by using the graduation on the bubble flow meter and the stop clock on the GC itself. The timer is graduated in units of min^{-1} and the bubble flow meter is graduated in ml. The flow rate is calculated by measuring the time it takes the soap bubble to travel a graduated distance of 1, 10 or 100ml and simply multiplying with the time reading on the GC LED.
6. The gas flow was allowed to equilibrate before flow rates were measured.
7. After measuring the He, the air valve was opened on the GC to take measurements. (the reading for the Air included that of the Helium)
8. To set the flow rate of the Hydrogen, the Air valve was closed and that of the hydrogen was opened. The same procedure as measuring for air was then

- repeated. (the GC calculates the split flow by itself as long as the desired split ratio is known).
9. Finally, after measuring both gas flow rates, both gases were opened at the GC in order to light the FID.
 10. The injector and detector temperatures were both set at 200°C and the Detector B was chosen, representing the FID.
 11. Once the gas flows were verified, the lighter button was depressed at the GC. The best way to make sure the FID was lit was to listen for a “pop” sound of the gases igniting. A continuous popping sound meant the gas flow rates were off and needed to be rechecked (only the hydrogen and air). After hearing the pop sound, a piece of glass was held over the detector opening and condensation was also a confirmation of the lit FID.
 12. The samples to be analyzed were transferred into small vials and loaded into the auto sampler tray, starting at position #1.
 13. The method set-up determine how the samples are going to run. The parameters that were pre-programmed include:
 - Oven temperature and ramp program
 - Injector and Detector temperatures
 - Injection volume
 - Number of injections per sample
 - The pre and post rinse for the injector needle

14. In developing the method, a generic method was first chosen from the list of methods already residing on the GC and saved as a new method with the name that could be easily recognized.
15. Getting a good analytical procedure then depended on making multiple runs of the compounds of interest and watching the resulting chromatograms while changing the injector, detector temperature and the oven temperature program until sharp, repeatable peaks were obtained for the compounds. This was achieved by experimenting with different temperatures and making adjustments as they were needed.
16. In order to obtain a certain level of reproducibility, some maintenance was necessary. After about 20 injections, due to the high concentration of salts in the samples, the injector port liner was removed and cleaned by replacing the wool trap in the glass inlet. The column was also removed at the injector and trimmed every 100 injections.
17. Three injections were made per sample and the average was used as the final value.
18. After finishing the analysis, the injector, detector and oven temperatures are all set to off. The gas valves are closed at the GC and then at the cylinders.

The chromatograms for the initial and final run for each of the experiments are shown in Figures 1a to 4b. The initial chromatograms show the samples taken at time zero, while the final chromatograms show the end of the experiment.

The samples were labeled based on the start dates of each of the experiments. The GC was re-calibrated each time the samples were to be analyzed for each experiment set. The calibration curves are also shown.

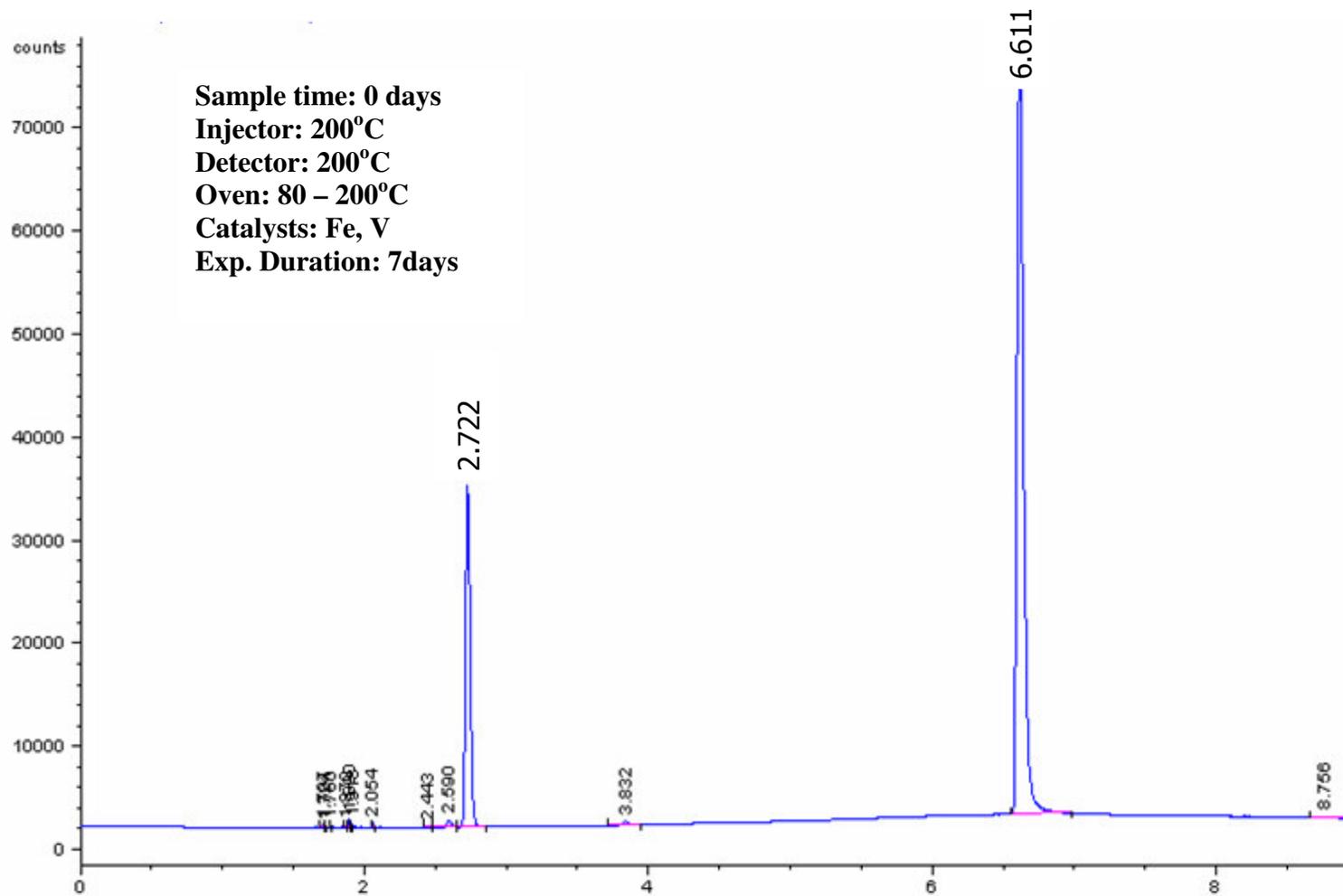


Figure B.1 GC Chromatogram for 6-13-2004, Initial

Sample time: 7 days
Injector: 200°C
Detector: 200°C
Oven: 80 – 200°C
Catalysts: Fe, V
Exp. Duration: 7days

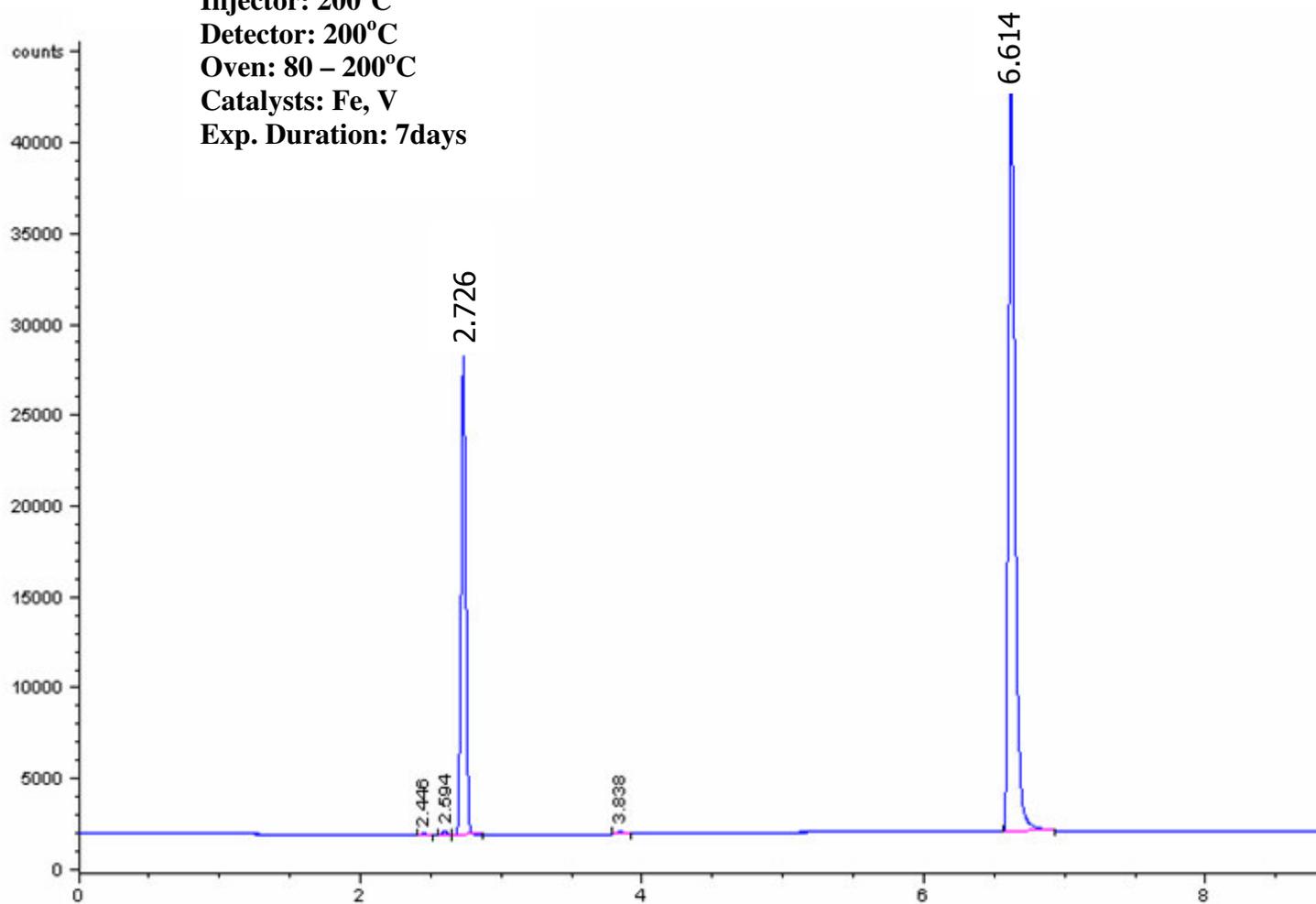


Figure B.2 GC Chromatogram for 6-13-2004, Final

Sample time: 0 days
Injector: 200°C
Detector: 200°C
Oven: 80 – 200°C
Catalysts: Fe
Exp. Duration: 7days

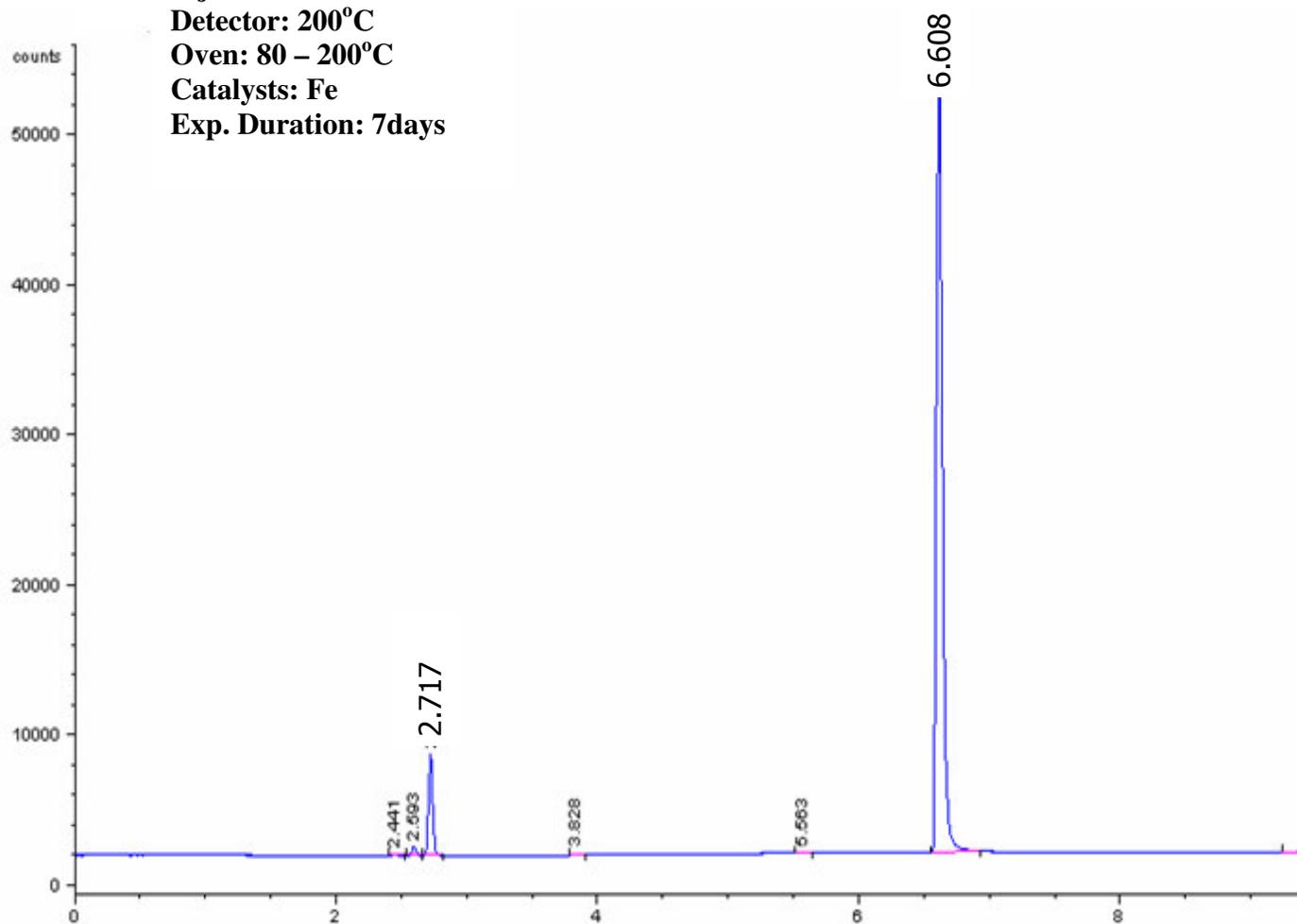


Figure B.3 GC Chromatogram for 6-21-04, Initial

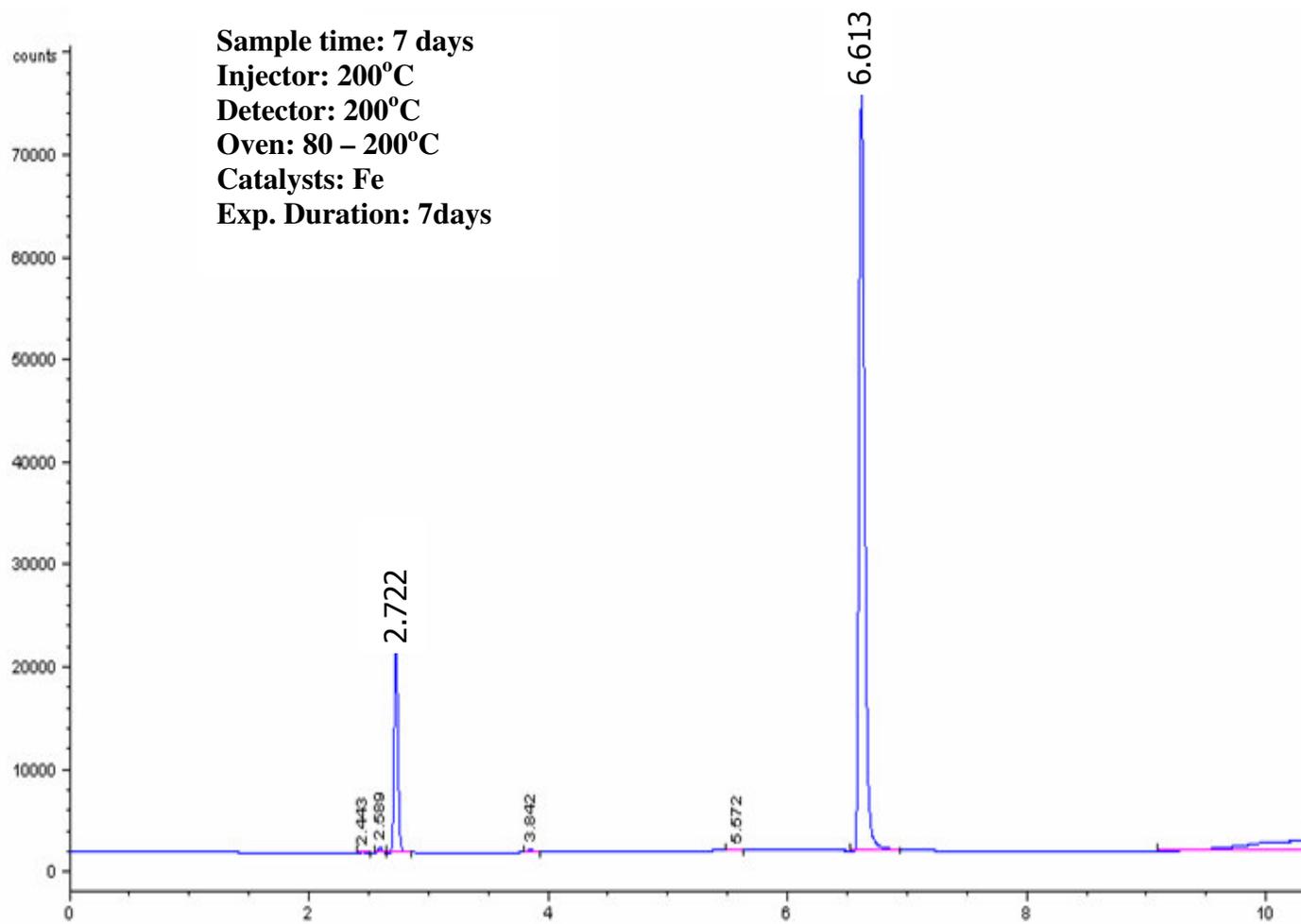


Figure B.4 GC Chromatogram for 6-21-2004, Final

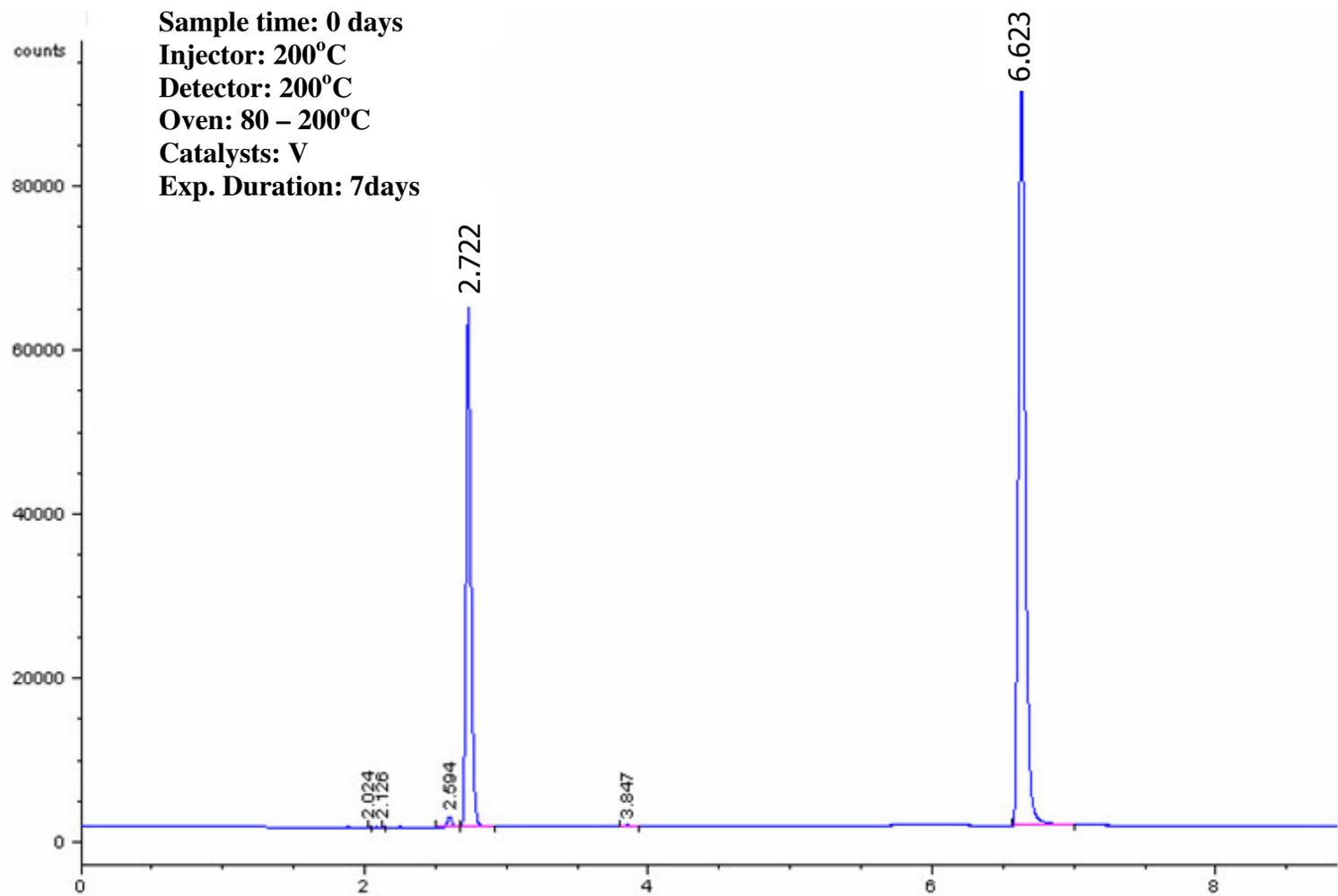


Figure B.5 GC Chromatogram for 6-30-2004, Initial

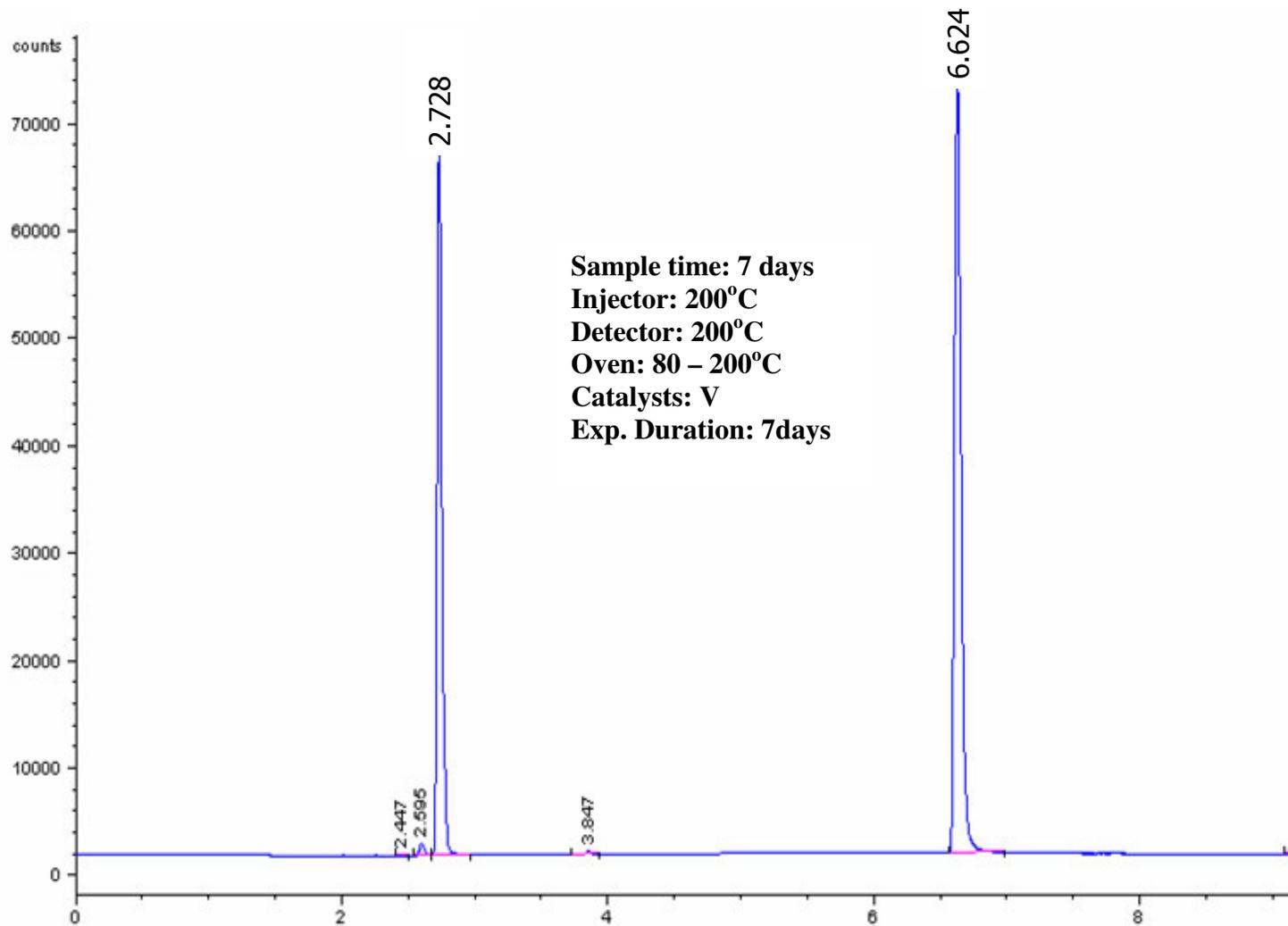


Figure B.6 GC Chromatogram for 6-30-2004, Final

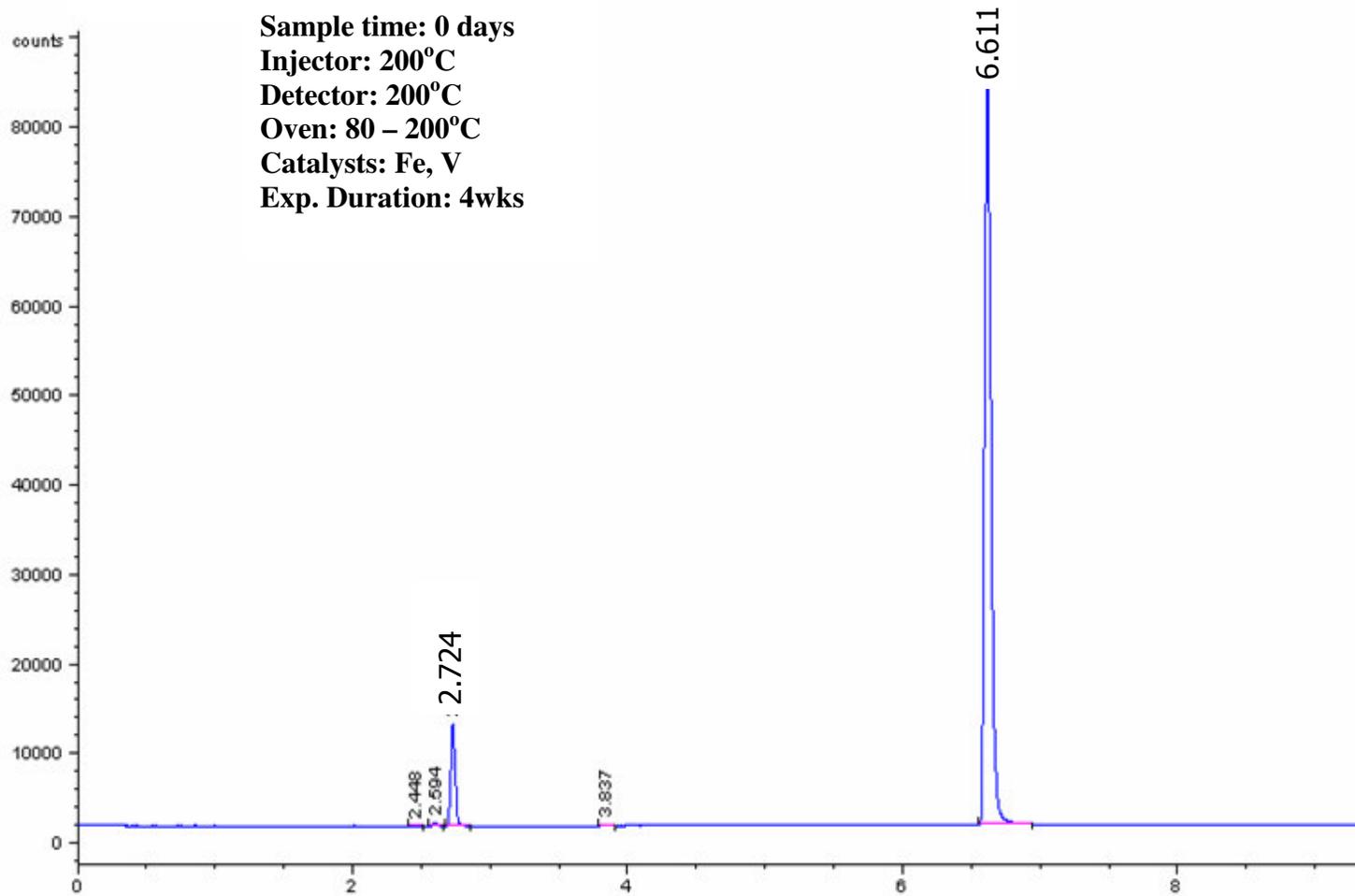


Figure B.7 GC Chromatogram for 7-10-2004, Initial

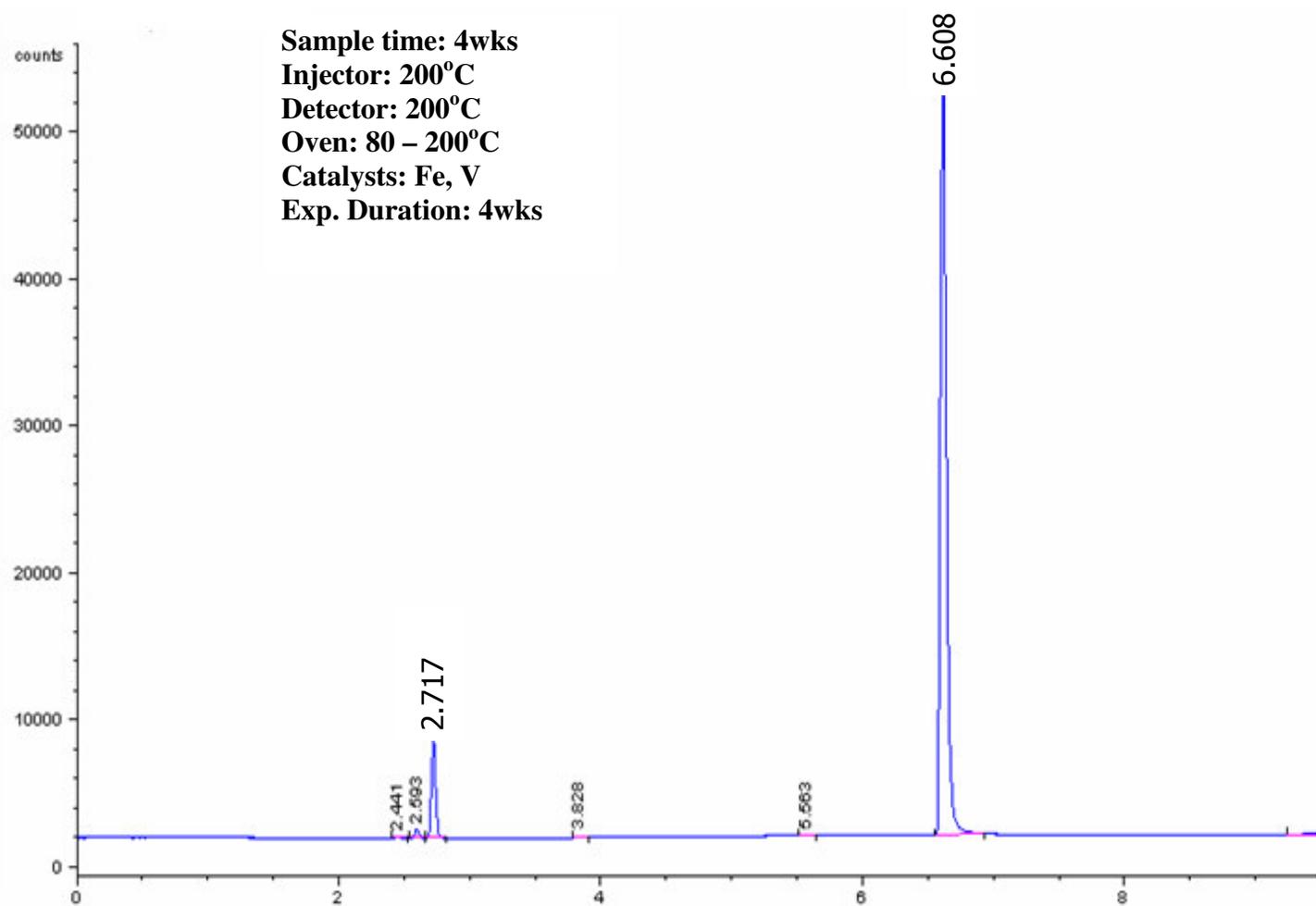


Figure B.8 GC Chromatogram for 7-10-2004, Final

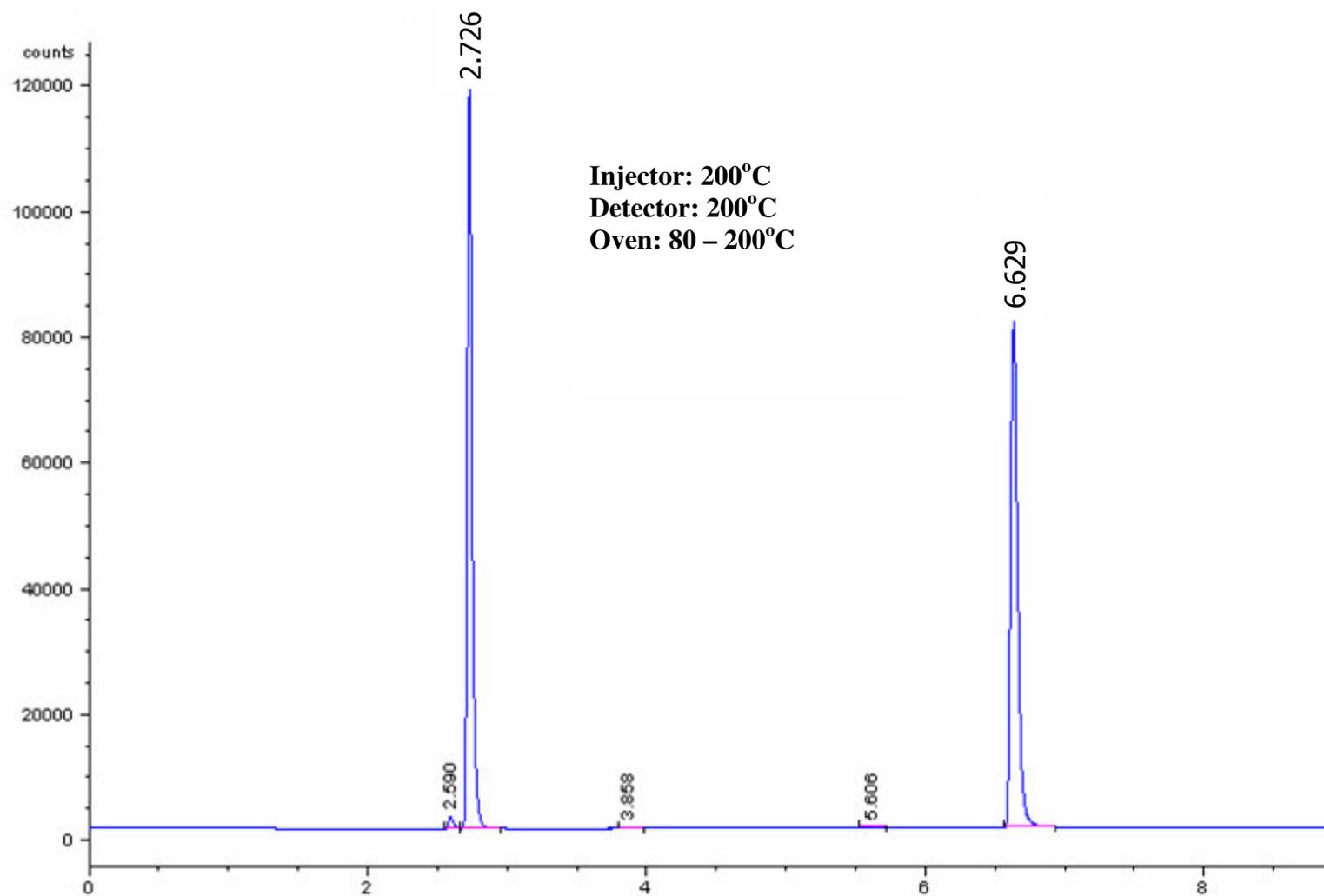


Figure B.9 GC Chromatogram for Calibration Sample 1

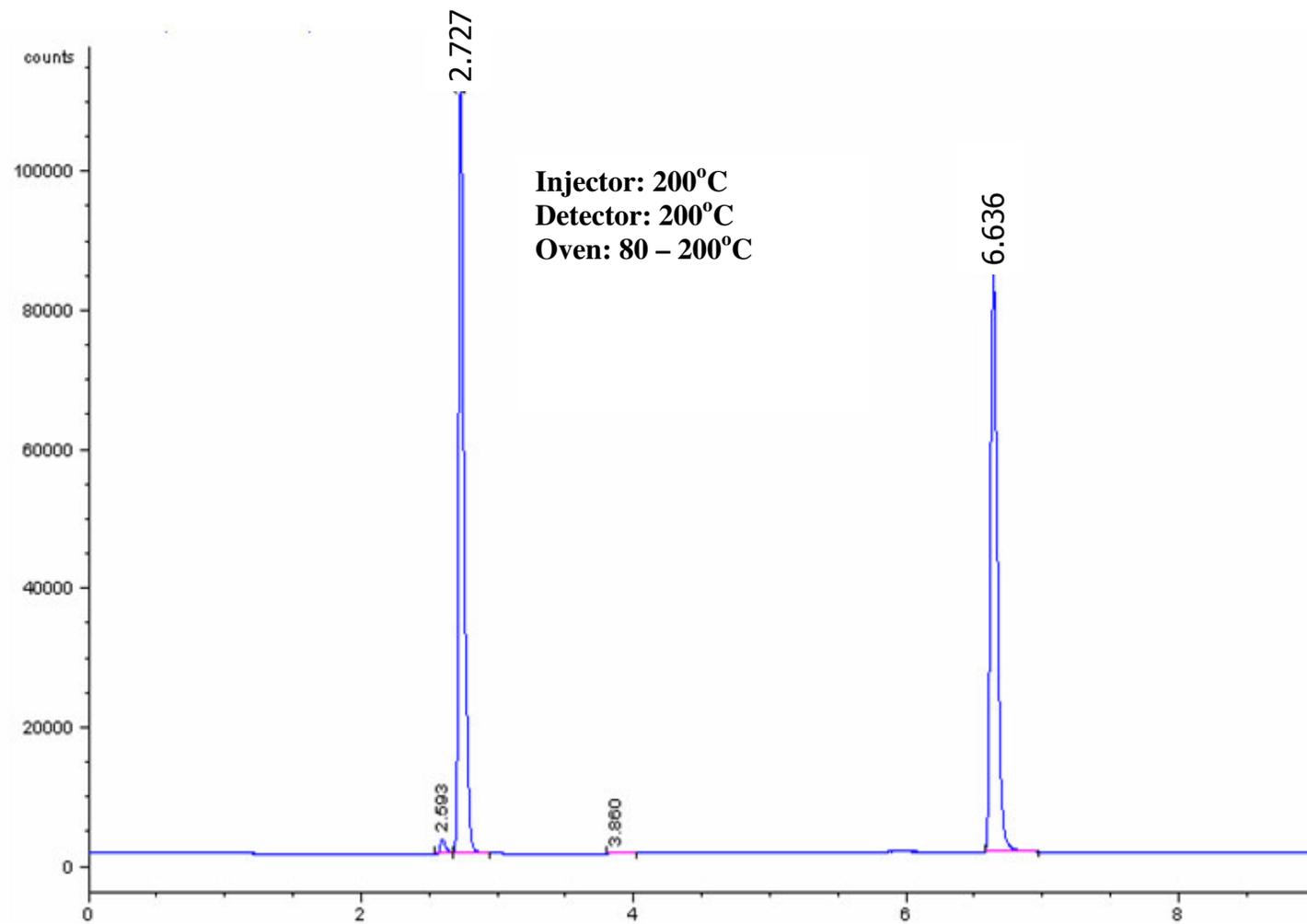


Figure B.10 GC Chromatogram for Calibration Sample 2

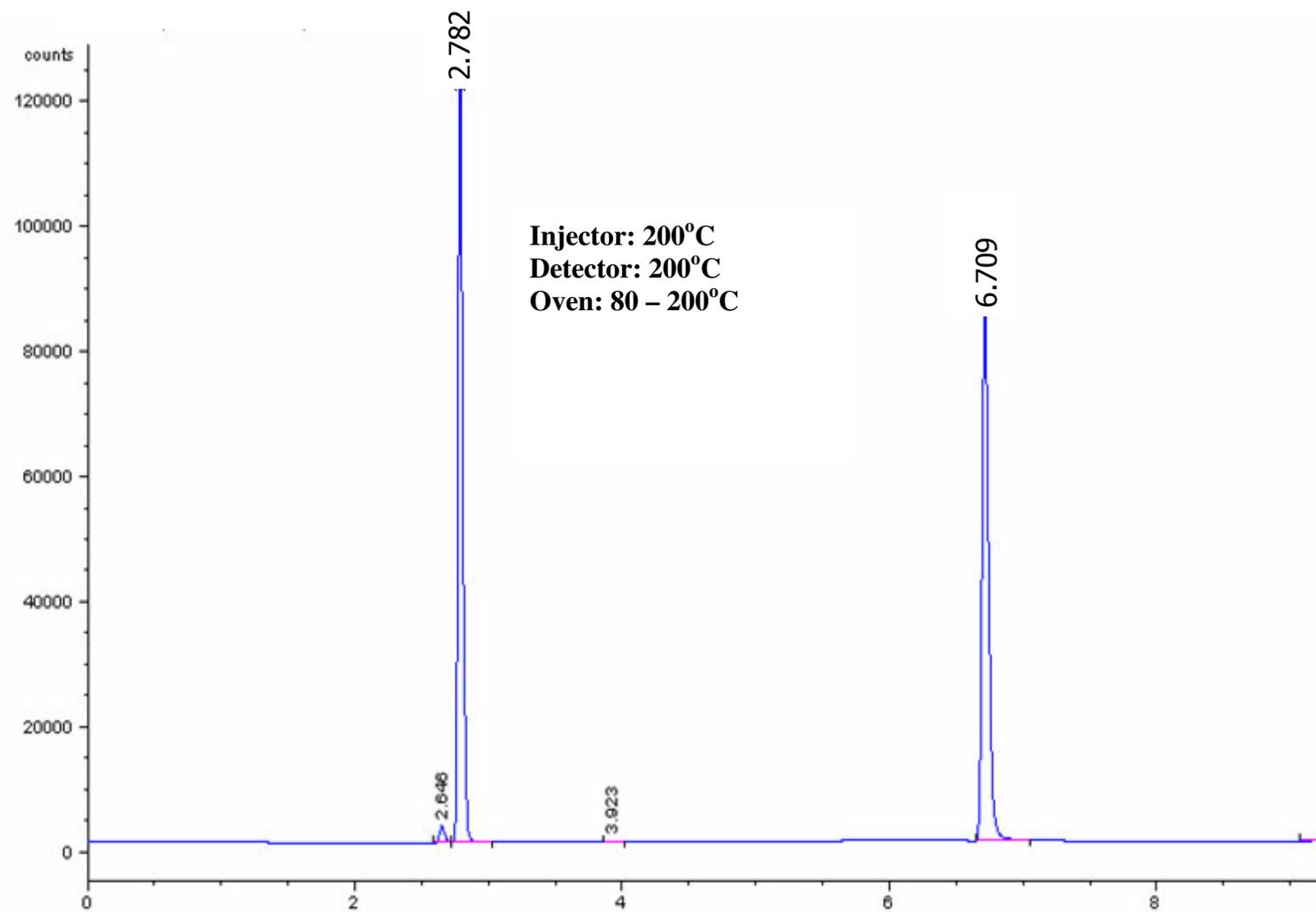


Figure B.11 GC Chromatogram for Calibration Sample 3

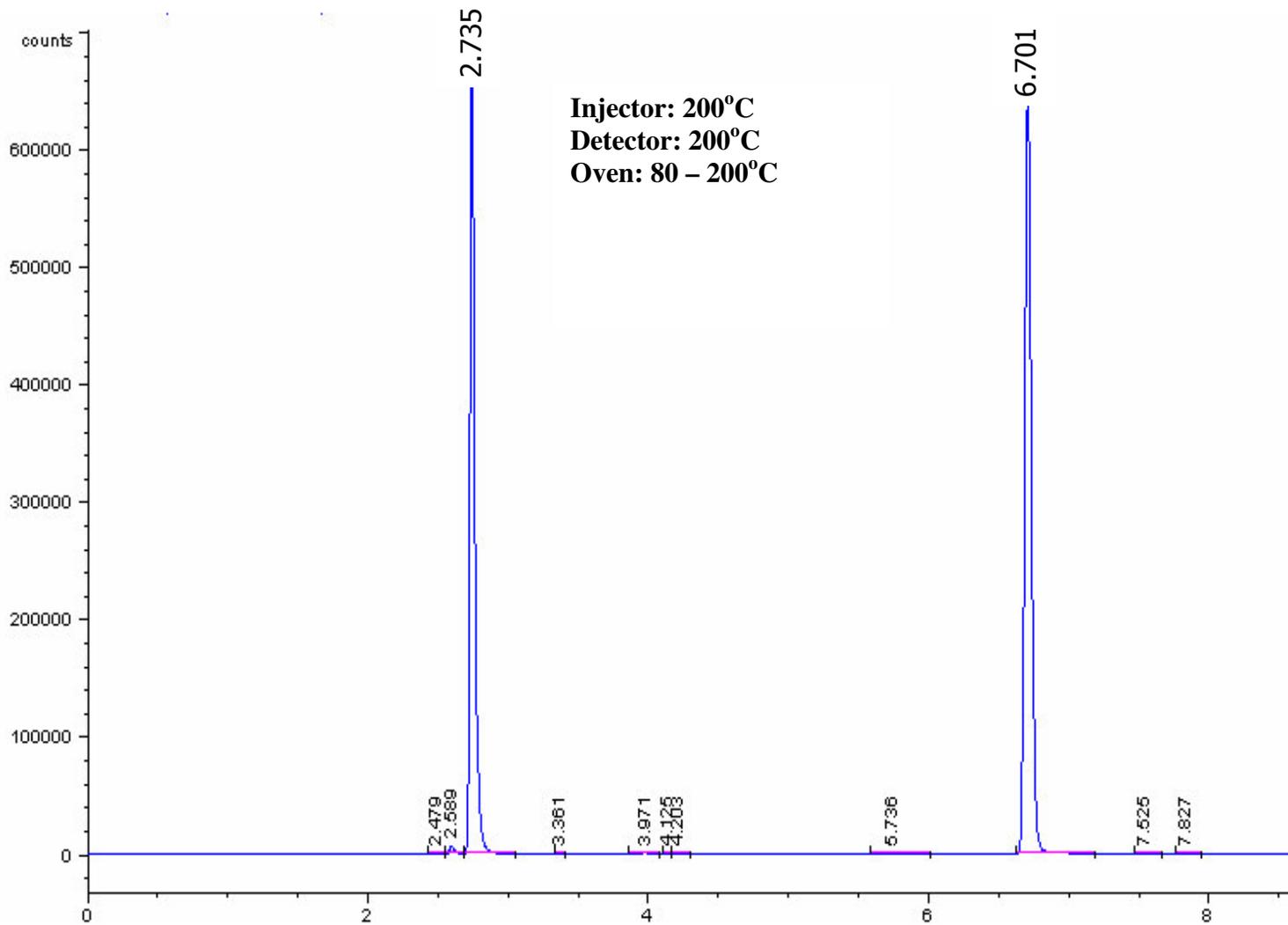


Figure B.12 GC Chromatogram for Calibration Sample 4

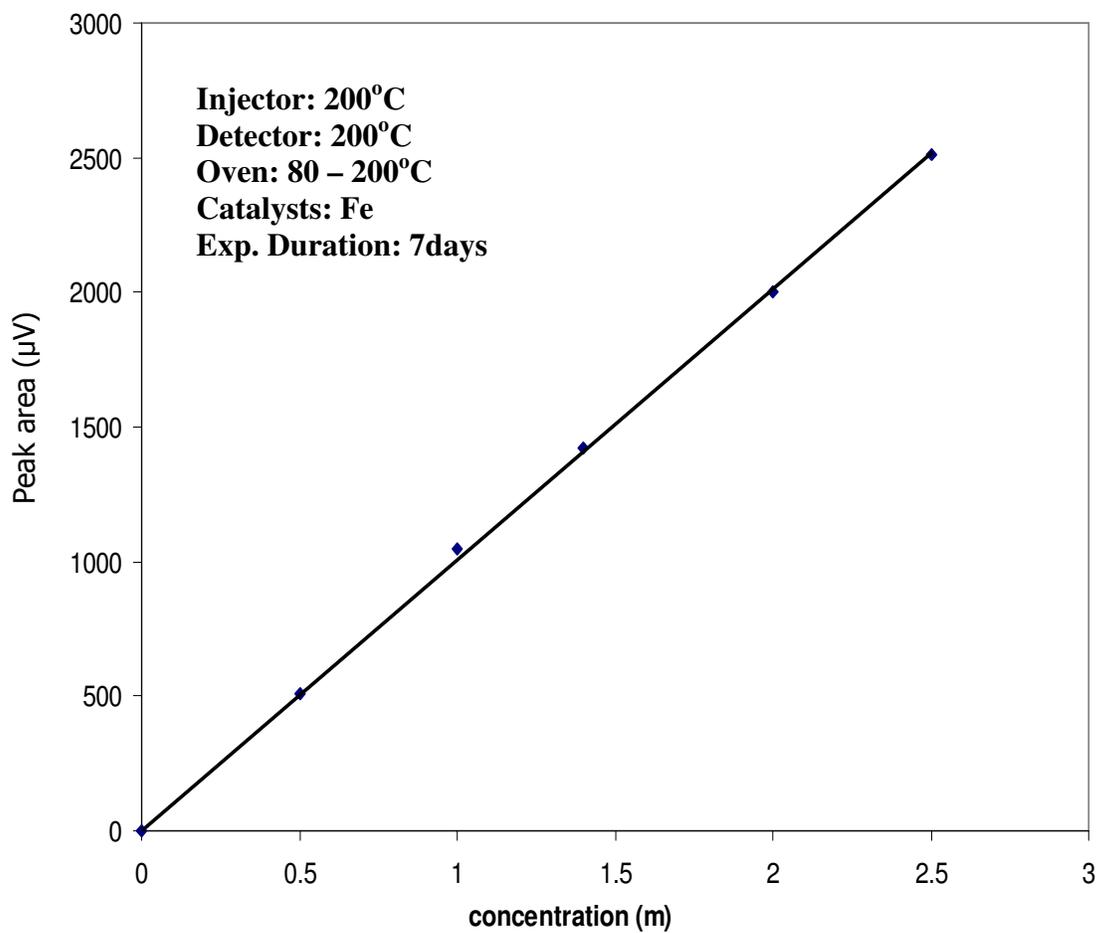


Figure B.13 GC Calibration Curve for 6-21-2004

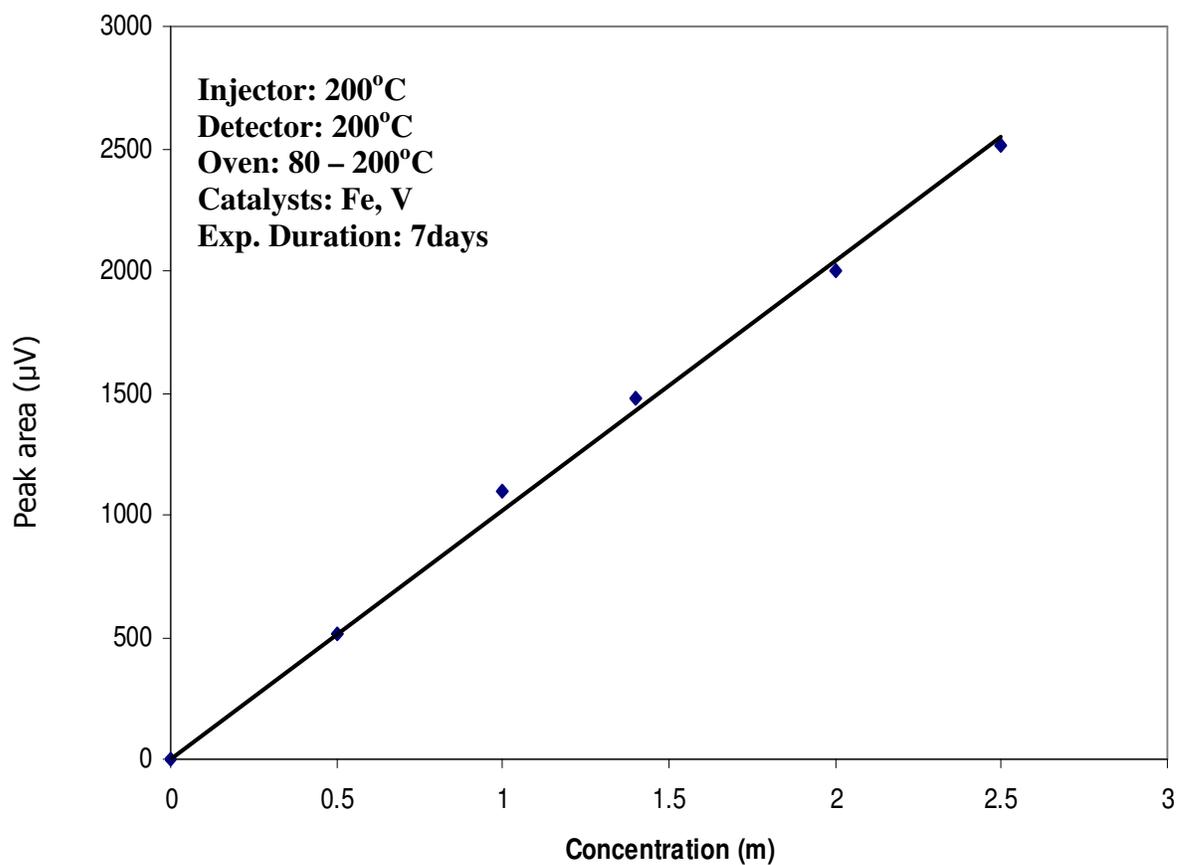


Figure B.14 GC Calibration Curve for 6-13-2004

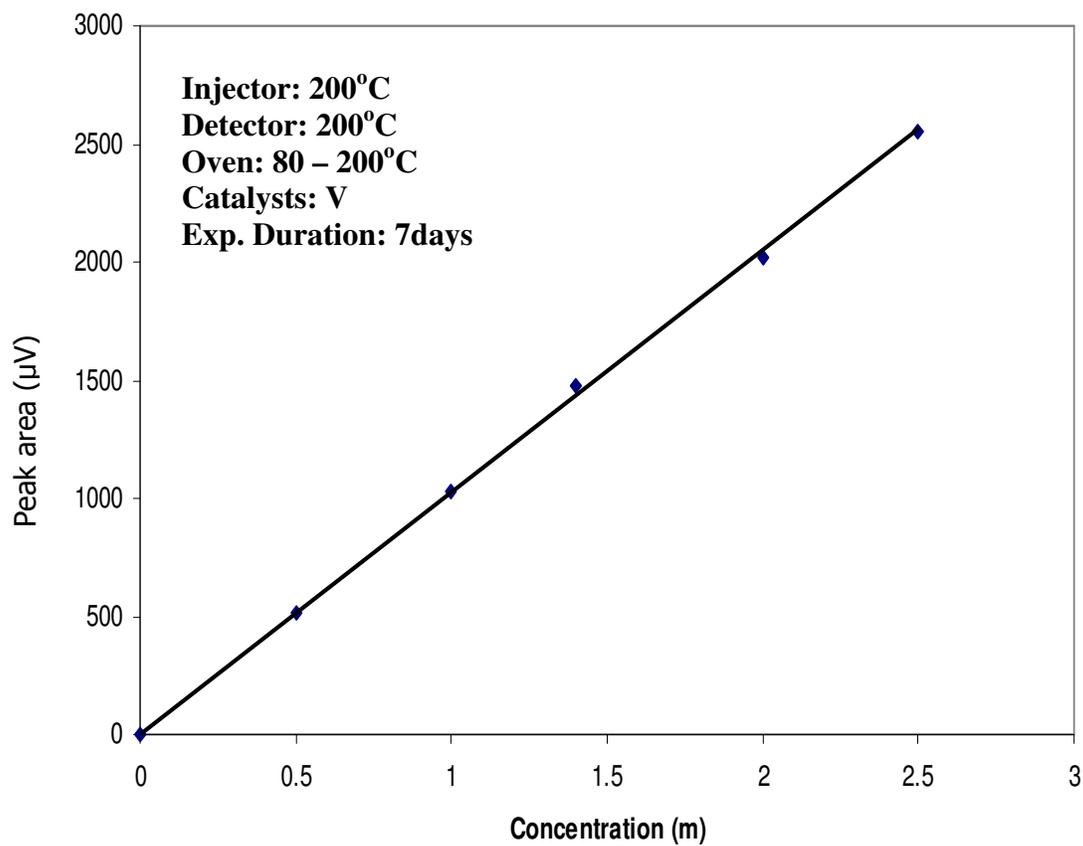


Figure B.15 GC Calibration curve for 6-30-2004

Appendix C

Ion Chromatography

C.1 Analytical information

The AS11 column uses a dilute KOH eluent that is made by the eluent generator, usually using a concentration gradient program that gradually increases the eluent concentration as the run progresses from 2mM to 30mM. It also uses a AG 11 guard column.

C.2 Sample Preparation

All samples were kept refrigerated and in the dark until they were ready to be analyzed. The samples contained highly concentrated potassium salts and piperazine and had to be diluted in order to avoid over-saturating the column. For each, 1microliter of sample is diluted in 1ml of distilled, deionized water. The volumes were measured by using a micropipette to ensure accuracy. There were no precipitates in the samples and therefore there was no need to profiler them, filter caps on the sample vials being sufficient traps for particles big enough to harm the column.

C.3 Procedure for IC

1. The Helium tank and deionized water valve are first opened.
2. The column oven and the conductivity detector switches are turned on and this should automatically turn on the pump, eluent generator and auto sampler.
3. On the front panel of the pump, MENU, 8, 7 sequence gives the chance to monitor the left and right “P-Point” values when the pump is running
4. At this time the computer and software program can be turned on
5. On the main menu bar of the software, the method is selected. This should get the pump started and the left and right p values should settle down within a few minutes. If they don't, the pump will have to be primed to get the bubbles out of the pump.
6. The run schedule can then be loaded (which is a list of all calibration and unknown samples)
7. There should be three test samples which have to be run through the system prior to running the calibration and unknown samples. These serve the purpose of flushing out the column and establishing a steady baseline.
8. The next set should be calibration standards, which are listed as such in the schedule under “Sample Type”. Two or more vials of distilled deionized water are inserted after the calibration samples to make sure the standards are flushed out before running the unknowns.

9. Last in line are two samples, one standard to make sure everything ran perfectly and DDI water which should run under the method “shut down” that will turn off the pump and other electronics at the end of the run.
10. After saving the run schedule, the samples are then loaded into the auto sampler rack.
11. The Hold/Run button on the auto sampler is then depressed so that the green is lit on the RUN side. This puts the auto sampler under the computer control.
12. From the menu bar of the software, the created schedule is then loaded and the run started by pressing the START button.
13. The run sequence starts automatically and the first chromatogram is monitored to make sure things are running as they should.

The calibration curves for all the experiments are shown in Figures 12 to 16. The samples were labeled based on the start dates of each of the experiments. The IC was recalibrated each time the samples were to be analyzed for each experiment set.

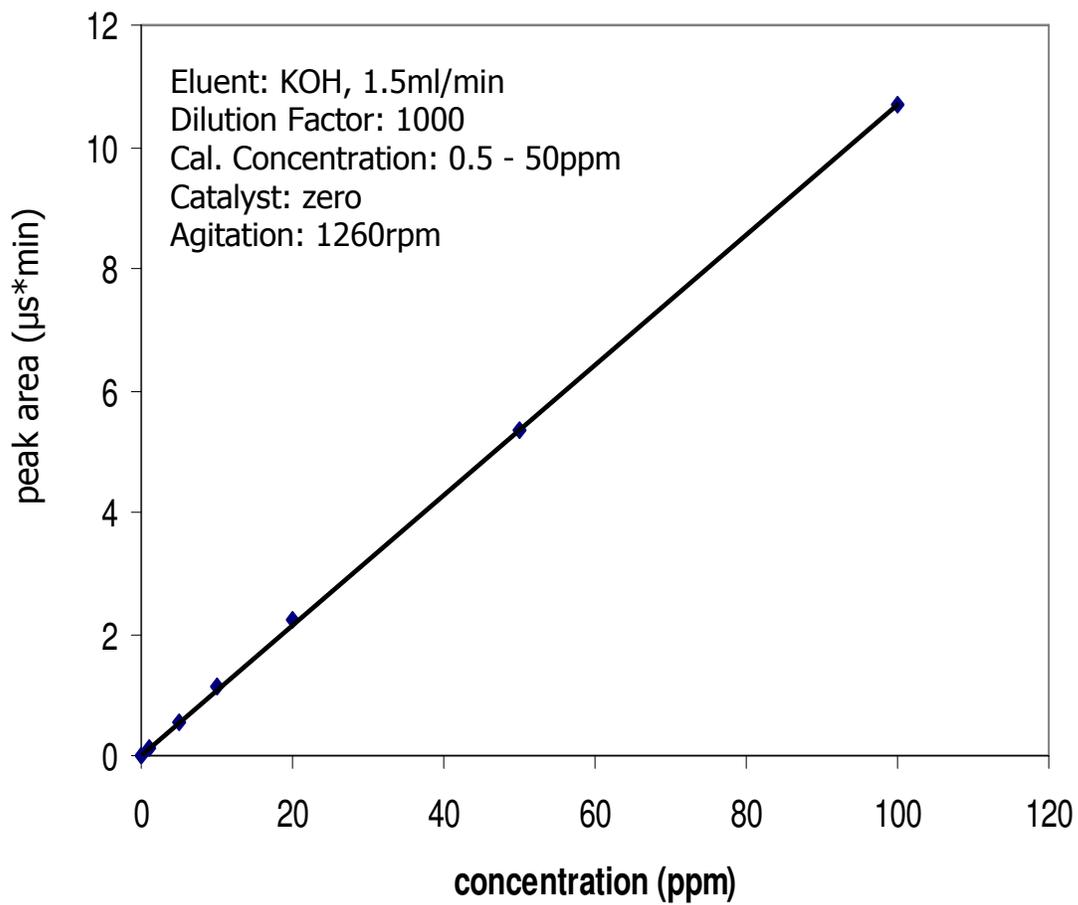


Figure C.1 IC Calibration curve for 1-10-2005

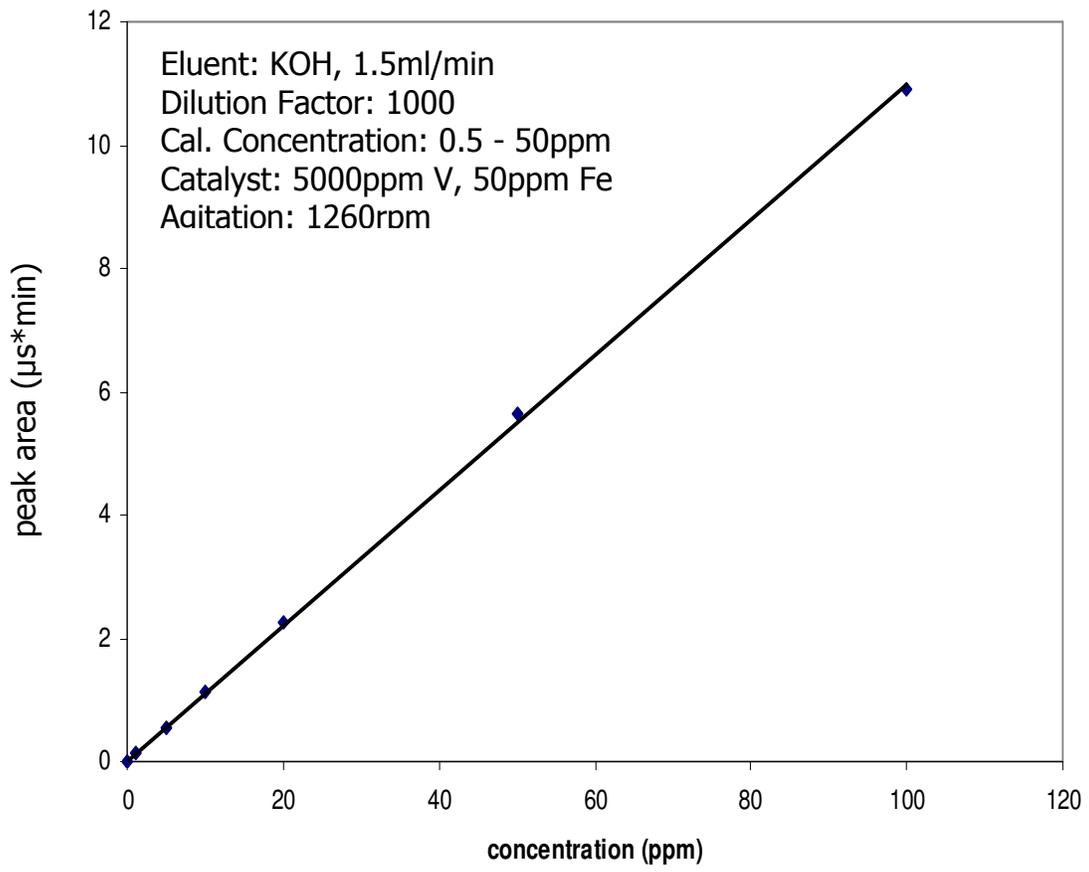


Figure C.2 IC Calibration Curve for 12-20-2004

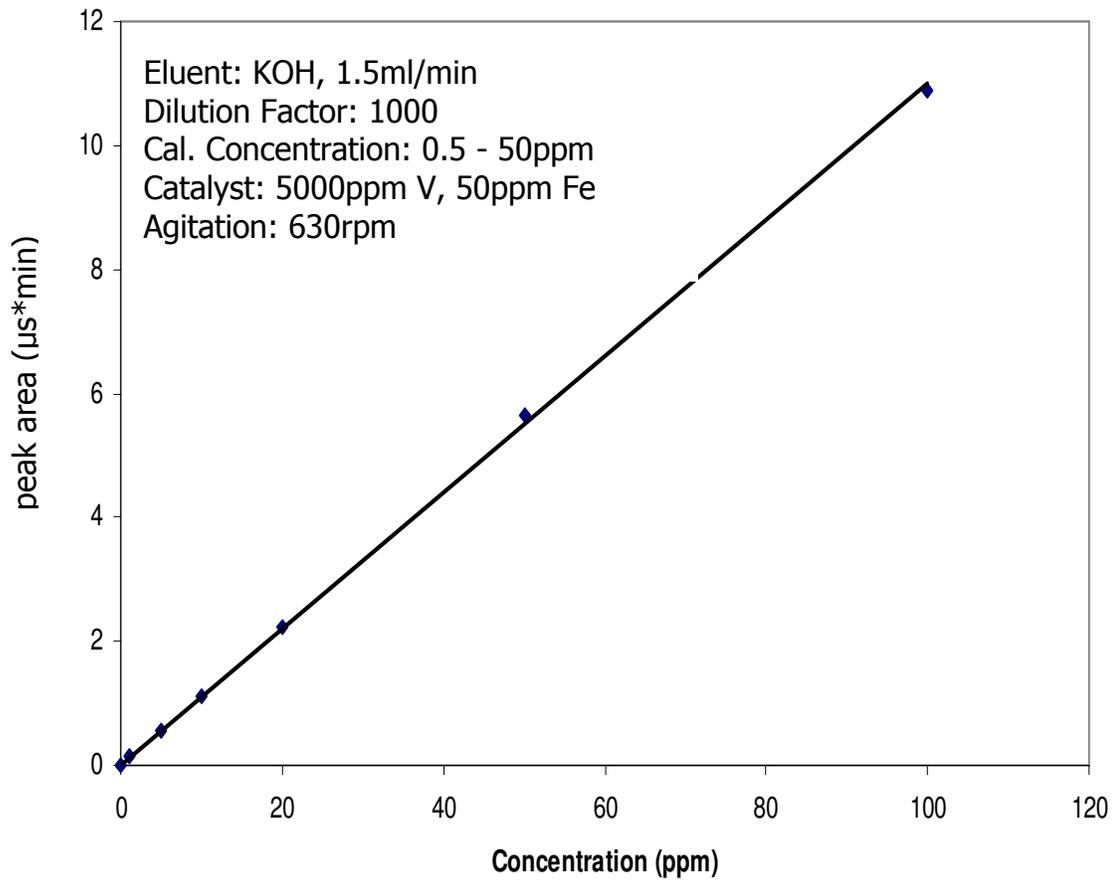


Figure C.3 IC Calibration curve for 1-2-2005

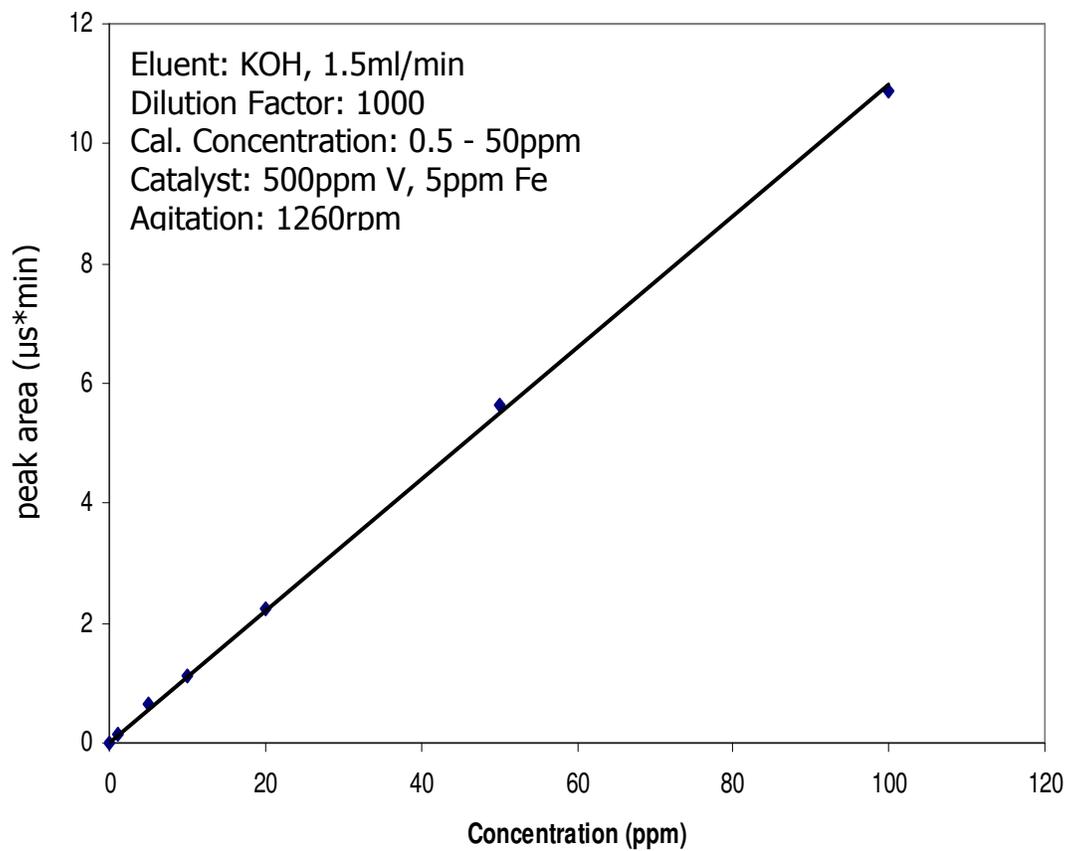


Figure C.4 IC Calibration Curve for 1-4-2005

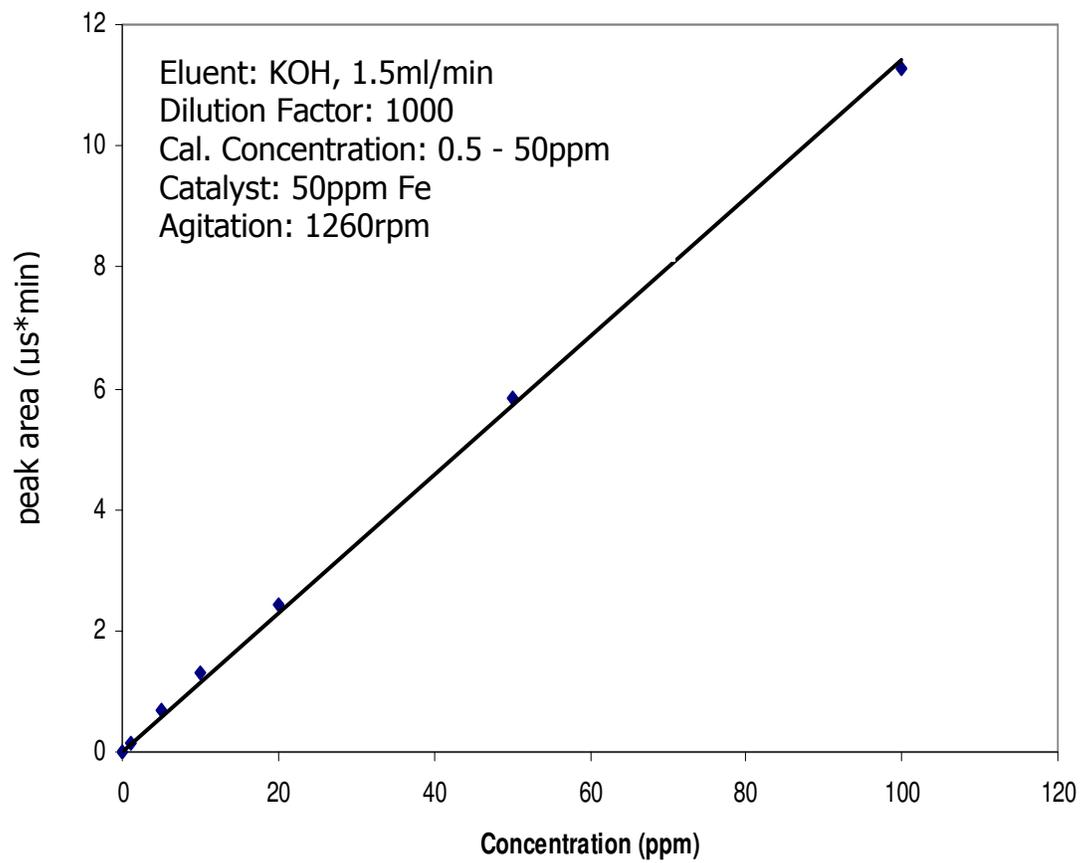


Figure C.5 IC Calibration Curve for 12-22-2004

Appendix D

NMR Peaks and Positions

The table shows the different peaks with their positions as observed in the spectra for the last five experiments.

Table D.5 Positions for Peaks in NMR Spectra

Position (ppm)	Peak
2.1	Acetone
2.2	Acetate
3.2	Unknown
3.25	Unknown
3.3	Unknown
3.35	Unknown
3.40	Piperazine
3.65	Unknown
3.85	Unknown
3.90	Unknown
4.00	Unknown
4.10	Unknown
4.70	Water/Deuterium
8.10	Formate

Diluent: 40% HCl
Solvent: D₂O
Reference: Acetone
Catalyst: none
Exp. Duration: 7days
Anitation: 1260nm

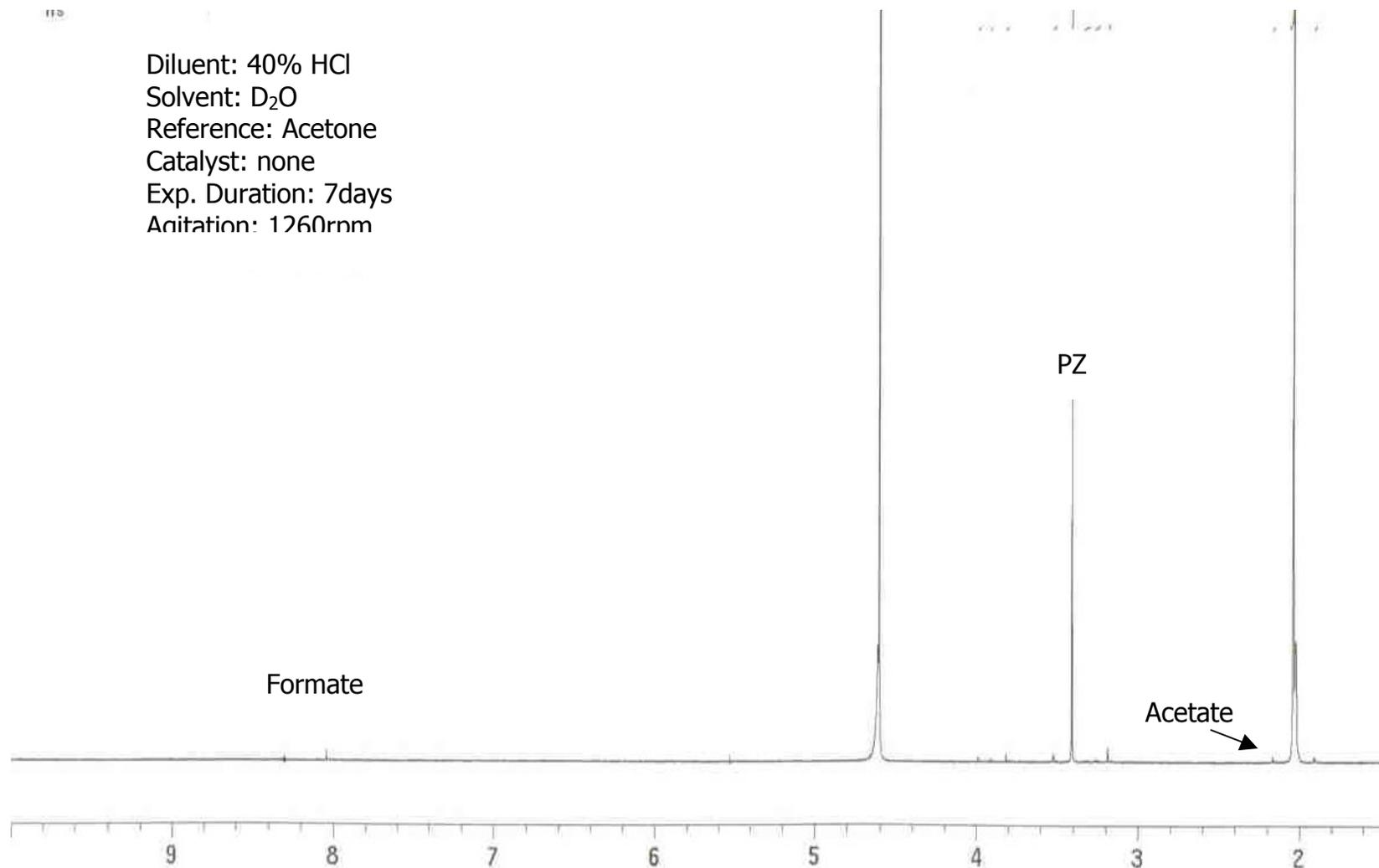


Figure D.1 NMR Spectrum for experiment 1-10-2005

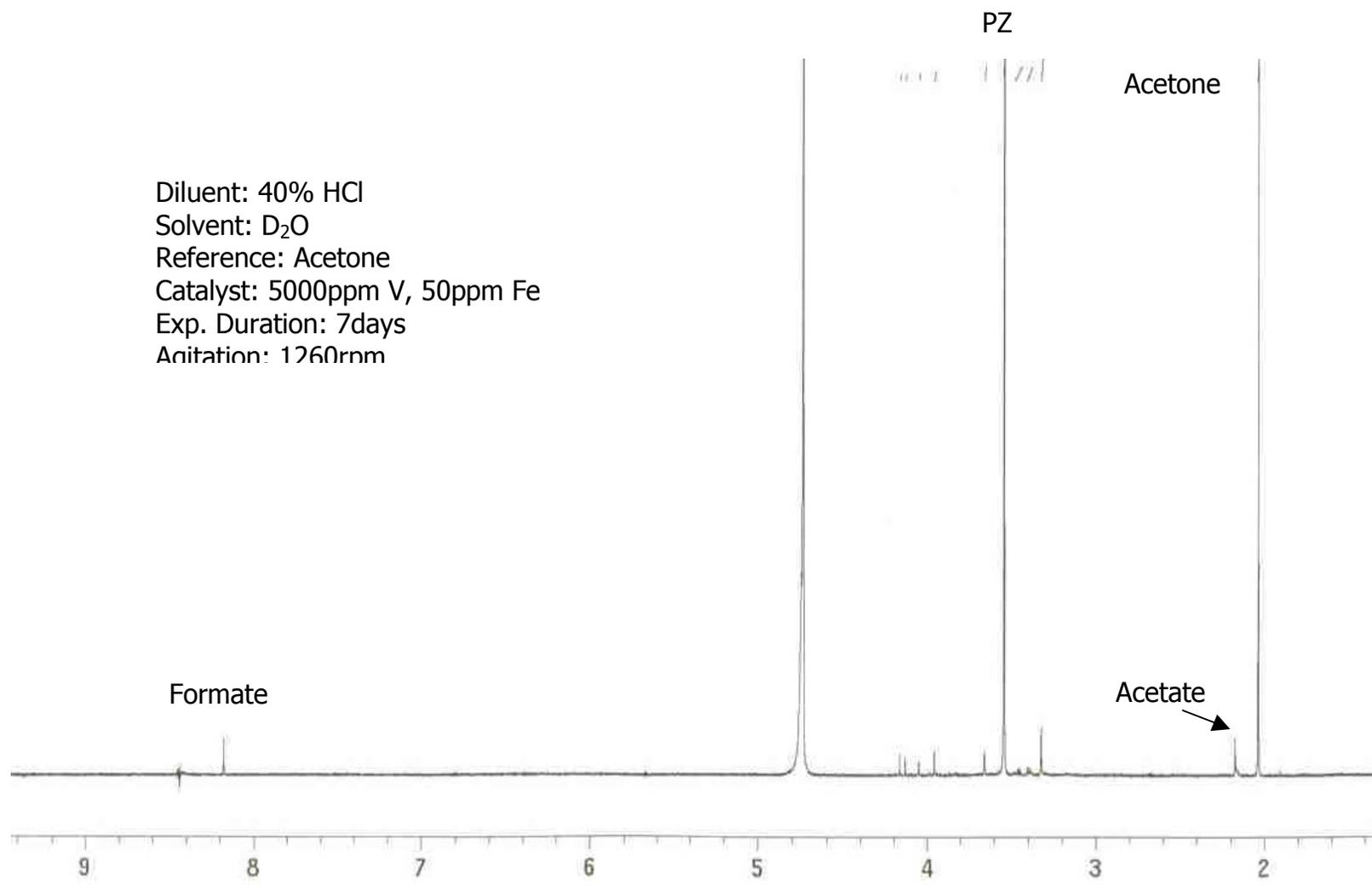


Figure D.2 NMR Spectrum for 12-20-2004

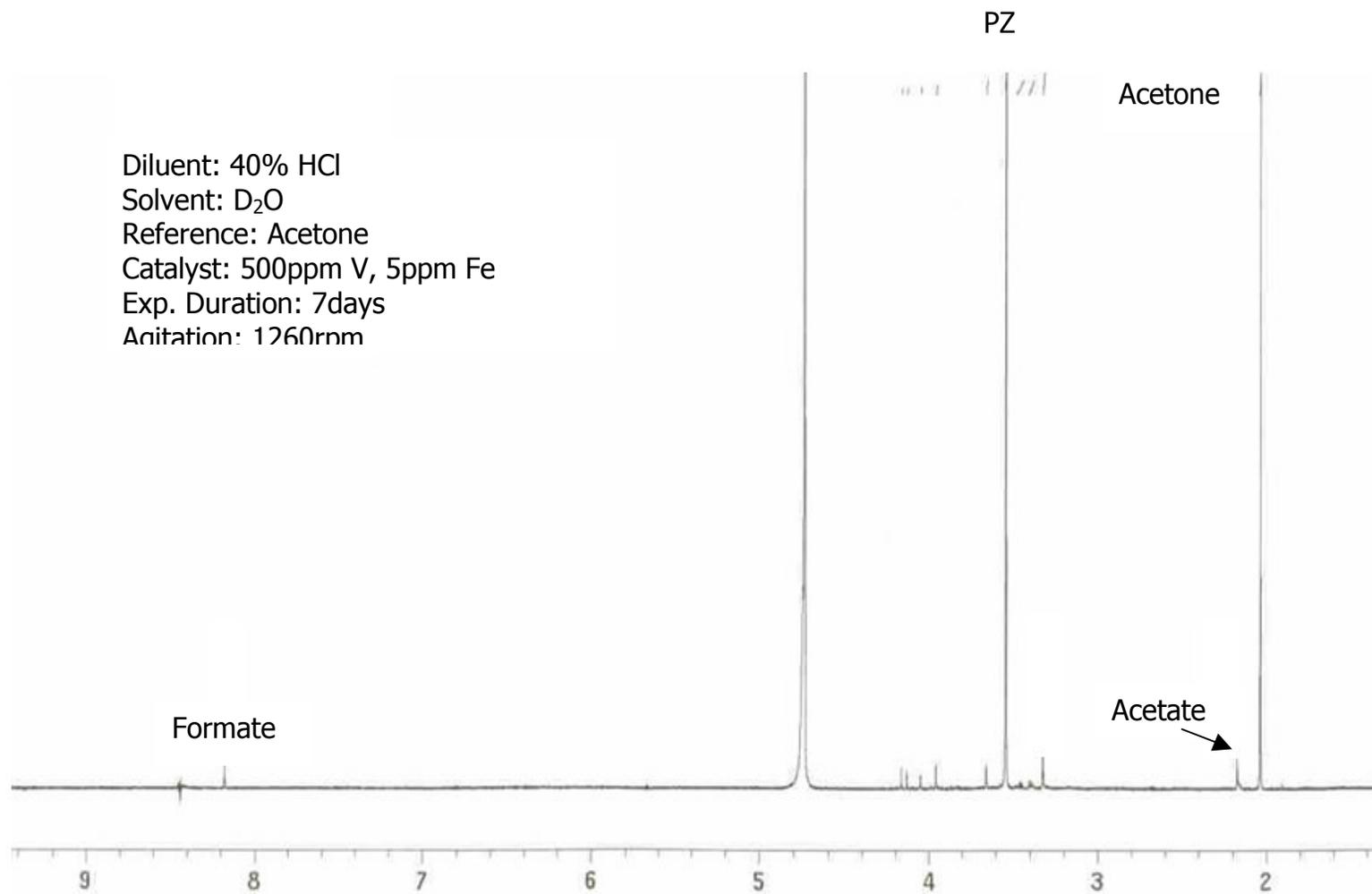


Figure D.3 NMR Spectrum for 1-4-2005

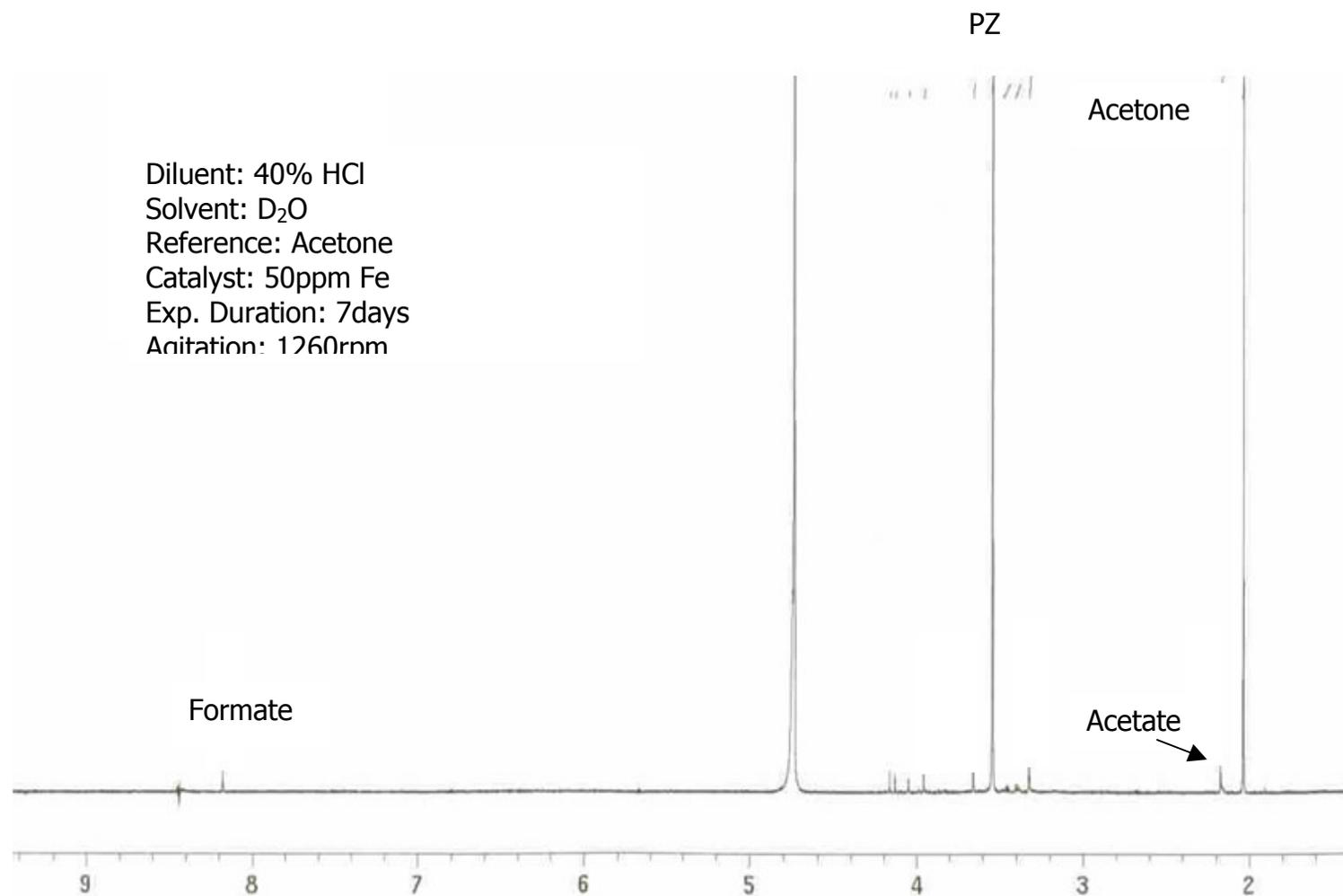


Figure D.4 NMR Spectrum for 12-22-2004

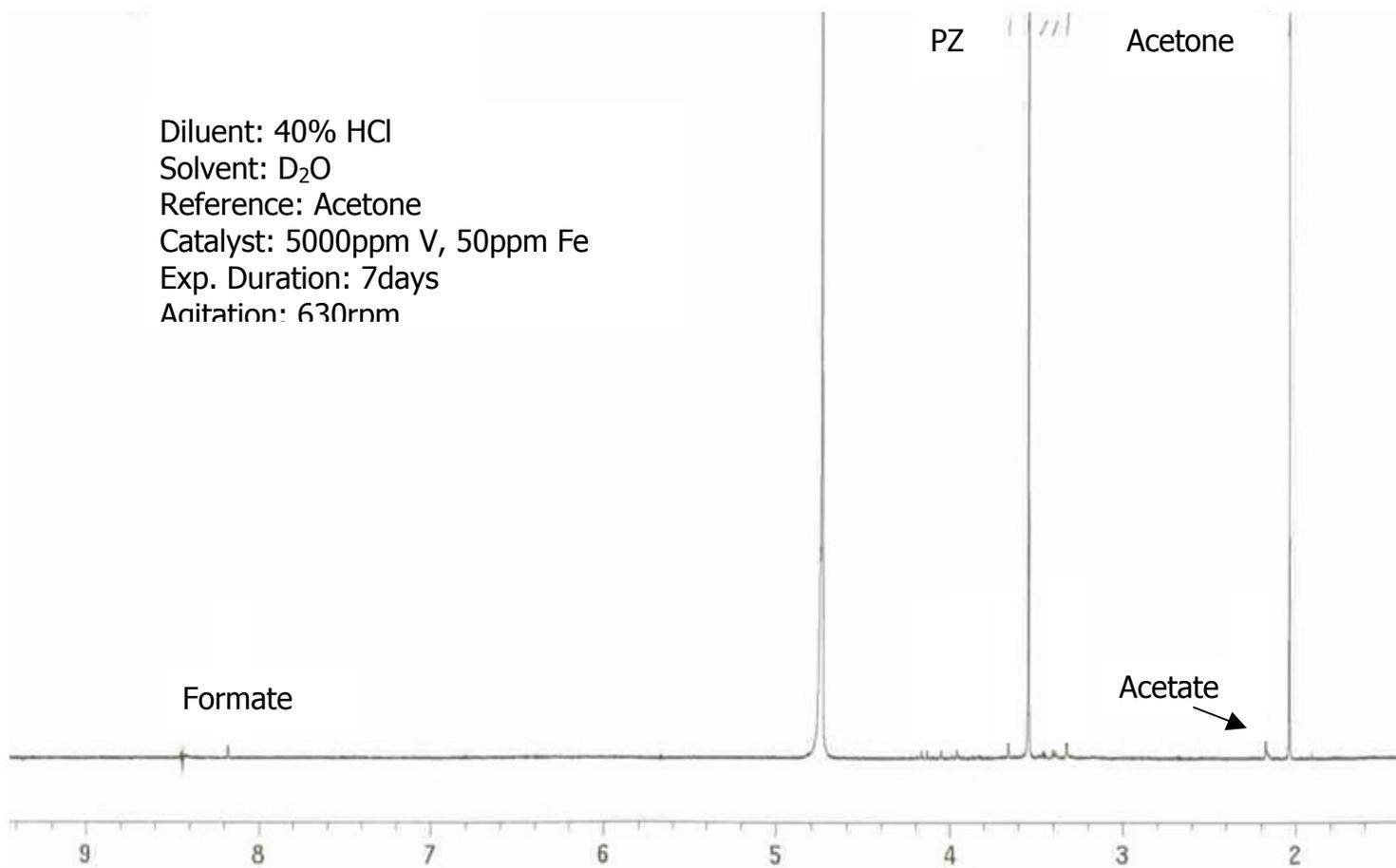


Figure D.5 NMR Spectrum for 1-2-2005

References

- Austgen, D.M. A Model of Vapor-Liquid Equilibria for Acid Gas-Alkanolamine-Water Systems. Ph.D. Dissertation, The University of Texas at Austin, 1989.
- Bishnoi, S. and G. T. Rochelle. "Absorption of Carbon Dioxide into Aqueous Piperazine: Reaction Kinetics, Mass Transfer and Solubility". *Chem. Eng. Sci* 55(22), 5531-5543, 2000.
- Goff, G. and G.T. Rochelle. "Monoethanolamine Degradation: O₂ Mass Transfer Effects under CO₂ Capture Conditions". *Ind. Eng. Chem.Res.* 43, 6400-6408, 2004.
- Chi, Susan and G.T. Rochelle. Oxidative Degradation of Monoethanolamine. M.S. Thesis, The University of Texas at Austin, 2001.
- Cullinane, J.T. Carbon Dioxide Absorption in Aqueous Mixtures of Potassium Carbonate and Piperazine. M.S. Thesis, The University of Texas at Austin, 2002
- Chakma, A.; Meisen A. Identification of Methyl-diethanolamine Degradation Products by Gas Chromatography-Mass Spectrometry. *J Chromatography* 457, 287-297, 1988.
- Critchfield, J.E., L. Jenkins. Evidence of MDEA Degradation in Tail Gas Treating Plants, *Pet. Tech Quart.*, Spring 1999.
- Dang, H. CO₂ Absorption Rate and Solubility in Monoethanolamine/Piperazine/Water. M.S. Thesis, The University of Texas at Austin, 2001.
- Dawodu, O.F., A. Meisen. Degradation of Alkanolamine Blends by Carbon Dioxide. *The Canadian Journal of Chemical Engineering.* 74, 960-966, 1996.
- Denisov, E.T., N.L. Mitskevich, V.E. Agabekov. Liquid-Phase Oxidation of Oxygen-Containing Compounds. Consultants Bureau, New York, 1977.
- Ding, Y., M.L. Lee, D.J. Eatough. *International Journal of Environmental Analytical Chemistry*, 69, 243-255, 1998.
- Ferris, J.P., R.D. Gerwe, G.R. Gapski. Detoxication Mechanisms III: The Scope and Mechanism of the Iron-Catalyzed Dealkylation of Tertiary Amine Oxides. *J. Org. Chem.*, 33, 3493-3498, 1968.

- Hull, L.A., G.T. Davis, D.H. Rosenblatt. Oxidation of Amines VII. Chemical and Electrochemical Correlations, *J. Phys. Chem.* 73, 2142-2146, 1969.
- Hull, L.A., G.T. Davis, D.H. Rosenblatt. Oxidation of Amines IX. Correlation of Rate Constants for Reversible One-Electron Transfer in Amine Oxidation with Reactant potentials, *JACS*, 91, 6247-6250, 1969c.
- Jones, Terraun and G.T. Rochelle. Oxidative Degradation of Piperazine. M.S. Thesis, The University of Texas at Austin, 2003.
- Kaganoi, S. "Carbon Dioxide Absorption in Methyl-diethanolamine with Piperazine or Diethanolamine: Thermodynamic Modeling and Rate Measurements," M.S. Thesis, The University of Texas at Austin, 1997
- Kennard, M.L., A. Meisen. Mechanism and Kinetics of DEA Degradation. *Ind. Eng. Chem. Fund.* 24, 129-140, 1985.
- Kim, C.J., G. Sartori. Kinetics and Mechanism of DEA Degradation in Aqueous Solutions Containing Carbon Dioxide. *Int. J. Chem. Kin.* 16, 1257-1266, 1984.
- Kim, C.J. Degradation of Alkanolamines in Gas Treating Solutions: Kinetics of Di-2-propanolamine Degradation in Aqueous Solutions Containing Carbon Dioxide. *Ind. Eng. Chem. Res.* 27, 1-3, 1988.
- Kindrick, R.C., R.E. Reitweier, M.R. Arnold. "A Prolonged Oxidation Test on Amine Solutions Resistant to Oxidation," Girdler Report No. T2. 15-1-31, in "Report: Carbon Dioxide Absorbents", Contract no. NObs-50023, by Girdler Corp., Gas Process Division, Louisville, Kentucky, for the Navy Department, Bureau of Ships, Washington 25, DC (Code 649P), June 1, 1950a.
- Majahani V.V., and P.V. Danckwartz. "The Stripping of CO₂ from Amine-Promoted Potash Solutions at 100oC," *Chem. Eng. Sci.*, 47(8), 2037-2045, 1992.
- Mahajani, V.V. and J.B. Joshi. "Kinetics of Reactions Between Carbon Dioxide and Alkanolamines". *Gas. Sep. and Purification*, 2(2), 50-64, 1988.
- Lee, Y.J., and G.T. Rochelle. Oxidative Degradation of Organic Additives for Flue Gas Desulfurization: Products, Kinetics, and Mechanisms," *Env. Sci. Tech.* 21, 266-272, 1987.
- Neta, P., R.E. Huie, A.B. Ross. Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution. *J. Phys. Chem. Ref. Data.*, 17, No. 3, 1027, 1988.

- Rochelle, G.T. S. Bishnoi, S. Chi, H. Dang, J. Santos. "Research Needs for CO₂ Capture from Flue Gas by Aqueous Absorption Stripping". Final Report, United States Department of Energy, Federal Energy Technology Center, P.O. No DE-AF26-99FT01029, 2000.
- Rooney, P.C., M.S. DuPart, T.R. Bacon. "Oxygen's Role in Alkanolamine Degradation," *Hydrogen Processing*, 77(7), 109, 1998.
- Rosenblatt, D.H., L.A. Hull, D.C. De Luca, G.T. Davis, H.K.R. Williams. Oxidations of Amines II: Substituent Effects in Chlorine Dioxide Oxidations. *JACS*, 89, 1158-1163, 1967.
- Rosenblatt, D.H., A.J. Hayes, B.L. Harrison, R.A. Streaty, K.A. Moore. (I) The Reaction of Chlorine Dioxide with Triethylamine in Aqueous Solution. *J. Org. Chem.*, 28, 2790-2794, 1963.
- Sajus, L., I. Seree De Roch. The Liquid Phase Oxidation of Aldehydes. *Comprehensive Chemical Kinetics*, 16, 89-124, Liquid-Phase Oxidation, Elsevier Scientific Publishing Co., Amsterdam, 1980.
- Schmidt, C.E., R.F. Sprecher, B.D. Batts. *Analytical Chemistry*, 59, 2027-2033.
- Seo, D.J., and W.H. Hong. "Effect of Piperazine on the Kinetics of Carbon Dioxide with Aqueous Solutions of 2-Amino-2-Methyl-1-Propanol," *Ind. Eng. Chem. Res.* 39, 2062, 2000.
- Strazisar, B.R., R.R. Anderson, C.M. White. Degradation Pathways for Monoethanolamine in a CO₂ Capture Facility. United States Department of Energy 2002.
- Tosh, J.S., J.H. Field, H.E. Benson, W.P. Haynes. "Equilibrium Study of the System Potassium Carbonate, Potassium Bicarbonate, Carbon Dioxide, and Water". United States Department of the Interior, Bureau of Mines Report of Investigation 5484, 1959.

Vita

Akinleye Olaolu Alawode was born on 2nd March, 1976 in Ile-Ife, Nigeria to Festus Akinyele Alawode and Olufunmilade Alawode. He graduated with a Bachelor of Science degree from the Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria in 2001. After a year of National Youth Service, he entered the graduate school of Chemical Engineering at the University of Texas at Austin.

Permanent Address: 2065 SE 44th Avenue, Apt. C212
Hillsboro, Oregon 97123

This thesis was typed by the author.