DEGRADATION OF DEA TREATING SOLUTIONS

by

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ABSTRACT

The objectives of this research were (i) to develop an
analytical method capable of measuring trace quantities of DEA
degradation products and (ii) to study DEA degradation under
carefully controlled experimental conditions.

The analytical method consisted essentially of removing
water by air stripping, silylating the residue with N,O-bis(trimethylsilyl)
acetamide (or "BSA"), and analyzing the silylated compounds by gas
chromatography. An OV-17 stainless steel column and H_2 flame
ionization detector were used. The effectiveness of this method
was subsequently confirmed by its ability to analyze numerous DEA
samples from laboratory experiments and industrial plants.

DEA degradation was first studied at atmospheric pressure
using an all glass and teflon apparatus. When a 30% DEA solution
was contacted with pure CO_2 for up to 23 days, no known DEA degradation
products were detected. However, the DEA concentration was observed
to decrease with time. This may be caused by the formation of heat-
stable salts which are undetectable by gas chromatography.

DEA degradation experiments were then conducted at elevated
pressures (up to 4238 kP_a (600 psig)) and temperatures (165 to 185° C)
using a stainless steel reactor. The results showed that DEA degradation
proceeded rapidly in the presence of CO_2 and N,N-bis(2-hydroxyethyl)
piperazine (HEP) was one of the major degradation products. Four other

degradation products called T, X, Y and Z were also observed when the column temperature of the chromatograph was set to 142° C. The concentration of HEP was found to increase uniformly with time whereas concentrations of T and Y increased only slightly. The concentration versus time plots of compounds X and Z exhibited a maximum which suggests that they are degradation intermediates. The overall DEA loss was governed by a first order rate equation of the following form:

$$\frac{d[DEA]}{dt} = - A \exp\left\{ - E_a /RT \right\}\left[DEA \right]$$

where A, E_a and R are 2.03×10^{10} hour^{-1}, 2.17×10^4 cal. g-mole^{-1}, 1.99 cal g-mole^{-1} ^{O}K^{-1} respectively.

A degradation mechanism is proposed which resembles that suggested by Polderman *et al.* (16):
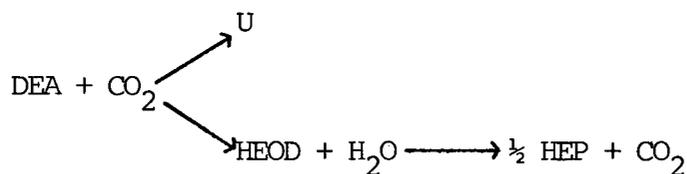
where U denotes one, or more, unidentified compounds.
The theoretical concentration values of DEA and HEP based on the above mechanism fitted the experimental data fairly well. However, the predicted concentrations of HEOD did not exhibit a sharp maximum and therefore failed to match the behavior of X or Z.

The DEA samples obtained from the high pressure tests were also analyzed using a higher G.C. column temperature of 174° C. In this case, seven additional peaks were observed indicating other degradation products. One of the seven peaks could be caused by THEED, which was previously reported by Hakka $et\ al.$ (17). It is therefore clear that the degradation of DEA is more complex than suggested by the above mechanism.

Special high pressure tests were conducted to discover the effects of acid gas composition, pressure, initial DEA concentration and metals on DEA degradation. It was found that CO_2 and temperature were the most important parameters affecting DEA degradation but purely thermal degradation was insignificant. CO_2 pressure appeared to be unimportant, between 2170 and 4238 kP_a (300 to 600 psig), probably due to a large excess of CO_2. When the initial DEA concentration was 10% (as opposed to 30%), the degradation of DEA proceeded more slowly than expected from the aforementioned rate expression. The reason for this behavior is presently unknown. When the DEA solution was saturated with H_2S at 1480 kP_a (200 psig) and room temperature prior to contact with CO_2 at 4238 kP_a (600 psig), it was observed that the degradation at 175° C decreased substantially. This was probably due to the fact that approximately half of the DEA combined with H_2S and was hence protected against CO_2 attack.

Initial results from preliminary paper chromatographic and mass spectroscopic studies are also reported. These studies provide guidance for future work.

TABLE OF CONTENTS

LIST OF TABLES

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I. INTRODUCTION

The pressure and composition of raw natural gas, i.e. gas as it leaves the geological formation, can vary greatly, but Table 1 gives some typical values for three Western Canadian gas fields. Most of the acid gases (H_2S and CO_2) as well as water have to be removed before the gas can be sold in order to minimize pipeline corrosion, pumping costs, health hazards and pollution when the gas is finally burnt or converted. For Western Canada and the United States, the product natural gas should usually contain less than 0.57 grams/100 cubic meter (0.25 grains/100 SCF) of H_2S and 6.4 grams/100 cubic meter (4 lbs/SCFx10^6) of water (1).

The removal of H_2S and CO_2, or "sweetening", is therefore a major process used by the natural gas processing industry. Sweetening by absorption with aqueous ethanolamine solutions has found greatest acceptance (2, 3), although other processes (4, 5) are used as well.

Monoethanolamine (MEA) is often preferred to diethanolamine (DEA) due to its lower cost and greater absorptive capacity on a unit weight basis, but DEA has the following advantages over MEA: greater resistance to COS and CS_2 attack, smaller vapour pressure, lower affinity for hydrocarbons, less energy requirements (up to 35%) for regeneration (6), reduced corrosiveness, increased filter life

TABLE 1: General information on three Western Canadian gas fields

Property	Field I	Field II	Field III
Pressure	6996 kP_a (1000 psig)	6996 kP_a (1000 psig)	6996 kP_a (1000 psig)
Temperature	32° C (90° F)	41° C (105° F)	43° C (110° F)
Gas composition (mole %)			
N_2	0.4	0.2	0.9
CO_2	2.2	6.4	5.2
H_2S	9.2	34.5	27.7
C_1	82.4	58.2	66.0
C_2	3.4	0.5	0.3
C_3	1.2		
$i-C_4$	0.3		
$n-C_4$	0.4		
$i-C_5$	0.2		
$n-C_5$	0.2		
Other hydrocarbons $> C_3$	0.1	0.1	0.2
Water	Saturated	Saturated	Saturated

by a factor of 5 to 10 (6) and reduced solution foaming. As a result, more and more gas treating plants are being converted to the DEA process (7).

A flowsheet of a typical industrial DEA sweetening unit is shown in Figure 1. Sour natural gas containing CO_2 and H_2S is contacted with an aqueous DEA solution (15 to 30 wt.% of DEA) by passing it counter-currently through an absorber. This unit usually contains 10 to 20 plates, but packed absorbers are also in use. The gas leaving the absorber is sweet, i.e. essentially free of acid gases, and it is passed through a knock-out drum to remove any entrained DEA solution. The sweet gas is then usually dehydrated before delivery to the user.

The pressure of the rich DEA solution leaving the absorber is let down in a vent tank and the majority of absorbed hydrocarbons are thus vaporized. After heating, the rich DEA solution is sent to a stripper where the absorbed H_2S and CO_2 are released. The overhead acid gases are flared or, in case of high H_2S concentrations, are sent to a Claus plant (8) for recovery of elemental sulphur.

The regenerated lean DEA solution from the bottom of the stripper is cooled and recycled to the absorber. In order to prevent the build-up of impurities (such as iron sulphide and other
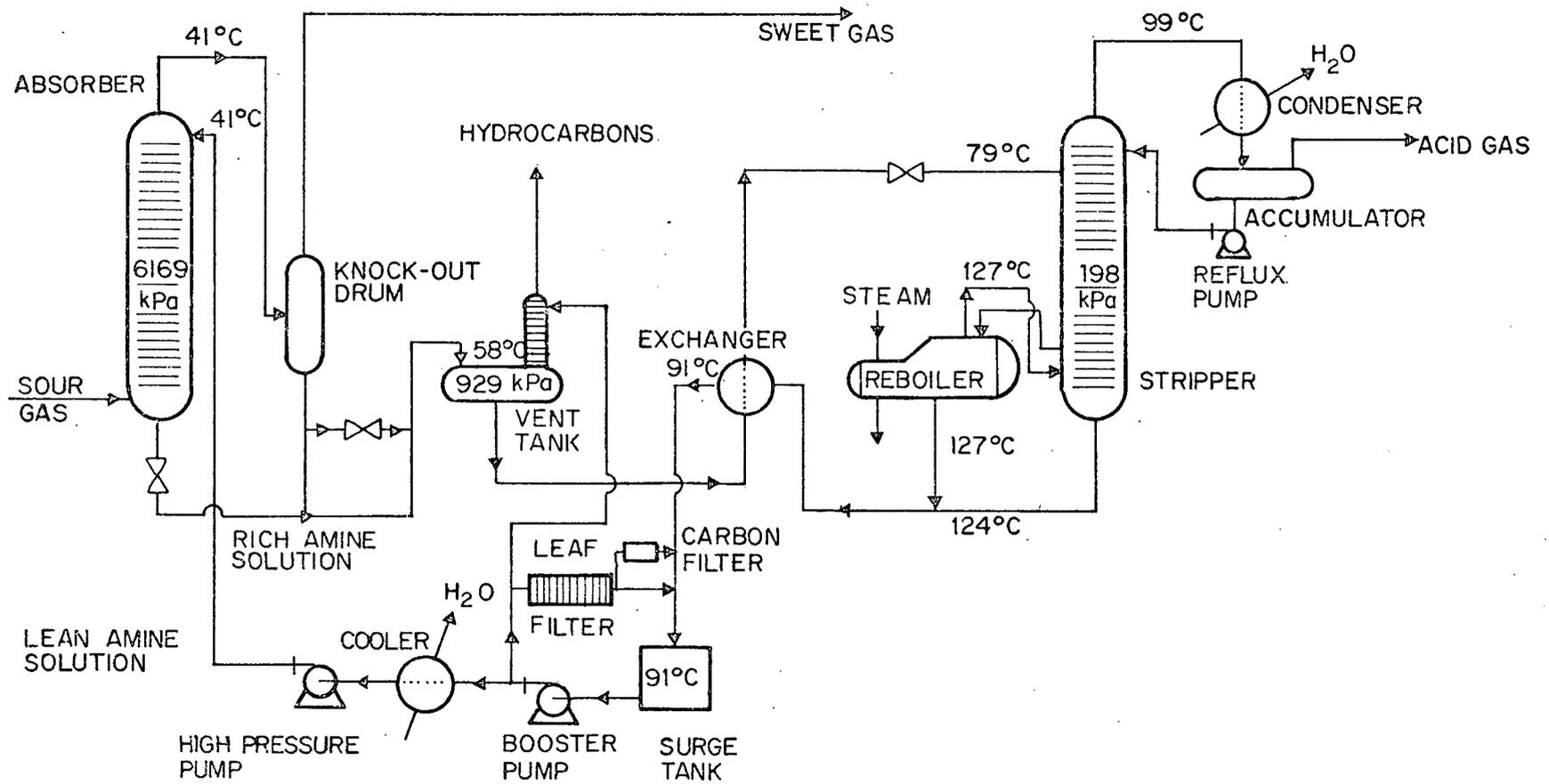
FIGURE 1: Flow sheet of a typical industrial amine unit.

non-regenerable compounds), a small slip stream of the DEA solution may be passed through a filter system (7, 9).

The principal reactions of DEA with H_2S and CO_2 can be represented by the following equations (10):

$$
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH \\
HO-CH_2-CH_2 \diagup
\end{array}
+ H_2S
\underset{116^\circ\,C}{\overset{38^\circ\,C}{\rightleftharpoons}}
\left[
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH_2 \\
HO-CH_2-CH_2 \diagup
\end{array}
\right] HS
\qquad (1)
$$

$$
2\,
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH \\
HO-CH_2-CH_2 \diagup
\end{array}
+ H_2S
\underset{116^\circ\,C}{\overset{38^\circ\,C}{\rightleftharpoons}}
\left[
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH_2 \\
HO-CH_2-CH_2 \diagup
\end{array}
\right]_2 S
\qquad (2)
$$

$$
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH \\
HO-CH_2-CH_2 \diagup
\end{array}
+ CO_2 + H_2O
\underset{149^\circ\,C}{\overset{38^\circ\,C}{\rightleftharpoons}}
\left[
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH_2 \\
HO-CH_2-CH_2 \diagup
\end{array}
\right] HCO_3
\qquad (3)
$$

$$
2\,
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH \\
HO-CH_2-CH_2 \diagup
\end{array}
+ CO_2 + H_2O
\underset{149^\circ\,C}{\overset{38^\circ\,C}{\rightleftharpoons}}
\left[
\begin{array}{c}
HO-CH_2-CH_2 \\
 \diagdown NH_2 \\
HO-CH_2-CH_2 \diagup
\end{array}
\right]_2 CO_3
\qquad (4)
$$
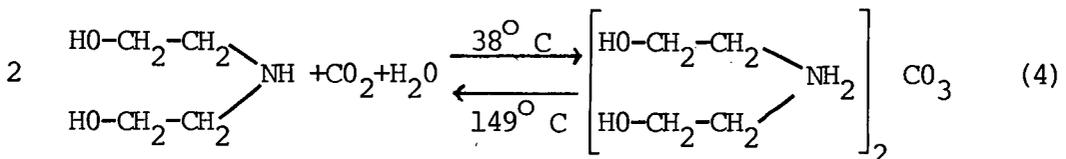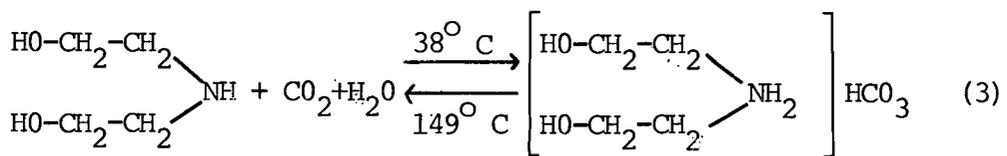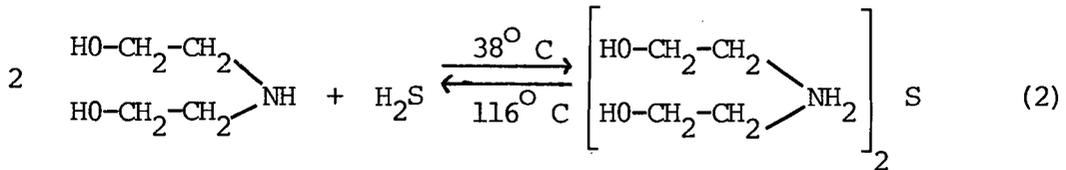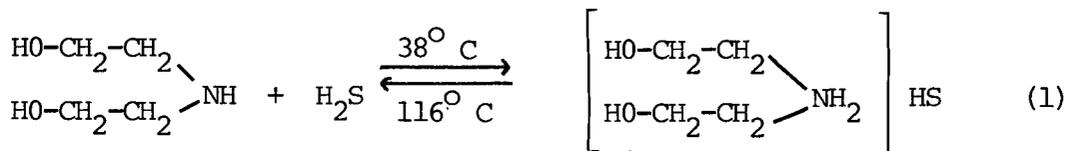
The reactions are reversible with the forward (absorption step) being exothermic and the backward (desorption step) being endothermic.

As explained more fully in the next Chapter, Eqs. 1 to 4 are accompanied by undesirable side reactions which result in amine degradation. The degradation products, some of which are summarized in Table 2, are either corrosive or give rise to corrosive compounds (1, 7). It is not possible to purify DEA solutions by distillation alone and a majority of the gas treating plants control the build-up of degradation products by purging or activated carbon absorption (7). The effectiveness of absorption has however not yet been fully established.

The DEA loss and increased corrosion can result in major costs and the incentive for suppressing the side reaction is therefore high. Plant experience has indicated that amine losses and corrosion rates are affected by the following operating variables (1, 7, 10): temperature, pressure, raw gas composition, amine concentration, pH of the amine solution and the presence of metal ions. The *quantitative* relationship between these variables is however unknown.

Although DEA samples from sweetening processes are routinely analyzed to monitor the purity of the solutions and to detect

TABLE 2: Some possible degradation products from DEA gas-treating solutions.

NAME	ABBREVIATION	STRUCTURAL FORMULA	MOLECULAR WEIGHT
Hydroxyethyl imidazolidone	HEI	CH_2——CH_2 │ │ CH_2 C==O \\ / N │ CH_2——CH_2——OH	113
3-(2-hydroxyethyl)-2-oxazolidinone	HEOD	CH_2——N——CH_2-CH_2——OH │ │ CH_2 C==O \\ / O	131
N,N-bis(2-hydroxyethyl) piperazine	HEP	HO-CH_2——CH_2——N ⟨ CH_2--CH_2 / CH_2--CH_2 ⟩ N-CH_2——CH_2——OH	174
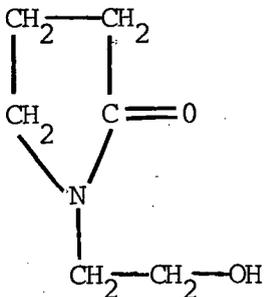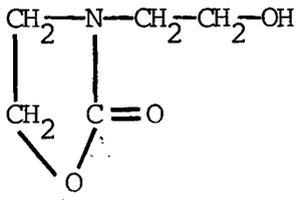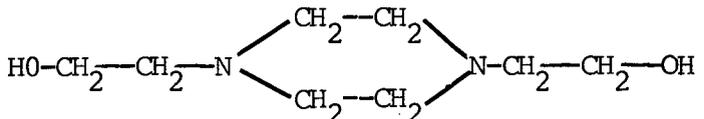
TABLE 2: Some possible degradation products from DEA gas-treating solutions. (continued)

NAME	ABBREVIATION	STRUCTURAL FORMULA	MOLECULAR WEIGHT
N,N,N-tris(2-hydroxyethyl) ethylenediamine	THEED	$HO-CH_2-CH_2$ $HO-CH_2-CH_2$ $>N-CH_2-CH_2-\overset{H}{N}-CH_2-CH_2-OH$	236
N-Methyldiethanolamine	MDEA	$HO-CH_2-CH_2$ $HO-CH_2-CH_2$ $>N-CH_3$	119
Oxazolidone	OZD	$\begin{array}{c} CH_2-N-H \\ \mid \quad\quad \mid \\ CH_2 \quad C=O \\ \diagdown_O \diagup \end{array}$	87
Aminoethylethanolamine	AEEA	$NH_2-CH_2-CH_2-\overset{H}{N}-CH_2-CH_2-OH$	104

corrosion related materials (7, 11, 12), very little has been
published in the open literature on the analytical precedures
used and their accuracy. The analysis is difficult because DEA
and its degradation products have fairly low vapour pressures,
readily decompose at elevated temperatures, are highly polar,
occur in aqueous solution and at small concentrations. Furthermore,
any relationships between the rates of degradation and process
conditions are generally unknown.

1. Specific Objectives of the Present Study

The main objective of the present study was to develop a
reliable, quantitative technique for determining DEA and its
degradation products. A further objective was to relate the
formation of degradation products to some processing parameters
such as temperature, pressure and DEA concentration.

II. LITERATURE REVIEW

The DEA sweetening process has been widely accepted for removing CO_2 and H_2S from natural gas streams and numerous studies have been conducted using DEA as a sweetening reagent (7, 8, 9, 13). In addition to general handbooks (14, 15) on natural gas engineering, the "Gas Conditioning Fact Book" (5) published by The Dow Chemical Company describes various gas-treating methods commonly used. It also presents general analytical methods for routine analysis of industrial gas-treating solutions.

However, there are surprisingly few references dealing specifically with DEA degradation. Furthermore, the open literature contains no information on fast, reliable and quantitative analytical methods suitable for measuring small concentrations of DEA and its degradation products in aqueous solutions. Such an analytical technique is of course a pre-requisite for quantitative studies on DEA degradation. The review of the literature is divided into two major parts: DEA Degradation and Analytical Techniques.

1. DEA Degradation

Polderman and Steele (16) were the first to publish a comprehensive investigation on DEA degradation in 1955. The authors used a stainless steel pressure autoclave as a reaction vessel in

which a 25 wt.% solution of DEA was first saturated with CO_2 at 25° C. The vessel was then sealed and heated to the desired temperature (between 100 and 175° C). The pressure inside the autoclave ranged from 1342 (180 psig) to 4238 (600 psig) kP_a. After 8 hours, the autoclave was cooled to 25° C and the contents were discharged and fractionally distilled. It was thus possible to determine the amount of DEA remaining and the amount converted to higher-boiling, nitrogenous compounds. The DEA conversion was reported to range from 0% (at 100° C and 1342 kP_a (180 psig)) to 97% (at 175° C and 4238 kP_a (600 psig)).

Using fractional distillation and crystallization, the authors attempted to analyze the nature of the degradation products. A white crystalline solid was isolated from the DEA residue and was identified as N,N'--bis (2-hydroxyethyl) piperazine ("HEP"). The authors also noted the presence of other degradation products, but did not characterize them further owing to the lack of suitable analytical and separation techniques at that time. For the same reason, the concentrations of HEP in the reacted DEA solutions could not be determined accurately. The authors postulated the following reaction scheme for the formation of HEP:

$$
\begin{array}{l}
HO-CH_2-CH_2 \\
 \diagdown \\
 NH \;+\; CO_2 \longrightarrow \\
 \diagup \\
HO-CH_2-CH_2
\end{array}
\qquad
HO-CH_2-CH_2-N
\begin{array}{c}
CH_2--CH_2 \\
| \qquad\quad | \\
\diagdown \qquad\quad O \\
\diagup \\
C \\
\| \\
O
\end{array}
\;+\; H_2O
\qquad (5)
$$

DEA   3-(2-hydroxyethyl)-2-oxazolidone, "HEOD"

$$2 \text{ HO-CH}_2\text{-CH}_2\text{-N} \overset{\text{CH}_2\text{-CH}_2}{\underset{\text{C}}{\diagdown}} O \longrightarrow \text{HO-CH}_2\text{-CH}_2\text{-N} \overset{\text{CH}_2\text{-CH}_2}{\underset{\text{CH}_2\text{-CH}_2}{\diamond}} \text{N-CH}_2\text{-CH}_2\text{-OH} + 2\text{CO}_2 \quad (6)$$

$N,N'\text{-}bis\,(2\text{-}hydroxyethyl)\ piperazine,\ "HEP"$
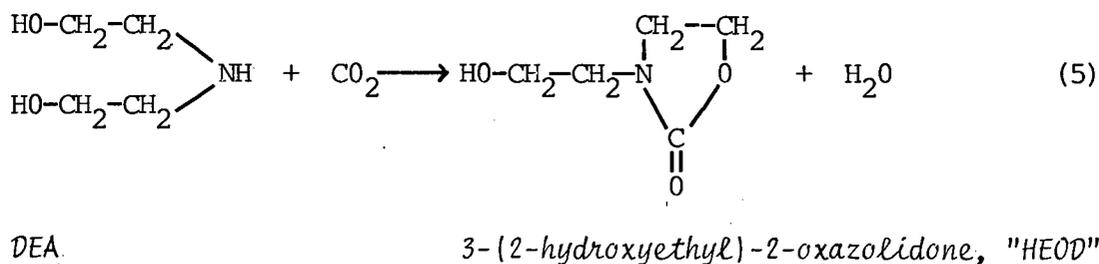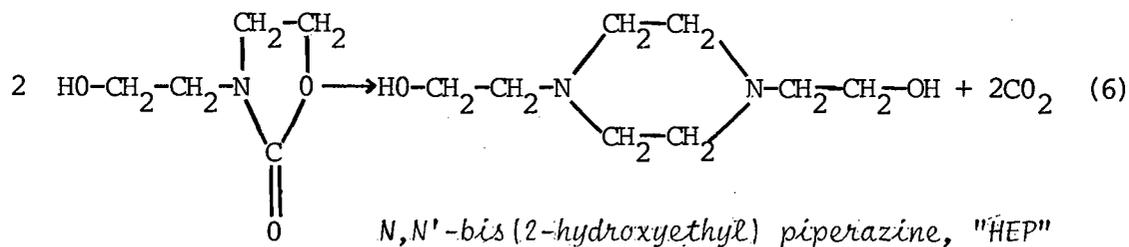
Hakka *et al.* (17) continued the work of Polderman *et al.* (16). Using modern techniques such as infrared (IR) spectroscopy, mass spectroscopy (M.S.), nuclear magnetic resonance (NMR), gas chromatography (G.C.) and thin layer chromatography (TLC), the authors were able to isolate another degradation product, N,N,N'-tris(2-hydroxyethyl)-ethylenediamine ("THEED"). Its chemical structure is shown below:

$$\overset{\text{HO-CH}_2\text{-CH}_2}{\underset{\text{HO-CH}_2\text{-CH}_2}{\diagdown}} \text{N-CH}_2\text{-CH}_2\text{-}\overset{H}{\underset{|}{N}}\text{-CH}_2\text{-CH}_2\text{-OH}$$
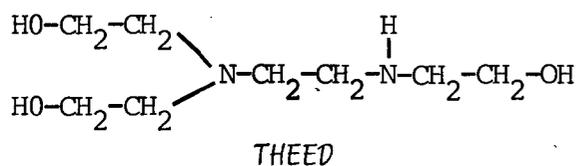
THEED

According to Hakka *et al.* (17), this degradation product occurred frequently at the level of 0.5 to 2 wt.% of the gas treating solution and was by far the major unidentified degradation product. The authors found that both HEP and THEED are able to combine with

CO_2 and H_2S and that their basicity is equivalent to that of triethanolamine (TEA). However, under gas-treating conditions, only one of the nitrogen atoms in the HEP or THEED molecule is likely to react with the acid gas. Hence, on a weight basis, the capacity of the gas-treating solution falls with increasing DEA degradation.

In addition to the work cited above, Smith and Younger (7) discussed DEA degradation and mentioned several other degradation products reported by gas plant operators. Among them was a compound which had the same retention time as triethanolamine (TEA) in gas chromatographic analysis.

Corrosion studies have been published by various researchers (5, 9, 16). DEA itself is not considered to be very corrosive, but degraded DEA solutions attack mild steel extremely readily (11, 12). So far, no quantitative studies that relate DEA degradation to processing conditions such as H_2S/CO_2 ratios, solution loadings, temperature and pressure have been published.

2. <u>Analytical Techniques for Amine Analysis</u>

Henry and Grennert (11, 12) in 1955 were amongst the first researchers interested in the detection and measurement of stable DEA salts present in refinery samples. The authors pointed out

that acid gases other than H_2S would also react with DEA. If these materials were more strongly acidic in aqueous solution than hydrosulfuric acid, they would form heat-stable salts with DEA from which the latter would not be liberated during the regeneration process. These acidic constituents, although, usually present in refinery gases in very small concentrations relative to H_2S, would still tend to accumulate in a closed system. This would result in a gradual decrease of the available (free) DEA, until finally its replenishment became necessary in order to maintain efficient absorption of H_2S.

Henry *et al.* (11, 12) investigated four types of acidic materials namely: (a) organic acids, (b) chloride, (c) cyanide and thiocyanate and (d) sulfite, sulfate and thiosulfate.

The investigation of organic acids was performed by potentiometric titration. The authors observed two inflection points in the titration curves of lean DEA samples at pH 6.3 and 3.5 respectively. The second one (at pH = 3.5) was not found in the titration curve of fresh, unused DEA but would become more pronounced with the accumulation of heat-stable salts. Further investigation using different synthetic solutions of DEA with acetic acid additions led to the discovery that the difference between the first and second inflection points in the titration curve was found to be a good measure of the added acetic acid. Also, the first

inflection point in the potentiometric titration of refinery samples
was a direct measure of the uncombined DEA. For pure DEA solutions,
this value was obtained by titration to the methyl red end point,
but for refinery DEA samples, the difference between the potentiometric
value and the end point value increased with organic acid content.
Hence this method might give a rather large discrepancy in the obtained
results.

Chlorides were found to have very little effect on the formation
of heat-stable salt. On the other hand, cyanide was found to be able
to react with constituents of H_2S-enriched DEA solution to form
thiocyanate, which reduced the available amine content of the solution.
The principal reaction appears to be:

$$\left[(HOC_2H_4)_2NH_2\right]_2 S_2 + 2 \ CN^- \longrightarrow 2\left[(HOC_2H_4)_2NH_2\right]SCN^- \qquad (7)$$
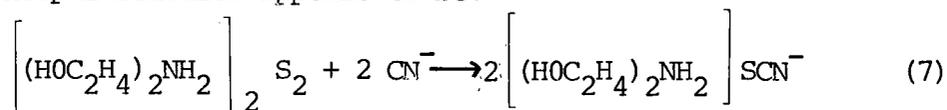
Further studies led to the conclusion that in solutions with
polysulfides, conversion of cyanide to thiocyanate occurs almost
immediately.

The formation of thiosulfate salt was reported by the authors
to be analogous to the formation of thiocyanate:

$$2 \left[(HOC_2H_4)_2NH_2\right]_2 S_2 + 3O_2 \longrightarrow 2 \left[(HOC_2H_4)_2NH_2\right]_2 S_2O_3 \qquad (8)$$
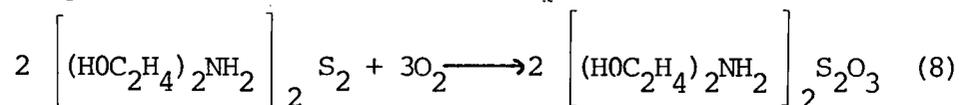
It was found that the above reaction takes place in H_2S-enriched
DEA solutions in the presence of even trace amounts of oxygen. The rate
of reaction depends on the degree of saturation of the DEA with H_2S.
For given H_2S and O_2 concentrations, the rate of formation of thiosulfate
was found to increase with temperature.

Henry *et al.* (11, 12) also discussed conventional wet
chemistry methods such as titration and Kjeldahl total nitrogen
determination, as well as other methods for the determination of
total sulfur, sulfide, mercaptide, sulfate, thiocyanate, cyanide,
chloride, carbonate, alkalinity and sodium. The above two
publications are by far the most complete investigation on heat-
stable DEA salts ever performed and published up to the present
time. Most of these methods have since been used extensively
by industrial laboratories for the analysis of DEA gas-treating
solutions. However, they fail to identify the presence of degraded,
organic compounds even in a qualitative manner. Furthermore, in
1955 Polderman *et al.* (16) noted some inconsistencies in the results
obtained with the above analytical methods. For example, chemical
analyses by conventional acid titration may show a decline of DEA
concentration in an industrial sample whereas the Kjeldahl total
nitrogen determination may indicate that the sample contains more
organic nitrogen than was possible in the form of DEA.

In 1957, the Dow Chemical Company published the "Gas
Conditioning Fact Book" (5) which listed all conventional, wet
chemistry methods for the testing of DEA gas-treating samples. However,
these procedures are unsuitable for identifying DEA degradation
products. Also, since the book was written in 1957, it does not
cover modern techniques such as gas chromatography (18, 19), Mass
spectroscopy (20, 21) and thin layer chromatography (18, 22).

Brydia *et al.* (23) discussed the inability of direct gas chromatographic methods to analyze ethanolamines quantitatively. This is because of the following adverse properties associated with these types of compounds: low vapour pressure ($<$ 1.3 Pa (0.01 mm Hg) @ 20° C for DEA), high polarity and instability at elevated temperatures, especially in the presence of metals (24). The authors showed however that G.C. analysis became possible once the ethanolamines are reacted with trifluoroacetyl ("TFA") anhydride. The latter compound attacks the amino and hydroxyl groups of DEA and forms a DEA--trifluoroacetyl derivative:

$$\text{HO-CH}_2\text{-CH}_2 \diagdown \atop \text{HO-CH}_2\text{-CH}_2 \diagup \text{NH} + 3 \; \text{CF}_3\text{-C} \diagup\diagdown \text{O} \longrightarrow \; \text{F}_3\text{C-C-O-CH}_2\text{-CH}_2 \diagdown \atop \text{F}_3\text{C-C-O-CH}_2\text{-CH}_2 \diagup \text{N-C-CF}_3 + 3\text{CF}_3\text{COOH} \quad (9)$$

    DEA   *TFA anhydride*   *DEA-TFA derivative*   *TFA acid*
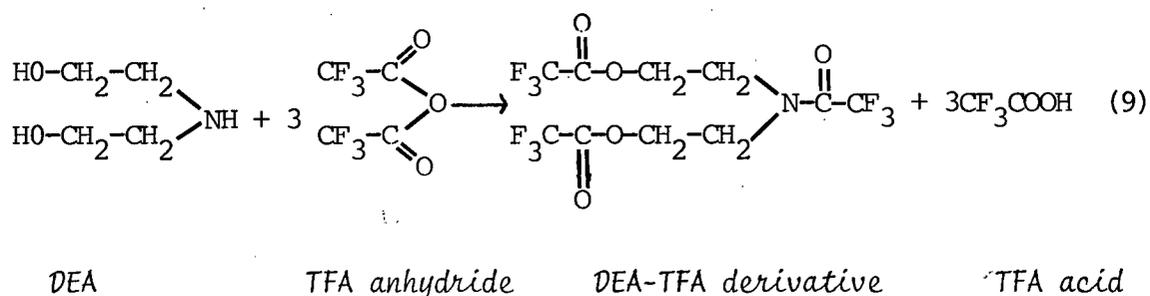
The analytical equipment and operating conditions are summarized in Table 3.

This method is fairly simple, rapid (complete elution of MEA, DEA and TEA takes less than 14 minutes) and capable of detecting some impurities which are unobtainable by chemical means. However,

TABLE 3: Analytical equipment and operating conditions used by
Brydia *et al.* (23).

Gas Chromatograph

Manufacturer	— F & M Scientific Corp.
Model	-- 810 with dual column
Detector	-- Thermal conductivity detector with W-2 filaments.

Chromatographic Column

Material	-- Aluminum
Dimensions	-- ¼" O.D., 5' long
Packing	-- 5% neopentylglycol succinate* coated on 60/100 mesh chromosorb G.

Operating Conditions

Injector port temperature	- 250° C
Column temperature	- 172° C
Detector temperature	- 250° C
Detector current	- 185 mA
Carrier gas	- Helium
Carrier gas flow	- 30 ml/min
Injected sample size	- 5 µl

* Refer to Appendix A for a more detailed description of this material.

when water is present, TFA anhydride reacts with it to give TFA acid (CF_3COOH) which results in severe G.C. peak tailing. The authors also used a flame ionization detector and found an increase in the sensitivity and decrease in TFA acid peak tailing. However, an unexplainable decrease in precision of the G.C. results was also observed.

Piekos *et al.* (25) eliminated the shortcomings discussed by Brydia *et al.* (23) by converting the ethanolamine mixtures to their trimethylsilyl ("TMS") derivatives instead. The silylation reagent, N,O-bis (trimethylsilyl) acetamide ("BSA") reacts with both the amino and hydroxyl groups of ethanolamines as shown in Eq. 10:

$$
\begin{array}{ccc}
\underset{\text{DEA}}{
\begin{matrix}
\text{HO-CH}_2\text{-CH}_2 \\
\text{HO-CH}_2\text{-CH}_2
\end{matrix}\!\!\!>\!\text{N-H}
} &
+\ 3\ \underset{\text{BSA}}{
\text{CH}_3\text{-C}\!<\!\!\begin{matrix}\text{O-Si(CH}_3)_3\\ \text{N-Si(CH}_3)_3\end{matrix}
} & \longrightarrow
\end{array}
$$

$$
\begin{array}{ccc}
\underset{\text{DEA - TMS Derivative}}{
\begin{matrix}
\text{(CH}_3)_3\!-\!\text{Si-O-CH}_2\text{-CH}_2 \\
\text{(CH}_3)_3\!-\!\text{Si-O-CH}_2\text{-CH}_2
\end{matrix}\!\!\!>\!\text{N-Si(CH}_3)_3
} &
+\ 3\ \underset{\text{MSA}}{
\text{CH}_3\text{-C}\!<\!\!\begin{matrix}\text{O}\\ \text{NH-Si(CH}_3)_3\end{matrix}
} & (10)
\end{array}
$$
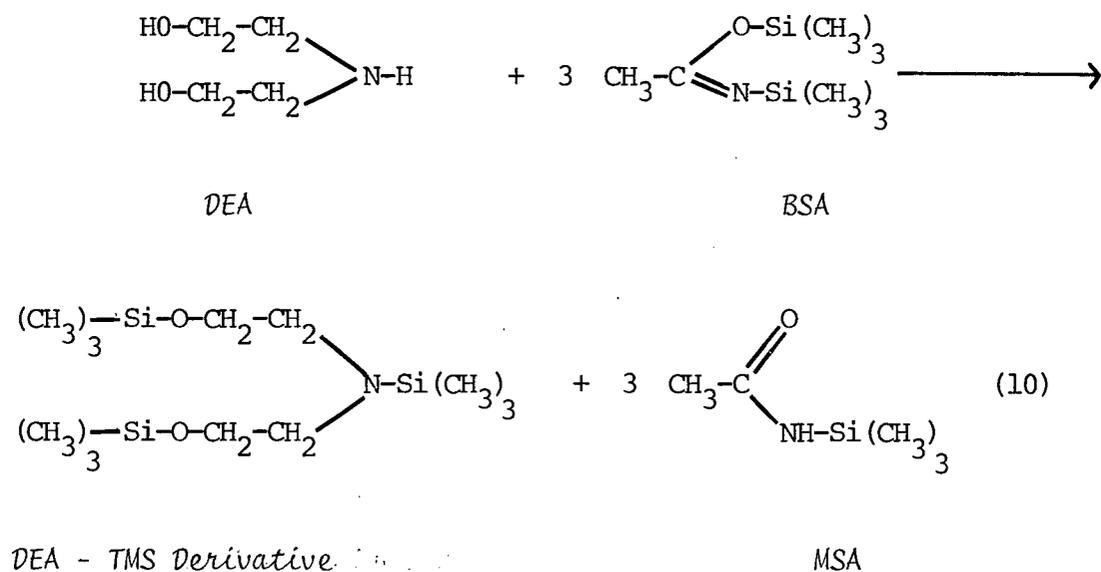
The abbreviation MSA denotes N-trimethylsilylacetamide.

The analytical equipment together with the operating conditions are summarized in Table 4.

The authors also reported the conditions under which ethanolamines reacted with BSA quantitatively (25). The primary advantages of this method are simplicity and rapidity. Complete elution of the MEA, DEA and TEA derivatives requires less than 10 minutes. MSA, excess BSA and trimethylsilanol (a by-product from the water - BSA reaction) are eluted ahead of the other compounds. Separate experiments showed that water concentrations up to 5% could be tolerated provided a large excess of BSA was employed.

Just recently, Saha et al. (26) renewed the interest in direct G.C. analysis of ethanolamines. The authors indicated that several disadvantages arise by converting the amines to G.C. stable derivatives prior to analysis. For example, derivative preparation is time consuming, derivative reactions may be incomplete and the derivatives may not be stable for long periods. These problems are of particular significance to laboratories where large numbers of samples have to be analyzed. On the other hand, hydroxyl and amino groups have a strong affinity for most column support materials. This leads to long elution times, significant peak broadening and peak asymmetry. Saha et al. (26) consequently investigated the use of organic

TABLE 4: Analytical equipment and its operating conditions used by Piekos *et al.* (25).

Gas Chromatograph

Manufacturer	-	W.G. Pye & Co. Ltd.
Model	-	104
Detector	-	H_2 flame ionization detector.

Chromatographic Column

Material	-	Glass
Dimensions	-	0.4 cm. I.D., 5' long
Packing	-	3% OV-1* coated on 100/120 mesh Diatomite CQ.*

Operating Conditions

Injector port temperature	- 190° C
Column temperature	- Isothermal at 130° C for 2 min. and 15 sec. then temperature programmed to 180° C at 49°/min.
Detector temperature	- 210° C
Carrier gas	- Argon or Nitrogen
Carrier gas flow	- 19 ml/min
Injected sample size	- 0.4 - 0.7 µl

---

* Refer to Appendix A for a more detailed description of this material.

polymer beads with varying pore geometries and weak interacting surfaces as potential G.C. column packing materials. These compounds, being in the solid state at the operating temperature, were expected to permit rapid mass transfer and hence fast elution and sharp peaks.

Saha *et al.* (26) discovered that a new column packing, Tenax-GC[*], which is a porous polymer based on 2, 6-diphenyl-P-phenylene oxide was able to separate ethanolamines with excellent results.

The analytical equipment and operating conditions are summarized in Table 5.

The authors reported that by using the above operating conditions, it was possible to separate a mixture of MEA, DEA and TEA in less than 8 minutes with excellent resolution, reproducibility and accuracy. Furthermore, aqueous solutions of amines could be injected into the chromatograph directly without difficulty.

Zimmerman *et al.* (27) investigated the separation of amines and related compounds by paper chromatography. The R_f[#] values obtained for three different solvents are summarized in Table 6.

---

* Refer to Appendix A for a more detailed description of this material.

\# R_f value is defined as the distance of sample spot from the origin divided by the distance travelled by the solvent front from the same origin.

TABLE 5: Analytical equipment and operating conditions used by

Saha *et al.* (26).

Gas Chromatograph

      Manufacturer   -   Perkin - Elmer Corp.

      Model   -   900

      Detector   - H_2 flame ionization detector.

Chromatographic Column

      Material   -   Stainless steel

      Dimensions   -   1/8" O.D., 4' long

      Packing   -   Tenax - G C porous polymer column
                                   packing, 60/80 mesh.

Operating Conditions

      Injector port temperature   - 350° C

      Column temperature   -   Isothermal at 135° C for
                                   1 min. then temperature
                                   programmed to 350° at 16° C/min.

      Detector temperature   - 325° C

      Carrier gas   -   Nitrogen

      Carrier gas flow   -   25 ml/min

TABLE 6: R_f values and solvent systems related to the separation of some hydroxyamines using paper chromatography (27).

Name	Solvent	System	
	A	B	C
Ethanolamine	0.19	0.32	0.54
Diethanolamine	0.21	0.47	0.62
Triethanolamine	0.22	0.45	0.62
HEP	0.13	0.43	0.55
N,N,N',N'-Tetrakis-(hydroxyethyl)-ethylene-diamine[*], ("TEHEED")	0.29	0.48	0.66

* This compound is very similar to THEED but is quartenary substituted by the hydroxyethyl group instead of tertiary substituted.

The solvent systems employed were:

Solvent A : n-butanol, 77%; acetic acid, 6%; water, 17%

Solvent B : n-butanol saturated with 0-1% aqueous NH_3

Solvent C : pyridine, 42%; ethyl acetate, 25%; water, 25%

With solvent system A and B, the migration was allowed to proceed for 4 hours. With solvent C, which moved more rapidly, the migration was stopped after 3 hours. Upon removal of the paper chromatograms, the solvent front was marked while still wet. After air-drying, the chromatograms were sprayed with 0.25% ninhydrin in 1:1 pyridine-ethanol and maintained at 105° C for 5 minutes to bring out the colour of the spots.

The authors observed that solvent systems A and B gave extensive tailing of the spots. In many cases, this made visual detection very difficult. On the other hand, solvent C gave good, coherent spots but the migration was comparatively rapid, leading to poorer separations.

Amines and amine related compounds are always of interest to scientists in biological fields. Extensive studies have been published in the analysis of amines in the past which include salting out chromatography (28), fractional distillation, potentiometric titration (11, 12, 29), Kjeldahl nitrogen (5, 30) and Van Slyke

analyses (5, 30). Modern publications using gas chromatographic (31, 32, 33, 34, 35) and thin layer chromatographic (27, 36) techniques are also common.

III. CHROMATOGRAPHIC ANALYSIS OF DEGRADED DEA SOLUTIONS

1. Introduction

Before a study of DEA degradation could be undertaken,
a reliable, quantitative method had to be available for the
analysis of both residue DEA and trace quantities of degradation
products. This method should be reliable, rapid, highly sensitive
and require minimal sample size and preparation time. In addition,
it should be applicable to DEA solutions degraded under laboratory
as well as industrial conditions.

2. Selection of a Suitable Analytical Technique

As mentioned in the previous chapter, virtually no information
has been published on an analytical technique with the aforementioned
attributes. Consequently the development of such a technique was
the primary objective of the present study.

Since conventional wet chemistry methods lack the desired
reliability, accuracy and specificity, attention had to be focused
on modern analytical methods such as infrared (37) and ultraviolet
(38, 39) spectroscopy, mass spectroscopy (20, 21) as well as paper
(18, 22, 27), high pressure liquid (18, 40) and gas (18, 19)
chromatography. A brief comparison of these techniques is given
in Table 7.

TABLE 7: Comparison of analytical techniques suitable for the analysis of degraded DEA solutions.

Technique	Principle	Advantages	Disadvantages
Infrared spectroscopy	Characteristic IR absorption of functional groups – OH and – NH in 3600–3700 and 3400 cm^{-1} regions respectively.	High sensitivity, rapid, very small sample requirement, simple operation and low cost; unique identification of organic compounds by its functional groups and "finger print" region (1600–600cm^{-1}) IR absorption characteristics, very good documentation on IR spectra available from the literature.	Applicability extends to single component, qualitative identification only; inability to analyze samples in aqueous and most organic solvents; lack of standards or information on degradation products; instrument not readily available.
Ultraviolet spectroscopy	Characteristic UV absorption bands in the region 190–400 mu.	High sensitivity, rapid, very small sample requirement, simple operation and low cost; ability to analyze simple mixtures in aqueous or organic solvents quantitatively; instrument readily available; good documentation on UV spectra.	No distinct UV absorption bands for DEA and its known degradation products, inability to convert the above compounds to UV absorptive species by chemical reaction.
Optical spectroscopy	Characteristic optical absorption bands in the region 400–800 mu.	High sensitivity, rapid, very small sample requirement and simple operation; ability to analyze simple mixtures in aqueous or organic solvents quantitatively; instrument readily available.	No distinct optical absorption bands for DEA and its known degradation products; inability to convert the above compounds to optically absorptive species by chemical reaction.

TABLE 7: Comparison of analytical techniques suitable for the analysis of degraded DEA solutions. (continued)

Technique	Principle	Advantages	Disadvantages
Mass spectroscopy	Characteristic ion fragmentation pattern and molecular ion peak detection.	Extreme sensitivity and small sample requirement; ability to analyze simple mixtures quantitatively; unique characterization and identification of compounds by molecular weights and ion fragmentation patterns; good documentation on M.S. spectra.	Inability to analyze DEA samples due to low volatility and fragile compounds present; lack of standards or information on degraded compounds relevant to M.S. analysis; difficult operation and high cost; instrument not readily available.
Paper and thin layer chromatography	Separation and identification by differences in partition coefficients between two solvents.	Combination of separation and identification technique with high sensitivity, small sample size, simple and low operation cost; ability to analyze mixtures in aqueous and organic solvents; simultaneous multiple analyses possible at room temperature; suitable for the analysis of high molecular weight fragile compounds with very simple detection devices; good documentation on paper or thin layer chromatograms.	Very slow and useable mainly as a qualitative identification technique; inavailability of some degradation products as standards and incomplete knowledge of DEA degradation products.

TABLE 7: Comparison of analytical techniques suitable for the analysis of degraded DEA solutions. (continued)

Technique	Principle	Advantages	Disadvantages
High pressure liquid chromatography	Separation and identification by differences in partitation coefficients between two phases.	Combination of separation and identification technique with high sensitivity, rapidity, small sample size, simple and low operation cost; ability to analyze mixtures in aqueous and organic solvents quantitatively; analysis at room temperature is particularly suitable for high molecular weight, fragile compounds; large variety of detection devices available and good documentation of this technique is available.	UV detection is impossible; instrument is unavailable for long term usage; inavailability of some degradation products as standards and incomplete knowledge of DEA degradation.
Gas chromatography	Separation and identification by differences in partitation coefficients between the two phases.	Combination of separation and identification technique with high sensitivity, rapidity, small sample size, simple and low operation cost; ability to analyze mixtures in aqueous and organic solvents quantitatively; capability to operate at room and elevated temperatures for effective separation of high molecular weight, low volatility compounds; large variety of detection devices available and good documentation of this technique is available; the instrument is readily available.	Heavy, fragile compounds might decompose in G.C. columns, high polarity compounds are difficult to separate; inavailability of some degradation products as standards and incomplete retention data of DEA degradation products.

Infrared* and ultraviolet spectroscopic techniques were quickly eliminated due to the disadvantages listed in Table 7. However, once individual components of DEA degradation products can be isolated, IR spectroscopy will become an invaluable characterization technique due to its ability to detect functional groups (37, 41).

Initially, mass spectroscopy was thought to be the ideal analytical technique for the present study because of its outstanding advantages listed in Table 7. Mass spectra of HEP and TEHEED, which were not available from the literature, were determined in this study. Figure 2 to 4 show the mass spectra of DEA, HEP and TEHEED. However, this technique was finally abandoned because of the disadvantages also listed in Table 7. Should all these undesirable factors be overcome, M.S. would once more be used extensively because of its unique characterization abilities.

From the drawbacks associated with the above three analytical techniques, it was concluded that a combined separation and identification technique was necessary for the present study. Paper chromatography was first investigated.

Initial results, which are discussed in Appendix C, showed

* Refer to Appendix B for IR spectra of DEA and some degradation products.
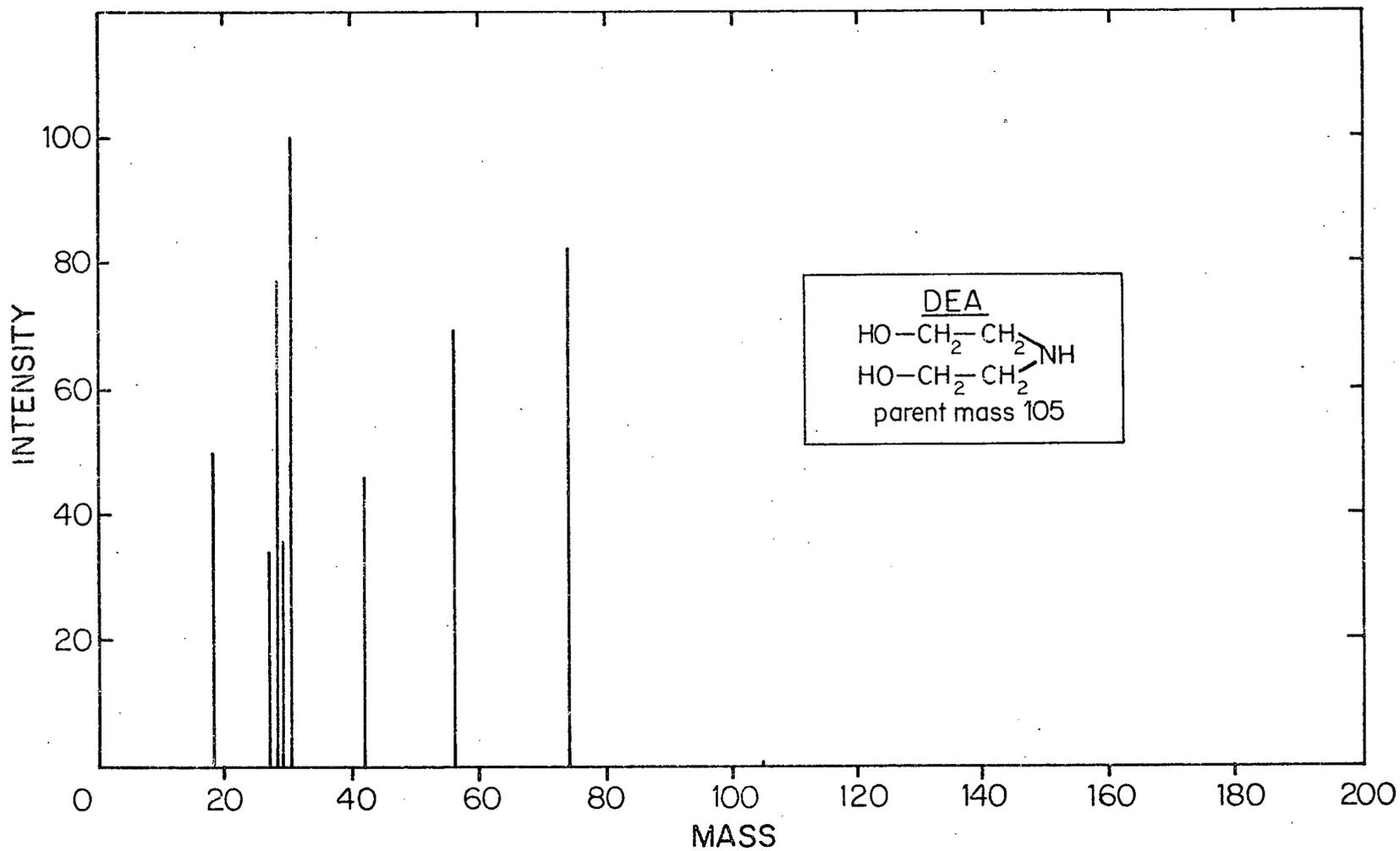
FIGURE 2: Mass Spectrum of DEA.
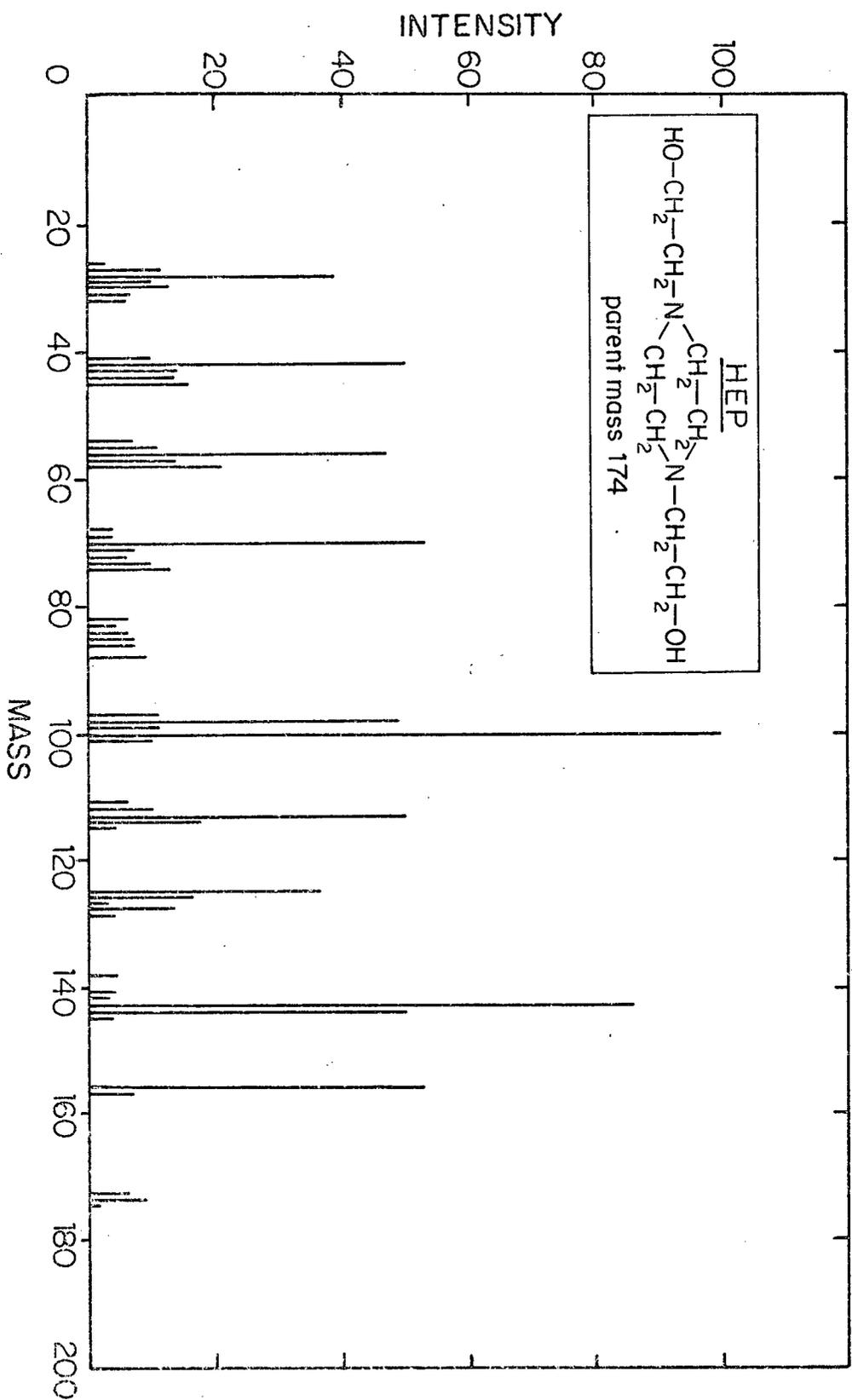
FIGURE 3: Mass Spectrum of HEP.

HEP

HO-CH₂-CH₂-N(CH₂-CH₂)₂N-CH₂-CH₂-OH

parent mass 174

FIGURE 4: Mass Spectrum of TEHEED.

great promise for this method as a qualitative separation technique. Ultimately, paper chromatography may be coupled with M.S. to give quantitative results.

High pressure liquid chromatography was also tested briefly using equipment available in the Chemistry Department. Although the initial experimental results were encouraging, this method had to be abandoned due to lack of access to the apparatus.

Hence, after several months of trials with the above six analytical techniques, it was decided to develop a gas chromatographic method for the present DEA study.

3. Adverse Properties of DEA and Its Degradation Products for G.C. Analysis

Until recently, the usage of G.C. for the analysis of hydroxyamines and related compounds has proved to be very difficult. This is due to four main adverse factors: low vapour pressure ($<$ 1.3 Pa (0.01mm Hg) @ 20° C), high polarity, instability at elevated temperatures (especially in the presence of metals (24)) and simultaneous occurrence with water. The low vapour pressure requires DEA to be subjected to high injector and column temperatures for effective G.C. analysis. However, the poor thermal stability

of DEA enhances the probability of amine decomposition and therefore leads to poor quantitative measurements and reproducibility. The polar hydroxyl and amino groups have a high affinity for most column packings and this results in long elution times, large peak broadening and peak asymmetry. Water is a further complicating factor since only a few column packings (18, 19, 31) can tolerate aqueous amine samples. If it is desired to extract DEA and its degradation products with an organic solvent, difficulties arise with selecting a suitable solvent.

These various shortcomings had to be overcome before G.C. could be used for the effective analysis of aqueous, degraded DEA solutions. Table 8 lists some physical properties of ethanolamines and HEP relevant to the present study.

4. Development of the Present Analytical Method

Derivative G.C. methods, as proposed by Brydia *et al.* (23) and Piekos *et al.* (25), indicated that the volatility and polarity characteristics of DEA solutions could be overcome. However, four main disadvantages arose with the derivative methods: (i) the inability to form amine-derivatives in the presence of excess water, due to the extreme reactivity of silylation reagents with moisture, (ii) the possibility of incomplete silylation resulting in extra G.C. peaks caused by partially silylated compounds,

TABLE 8: Selected physical properties of ethanolamines and HEP.

Property	MEA	DEA	TEA	HEP
Formula	$H_2NCH_2CH_2OH$	$HN(CH_2CH_2OH)_2$	$N(CH_2CH_2OH)_3$	$C_8H_{18}N_2O_2$
Molecular weight	61.08	105.14	149.19	174.24
Sp. gr. @ 20° C	1.0179	1.0919	1.1258	
Δ Sp.gr./Δt, @ 20 to 30° C	0.00078		0.00055	
30 to 40° C		0.00065		
Vapour pressure, @ 20° C	<133 Pa (1 mm Hg)	<1.3 Pa (0.01 mm Hg)	<1.3 Pa (0.01 mm Hg)	
Boiling point, @ 101 kP_a (760 mm Hg)	170.4° C	268.4° C (dec.)	335.4° C (dec.)	$215-220^{\circ}$ C
6.67 kP_a (50 mm Hg)			245	
4.00 kP_a (30 mm Hg)	143	237		
13.3 P_a (0.10 mm Hg)	71	152	205	
Flash point	93° C	138° C	193° C	
Viscosity @ 20° C, Cp	24.1	867	921	

TABLE 8: Selected physical properties of ethanolamines and HEP. (continued)

Property	MEA	DEA	TEA	HEP
Melting point, ^{o}C	10.3	28.0	21.6	133.5–136
Refractive index, n_D^{20} @ 20° C	1.4549		1.4852	
30° C		1.4747		
$\Delta n_D^{20}/\Delta t$ @ 20 to 40° C	0.00034	0.00028	0.00020	
Solubility @ 20° C in water	Complete	95.4 wt.%	Complete	Very soluble
water in	Complete		Complete	
Solubility in organic liquids @ 25° C				
acetone	Complete	Complete	Complete	Insoluble
benzene	0.6 wt.%	0.03 wt.%	2 wt.%	Insoluble
carbon tetrachloride	0.1	0.01	Complete	Slightly soluble
ethyl ether	0.7	0.5	2 wt.%	Insoluble
heptane	0.1	0.03	0.03	Insoluble
methanol	Complete	Complete	Complete	Very soluble
dimethyl formamide	Complete	Complete	Complete	Soluble

(iii) the long-term instability of the derivatives and (iv) the limited choice of silylation solvents due to the high reactivity of the reagent and the low solubility of various DEA degradation products. These drawbacks made the application of derivative G.C. to the present work quite difficult.

5. Choice of Silylation Reagent

Since its discovery, silylation reagents have been widely used to react with the active hydrogen in hydrogen-bonded materials such as carboxylic acids, alcohols, amines and amides to produce fairly stable, easily separated and identifiable derivatives (33, 42, 43, 44). Even very delicate and complex biochemicals such as carbohydrates, amino acids, peptides and steroids can be analyzed by G.C. after stabilization with suitable silylation reagents (32, 33, 43).

Table 9 lists some commonly used silylation reagents capable of forming trimethylsilyl (TMS) derivatives with a large variety of important chemicals having active hydrogen atoms (42, 44). However, all these reagents have one common undesirable property, viz. their extreme sensitivity to moisture.

A comprehensive study of BSA silylating properties was made by Klebe et $al.$ (45). Their investigation showed BSA to be a highly effective silylation reagent. Furthermore, it is rather

TABLE 9: Some common silylation reagents capable of forming trimethylsilyl derivatives.

Name	Abbreviation	Chemical formula	Molecular weight	Boiling point	Usage	Special features
N, O-bis-(trimethylsilyl) acetamide	BSA	$\overset{\displaystyle Si(CH_3)_3}{\underset{\displaystyle CH_3-C=N-Si(CH_3)_3}{\overset{\displaystyle O}{|}}}$	203.43	71-73°C @ 35 mm	General silylation	
N,O-bis-(trimethylsilyl) trifluoroacetamide	BSTFA	$\overset{\displaystyle Si(CH_3)_3}{\underset{\displaystyle CF_3-C=N-Si(CH_3)_3}{\overset{\displaystyle O}{|}}}$	257.40	40° C @ 12 mm	General silylation	Greater volatility than BSA.
N-methyl-N-TMS trifluoroacetamide	MSTFA	$CF_3-CONCH_3\left[Si(CH_3)_3\right]$	199.25	132° C	General silylation	Most volatile derivative with extremely low retention time of its by-products.
Hexamethyldisilazane	HMDS	$(CH_3)_3-SiNHSi(CH_3)_3$	161.41	126° C	Carbohydrates	Evolves NH_3 during silylation reaction.
Trimethylchlorosilane	TMCS	$(CH_3)_3-SiCl$	108.7	57° C	Biochemicals	Often used as catalyst for silylation reaction; evolves Cl_2 during silylation reaction.

inexpensive and does not produce noxious, gaseous by-products.
Hence, it was chosen to be the silylation reagent for the present
study.

The silylation of DEA and HEP can be represented by the
following equations:

$$HO-CH_2-CH_2 \diagdown \atop HO-CH_2-CH_2 \diagup N-H \quad + \quad 3 \ CH_3-C \diagup^{O-Si(CH_3)_3} _{\diagdown N-Si(CH_3)_3} \longrightarrow$$

DEA   BSA

$$(CH_3)_3Si-O-CH_2-CH_2 \diagdown \atop (CH_3)_3Si-O-CH_2-CH_2 \diagup N-Si(CH_3)_3 \quad + \quad 3 \ CH_3-C \diagup^{O} _{\diagdown N-Si(CH_3)_3 \atop H} \qquad (11)$$

DEA -- TMS Derivative   MSA
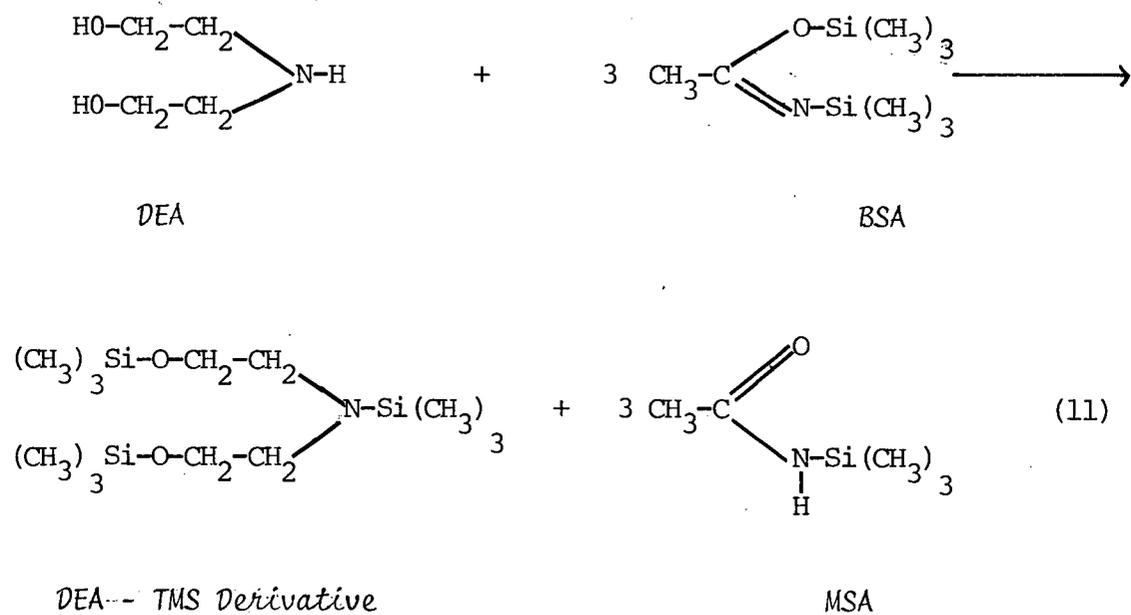
The abbreviation MSA denotes N-trimethylsilylacetamide. Similarly
the reaction between HEP and BSA is given by:

$$HO-CH_2-CH_2-N \diagup^{CH_2-CH_2} _{\diagdown CH_2-CH_2} N-CH_2-CH_2-OH \ + \ 2 \ CH_3-C \diagup^{O-Si(CH_3)_3} _{\diagdown N-Si(CH_3)_3} \longrightarrow$$

HEP   BSA

$$(CH_3)_3\text{-}Si\text{-}O\text{-}CH_2\text{-}CH_2\text{-}N \overset{CH_2\text{-}CH_2}{\underset{CH_2\text{-}CH_2}{\diagup \diagdown}} N\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Si\text{-}(CH_3)_3 \; + \; 2 \; CH_3\text{-}\overset{O}{\underset{H}{\overset{\|}{C}}} \underset{N\text{-}Si(CH_3)_3} \quad (12)$$

HEP-TMS *Derivative*   MSA
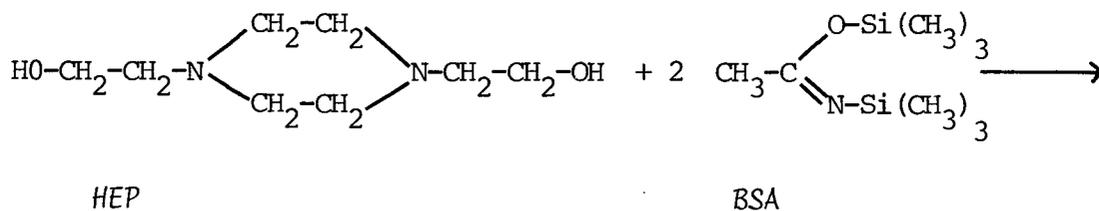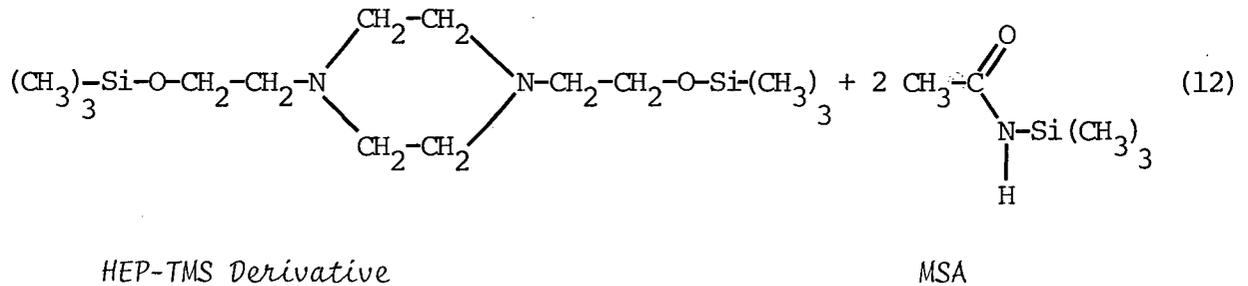
6. Choice of Chromatographic Column

The G.C. column is the heart of the Chromatograph where actual separation of sample components is achieved. For direct G.C. analysis, the choice of columns is often the most critical factor, due to the strong physico-chemical interactions and slow diffusion of the compounds to be separated. For derivative G.C. analysis, however, the choice of silylation method is more important, since this method alleviates factors that prevent direct G.C. analysis in the first place. High molecular weight, silicone stationary phases often prove to be quite satisfactory for the separation of silylated compounds (32, 33, 40, 41, 44).

During the initial development of a suitable G.C. method for analyzing DEA gas-treating solutions, a ¼" O.D., 6' long glass column containing 4% Carbowax* 20 M on 60/80 mesh Carbopack B deactivated with 0.8% KOH was purchased from the Supelco, Inc. Carbopack is a highly inert graphitized carbon stationary phase

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* Refer to Appendix A for a more detailed description of this material.

and the above column was reported to be very effective in the separation of trace amounts of aliphatic amine mixtures in aqueous solutions (31). Initial direct G.C. analysis of methyl and t-butyl amines confirmed this. However, when aqueous DEA solutions were subjected to the same procedure, extreme sensitivity settings were required to produce a small DEA peak. This was due to the low volatility of DEA up to 140° C. At higher temperatures, the DEA started to decompose in the injector and/or column and deactivated the column. This showed that direct G.C. analysis using the Carbopack column was not suitable for the analysis of ethanolamines. Attention was therefore switched to G.C. derivative analysis.

In the course of the development of DEA silylation techniques, two OV columns have been tested extensively. The first one was a 1/8" O.D., 6' long glass column containing 10% OV-11[*] on 100/120 mesh chromosorb WHP purchased from Supelco Chromatography Supplies. The second was a 1/8" O.D., 6' long stainless steel column containing 8% OV-17[*] on 80/100 mesh Chromosorb WHP supplied by Western Chromatography Supplies. Tests showed that both columns separated DEA and its degradation compounds effectively even at very low concentrations. Although the OV-11 glass column gave somewhat better resolution and less baseline drifting, the OV-17 stainless steel column was chosen because it was cheaper, more rugged and had somewhat shorter elution times at the same column temperatures.

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[*] Refer to Appendix A for a more detailed description of this material.

7. Column Conditioning

Columns used for the analysis of silylation derivatives must be thoroughly conditioned before use. A powerful column conditioner, Silyl-8, has been developed for such purpose (44). This reagent is a silylating reagent which reacts with the active sites in the column and renders them inert. 10 to 25 μl samples of Silyl-8 are injected directly into the chromatograph with the column at a temperature of 150° C and the flame ionization detector in operating mode. Such treatment should be repeated until a stable baseline is attained. Thereafter, samples containing BSA should keep the column conditioned. However, if the column has been used for non-silylated samples, it might be necessary to repeat the above conditioning treatment to remove non-volatile residues which can be silylated.

8. Choice of Solvent

The selection of a solvent to dissolve degraded DEA samples for silylation proved to be quite challenging since the solvent must not react with the silylation reagent. Thus many common organic solvents such as alcohols cannot be used because they contain active hydrogen atoms. The following solvents which are commonly used for silylation reactions (44), were therefore evaluated for the present study: acetonitrile (CH_3CN), dimethyl sulfoxide ($(CH_3)_2SO$),

tetrahydrofuran $(CH_2(CH_2)_2CH_2O)$, pyridine (C_5H_5N), Chloroform $(CHCl_3)$, furan (C_4H_4O) and dimethyl formamide $(HCON(CH_3)_2)$.

Acetonitrile, tetrahydrofuran, pyridine, Chloroform and furan had to be eliminated because they did not dissolve HEP and other DEA degradation products. Dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) did not suffer from this disadvantage but the former is expensive and hazardous. Consequently, DMF was finally chosen as the solvent.

A further advantage of DMF is its high boiling point $(153^O$ C @ S.T.P.) which made high temperature silylation possible without appreciable loss of solvent. DMF samples containing reacted DEA residues were also found to be stable for months if the samples were kept at room temperature.

9. Drying of Aqueous DEA Samples

As mentioned previously, BSA and other silylation reagents react quickly with water (42, 44):

$$CH_3-C \begin{matrix} O-Si(CH_3)_3 \\ \\ N-Si(CH_3)_3 \end{matrix} + H_2O \longrightarrow (CH_3)_3-Si-O-Si-(CH_3)_3 + CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \qquad (13)$$
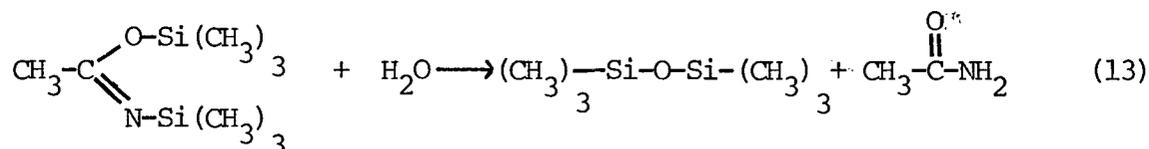
BSA   Hexamethyl disiloxane   Acetamide

Although some attempts have been made to perform silylation in the presence of water (42, 43, 46), this approach was not adopted here since the effect of acidic gases in the DEA samples was unknown. Instead, the aqueous DEA samples were dried by placing them in a sand bath at 80° C and passing bone-dry air over them for 40 minutes. To remove the last trace of water, a few millilitres of methylene chloride were added to the DEA residue and the evaporation repeated to ensure the complete azeotropic removal of water (32). This procedure also stripped H_2S and CO_2 from the samples.

10. Internal Standard

In quantitative G.C. analysis, the peak area is usually used to determine concentration and all operating parameters, which influence the peak size, must therefore be held constant. Since it is very difficult to keep parameters such as carrier flow rate, column temperature, injected sample size etc. absolutely constant, an "internal standard" is frequently employed. In this method a substance, is added to each sample in fixed amounts. The peak size of the sample relative to that of the internal standard is then used for all concentration determinations. Moderate variations in operating parameters do not affect the quantitative determination of concentrations since both the sample and the internal standard are affected to a similar extent. The requirements for an internal standard are:

(i) Elution times similar to but not identical to other peaks.

(ii) Availability in high purity and at reasonable cost.

(iii) Concentrations similar to those of unknown compounds.

For derivative G.C. analysis involving BSA as a silylation reagent, various internal standards have been proposed depending on the types of compounds to be separated. Brittain *et al.* (42) in their work on sugar analysis suggested 2, 3'-difluorobenzo-phenone and tetraphenyl silane for separations at high column temperature (175 to 252° C). Gehrke *et al.* (32) in their analysis of amino acids reported phenanthrene, decanolic acid and fluorene to be suitable internal standards for column temperature between 154 and 265° C.

After some initial trials, the column temperature was chosen to be 142° C for optimum separations of DEA, HEP and other degradation products. Based on the above literature sources, one would therefore suspected a member of the fatty acid family to be an appropriate internal standard. This fatty acid should produce a trimethylsilyl derivative with an elution time slightly longer than DEA-TMS (3.5 min. @ 142° C column temperature). This would ensure maximum accuracy in the determination of DEA concentrations since any deviation the operating conditions would affect the DEA and the internal standard in a very similar manner. Furthermore, the elution of the internal

standard right after DEA would eliminate possible interference with other DEA degradation products.

After some trials with dodecyl (C_8), decanolic (C_{10}) and tetradecyl (C_{14}) fatty acids, decanolic acid ($CH_3-(CH_2)_8-COOH$, "DECA") was chosen. Its trimethylsilylated product (DECA-TMS) has a retention time of 5 minutes. For the present study, a large batch of DECA in DMF solvent was prepared with a concentration of 7.46×10^{-5} mole/ml.

11. Choice of Septum

The choice of septum depends on how it is to be used. For high injector and column temperatures, ordinary rubber septa tend to bleed and deteriorate rapidly. Furthermore, small broken pieces of septum materials (dirt) tend to accumulate just inside the injector port and may result in high background noise, peak tailing and sample loss. Hence, in the present work where the chromatograph had to be operated at extremely high sensitivities, only high quality septa could be used.

After considerable testings, it was found that Septum #2015 developed by the Unimetric Corporation was suitable. This septum is made of high quality silicone rubber reinforced by fiber glass. An inert Teflon layer is also bonded to the side of the septum facing the column.

A G.C. needle guide was used in conjunction with the above septum. This allows the needle to be guided into the "cool" needle entrance thus eliminating premature flashing of volatile components. In addition, it serves as a spacer for needle penetration depth and it lengthens septum life by using only a single pierced hole for repeated injections.

Needle guides are indispensable for high precision, delicate analytical analyses where the sample from the syringe is to be delivered inside a glass chromatographic column without metal contact.

12. Choice of Operating Conditions

Attempts were made to optimize all operating variables in order to achieve the best separation of DEA and its degradation products. It may be noted that temperature programming equipment (18, 19) was unavailable.

Initially, the column temperature (130° C) and nitrogen carrier gas flow rate (19 ml/min.) were adapted from Piekos *et al.* (25). After some trials, the column temperature was adjusted to 142° C which was high enough to give good separation with low elution times and the carrier flow rate was increased to 20 ml/min. At this carrier flow rate, the optimum H$_2$ and air flow rates to the flame ionization detector were determined to be 35 and 350 ml/min, respectively.

The injector port temperature was set to 195° C which was sufficient to vaporize the sample instantaneously without thermal decomposition. The temperature of the flame ionization detector is not very critical and was chosen to be 220° C to avoid condensation of samples.

13. Equipment Specifications

A summary of the final analytical equipment used and its operating conditions are given in Table 10.

14. Sample Preparation Procedure

The sample preparation procedure consists of 3 main steps, namely, *drying of sample, silylation with BSA* and *G.C. analysis.*

After drying 1 ml of aqueous DEA sample by the method discussed previously, DMF was used as a solvent for the re-dissolution of the DEA residue. 2 ml DECA spiked DMF solution were added to each DEA sample so that each contained 1.49×10^{-4} mole of decanolic acid . Pure DMF was then added until the final solution was exactly 25.0 ml.

Exactly 4.0 ml of the above solution were transferred to a 12 ml sampling bottle equipped with a Teflon-lined screw cap. A large excess of 2 ml BSA (8.31×10^{-3} mole) was then added to the sampling bottle and the cap was replaced and screwed tight. Special

TABLE 10: Analytical equipment and its operating conditions for
G.C. analysis.

Gas Chromatograph

Manufacturer	-	Varian Aerograph
Model	-	1440 Series, single column model
Detector	-	H_2 flame ionization detector.

Chromatographic Column

Supplier	-	Western Chromatography Supplies, New Westminster B.C.
Material	-	316 Stainless Steel
Dimensions	-	1/8" O.D., 6' long
Packing	-	8% OV-17 on 80/100 mesh chromosorb WHP

Operating Conditions

Injector Port Temperature	- 195° C
Column temperature	- 142° C
Detector temperature	- 220° C
Carrier gas	- N_2
Carrier gas flow	- 20 ml/min
Air flow	- 350 ml/min
H_2 flow	- 35 ml/min

Recorder

Supplier	-	Corning
Model	-	840 Series with mechanical disc integrator
Response	-	1 mv, 1 sec. full scale
Chart speed	-	Variable

Syringe

Supplier	-	Precision Sampling Corporation
Model	-	Pressure-Lok liquid syringe, series D 2 μl volume
Injected sample size	-	0.3 μl

oil-resistant, electro-plating adhesive tape developed by the 3M Company was then wrapped around the sampling cap to ensure a perfect seal. The bottle was then well shaken and immersed in a 60° C oil bath for 1 hour which was sufficient to complete the silylation reactions. Silylation at 70° C gave essentially the same results.

When the silylation reaction was complete, the sampling bottle was removed from the oil bath and the Teflon lined stopper cap replaced by a silicon rubber septum which permitted syringe withdrawal of a sample.

This procedure was adopted to minimize the contact between the sample and atmospheric moisture. Finally, sample volumes of 0.3 μl were injected into the chromatograph pre-set to the previously described conditions.

15. Calibration Method for Quantitative Analysis

The calibration plot for DEA was prepared by determining the ratio of DEA to DECA peak areas as a function of the amount of DEA injected into the chromatograph. The calibration plot for HEP was obtained in an analogous manner. The plots are shown in Figs. 5 and 6.

Whenever possible, the peak areas were measured by the disc integrator included in the Corning recorder.
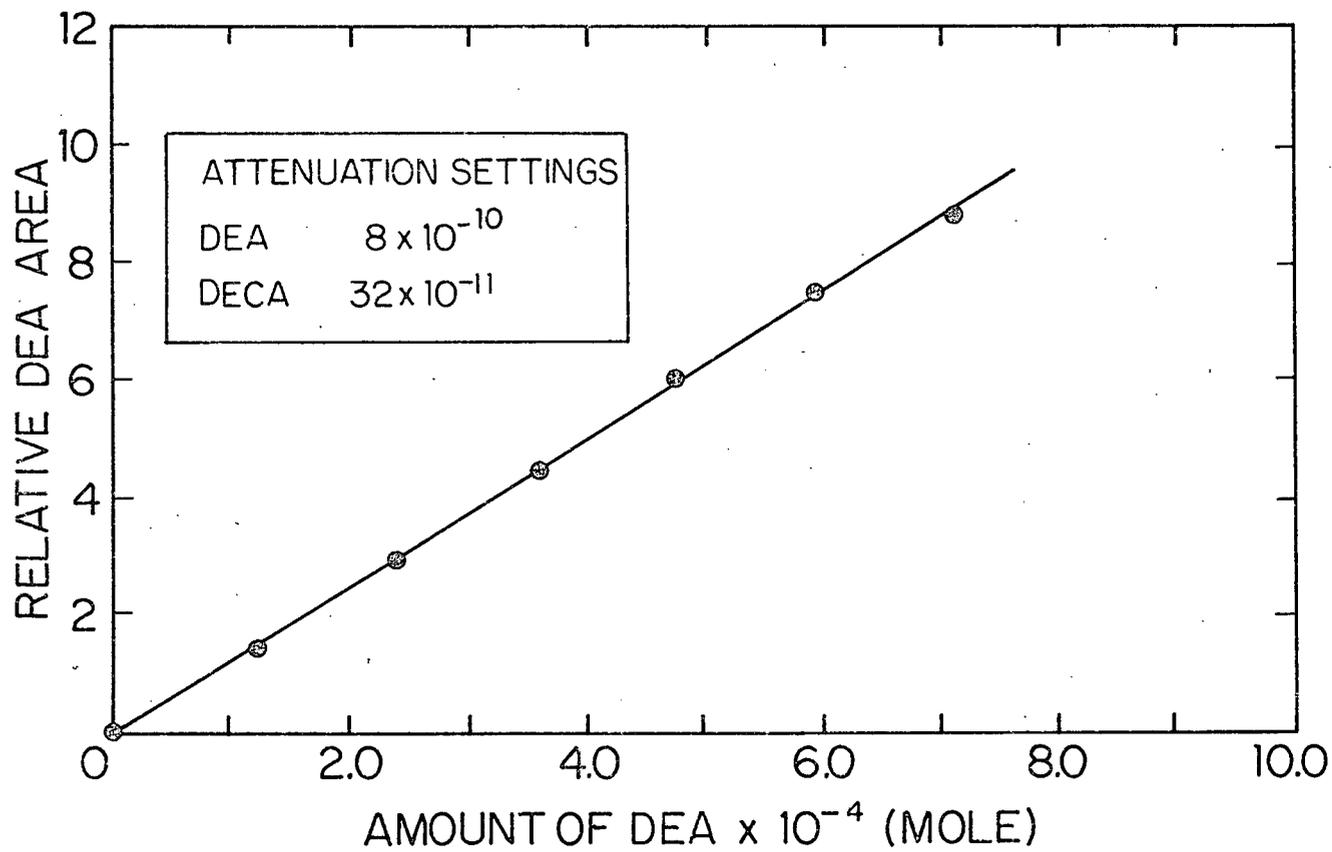
FIGURE 5: Calibration plot of the peak area ratios of DEA/DECA as a function of the amount of DEA present.
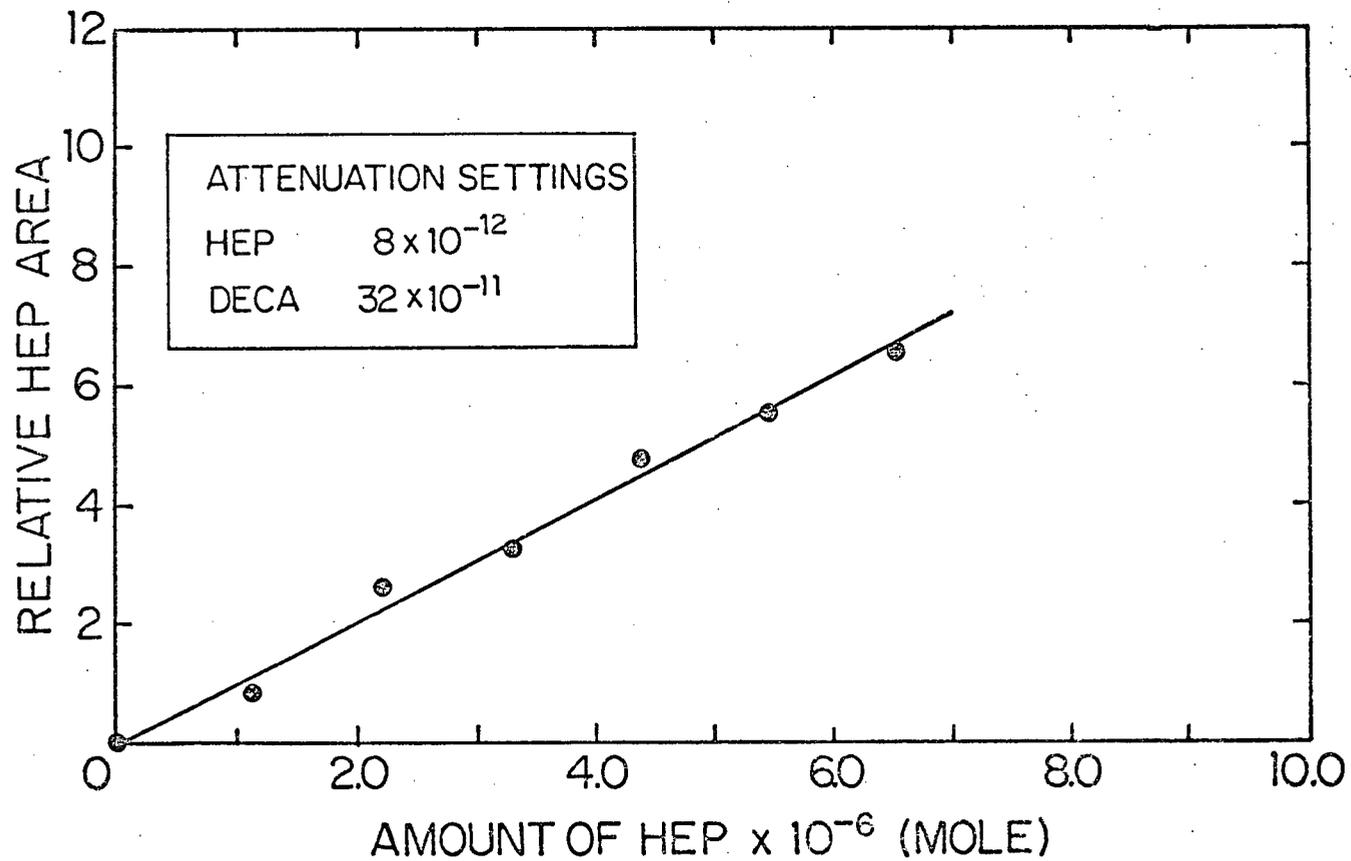
FIGURE 6: Calibration plot of the peak area ratios of HEP/DECA as a function of the amount of HEP present.

16. <u>Maintenance of Analytical Equipment</u>

The gas chromatograph and microsyringes must be kept extremely clean at all times. This was most important when operating in high sensitivity ranges since contaminants might produce extra or "ghost" peaks. Sometimes a rapid loss of sample peak size with repeated injection resulted, due to the absorption of sample on dirty surfaces. Routine maintenance and cleaning methods are described in the "Varian Chromatograph Operation Manual" (47).

In using gas chromatography for the analysis of trimethylsilyl derivatives, SiO_2 deposits tend to accumulate slowly in the flame ionization detector. Bleeding of the silicone column phases also results in silicone oxide formation. The deposition of such material on electrodes and Teflon insulators results in increased noise and decreased detector sensitivity.

These deposits can be removed effectively from the detector cap and collector cylinder by immersing them in acetone or chloroform followed by gentle scrubbing. The detector tower, ignitor coil etc. can be similarily cleaned by scrubbing with wetted tissue paper. However, the flame tip assembly is hard to reach and the complete removal of the probes (which are very fragile)(47) is not recommended unless absolutely necessary.

An easier method is to inject 10 to 35 μl of Freon 113 flame ionization detector cleaner directly into the chromatograph with the

equipment operating and the G.C. column temperature at 150° C. The Freon elutes from the column within a few seconds and, when burnt in the hydrogen flame, produces HF as the cleaning agent. Usually a few injections are needed to restore the detector to its normal behavior.

IV. DEA DEGRADATION UNDER CONTROLLED CONDITIONS

As pointed out in the Introduction, very little information
has been published on DEA degradation. Plant experience indicates
that DEA losses are affected by the following variables: temperature,
pressure, raw gas composition, DEA concentration and pH of the DEA
solutions. Due to the complexity of the problem, little effort
has however been made to correlate these variables with DEA losses.

One of the objectives of the present study was therefore to
determine the degradation of DEA and the formation rates of degradation
products in a series of well controlled experiments.

Two types of equipment were constructed. The first one was
suitable for operating at atmospheric pressures and moderate
temperatures, whereas the second equipment was suitable for operating
at elevated pressures (up to 5617 kP_a (800 psig)) and temperatures
(up to 190° C).

1. Atmospheric Pressure Equipment

As discussed in Chapter III in connection with the chromatographic
analysis of degraded DEA solutions, metallic surfaces tend to accelerate
DEA degradation (24). Hence, the equipment built for atmospheric
pressure operation was constructed so that only Pyrex glass or Teflon
came in contact with the DEA solution. As seen from Fig. 7, the DEA
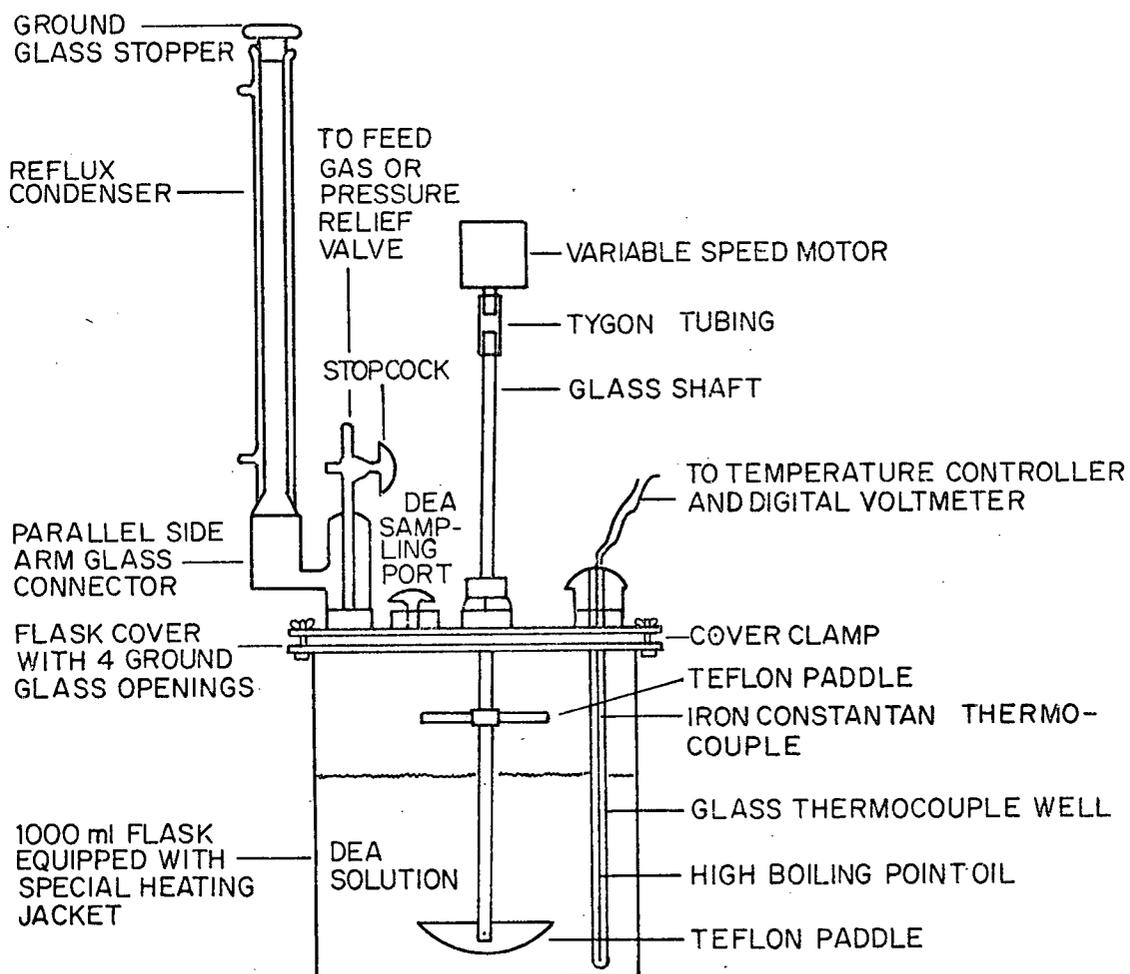
FIGURE 7: Schematic diagram of the atmospheric pressure apparatus for DEA degradation reaction studies.

solution was contained in a 1000 ml glass flask. A cover plate containing four ground glass openings and lined with a silicon rubber gasket could be attached to the flask by means by 3 cover clamps, thus providing a gas-tight seal. A commercial all glass stirrer assembly was installed in one of the four cover plate openings. It was designed for gas-tight operation and was powered by a variable speed motor. Two Teflon paddles were attached to the glass stirrer, one for agitating the DEA solution and the other for mixing the gases above the solution.

A reflux condenser and sampling valve were attached to the reaction flask by means of a parallel side arm connector. The condenser was used to prevent the build-up of pressure and return any vaporized water. Using the sampling valve adjacent to the condenser, in conjunction with a two-way flow valve, acid gas could either be introduced into the reaction flask or the flask could be connected to a pressure relief valve.

The solution temperature was maintained constant by placing the reaction flask into an electric heating jacket. The power input to the heating jacket was regulated by a Thermal Electric proportional controller. (Model 232), which was capable of keeping the temperature within $\pm$ 3° C of the desired value. The solution temperature was measured and fed back to the temperature controller by an Iron-Constantan thermocouple immersed in a thermocouple well filled with

high boiling point oil. A digital millivoltmeter was used in conjunction with the thermocouple to monitor the solution temperature.

Chemically pure CO_2, CH_4 and H_2S gases were metered by three precision rotameters before mixing and introducing them into the reaction vessel. The acid gas composition was determined from previous, carefully prepared calibration plots of the three rotameters. Due to the hazardous nature of H_2S (48), the entire apparatus was placed in a fume-cupboard.

A typical run consisted of introducing 350 ml of aqueous DEA solution of the desired strength into the reaction flask. Acid gas was passed over the solution for about 90 minutes, which was sufficient to saturate the solution. Once a day, a 3 ml liquid sample was withdrawn from the DEA sampling port before resaturating the solution with an acid gas of the same composition. Runs lastings up to 23 days were conducted at a maximum temperature of 90° C.

2. High Pressure Equipment

The primary purpose of this equipment was to check whether it was possible to reproduce the high rates of HEP formation reported by Polderman et al. (16) at elevated temperatures and pressures.

The high pressure reaction vessel was a modified 316 stainless steel miniature sample cylinder manufactured by Nupro. It has a maximum service pressure of 6996 kP_a (1000 psig) and a capacity of

25 ml. The approximate internal dimension of the reactor are 22 mm dia. x 80 mm high. Figure 8 shows the schematic diagram of the high pressure apparatus. All other parts used in conjunction with the reaction vessel were also made from 316 stainless steel.

The reaction vessel was submerged in a high temperature bath filled with glycerine and equipped with a mechanical stirrer. The power input to the temperature bath was regulated by a Thermal Electric proportional controller (Model 232) which was capable of keeping the temperature within $\pm$ 3° C of the desired value. The solution temperature was measured and fed back to the temperature controller by an Iron-Constantan thermocouple immersed in a thermocouple well (filled with high boiling point oil) which was placed inside the temperature bath. A digital millivoltmeter was used in conjunction with the thermocouple to monitor the solution temperature.

No attempt was made to withdraw samples from the high pressure apparatus during a run. Instead, 15 ml of aqueous DEA solution of the desired strength was allowed to be in contact with the acid gas at the desired pressure and temperatures for a specific period. The reaction vessel was then removed from the oil bath, cooled to room temperature and brought down to atmospheric pressure by means of a purge valve. Only then was the DEA solution withdrawn from the reaction vessel and analyzed.

Experiments lasting as long as 11 hours were conducted at temperatures and pressures of up to 185° C and 4238 kP$_a$ (600 psig) respectively.
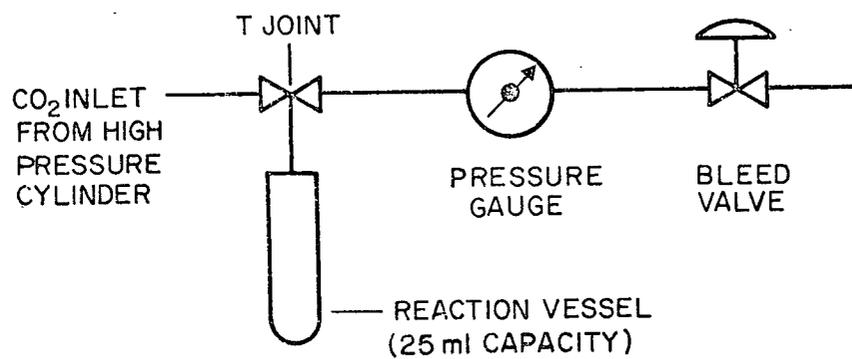
FIGURE 8: Schematic diagram of the high pressure apparatus for DEA degradation reaction studies.

V. DATA ANALYSIS

According to Polderman and Steele (16), DEA degradation by CO_2 can be represented by

$$DEA + CO_2 \longrightarrow HEOD + H_2O \qquad (14)$$

$$2 \ HEOD \longrightarrow HEP + 2CO_2 \qquad (15)$$
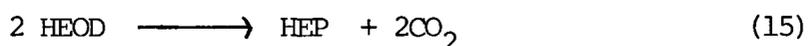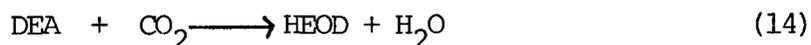
These equations suggest that only two degradation products (HEOD and HEP) should be formed. However, both Hakka *et al.* (17) and Smith *et al.* (7) reported the presence of other degradation products in industrial gas-treating solutions. Hence, Eqs. 14 and 15 cannot explain DEA degradation fully. Nevertheless, the equations may be used to form at least a partial basis for a mathematical model describing DEA degradation.

1. Theory of DEA Decomposition

Initial analyses of a series of lean DEA samples obtained from high pressure operations showed that the DEA concentration decreased uniformly with time and could be explained in terms of a first order reaction. Hence,

$$\frac{d\left[DEA\right]}{dt} = - k_{DEA}\left[DEA\right] \qquad (16)$$

where $\left[DEA \right]$ = Concentration of DEA

t = Time

k_{DEA} = Overall reaction rate constant

The integrated form of the above equation is

$$\log_{10} \left[DEA \right] = \log_{10} \left[DEA \right]_o - \frac{k_{DEA} t}{2.303} \qquad (17)$$

If the reaction is first order, a semi-logarithmic plot of the experimentally determined DEA concentrations versus time should fall on a straight line. Systematic departure from the straight line would indicate a reaction mechanism of order other than unity. It should be pointed out that Eqs. 16 and 17 are based on the assumption that CO_2 is present in excess, which was the case in the present study.

Once the overall reaction order and the reaction rate constant are obtained, the activation energy can be found from the Arrhenius equation (49, 50):

$$k_{DEA} = A \exp(- E_a/RT) \qquad (18)$$

or $$\log_{10} k_{DEA} = \log_{10} A - \frac{E_a}{2.303\ RT} \qquad (19)$$

where   A = Frequency factor

E$_a$ = Activation energy

R = Universal gas constant

T = Absolute temperature

The valves of A and E$_a$ can therefore be found by plotting k$_{DEA}$ versus 1/T on semi-logarithmic graph paper.

2.   Theory of Degradation Product Formation

Since DEA degradation is more complex than suggested by Eqs. 14 and 15, the reaction scheme could be modified as follows:

$$DEA \begin{array}{l} \xrightarrow{k_1'} U \\ \xrightarrow{k_1} HEOD \xrightarrow{k_2} \tfrac{1}{2} HEP \end{array} \qquad (20)$$
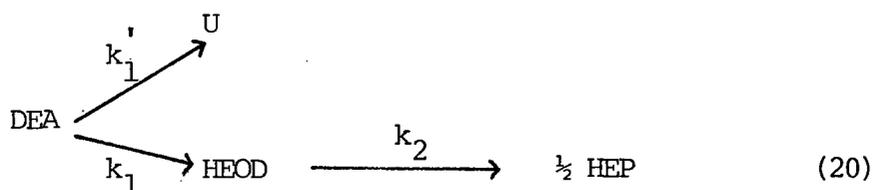
U denotes an unspecified degradation product which may decompose further, but tests have shown that HEP is stable at the high pressure and temperatures used in this study. The rate equations corresponding to the more general reaction scheme (Eq. 20) are:

$$\frac{d\left[DEA\right]}{dt} = -(k_1' + k_1)\left[DEA\right] = -k_{DEA}\left[DEA\right] \qquad (21)$$

$$\frac{d\left[HEOD\right]}{dt} = k_1\left[DEA\right] - k_2\left[HEOD\right]^2 \qquad (22)$$

$$\frac{d[\text{HEP}]}{dt} = k_2 [\text{HEOD}]^2 /2 \qquad\qquad (23)$$

with initial conditions (at $t = 0$):

$$[\text{DEA}] = [\text{DEA}]_o, \quad [\text{HEOD}] = 0, \quad [\text{HEP}] = 0$$

Exponents of HEOD ranging from 0.5 to 4 were considered for Eqs. 22 and 23. An exponent of 2 gave the best agreement between the predicted and measured HEP concentrations.

Since Eqs. 22 and 23 are non-linear, they had to be solved numerically and a standard Runge-Kutta method, which was available from the UBC computer library, was chosen.

Since k_{DEA} was known from the DEA measurements, only k_1 and k_2 needed to be specified to determine the theoretical values of HEOD and HEP. The specifications were made using a Simplex search routine which minimize the difference between the measured and theoretical HEP values. A listing of the computer program is given in Appendix D.

VI RESULTS AND DISCUSSION

1. Interpretation of Chromatograms

After considerable preliminary testing, the important parameters discussed in Chapter III were optimized for the analysis of DEA solutions (as shown in Table 10). Figure 9 shows a chromatogram for a mixtures of various commercially available ethanolamines and degradation products after BSA silylation.

Figure 10 shows a typical chromatogram of a lean DEA sample obtained from a high pressure experiment. In this particular case, a 30% DEA solution was contacted with pure CO_2 at 4238 kP_a (600 psig) and 185° C for 4 hours. For comparison, a chromatogram of the parent, 30% DEA sample used for the high pressure experiments is given in Fig. 11.

1.1 *Measurement of DEA Peaks*

The DEA peaks (Figs. 9 to 11) are symmetrical and sharp, indicating proper selection of the G.C. column, operating conditions and sample injection technique.

The reproducibility of DEA measurements was good (within $\pm$ 4%) and the lower limit of measuring DEA was found to be about 1.44×10^{-6} moles (for a 30% DEA parent solution this corresponds to 1.38×10^{-2}% DEA). The detection of DEA peaks was possible at an even lower level. However, at such low concentrations, the peaks
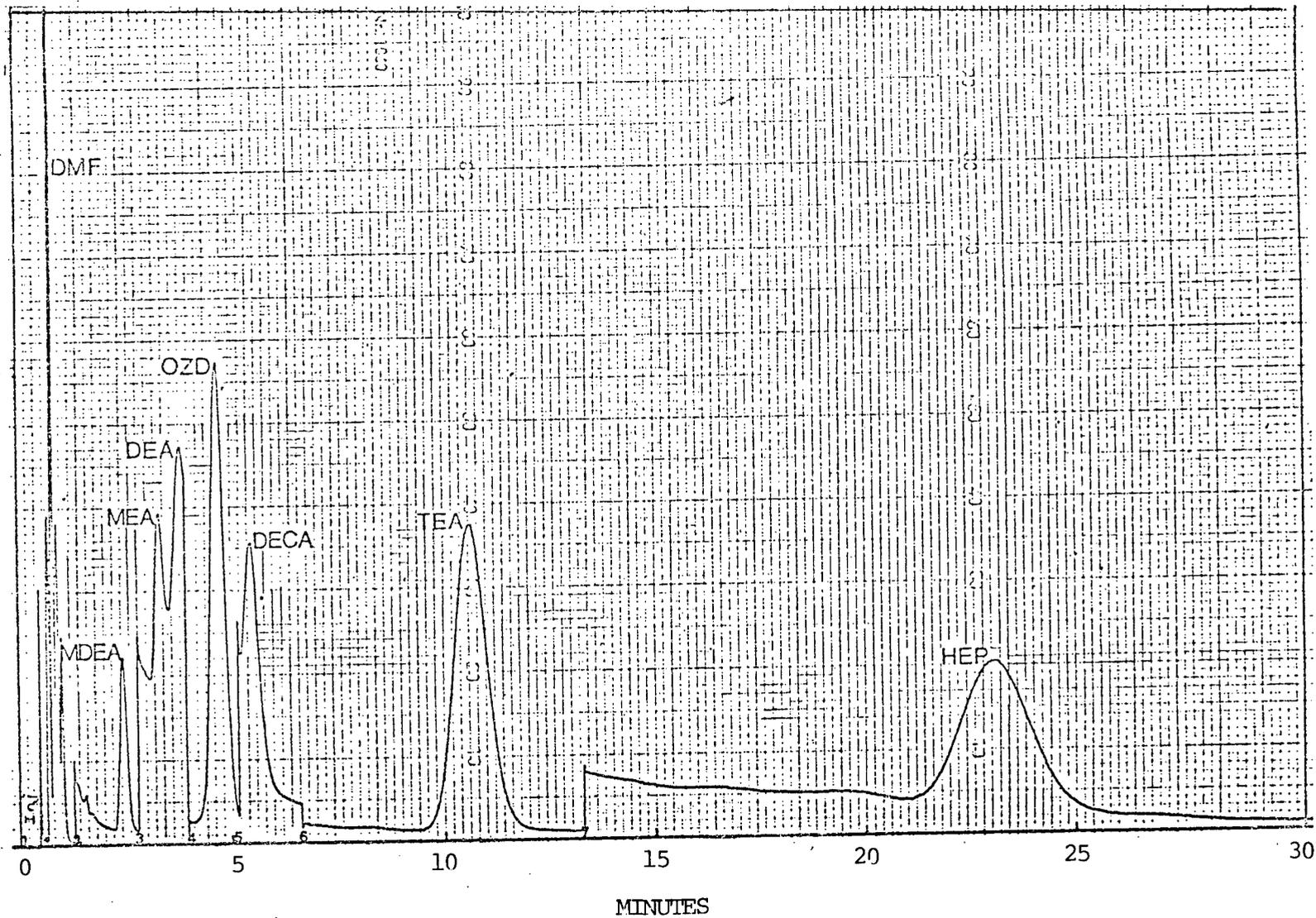
FIGURE 9: Chromatogram of ethanolamines and some previously reported degradation products. (Sensitivity: $1\text{-}512 \times 10^{-10}$ AFS; $2\text{-}125 \times 10^{-11}$ AFS; $3\text{-}8 \times 10^{-11}$ AFS; $4\text{-}128 \times 10^{-11}$ AFS; $5\text{-}16 \times 10^{-11}$ AFS; $6\text{-}32 \times 10^{-11}$ AFS; $7\text{-}4 \times 10^{-11}$ AFS. Conditions as given in Table 10.)
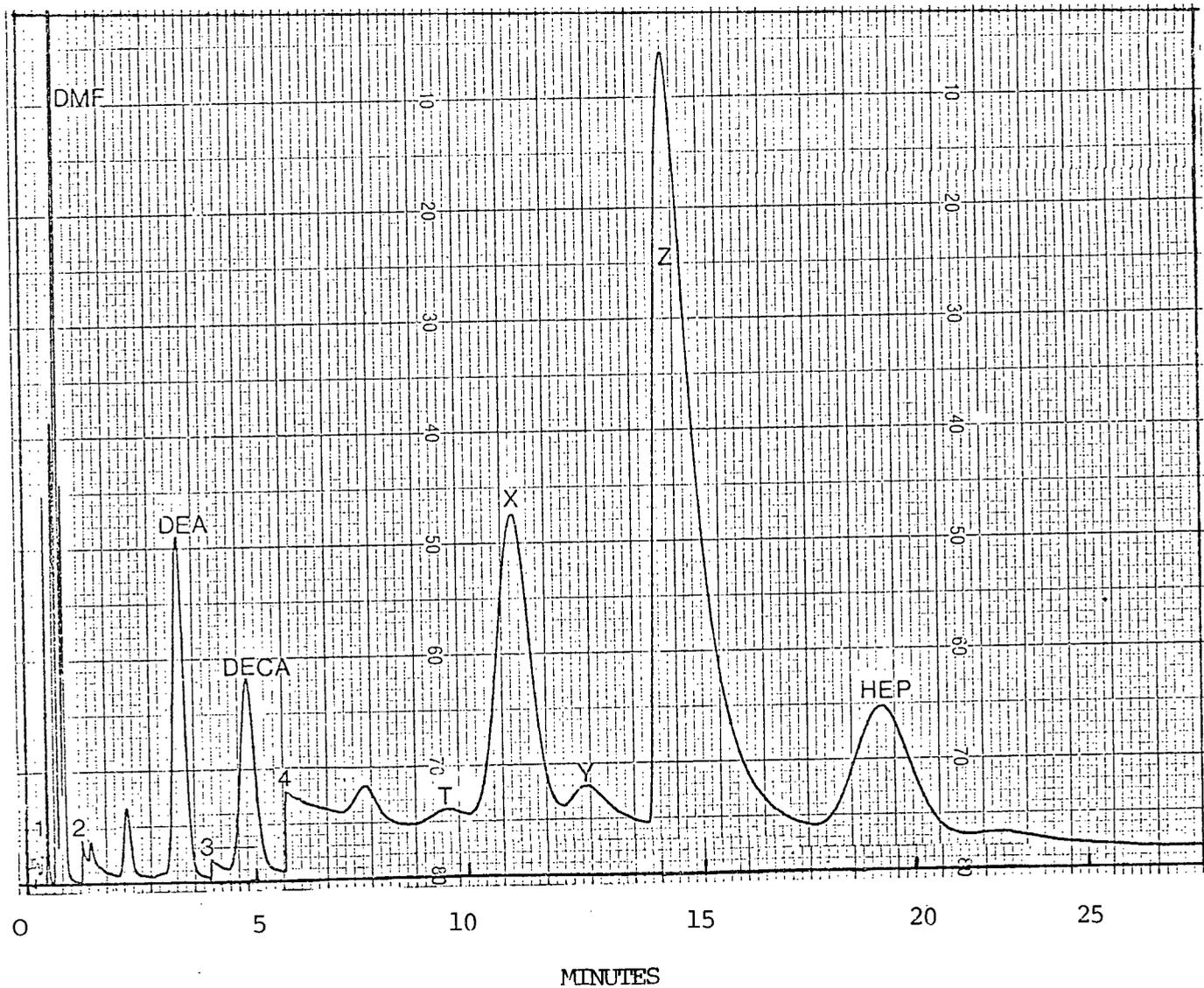
FIGURE 10: Typical chromatogram of a lean DEA sample obtained with the high pressure equipment. (Sensitivity: $1-512 \times 10^{-10}$ AFS; $2-16 \times 10^{-10}$ AFS; $3-32 \times 10^{-11}$ AFS; $4-32 \times 10^{-12}$ AFS. Conditions as given in Table 10.)
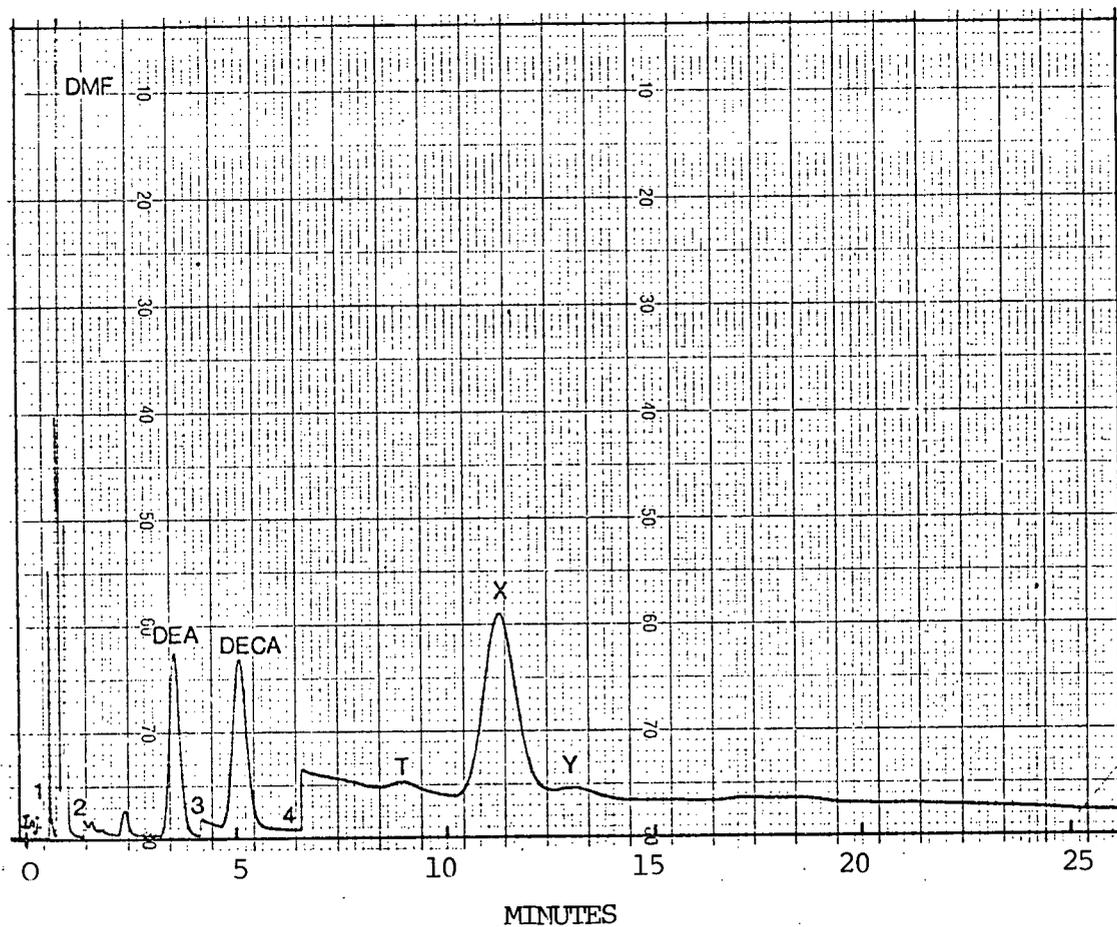
FIGURE 11: Chromatogram of parent, 30% DEA solution. (Sensitivity: 1-512x10^{-10} AFS; 2-32x10^{-10} AFS; 3-32x10^{-11} AFS; 4-32x10^{-12} AFS. Conditions as given in Table 10.)

suffer some distortion which is probably due to the interference from the solvent and residual BSA.

1.2 *Measurement of Degradation Product Peaks*

As shown in Fig. 10, five other peaks labelled "HEP", "T", "X", "Y" and "Z" were observed, when samples obtained with the high pressure equipment were analyzed. HEP and T are degradation compounds previously reported by other researchers (7, 17). The compound Y might be a degradation product or a trace impurity since this compound was also present in the parent chromatogram (Fig. 11). The compounds X and Z are also thought to be caused by degradation products, although the parent DEA chromatogram (Fig. 11) also contains compound X but at a very much smaller concentration.

Since all degradation products were present at very low concentrations, the chromatograph had to be set to extremely high sensitivity ranges (32×10^{-12} AFS or less). At such sensitivity levels, very minor contaminents and high line-voltage fluctuations can induce disturbances and distort the peaks somewhat. The former often resulted in baseline drift and the latter in minor peaks at regular intervals. If a mechanical disc integrator is used to estimate peak areas, the baseline drift can introduce significant errors.

This problem was overcome by using a triangulation method (19) for measuring the peak areas. As shown in Fig. 12, a level baseline was first estimated and drawn on the chromatogram. The width of the peak, W was regarded as the distance between the start and end points of the peak. The peak height, H, was taken to be the perpendicular distance between the baseline and the apex of the peak. The area was calculated from

$$Area = \frac{1}{2} \cdot W \cdot H \qquad (24)$$

The concentration of HEP in the experimental samples was measured by this method and evaluated from the previously prepared calibration plot (Fig. 6). However, the concentrations of other products could not be determined quantitatively since these compounds have not yet been identified. Hence, only the area ratios of these peaks to the decanolic acid (DECA) peaks are reported at present.

Although the triangulation method was time consuming, the precision was found to be good provided that the peaks were large and not too different from Gaussian shapes (19). The reproducibility was also good (within $\pm$ 7%) and the lower limit for quantitative HEP measurements was found to be approximately 6.25×10^{-7} mole/ml.
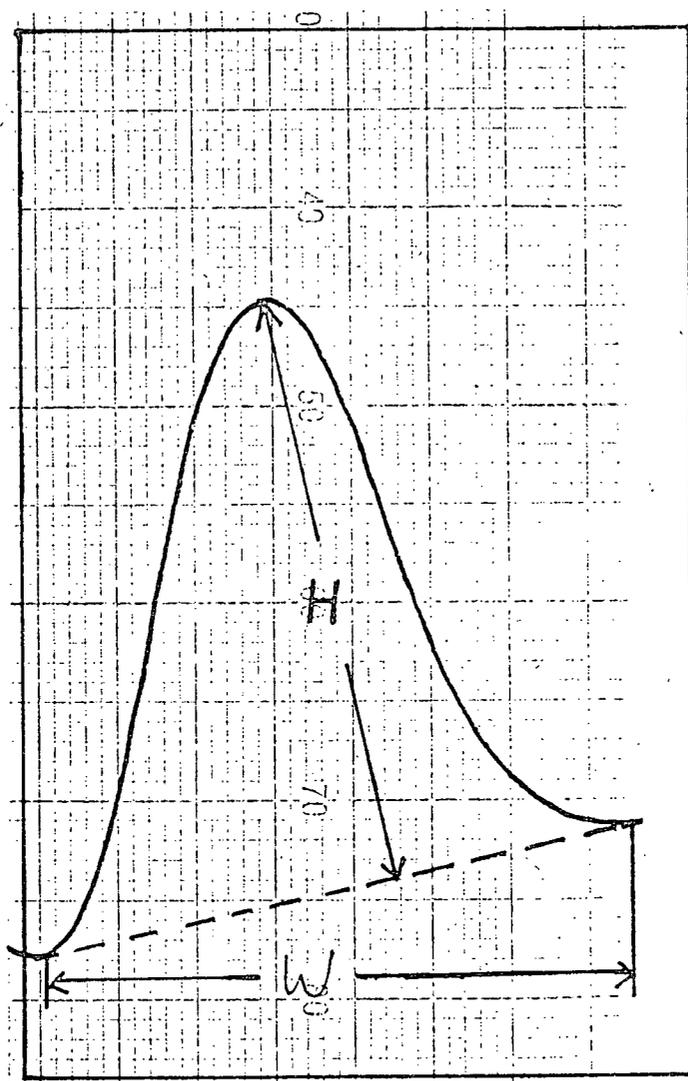
FIGURE 12: Illustration to show how triangulation method
was used to evaluate distorted G.C. peak areas.

2. High Molecular Weight Degradation Products

Apart from HEP, Hakka *et al.* (17) also reported that the
compound THEED is often present in industrial DEA solutions. This
compound is unavailable commercially and the authors reported
that it decomposes during G.C. analysis. However, the compound
TEHEED, which has a structure very similar to THEED could be purchased.
The present silylation procedure made G.C. analysis and detection
of TEHEED possible even at concentrations as low as 2.95×10^{-5} mole/ml
provided the column temperature was raised to about 174° C. The
TEHEED peak was Gaussian in shape and gave no indication of sample
decomposition. Hence the ability to separate fragile compounds
like THEED does exist.

When the column temperature is raised to 174° C,[*] HEP and
TEHEED eluted after 5.6 and 31.3 minutes, respectively. A high
temperature chromatogram for a typical lean DEA sample obtained
with the high pressure equipment is shown in Fig. 13. Two significant
peaks were observed at 10.7 and 13 minutes after injection and were
followed by 5 other smaller peaks at 17.2, 23.4, 29.0, 33.0 and 42.4
minutes. These latter seven peaks are caused by unknown compounds
and indicate the presence of species of much higher molecular weight
than HEP. Consequently they cannot be the other degradation products
listed in Table 2. The possibility that one of the seven compounds

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[*] This column temperature did not cause DEA degradation in
the gas chromatograph as confirmed by injecting a sample
of the initial DEA solution.
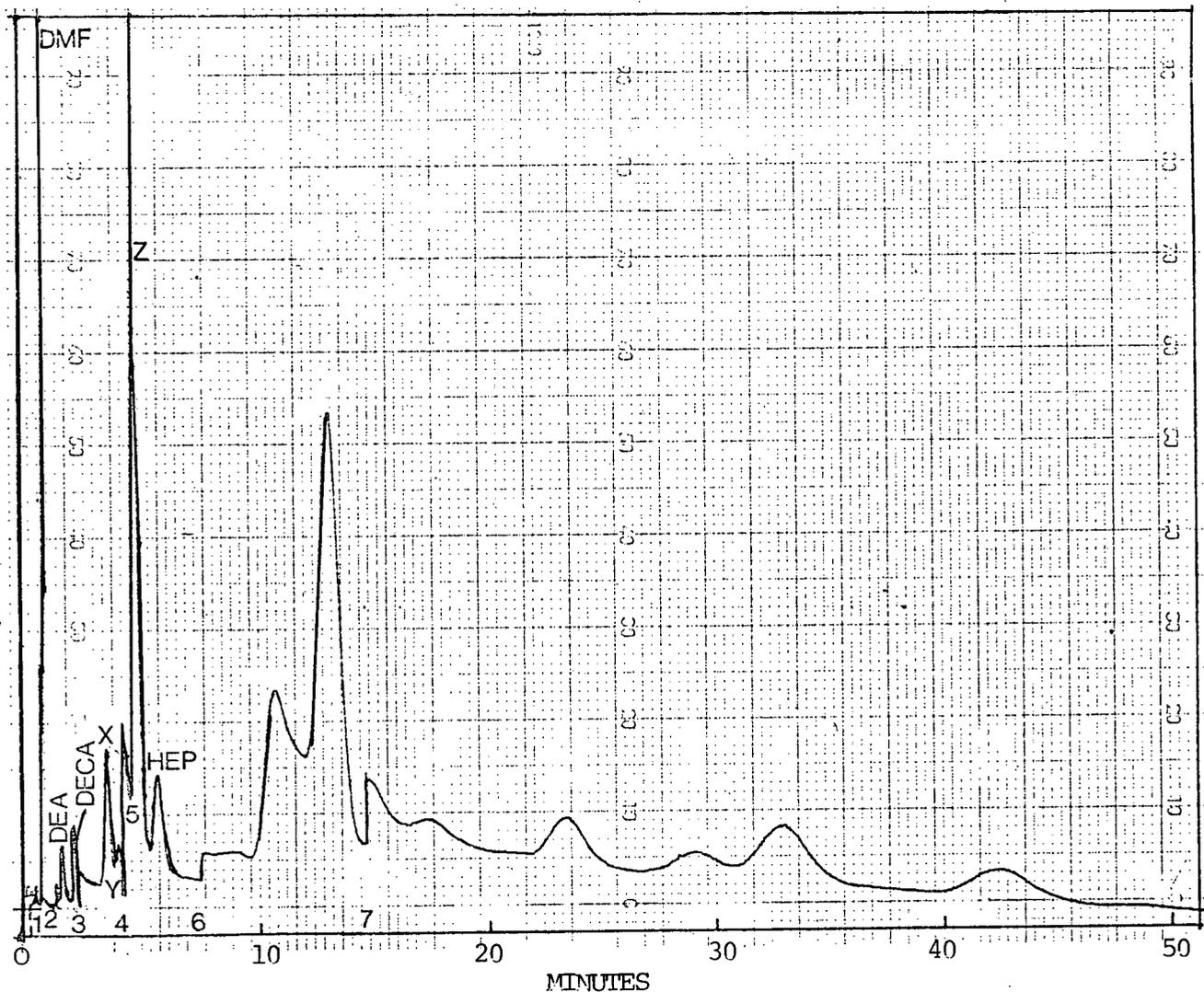
FIGURE 13: A typical high temperature chromatogram of a lean DEA sample obtained with the high pressure equipment. (Sensitivity: 1-512x10^{-10} AFS; 2-16x10^{-10} AFS; 3-32x10^{-11} AFS; 4-64x10^{-12} AFS; 5-128x10^{-12} AFS; 6-64x10^{-12} AFS; 7-32x10^{-12} AFS. Conditions as given in Table 10 with the column temperature at 174° C.)

is THEED does exist but further work is required to confirm this
as well as to establish the formation rates of such compounds. A
second internal standard should be added to the existing system
for effective, quantitative determinations. Based on the existence
of high molecular weight degradation products, which have not been
previously reported, the DEA degradation mechanism must be more
complex than postulated by Polderman *et al.* (16).

3. Analytical Technique

The reliability of the newly developed G.C. technique is
confirmed by the numerous tests of samples which contain DEA and
its degradation products in a wide range of concentrations. This
method is fast, has good reproducibility, has high sensitivity and
is capable of analyzing fragile compounds. Relatively inexpensive
G.C. columns of the OV type could be used for the analyses of high
boiling point, fragile compounds with long column life and good
separation characteristics. Furthermore, more than 36 samples from
Canadian gas-processing plants and oil refineries have been received
and analyzed in this laboratory. The results are tabulated in
Appendix E for future reference. The capability of handling
industrial samples, which contain a wide variety of contaminants
(11, 12) demonstrates the versatility and effectiveness of the newly
developed G.C. method.

4. Results of Atmospheric Pressure Tests

The all glass apparatus discussed in Chapter III, section 1 was used under the following operating conditions listed in Table 11.

Table 11 : Operating conditions for the atmospheric pressure equipment.

Temperature: 30 – 90° C

DEA Concentration: 10 – 30%

Gas Composition:

     H_2S 0 – 50%

     CO_2 0 – 50%

     CH_4 0 – 100%

It was observed that the DEA solutions changed to a light yellow colour after about 1 day and that the colour darkened with time. After about 7 days of operation, the solution changed to a deep yellow colour.

However, in spite of the colour change, none of the degradation products previously reported (7, 17) were detected after conducting the experiments for up to 23 days. These observations indicate that the conversion of DEA into these compounds either did not occur or take place at an extremely slow rate.

However, as shown in Fig. 14 the DEA concentration decreased steadily with time. It is quite unlikely that the DEA loss resulted from volatilization since water has a higher vapour pressure than DEA. A more probable explanation is that heat-stable salts were formed which are undetectable by G.C. analysis. As discussed in greater detail in Chapter II, the formation of these heat-stable salts is quite common in industrial plants where acidic gases (COS, HCN), organic acids and polysulfide compounds are frequently present. In the present case, the formation of these heat-stable salts might be caused by the impurities present in the commercial CO_2 gas supply and the large concentration of O_2 present. The latter was introduced by leakage as well as during sample withdrawl.

5. Results of High Pressure Tests

Preliminary work using the high pressure equipment gave essentially the same results as those obtained with the atmospheric pressure equipment for temperatures up to 140° C. However, by increasing the DEA solution temperature to 175° C, complete conversion
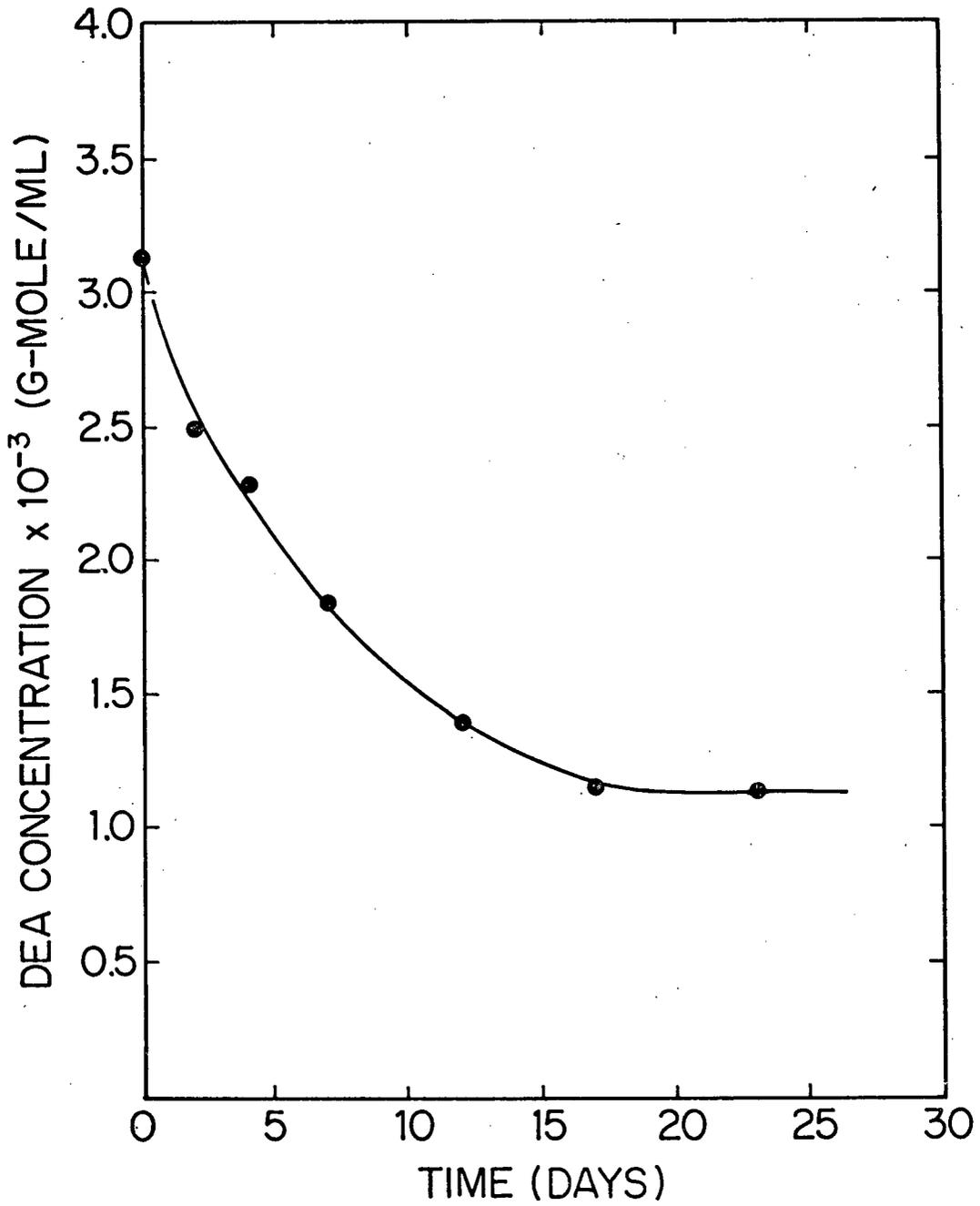
FIGURE 14: DEA loss as a function of time obtained with the atmospheric pressure equipment. (Operating conditions: pressure--101 kP_a (14.7 psi); temperature--60° C; acid gas--pure CO_2; initial DEA strength--30%.)

of DEA to its degradation products including HEP was observed after

8 hours of contact with CO_2 at 4238 kP_a (600 psig). These results

are in good agreement with the findings of Polderman *et al* (16).

Furthermore, degradation product peaks were observed in the chromatograms.

The peak areas of those degradation products also changed with time.

It was concluded that further experiments with the high pressure

equipment were desirable especially because the reaction times were

short (a few hours as compared to several days for the atmospheric

pressure equipments).

Table 12 lists the results obtained with the high pressure

equipment conducted at 165, 175 and 185° C. In all cases, 15 ml of

30% DEA aqueous solutions were subjected to pure CO_2 at a pressure

of 4238 kP_a (600 psig). The analysis of the initial 30% DEA solution

is also included for reference. The concentrations of DEA, HEP, X

and Z are shown as a function of time in Figs. 15 to 18.

The DEA degradation is governed by a first order reaction as

demonstrated by the semi-logarithmic plot shown in Fig. 15. The

solid lines represent the best fit using a least square method with

the intercept fixed at 3.12 x 10^{-3} mole/ml (the parent, 30% DEA

concentration). The overall reaction rate constants were then

estimated from the slopes of the lines. Since the high pressure

experiments were conducted at three different temperatures, the

activation energy and the frequency factor could also be determined.

The overall rate constants are summarized in Table 13 and Fig. 19 is

Table 12: Results of high pressure tests.

Temperature, ^{o}C	Time, hours	Concentrations					
		DEA, g-mole/ml	HEP, g-mole/ml	T	X	Y	Z
185	1	8.7×10^{-4}	6.25×10^{-7}	0.0	6.84	5.55×10^{-2}	3.40
"	2	3.2×10^{-4}	1.19×10^{-5}	0.0	10.7	1.79×10^{-2}	4.51
"	3	1.88×10^{-4}	2.16×10^{-5}	0.0	8.99	0.0	5.38
"	4	9.38×10^{-5}	3.26×10^{-5}	0.0	6.35	7.44×10^{-2}	5.59
"	5	0.0	4.75×10^{-5}	3.75×10^{-2}	3.23	2.89×10^{-2}	6.45
"	6	0.0	6.06×10^{-5}	6.2×10^{-2}	2.41	5.43×10^{-2}	5.76
"	7	0.0	8.44×10^{-5}	1.14×10^{-1}	1.30	5.61×10^{-2}	5.07
"	8	0.0	1.16×10^{-4}	9.0×10^{-2}	0.24	4.09×10^{-2}	4.07
175	1	2.0×10^{-3}	0.0	0.0	6.08	0.0	3.46
"	2	1.1×10^{-3}	1.0×10^{-6}	0.0	8.60	0.0	4.93
"	3	8.2×10^{-4}	6.88×10^{-6}	0.0	10.55	4.74×10^{-2}	6.64
"	4	5.4×10^{-4}	1.05×10^{-5}	0.0	10.1	4.36×10^{-2}	6.99
"	5	2.94×10^{-4}	2.11×10^{-5}	0.0	8.23	2.48×10^{-2}	8.12
"	6	2.1×10^{-4}	2.81×10^{-5}	0.0	6.33	4.41×10^{-2}	6.69

Temperature, $^\circ$C	Time, Hours	Concentrations					
		DEA, g-mole/ml	HEP, g-mole/ml	T	X	Y	Z
175	7	1.63×10^{-4}	3.56×10^{-5}	1.47×10^{-2}	5.18	4.43×10^{-2}	6.21
"	8	9.0×10^{-6}	5.31×10^{-5}	8.01×10^{-2}	4.4	4.77×10^{-2}	5.26
165	3	1.2×10^{-3}	0.0	0.0	8.88	4.64×10^{-2}	6.46
"	4	1.03×10^{-3}	1.56×10^{-6}	0.0	9.85	0.0	7.93
"	5	6.0×10^{-4}	4.06×10^{-6}	0.0	11.65	0.0	8.78
"	6	4.0×10^{-4}	6.56×10^{-6}	0.0	9.25	0.0	9.28
"	7	2.8×10^{-4}	1.11×10^{-5}	0.0	6.97	7.07×10^{-2}	8.51
"	8	2.19×10^{-4}	1.53×10^{-5}	0.0	5.46	0.0	8.76
"	9	1.44×10^{-4}	2.11×10^{-5}	0.0	4.88	3.51×10^{-2}	8.0
"	10	1.06×10^{-4}	3.17×10^{-5}	0.0	4.17	2.77×10^{-2}	7.12
"	11	8.75×10^{-5}	4.31×10^{-5}	0.0	3.27	4.2×10^{-2}	6.67
*	0	3.12×10^{-3}	0.0	6.93×10^{-3}	0.566	3.41×10^{-2}	0.0

Note. The concentrations of T, X, Y and Z are expressed as $\dfrac{\text{peak area of compound}}{\text{peak area of DECA}}$. The sensitivity level for the detection of the compounds and DECA were set at 32×10^{-12} AFS and 32×10^{-11} AFS respectively.

*   Initial 30% DEA solution
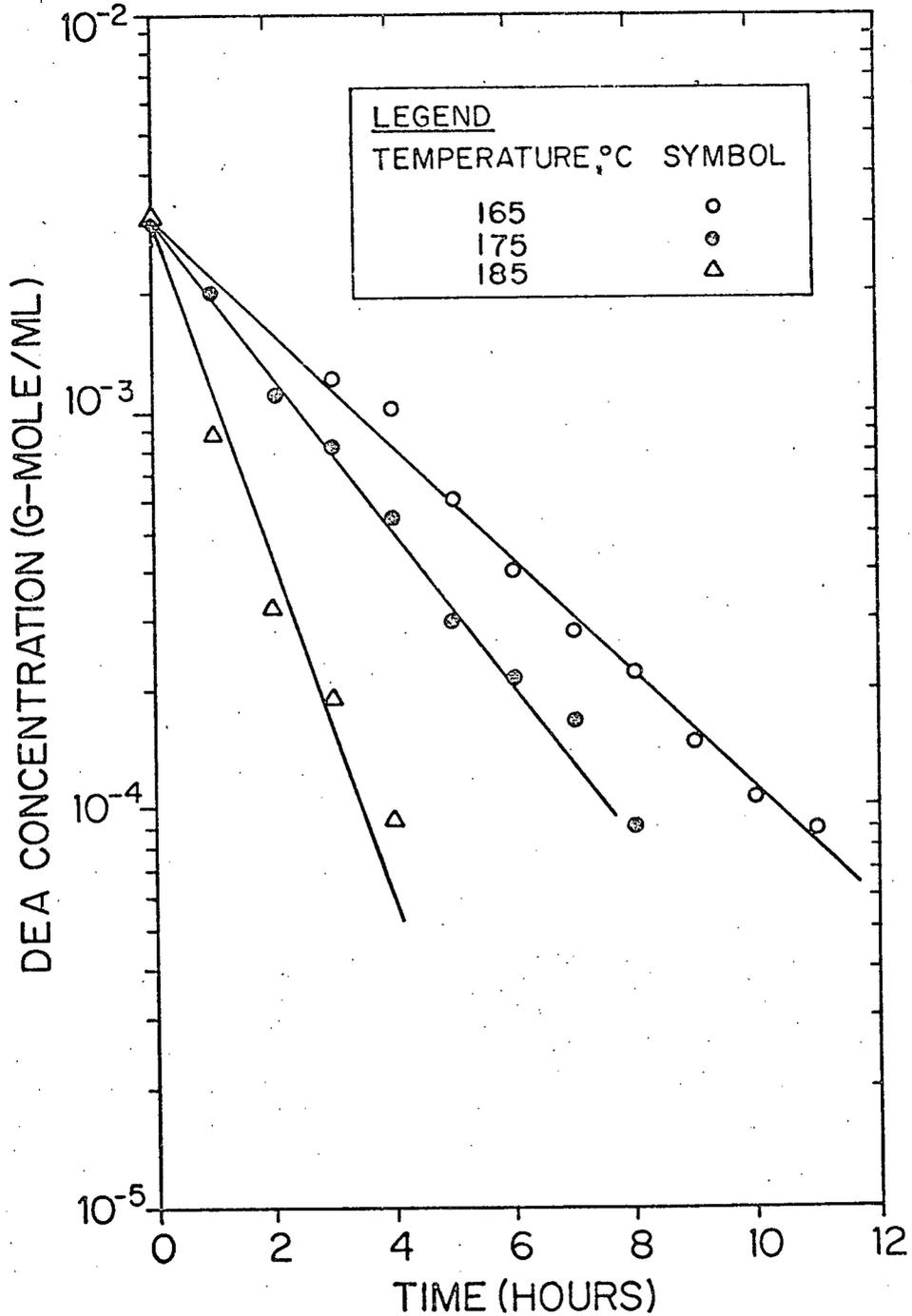
FIGURE 15: DEA concentration as a function of time obtained
with the high pressure equipment. (Operating
conditions: pressure--4238 kP$_a$ (600 psig);
acid gas--pure CO_2; initial DEA strength--30 wt.%;
the symbols are based on experimental measurements
whereas the lines represent the model predictions.)
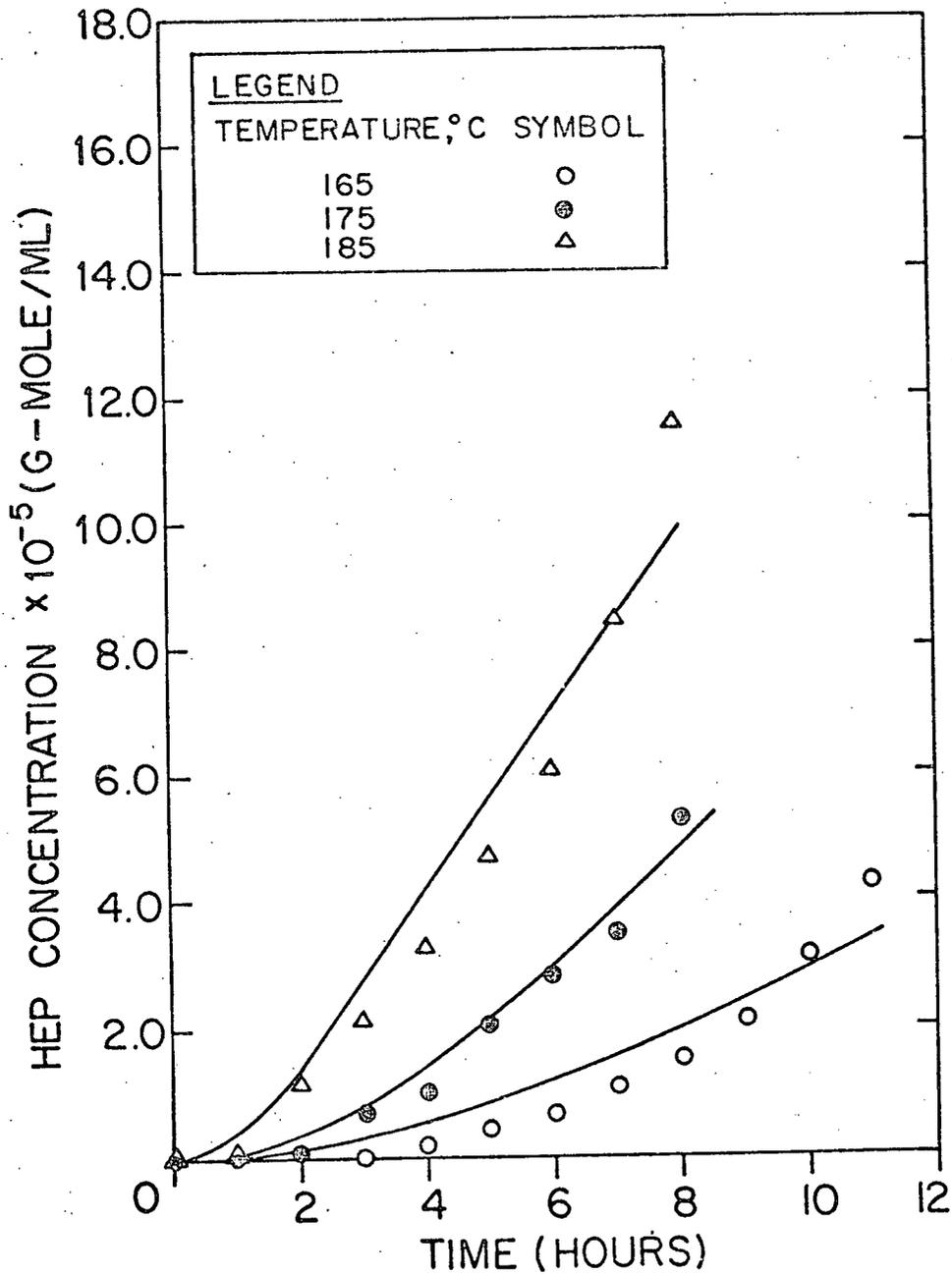
FIGURE 16: HEP concentration as a function of time obtained with the high pressure equipment. (Operating conditions: pressure--4238 kP_a (600 psig); acid gas--pure CO_2; initial DEA strength--30 wt.%; the symbols are based on experimental measurements whereas the lines represent the model predictions.)
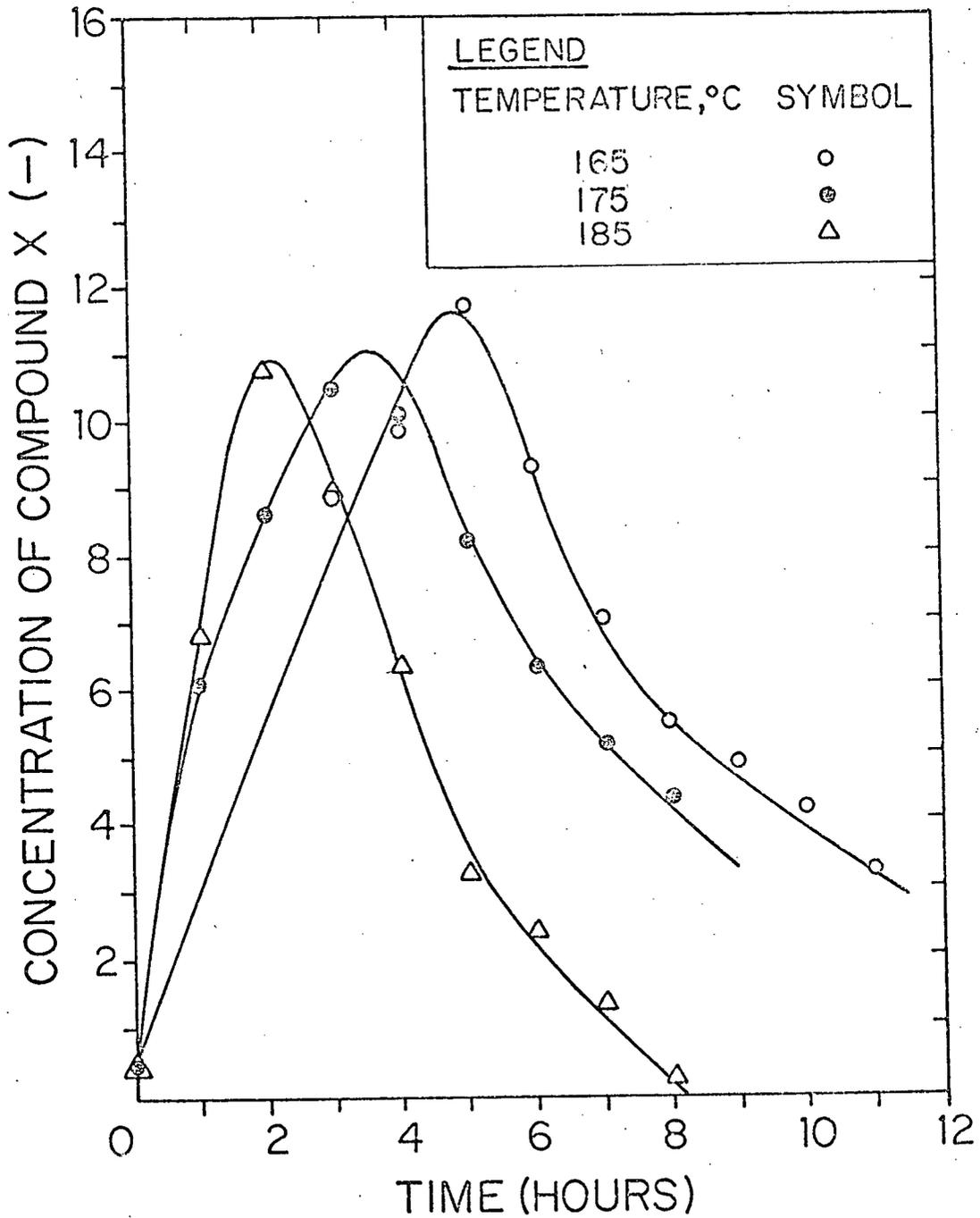
FIGURE 17: Formation of compound X as a function of time
obtained with the high pressure equipment.
(Operating conditions: pressure--4238 kP$_a$
(600 psig); acid gas--pure CO_2; initial DEA
strength--30 wt.%; the symbols are based on
experimental measurements and the lines were
drawn to pass through these data points.)
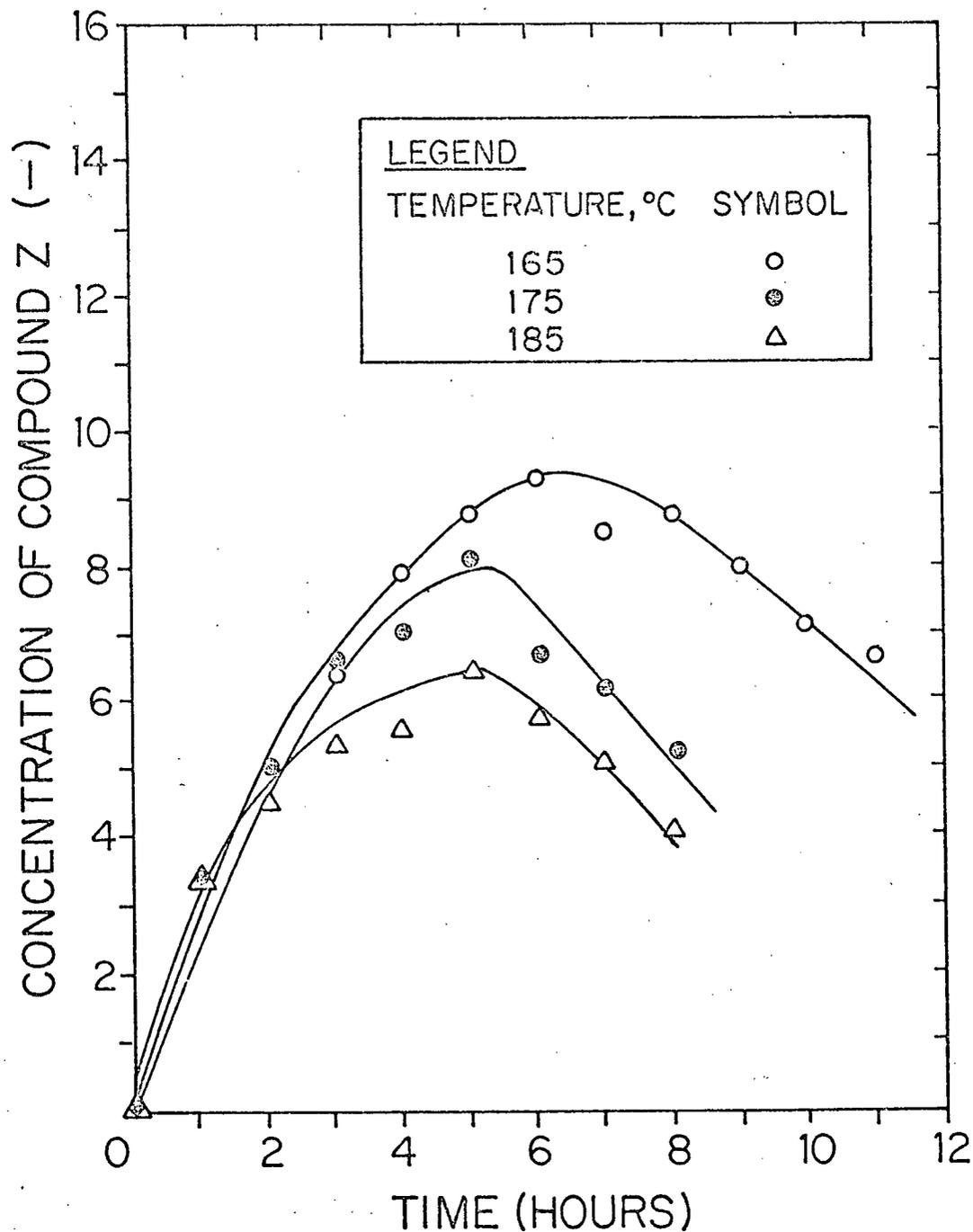
FIGURE 18: Formation of compound Z as a function of time obtained with the high pressure equipment. (Operating conditions: pressure—4238 kP_a (600 psig); acid gas—pure CO_2; initial DEA strength—30 wt.%; the symbols are based on experimental measurements and the lines were drawn to pass through these data points.)
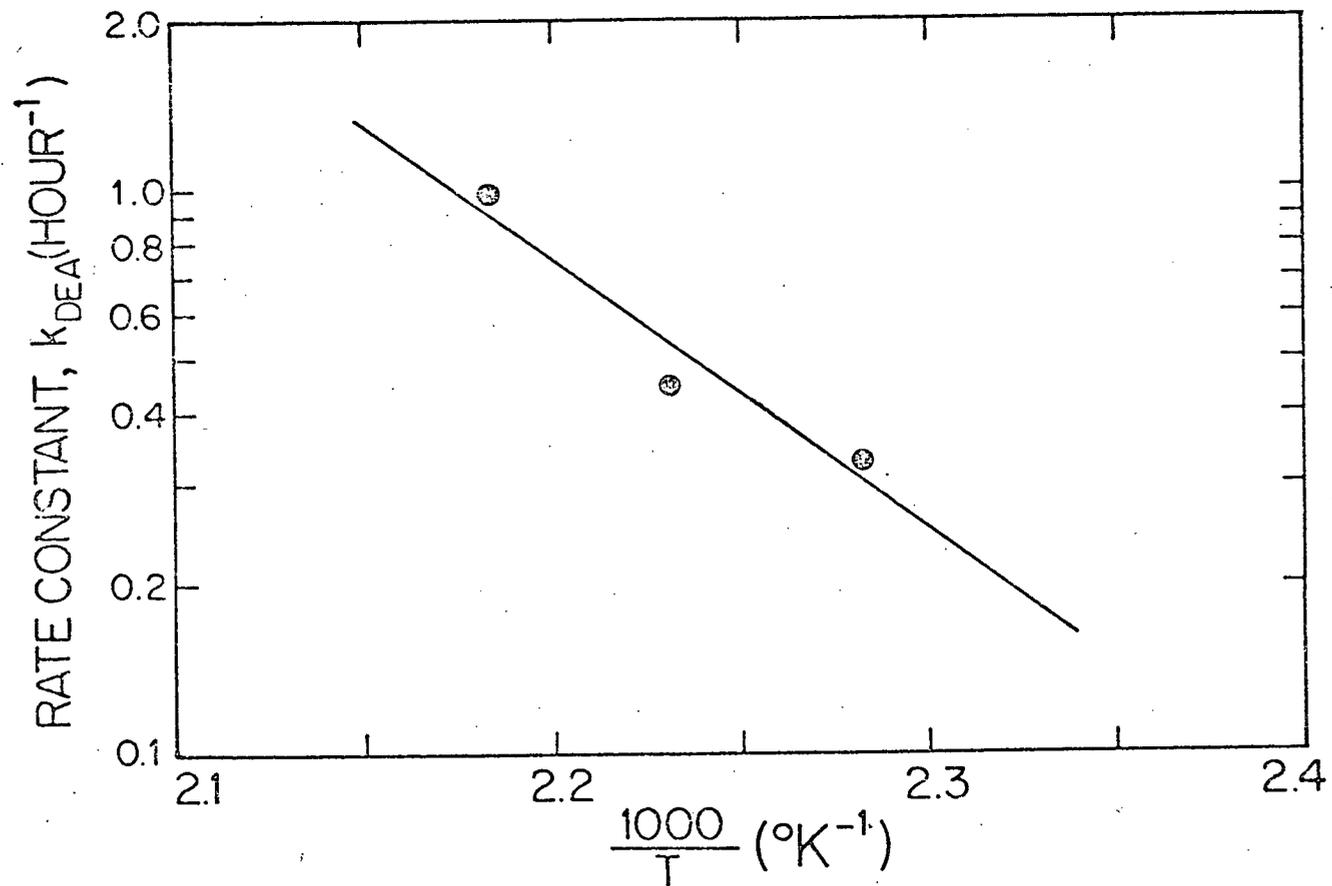
FIGURE 19: Overall DEA reaction rate constants as a function of absolute
temperature as listed in Table 13.

the corresponding Arrhenius plot. The activation energy and frequency factor were found to be 2.17×10^4 cal g-mole^{-1} and 2.03×10^{10} hour^{-1}, respectively.

Table 13: Overall reaction rate constants obtained with the high pressure equipment. (Operating conditions: pressure -- 4238 kP_a (600 psig); acid gas -- pure CO_2; initial DEA strength -- 30 wt.%)

Temperature		Overall rate constant, k_{DEA}
^{O}C	^{O}K	hour^{-1}
165	438	0.331
175	448	0.450
185	458	0.987

The HEP concentration is a function of time and temperature as shown in Fig. 16. The solid lines represent the best fitted lines to the experimental HEP data obtained from the kinetic model discussed in Chapter V.

Polderman *et al.* (16) reported that the formation of HEP from DEA might not be a simple process and that an intermediate compound, HEOD, may be present. If this hypothesis is true, the concentration of HEOD should pass through a maximum. Figures 17 and 18 show the concentration of X and Z respectively as a function of time. The concentrations of these two, as yet unidentified, compounds exhibit a maximum. It is therefore probable that both of them are reaction intermediates and one of them may be HEOD. Since no commercial HEOD standard was available, the identification of HEOD in the degraded samples was not possible.

The concentrations of the other two unidentified compounds (T and Y) were not plotted but are only tabulated in Table 12 for future reference. This was done because the compounds gave very small peaks even at extreme detector sensitivity settings and they may therefore be regarded as very minor constitutents or DEA impurities. For example, the chromatogram of the parent DEA solution (Fig. 11) also contained the compounds T, X and Y. By comparing the concentration values of T and Y with other high pressure samples, it was found that they did not change substantially. Hence, the variation in these two compounds concentrations could be caused by measurement error

since the peak size was extremely small and the peaks were situated between the large peaks of compounds X and Z.

From the above results, it is clear that temperature plays an important role in DEA degradation.

6. Results of the Kinetic Model Study

Some exploratory studies were undertaken to test the DEA degradation mechanism proposed in Chapter V. The reaction rate constants, which are summarized in Table 14, do not obey the usual Arrhenius equation. This implies that the kinetic model may be inadequate.

Table 14: Reaction rate constants giving the best fit between the theoretical and experimental HEP concentrations.

Temperature		Rate Constants		
$^\circ C$	$^\circ K$	k_1, hour^{-1}	k_1', hour^{-1}	k_2, ml g-mole^{-1}hour^{-1}
165	438	0.329	0.002	1.09
175	448	0.327	0.123	4.02
185	458	0.324	0.663	3.49

Table 15: Experimental and theoretical concentrations of DEA, HEP and HEOD.

Temperature, °C	Time, hours	Concentration				
		DEA expr., g-mole/ml	DEA ther., g-mole/ml	HEP expr., g-mole/ml	HEP ther., g-mole/ml	HEOD ther., g-mole/ml
185	0	3.12×10^{-3}	3.12×10^{-3}	0.0	0.0	0.0
"	1	8.7×10^{-4}	1.17×10^{-3}	6.25×10^{-7}	3.01×10^{-6}	6.38×10^{-4}
"	2	3.2×10^{-4}	4.35×10^{-4}	1.19×10^{-5}	1.34×10^{-5}	8.57×10^{-4}
"	3	1.88×10^{-4}	1.62×10^{-4}	2.16×10^{-5}	2.74×10^{-5}	9.19×10^{-4}
"	4	9.38×10^{-5}	6.05×10^{-5}	3.26×10^{-5}	4.23×10^{-5}	9.22×10^{-4}
"	5	0.0	2.26×10^{-5}	4.75×10^{-5}	5.69×10^{-5}	9.06×10^{-4}
"	6	0.0	8.42×10^{-6}	6.06×10^{-5}	7.09×10^{-5}	8.82×10^{-4}
"	7	0.0	3.14×10^{-6}	8.44×10^{-5}	8.41×10^{-5}	8.58×10^{-4}
"	8	0.0	1.17×10^{-6}	1.16×10^{-4}	9.66×10^{-5}	8.33×10^{-4}
175	0	3.12×10^{-3}	3.12×10^{-3}	0.0	0.0	0.0
"	1	2.00×10^{-3}	2.00×10^{-3}	0.0	5.09×10^{-7}	8.24×10^{-4}

Table 15: Experimental and theoretical concentrations of DEA, HEP and HEOD (continued).

Temperature, °C	Time, hours	Concentration				
		DEA expr., g-mole/ml	DEA ther., g-mole/ml	HEP expr., g-mole/ml	HEP ther., g-mole/ml	HEOD ther., g-mole/ml
175	2	1.10×10^{-3}	1.27×10^{-3}	1.00×10^{-6}	3.01×10^{-6}	1.35×10^{-3}
"	3	8.20×10^{-4}	8.12×10^{-4}	6.88×10^{-6}	7.69×10^{-6}	1.67×10^{-3}
"	4	5.40×10^{-4}	5.18×10^{-4}	1.05×10^{-5}	1.41×10^{-5}	1.87×10^{-3}
"	5	2.94×10^{-4}	3.31×10^{-4}	2.11×10^{-5}	2.17×10^{-5}	2.00×10^{-3}
"	6	2.10×10^{-4}	2.11×10^{-4}	2.81×10^{-5}	3.00×10^{-5}	2.07×10^{-3}
"	7	1.63×10^{-4}	1.35×10^{-4}	3.56×10^{-5}	3.87×10^{-5}	2.10×10^{-3}
"	8	9.00×10^{-5}	8.58×10^{-5}	5.31×10^{-5}	4.77×10^{-5}	2.12×10^{-3}
165	0	3.12×10^{-3}	3.12×10^{-3}	0.0	0.0	0.0
"	1	--	2.25×10^{-3}	--	1.51×10^{-7}	8.76×10^{-4}
"	2	--	1.61×10^{-3}	--	9.63×10^{-7}	1.50×10^{-3}
"	3	1.20×10^{-3}	1.16×10^{-3}	0.0	2.62×10^{-6}	1.95×10^{-3}
"	4	1.03×10^{-3}	8.32×10^{-4}	1.56×10^{-6}	5.08×10^{-6}	2.27×10^{-3}

Table 15: Experimental and theoretical concentrations of DEA, HEP and HEOD (continued).

Temperature °C	Time, hours	Concentration				
		DEA expr., g-mole/ml	DEA ther., g-mole/ml	HEP expr., g-mole/ml	HEP ther., g-mole/ml	HEOD ther., g-mole/ml
165	5	6.00×10^{-4}	5.98×10^{-4}	4.06×10^{-6}	8.19×10^{-6}	2.50×10^{-3}
"	6	4.00×10^{-4}	4.29×10^{-4}	6.56×10^{-6}	1.18×10^{-5}	2.66×10^{-3}
"	7	2.80×10^{-4}	3.08×10^{-4}	1.11×10^{-5}	1.59×10^{-5}	2.77×10^{-3}
"	8	2.19×10^{-4}	2.21×10^{-4}	1.53×10^{-5}	2.02×10^{-5}	2.85×10^{-3}
"	9	1.44×10^{-4}	1.59×10^{-4}	2.11×10^{-5}	2.47×10^{-5}	2.90×10^{-3}
"	10	1.06×10^{-4}	1.14×10^{-4}	3.17×10^{-5}	2.93×10^{-5}	2.94×10^{-3}
"	11	8.75×10^{-5}	8.19×10^{-5}	4.31×10^{-5}	3.40×10^{-5}	2.96×10^{-3}

The experimental and theoretical concentrations of DEA and HEP are

shown in Figs. 15 and 16. The theoretical HEOD concentrations predicted

by the proposed kinetic model are shown in Fig. 20.

The experimental and theoretical results for DEA and HEP

(Figs. 15 and 16) were found to be in moderately good agreement. The

discrepancies are largely due to experimental error, with inadequate

temperature control being the most prominent one. The temperature

controller was only capable of maintaining the oil bath temperature

within $\pm 3^{\circ}$ C which is unsatisfactory for high reaction rates. Figure 20

shows that the HEOD concentration should rise rapidly before gradually

decreasing again. This is in marked contrast to the behavior of

compounds X and Z which decompose rapidly. Hence, the likelihood

that either compound X or Z is HEOD is small. However, since this

part of the study was exploratory, no efforts were made to improve

the accuracy of the analysis of compounds X and Z. This could be

done by using a larger sample size for G.C. injection, which would

lower the detection sensitivity and give better base-line control.

Alternatively, another internal standard with a retention time slightly

greater than HEP could be used.

7. DEA Degradation Under Special Conditions

In addition to the high pressure tests summarized in Table 12,

a number of special tests were performed. The main objective was to

find the effects of CO_2 pressure, DEA solution strength, the presence
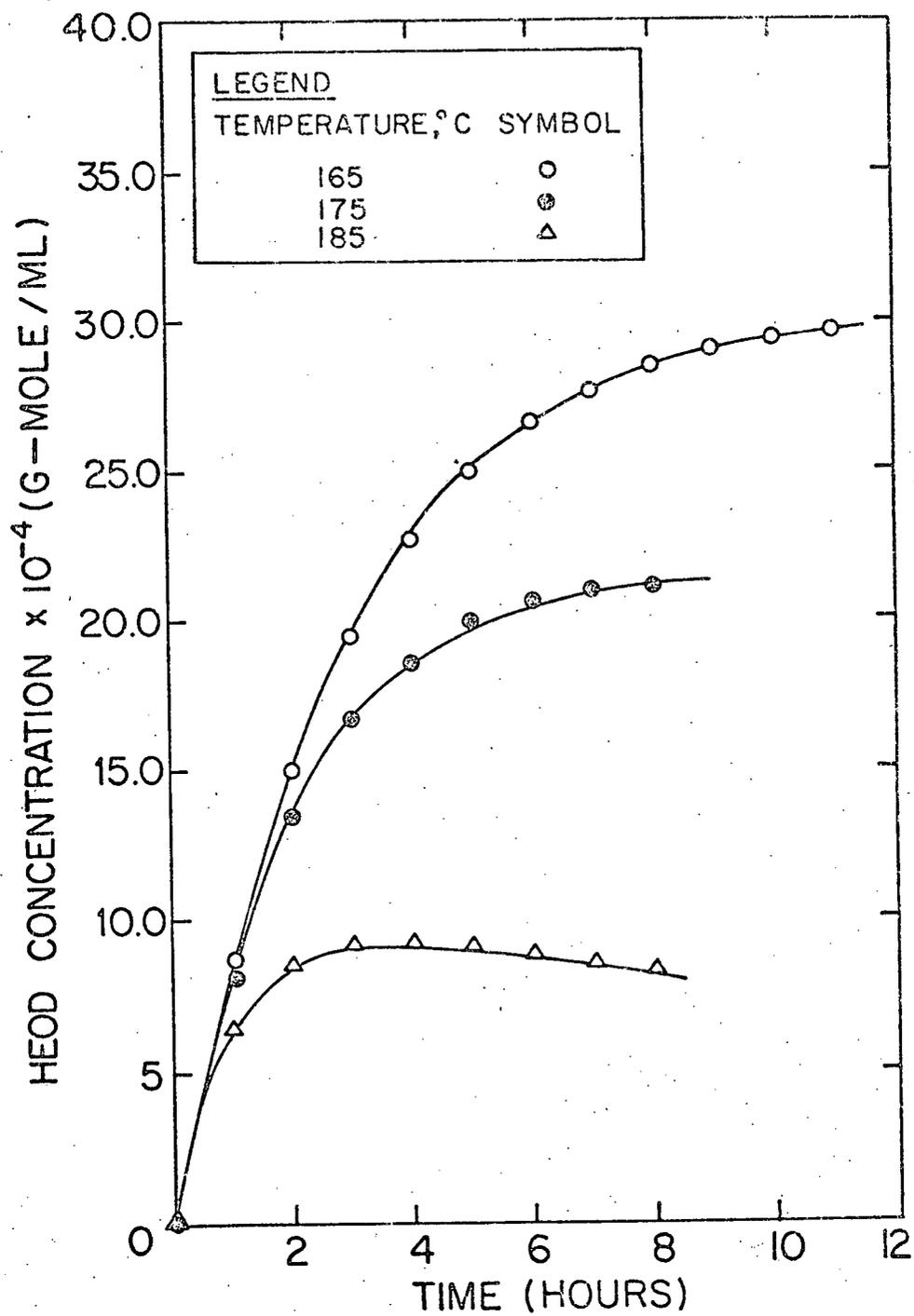
FIGURE 20: Formation of HEOD as a function of time predicted by the kinetic model.

of H_2S and metal surfaces on DEA degradation.

Table 16 lists the experimental conditions under which the special tests were performed and the corresponding results. In addition to the analysis for the initial 30% DEA solution, results obtained by contacting this DEA solution with 4238 kP_a (600 psig) CO_2 for 4 hours at 175° C is also included for reference. The latter is subsequently called the "base run".

The first special experiment involved contacting a 30% DEA solution with He at 1274 kP_a (170 psig) and 185° C for 8 hours. The reason for the selection of this relatively low contacting pressure was due to the lack of suitable high pressure regulator. However, this He pressure was sufficient to prevent boiling of the DEA sample at 185° C and, since helium is an inert gas, the He pressure should have no effect on the experimental results. By comparing the results obtained from the He run and the "base run", it was found that CO_2 is a major factor affecting DEA degradation since, in an inert atmosphere, the resulting DEA concentration (3.02×10^{-3} mole/ml) is very close to that of the initial 30% DEA solution (3.12×10^{-3} mole/ml). However, even in an inert atmosphere, the concentration of degradation compounds T and X increased slightly. Furthermore, a trace of compound Z was also detected. The latter compound was not present in the initial DEA solution and this indicates that DEA degradation does occur to a small extent at high temperatures and in the presence

Table 16: Special experimental conditions and the results obtained with the high pressure equipment.

Experimental Conditions						Concentration					
Initial DEA strength	Pressure	Temperature, $^\circ$C	Gas	Reaction time	Special feature	DEA, g-mole/ml	HEP, g-mole/ml	T	X	Y	Z
30%	1274 kP$_a$ (170 psig)	185	Pure He	8		3.02×10^{-3}	0.0	8.09×10^{-3}	0.766	0.0122	0.0188
30%	2170 kP$_a$ (300 psig)	175	Pure CO$_2$	4		5.4×10^{-4}	1.05×10^{-5}	0.0	10.81	0.0	3.90
10%	4238 kP$_a$ (600 psig)	175	Pure CO$_2$	4		3.06×10^{-4}	0.0	0.021	0.705	0.0398	2.57
30%	4238 kP$_a$ (600 psig)	175	H$_2$S + CO$_2$	4	Presaturating with 1480 kP$_a$ (200 psig) H$_2$S followed by contact with 4238 kP$_a$ (600 psig) CO$_2$	2.22×10^{-3}	0.0	0.0	4.67	0.0316	0.359
30%	4238 kP$_a$ (600 psig)	175	Pure CO$_2$	4	DEA solution contained in a glass vial	6.06×10^{-4}	1.03×10^{-5}	0.0	6.58	0.0	6.59
30%	--	--	--	--	initial DEA	3.12×10^{-3}	0.0	6.93×10^{-3}	0.566	0.034	0.00
30%	4238 kP$_a$ (600 psig)	175	Pure CO$_2$	4	"Base run"	5.4×10^{-4}	1.05×10^{-5}	0.0	10.1	0.0436	6.99

Note. The concentration of T, X, Y and Z are expressed as $\dfrac{\text{peak area of compound}}{\text{peak area of DECA}}$. The sensitivity level for the detection of these compounds and DECA were set at 32×10^{-12} AFS and 32×10^{-11} AFS respectively.

of metal surfaces.

The results obtained from the 2170 kP_a (300 psig) CO_2 run are quite similar to those of the "base run" except for the concentration of compound Z. The CO_2 pressure therefore has little effect on the degradation of DEA and the formation of HEP. This is probably due to the fact that CO_2 is present in great excess in all runs performed.

The results from the 10% DEA run showed that the concentration of degradation products were reduced. This is expected from the reaction mechanism postulated by Polderman *et al.* (16). However, the measured DEA concentration is much greater than the predicted value of 1.84×10^{-4} mole/ml. The latter concentration was calculated on the basis of 10% DEA in the initial solution and an overall reaction rate constant, k_{DEA}, of 0.45 hr^{-1}. The difference between the measured and predicted DEA concentration after 4 hours is $3.06 \times 10^{-4} - 1.84 \times 10^{-4}$ or 1.22×10^{-4} mole/ml. The corresponding difference in the overall reaction rate constant is 0.128 hr^{-1}. Such deviations cannot be explained in terms of experimental errors. For example, a drop of 5° C is necessary to explain the decrease in the overall reaction rate constant and this is much greater than the precision of the temperature controller ($\pm 3^{\circ}$ C). The reasons for the unexpected behavior of the 10% DEA solution are not known and merit further investigation in future.

The results from the H_2S - CO_2 run showed a higher DEA concentration (2.22 x 10^{-3} g-mole/ml), absence of HEP and much lower concentrations of other degradation products than the "base run". This can be explained by assuming that most of the DEA is tied up by H_2S and hence protected against CO_2 attack. Calculations based on the absorption of H_2S in aqueous DEA solutions (5) confirmed such an interpretion. At 21° C (70° F) and an H_2S pressure greater than 133 kP_a (1000 mm Hg), 1.08 moles of H_2S are associated with 1 mole of DEA at equilibrium. This means that pre-saturating a 30% DEA solution with H_2S before contacting it with CO_2, leaves only 46% of the original DEA (1.43 x 10^{-3} mole/ml) free to react with CO_2. Based on the overall reaction rate constant at 175° C and an initial DEA solution strength of 1.43 x 10^{-3} mole/ml, a calculated value of 2.48 x 10^{-4} mole/ml is obtained for the residue DEA after CO_2 contact. This is in good agreement with the measured concentration of 2.22 x 10^{-4} mole/ml.

The slightly higher residue DEA concentration (6.06 x 10^{-4} g-mole/ml) obtained by reacting DEA in a glass vial with CO_2 demonstrates that metal surfaces accelerate DEA degradation somewhat. This finding is in agreement with the results published by S.G.E. (24). The rest of the degradation products were present in concentrations similar to those of the "base run". This shows that, even in the presence of glass surfaces, CO_2 causes DEA degradation at high temperatures.

8. Analysis of Industrial Samples

Thirty six samples from Canadian gas-processing plants and oil refineries were analyzed. The results are tabulated in Appendix E.

There are strong similarities between the composition of industrial samples and DEA solutions degraded under laboratory conditions. It may therefore be concluded that DEA undergoes essentially the same kind of degradation in both cases.

The concentration ranges of DEA and HEP were in very good agreement. This demonstrates that, when DEA samples of similar concentrations are in contact with acid gases, one of the end products is HEP. Industrial samples generally contain much greater amounts of T (up to 100 times). A probable reason is that the industrial DEA feed, being less pure than the laboratory reagent, contains triethanolamine (TEA) as well as other impurities. The TEA, which has the same retention time as compound T in G.C. analysis, would increase the T peak. Small deviations in the peaks of compounds X, Y and Z might be caused by the presence of other contaminants that were always present in industrial processes.

VII   CONCLUSIONS

1. A reliable analytical method has been developed for the
    analysis of DEA gas-treating solutions. This method
    is based on the gas chromatographic separation of
    silylated derivatives. It can detect trace quantities
    of DEA, HEP and other degradation products in samples
    from laboratory experiments as well as industrial gas
    plants and petroleum refineries.

2. Degradation experiments at atmospheric pressure showed
    that DEA solutions change colour after 1 day of contact
    with CO_2 and H_2S at temperatures between 30° C and 90° C.
    However, no known degradation products were detected
    even after 23 days of operation. However, the DEA
    concentration decreased with time and the formation of
    heat-stable salts, which was undetectable by G.C. analysis
    was suspected.

3. Degradation tests at pressures and temperatures greater
    than 300 psig and 165° C, respectively, resulted in
    the formation of HEP, T, X, Y and Z plus seven other
    unidentified compounds. The first five degradation
    products could be detected by using a G.C. column temperature
    of 142° C whereas the latter seven compounds could only
    be readily observed by using column temperature of 174° C.

4. Compounds X or Z are suspected to be intermediates of
    DEA degradation since their concentration versus time
    plots exhibit maxima.

5. Based on the results obtained from high temperature
    (174° C) G.C. analysis, degradation products with
    molecular weights similar to that of TEHEED (m.w. 236)
    are suspected. If this is true, then this is the first
    report of the separation of high molecular weight DEA
    degradation products by gas chromatography.

6. The loss of DEA at elevated temperatures (data from high
    pressure experiments) was found to be governed by a
    first order reaction. The rate constants and activation
    energy of this reaction were also determined.

7. A simple DEA degradation scheme has been proposed and
    is compared with DEA and HEP measurements. The reaction
    rate constants for the formation of HEOD and HEP have
    been obtained by fitting the model to the experimental
    data. The theoretical DEA and HEP concentrations were
    found to be quite similar to the experimental values.
    However, the theoretical HEOD concentrations was very
    different from experimental measurements of the compounds
    X and Z. The former concentration was found to increase
    rapidly and then level off instead of passing through a

maximum as observed for compounds X and Z.

9. DEA degradation is complex and leads to the formations of many degradation products. The reaction mechanism proposed by Polderman *et al.* (16) is too simple to explain the experimental results fully.

10. Chromatograms obtained from samples of high pressure laboratory tests were very similar to those of industrial samples. The concentrations of DEA and HEP as well as other degradation products were present in similar concentrations in the laboratory and industrial samples.

11. Based on the present study, CO_2 and temperature appear to be the crucial factors in DEA degradation.

12. The results obtained from high pressure tests conducted with a 10% DEA solution indicated lower degradation rates than expected. The reasons for this are not understood at this time.

13. H_2S was found to inhibit DEA degradation. Saturating a 30% DEA solution with H_2S at 1480 kP_a (200 psig) prior to CO_2 contact, reduced the DEA loss by possibly limiting the amount of free DEA (up to 54 mole %) available to CO_2 attack.

14.   Stainless steel surfaces were found to accelerate DEA

        degradation somewhat.

VIII   RECOMMENDATION FOR FURTHER RESEARCH

1.   The direct G.C. technique proposed by Saha $et.$ $al.$ (26)

        should be investigated for the analysis of DEA and its

        degradation products. This method has proved to be

        capable of detecting ethanolamines in aqueous solution.

        However, it is uncertain whether it can also separate

        fragile compounds like HEP, TEHEED et. at the recommended

        high temperatures for injector and G.C. column (350° C

        and 135° C -- 350° C temperature programming, respectively)

        recommended by Saha et $al.$ (26). Thermal decompositions

        of the above compounds is very likely.

2.   A reliable analytical technique should be developed to

        analyze the amounts of DEA tied up in the form of heat-

        stable salts. These compounds cannot be detected by

        G.C. analysis and must be determined by wet chemistry

        methods (5, 11, 12, 29) which are time consuming. Perhaps

        physical properties such as the refractive index of DEA

        can be used to establish the DEA concentration.

3.   The identification of all other compounds detected by the

        present chromatographic technique is also desirable.

        Normally, a separation method, such as paper chromatography

        or TLC has to be used to isolate sufficient quantities of

        material for other instrumental methods such as M.S. and

        I.R.   High purity standards of HEOD and THEED should be

prepared or obtained from commercial suppliers which
specialize in synthesising rare chemicals.

4.   Atmospheric pressures tests should be resumed and carefully
controlled experiments should be carried out to elucidate
the DEA degradation process. It would be desirable to
find out whether DEA undergoes the same degradation
process with acid gases at low temperatures (but at a
very much slower rate) or an entirely different DEA
degradation process is taking place. The present study of
DEA degradation using the all glass equipment is inconclusive
but the inability to detect degradation products such
as HEP, X, Z etc. might mean that the DEA degradation
reaction at low temperature is entirely different than
the high temperature mechanism.

5.   More high pressure tests should also be performed using
better temperature control (to $\pm$ 0.5° C). Tests should
also be performed using initial DEA concentrations
ranging from about 5 to 40%. These experiments would be
helpful in explaining the present results obtained with
an initial DEA concentration of 10%.

6.   Isolation and identification of other degraded products present in the high pressure samples should be made so that the DEA degradation mechanism at high temperatures can be elucidated.

7.   The effect of pH, other acidic gases (CS_2 and COS) and metal surfaces on DEA degradation should be studied. Chemical additives, which may be used as degradation inhibitors, should also be examined.

8.   The effectiveness of activated carbon for cleaning degraded DEA solutions should be investigated.

IX   NOMENCLATURE

Symbol	Explanation and typical units
A	Frequency factor in the Arrhenius Eq. 18, hour^{-1}.
AEEA	Aminoethylethanolamine
AFS	Amps full scale
BSA	N,O-Bis-(trimethysilyl)acetamide
DEA	Diethanolamine
DECA	Decanolic acid
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
E_a	Activation energy in the Arrhenius Eq. 18, Cal g-mole^{-1}
G.C.	Gas chromatography
H	Peak height used for the triangulation Eq. 19, mm.
HEI	Hydroxyethyl imidazolidone
HEOD	3-(2-Hydroxyethyl)-2-oxazolidinone
HEP	N,N-Bis-(2-hydroxyethyl)piperazine

Symbol	Explanation and typical units
IR	Infrared
k_{DEA}	Overall reaction rate constant for Eq. 16, $hour^{-1}$
k_1'	Reaction rate constant for Eq. 20 & 21, $hour^{-1}$
k_1	Reaction rate constant for Eq. 21 & 22, $hour^{-1}$
k_2	Reaction rate constant for Eq. 23, cm^3 $g\text{-mole}^{-1}hour^{-1}$
M.S.	Mass spectroscopy
MDEA	N-Methyldiethandamine
MEA	Monoethanolamine
n_D^{20}	Refractive index at 20° C as measured by the Sodium D line
$\Delta n / \Delta t$	The change in refractive index value with respect to a change in temperature, $^{\circ} C^{-1}$
NMR	Nuclear magnetic resonance
OV	Trade name (Ohio Valley)
OZD	oxazolidone
R	Universal gas constant, 1.99 Cal $g\text{-mole}^{-1} {}^{\circ}K^{-1}$
R_f	A term used frequently in paper chromatography

Symbol	Explanation and typical units
	which is defined as the distance of sample spot from the origin divided by the distance travelled by the solvent front from the same origin.
SCF	Standard cubic foot
SCFD	Standard cubic foot per day
Sp. gr.	Specific gravity
Δ Sp. gr./Δt	The change in specific gravity value with respect to a change in temperature, $^{o}C^{-1}$.
S.T.P.	Standard temperature and pressure, 0° C and 760 mm Hg.
T	Absolute Temperature, ^{o}K
t	Time, hour
TEA	Triethanolamine
TEHEED	N,N,N',N'-Tetrakis-(hydroxyethyl)ethylenediamine
TFA	Trifluoroacetyl
THEED	N,N,N-Tris(2-hydroxyethyl)ethylenediamine
TLC	Thin layer chromatography
TMS	Trimethylsilyl
UV	Ultraviolet

Symbol	Explanation and typical units
W	Peak width used for the triangulation Eq. 19, mm
[ ]	Denotes concentration term, g-mole/ml
[ ]$_0$	Denotes concentration term for the initial solution, g-mole/ml
expr.	values obtained from experiments
ther.	values obtained from computer data fittings

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APPENDIX   A

GENERAL INFORMATION ON SIX G.C. ACTIVE PHASES RELEVANT TO DEA ANALYSIS

Once a choice has been made on whether a direct or derivative
G.C. technique should be used, the selection of suitable G.C. column
is the most critical factor to be considered. Usually packed
columns contain an inert support, e.g. Chromosorb, with a thin coating
of an active phase. Uniform particle sizes of the support (typically
40-120 mesh) give the highest efficiency and the active phase should
have a low viscosity and good selectivity for the mixture components
to be separated. A loading of 2 to 10% of the active phase is generally
used. The lower coating content can enable a column to give faster
separations at a lower temperature but also restrict the injected
sample capacity. The maximum column temperature is limited by the
onset of "bleeding" (i.e. volatilization of the active phase) or
reaction with the column support. The characteristics of six active
phases, which are relevant for DEA analysis, are summarized in
Table A-1 (18, 19, 31 51).

Table A-1: General information on active phases relevant to G.C. analysis of DEA solutions.

Name	Chemical Structure	Type	Maximum column temperature limit	Use	Recommended solvent	Suppliers
Neopentylglycol	$\left[\text{O-CH}_2\text{-C(CH}_3)_2\text{-CH}_2\text{-O-C(=O)-CH}_2\text{-CH}_2\text{-C(=O)-O-}\right]_n$	Mildly polar	$240°$ C	Separation of silylated derivatives which cannot be separated by non-polar phases.	methylene chloride, chloroform	Chromatographic Specialties Ltd.
OV-1	$\left[\text{Si(CH}_3)_2\text{-O}\right]_n$	Nonpolar dimethyl silicone gum	$325\text{-}375°$C	General G.C. separations and in biomedical research.	toluene, chloroform	Chromatographic Specialities Ltd.
OV-17	$\text{CH}_3\text{-Si(CH}_3)_2\text{-O-}\left[\text{Si(CH}_3)(\text{C}_6\text{H}_5)\text{-O}\right]_n\text{-Si(CH}_3)_2\text{-CH}_3$	Moderately polar 50% phenyl substituted phenyl methyl silicone	$350\text{-}375°$C	General G.C. separations particularly in biochemical research	toulene, chloroform	Chromatographic Specialties Ltd.

Table A-1:   General information on activie phases relevant to G.C. analysis of DEA solutions (continued).

Name	Chemical Structure	Type	Maximum column temperature limit	Use	Recommended solvent	Suppliers
OV-11	$CH_3-Si-O-[Si-O-]-[Si-O-]_n Si-CH_3$ (with CH_3 and phenyl/CH_3 substituents)	Mildly polar 35% phenyl methyl dimethyl silicone	$325-375^\circ C$	Separation of TMS-amino compounds	toulene, chloroform, acetone	Chromatographic Specialties Ltd.
Carbowax	$HO-[-CH_2-CH_2-O-]_n-H$	Polar polyglycol	$225^\circ C$	General G.C. separation.	methylene chloride	Supelco, Inc.
Tenax-GC	(porous diphenyl-p-phenylene oxide polymer structure) —O— [ ]$_n$ —OH	Porous, high molecular weight linear polymer based on 2, 6-diphenyl-p-phenylene oxide	$375-450^\circ C$	Separation of high boiling point polar compounds.	tetrahydro-furan, carbon disulphide, dioxane	Alltech Associates, Inc.

120

APPENDIX B

IR AND NMR SPECTRA OF DEA AND RELATED DEGRADATION PRODUCTS

Figures B-1 (a) & (b), and B-2 (a) & (b) give IR spectra of DEA, HEOD, HEP and TEHEED respectively. Once pure components can be isolated from the degraded DEA solutions, their identification by infrared spectroscopy should be very straight forward. Furthermore, other isolated components may also be characterized according to their functional groups (37, 41).

NMR spectroscopy has apparently not been considered for the analysis of DEA samples because of its complexity (52, 53) The main usage of NMR in organic chemistry is to provide information on the structural formula of compounds that have previously been analyzed by IR and MS and whose empirical formula and functional groups are therefore known.

Figure B-3 through B-5 are NMR spectra of DEA, HEP and HEOD respectively obtained from the Sadtler NMR Spectra (54). Since this instrument is also available in this laboratory, it may be used to confirm the findings of other characterization techniques by comparing the NMR spectrum of an isolated component to the published spectra of a list of possible compounds.
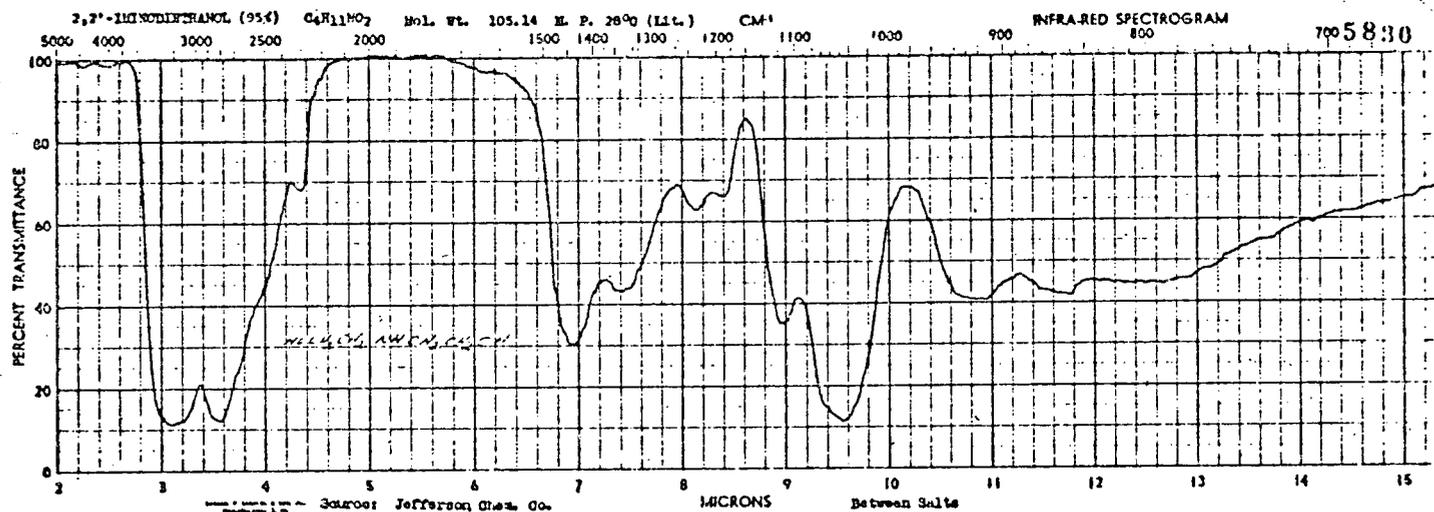
(a)
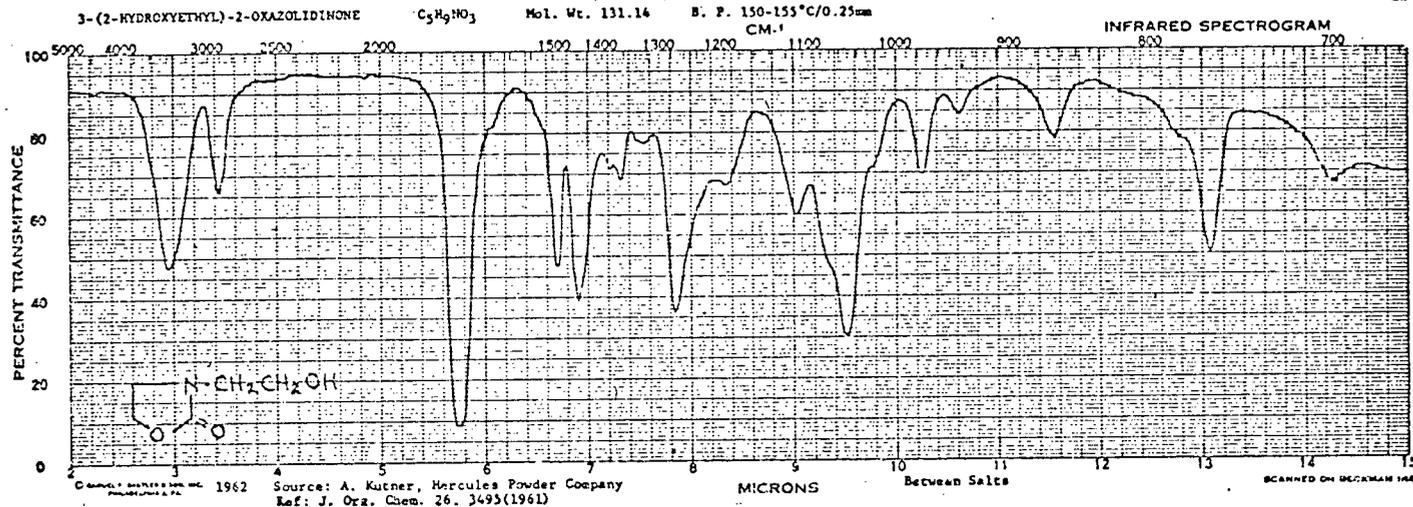
(b)

FIGURE B-1   IR spectra of (a) DEA and (b) HEOD.

1,4-PIPERAZINEDIETHANOL   C₈H₁₈N₂O₂   Mol. Wt. 174.25   INFRARED SPECTROGRAM

(a)

(ETHYLENEDINITRILO)TETRAETHANOL   C₁₀H₂₄N₂O₄   Mol. Wt. 236.32   INFRA-RED SPECTROGRAM   15047
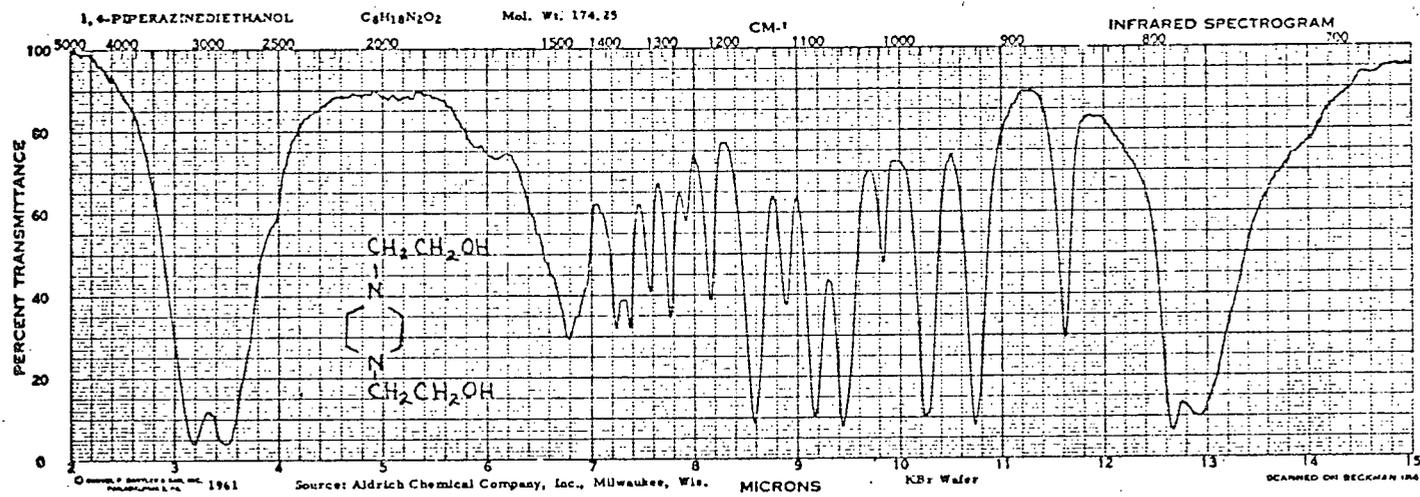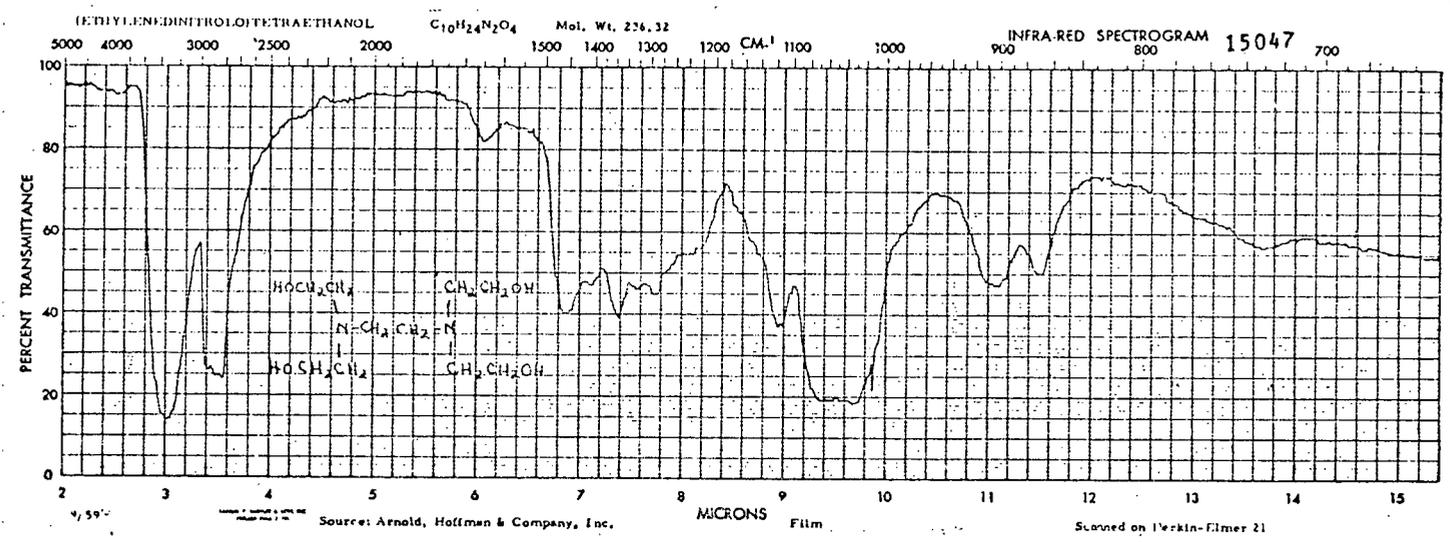
(b)

FIGURE B-2:   IR spectra of (a) HEP and (b) TEHEED.

DO-CH₂CH₂-ND-CH₂CH₂-OD
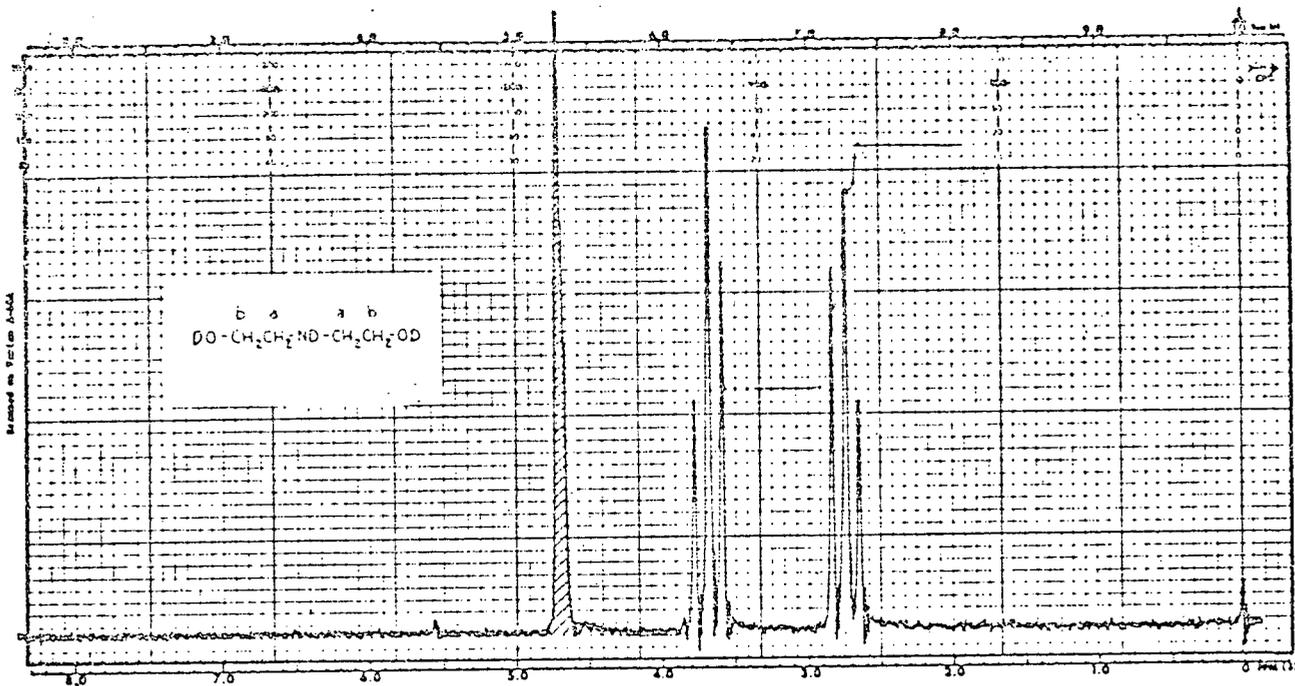
2,2'-IMINODIETHANOL

IR 5830; 10637

$C_4H_{11}NO_2$ Mol. Wt. 105.14   M. P. 28°C

Source: Jefferson Chemical Company, Inc.,
Houston, Texas

			ASSIGNMENTS		
Filter bandwidth:	4	cps	a	2.74	h
Sweep time:	250	sec	b	3.69	i
Sweep width:	500	cps	c	4.70 HDO	j
Sweep offset:	-	cps	d		k
Spectrum amp:	10		e		l
Integral amp:	80 (spec. amp. 3.2)		f		m
Conc. 60mg/0.5ml D₂O			g		n

FIGURE B-3:   NMR spectrum of partially deuterated DEA.

1,4-PIPERAZINEDIETHANOL
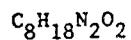
$C_8H_{18}N_2O_2$ 　　　　 Mol. Wt. 174.24

Source: Aldrich Chemical Company, Inc.,
　　　　　Milwaukee, Wisconsin

Filter bandwidth:	4	Hz	
Sweep time:	250	sec	
Sweep width:	500	Hz	
Sweep offset:	-	Hz	
Spectrum amp:	32		
Integral amp:	80 (spec. amp. 12.5)		
Solvent: Dimethyl sulfoxide-d_6			

ASSIGNMENTS

a	ca 2.40	h	
b	3.48	i	
c	4.25	j	
d	2.52 DMSO-d_5	k	
e	3.30 H_2O	l	
f		m	
g		n	
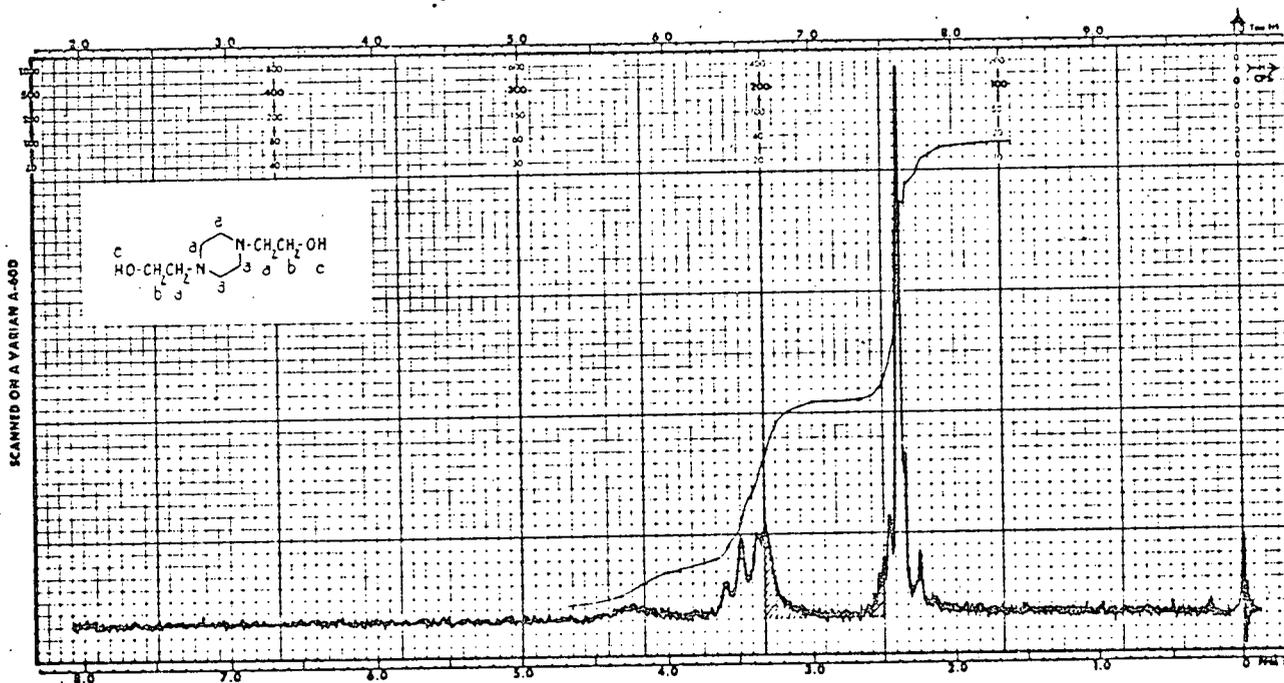
FIGURE B-4:　　NMR spectrum of HEP.
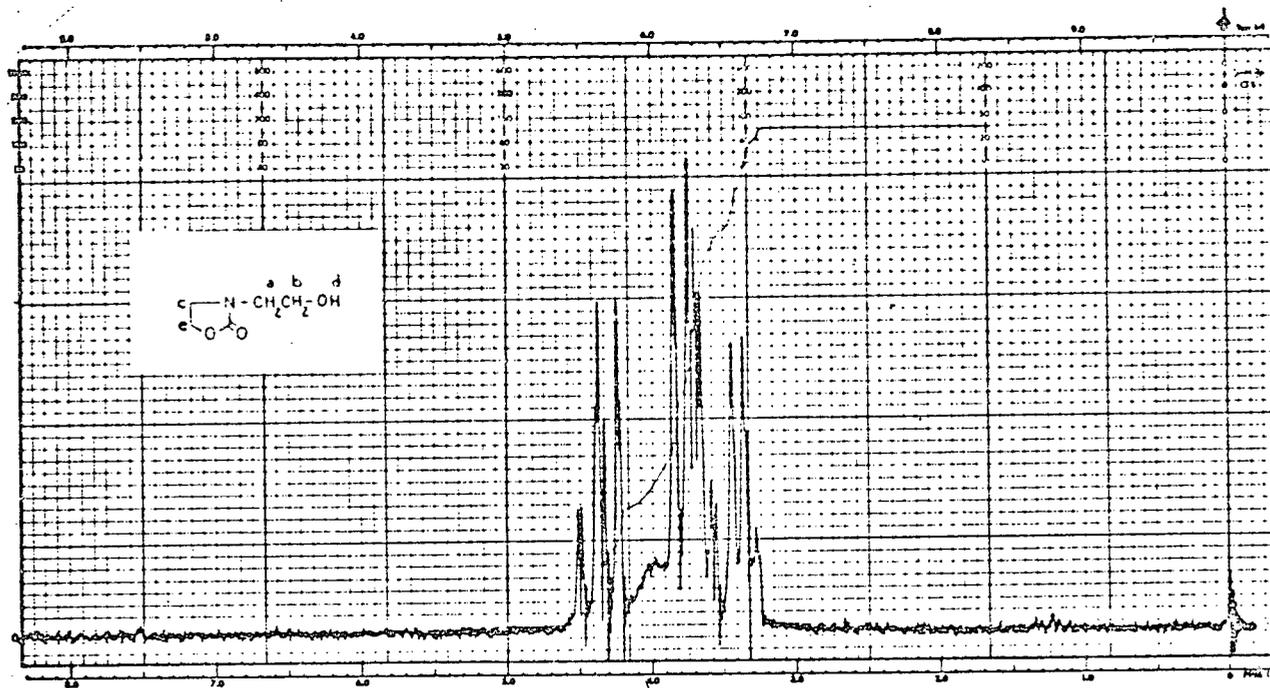
3-(2-HYDROXYETHYL)-2-OXAZOLIDINONE   IR 20793

$C_5H_9NO_3$ Mol. Wt. 131.13   B. P. 150-155°C/0.25mm

Source: A. Kutner, Hercules Powder Co.,
                    Wilmington, Delaware   ASSIGNMENTS

Filter Bandwidth:	4	cps	a 3.36
Sweep time:	250	sec	b 3.66
Sweep width:	500	cps	c 3.75
Sweep offset:	-	cps	d 3.99
Spectrum amp:	12.5		e 4.37
Integral amp:	80 (spec. amp. 1.6)		

Conc. 80mg/0.5ml CDCl₃

Filter Bandwidth: ___4___ cps   a ___3.36___   f _____
Sweep time: ___250___ sec   b ___3.66___   g _____
Sweep width: ___500___ cps   c ___3.75___   h _____
Sweep offset: ___-___ cps   d ___3.99___   i _____
Spectrum amp: ___12.5___   e ___4.37___   j _____
Integral amp: __80 (spec. amp. 1.6)__
Conc. 80mg/0.5ml CDCl₃

FIGURE B-5:   NMR spectrum of HEOD.

APPENDIX C

PAPER CHROMATOGRAPHIC SEPARATION OF SOME DEA DEGRADATION PRODUCTS

As Zimmerman (27) has reported, amino compounds can be
separated and identified by paper chromatography using very common
chemical reagents and detection techniques. Once the separation
has been accomplished, individual components can then be re-dissolved
in suitable solvents for further analysis by other analytical
techniques which are not suitable for mixtures.

Initial experiments with paper chromatography have achieved
some success with the separation and identification of DEA, HEP
and TEHEED. The procedure was as follows:

Whatman No. 1 filter paper was spotted with aqueous solutions
of the above compounds about an inch from the bottom. Then the
paper was lowered into a tank containing the solvent system: butanol,
4 parts/glacial acetic acid, 1 part/water, 5 parts/. After the
end of a run, the paper was withdrawn from the solvent tank and the
solvent front marked while still wet. Next, the paper was dried in
air and the paper was sprayed with 0.25 wt % ninhydrin in acetone
followed by heating at 105° C for 5 minutes to develop the chromatogram.

The DEA, HEP and TEHEED reacted with ninhydrin producing
spots of white, reddish brown and dark brown colours, respectively.
The separation of the three compounds was not too good but it was
believed that successful and effective separations could be achieved

by changing the polarity of the solvent and switching the stationary phase medium from paper to special TLC plates, thus minimizing the spreading of the spots (18, 36).

The successful development of TLC will enable the separation of individual components in aqueous solution, at room temperatures thus minimizing the possibility of sample decomposition and/or further degradation. Furthermore, the isolated compounds can then be subjected to IR and M.S. analyses without interferences from other components. These two techniques are often sufficient to identify and characterize unknown compounds.

APPENDIX D

A LISTING OF THE COMPUTER PROGRAM USED IN PREDICTING THE THEORETICAL CONCENTRATIONS OF DEA, HEP AND HEI AS WELL AS THE REACTION RATE CONSTANTS OF THE PROPOSED DEA DEGRADATION MODEL

```
 1      C       PROGR. NAME: EC3 (A.M., MARCH 1978)
 2      C       PROGR. CALCULATES DEA, HEOD AND HEP CONCENTRATIONS FOR
 3      C       GIVEN VALUES OF K1 AND K2
 4      C       REACTIONS:     DEA + CO2 -> HEOD + H2O     (RATE CONST. IS K1)
 5      C                      2HEOD  -> HEP + 2CO2        (RATE CONST. IS K2)
 6      C       LET CTHE(I,1),CEXP(I,1)=THEOR., EXP. CONC OF DEA AT I-1 HRS
 7      C           CTHE(I,2),CEXP(I,2)=THEOR., EXP. CONC OF HEOD AT I-1 HRS
 8      C           CTHE(I,3),CEXP(I,3)=THEOR., EXP. CONC OF HEP AT I-1 HRS
 9              COMMON /RATE/NDATA,KDEA,K1,K2
10              REAL KDEA,K1,K2
11              COMMON /OUT/CTHE(12,3),CEXP(12,3),EDEA(12),EHEP(12),SDEA,SHEP
12      C       READ TEMP. AND EXPERIMENTAL VALUES OF DEA,HEP
13              READ(5,1000)NDATA,TEMP,KDEA
14      1000    FORMAT(I2,2F10.1)
15              DO 100 I=1,NDATA
16              READ(5,2000)T,CEXP(I,1),CEXP(I,3)
17      2000    FORMAT(F7.1,2E15.5)
18      100     CONTINUE
19      C       READ VALUES OF K1 AND K2
20              READ(5,3000)K1,K2
21      3000    FORMAT(2F10.2)
22      C       ENTER SEARCH ROUTINE
23              CALL SEARCH
24      C       WRITTEN OUTPUT
25              WRITE(6,10000)TEMP,K1,K2
26      10000   FORMAT('1','TEMP=',F6.1,' DEGR.C',5X,'K1=',1PE14.5,' 1/HR',
27              15X,'K2=',E14.5,' CM**3/(GMOLE*HR)',//)
28              WRITE(6,1111)
29      1111    FORMAT(' HR DEA TH   DEA EXP   DEA DIF   HEOD',
30              14X,'HEP TH   HEP EXP   HEP DIF')
31              DO 400 I=1,NDATA
32              IT=I-1
33              IF(CEXP(I,1).GE.0.0.AND.CEXP(I,3).GE.0.0)GO TO 410
34              IF(CEXP(I,1).LT.0.0.AND.CEXP(I,3).LT.0.0)GO TO 420
35              IF(CEXP(I,1).LT.0.0.OR.CEXP(I,3).LT.0.0)GO TO 430
36      410     WRITE(6,12000)IT,CTHE(I,1),CEXP(I,1),EDEA(I),CTHE(I,2),
37              1CTHE(I,3),CEXP(I,3),EHEP(I)
38      12000   FORMAT(' ',I2,1PE9.2,6E9.2)
```

```
 39           GO TO 400
 40     420   WRITE(6,13000)IT,(CTHE(I,J),J=1,3)
 41   13000   FORMAT(' ',I2,1PE9.2,18X,2E9.2)
 42           GO TO 400
 43     430   IF(CEXP(I,1).GE.0.0)GO TO 440
 44           WRITE(6,14000)IT,CTHE(I,1),CTHE(I,2),CTHE(I,3),
 45          1CEXP(I,3),EHEP(I)
 46   14000   FORMAT(' ',I2,1PE9.2,18X,5E9.2)
 47           GO TO 400
 48     440   WRITE(6,15000)IT,CTHE(I,1),CEXP(I,1),EDEA(I),CTHE(I,2),
 49          1CTHE(I,3)
 50   15000   FORMAT(' ',I2,1PE9.2,4E9.2)
 51     400   CONTINUE
 52           WRITE(6,17000)SDEA,SHEP
 53   17000   FORMAT(/, 'SDEA=',1PE15.5,5X,'SHEP=',E15.5)
 54           STOP
 55           END
 56           SUBROUTINE SUBINT
 57   C       SUBR. SOLVES THE RATE EQUATIONS
 58           EXTERNAL FUNC
 59           COMMON /OUT/CTHE(12,3),CEXP(12,3),EDEA(12),EHEP(12),SDEA,SHEP
 60           DIMENSION C(3),F(3),G(3),S(3),T(3)
 61           COMMON /RATE/NDATA,KDEA,K1,K2
 62           REAL KDEA,K1,K2
 63           TI=0.
 64           C(1)=CEXP(1,1)
 65           C(2)=0.
 66           C(3)=CEXP(1,3)
 67           CTHE(1,1)=CEXP(1,1)
 68           CTHE(1,2)=0.
 69           CTHE(1,3)=CEXP(1,3)
 70           H=0.02
 71           HMIN=0.005
 72           E=1.0E-05
 73           ND1=NDATA-1
 74           DO 100 I=1,ND1
 75           TF=TI+1.
 76           CALL RKC(3,TI,TF,C,F,H,HMIN,E,FUNC,G,S,T)
 77           DO 120 J=1,3
 78     120   CTHE(I+1,J)=C(J)
 79     100   CONTINUE
 80           RETURN
 81           END
 82           SUBROUTINE FUNC(T,C,F)
 83           DIMENSION C(3),F(3)
 84           COMMON /RATE/NDATA,KDEA,K1,K2
 85           REAL KDEA,K1,K2
 86           K1=SQRT(K1*K1)
```

```
87              K2=SQRT(K2*K2)
88              F(1)=-KDEA*C(1)
89              F(2)=K1*C(1)-K2*C(2)**2
90              F(3)=(K2*C(2)**2)/2.
91              RETURN
92              END
93              SUBROUTINE SEARCH
94        C     ROUTINE PERFORMS SIMPLX SEARCH
95              COMMON /RATE/NDATA,KDEA,K1,K2
96              COMMON /OUT/CTHE(12,3),CEXP(12,3),EDEA(12),EHEP(12),SDEA,SHEP
97              REAL KDEA,K1,K2
98              DIMENSION XK(3,2),STEP(2)
99              EXTERNAL FUNCT
100             XK(1,1)=K1
101             XK(1,2)=K2
102             CALL SIMPLX(F,XK,3,3,STEP,1,50,25,1.E-6,FUNCT,&999)
103             GO TO 100
104       999   WRITE(6,1000)
105       1000  FORMAT(' SIMPLX SEARCH FAILED')
106       100   RETURN
107             END
108             FUNCTION FUNCT(XK,NDIMX,IZ)
109             DIMENSION XK(NDIMX,1)
110             REAL KDEA,K1,K2
111             COMMON /RATE/NDATA,KDEA,K1,K2
112             COMMON /OUT/CTHE(12,3),CEXP(12,3),EDEA(12),EHEP(12),SDEA,SHEP
113             K1=XK(IZ,1)
114             K2=XK(IZ,2)
115       C     CALL TO INTEGRATION SUBROUTINE
116             CALL SUBINT
117       C     ERROR CALCULATIONS FOR DEA AND HEP CONCS
118             SDEA=0.
119             SHEP=0.
120             DO 300 I=1,NDATA
121             IF(CEXP(I,1).LT.0.)GO TO 250
122             EDEA(I)=CTHE(I,1)-CEXP(I,1)
123             IF(CTHE(I,1).LE.0.0.OR.CEXP(I,1).LE.0.)GO TO 250
124             SDEA=SDEA+(CTHE(I,1)-CEXP(I,1))**2
125       250   IF(CEXP(I,3).LT.0.)GO TO 300
126             EHEP(I)=CTHE(I,3)-CEXP(I,3)
127             IF(CTHE(I,3).LE.0.0.OR.CEXP(I,3).LE.0.)GO TO 300
128             SHEP=SHEP+(CTHE(I,3)-CEXP(I,3))**2
129       300   CONTINUE
130             SHEP=SHEP*(1.0E+10)
131             FUNCT=SHEP
132             IF(ABS(K1).GT.0.32891)FUNCT=FUNCT+100.*ABS(K1)
133             RETURN
134             END
END OF FILE
```

APPENDIX E

INDUSTRIAL DEA SAMPLES

Thirty four DEA and two MEA gas-treating samples were received from Canadian natural gas processing plants and petroleum refineries. These samples were analyzed by the newly developed G.C. technique. Figure E-1 and E-2 show typical chromatogram of an industrial DEA sample analyzed by a G.C. column temperature of 142° C and 174° C respectively. In general, the chromatograms of industrial samples were found to be very similar to the high pressure DEA samples produced in laboratory tests, thus confirming that DEA and CO_2 react similarly under the two conditions.

For the low column temperature analysis (Fig. E-1), only the peak size of degradation products varied and this might have been caused by different operating conditions. As for the high column temperature analysis (Fig. E-2), the unidentified compound with an elution time of 33 minutes is missing from the industrial sample. Furthermore, the peak with an elution time of 42.6 minutes is very broad and irregular, thus indicating that more than one compound is eluted.

The results obtained for the 36 industrial samples are tabulated in Table E-1 together with a sample obtained from the UBC high pressure test. In the latter case (sample #37), a 30% DEA solution was subjected to pure CO_2 for 4 hours at a temperature and pressure of 185° C and 600 psig, respectively.
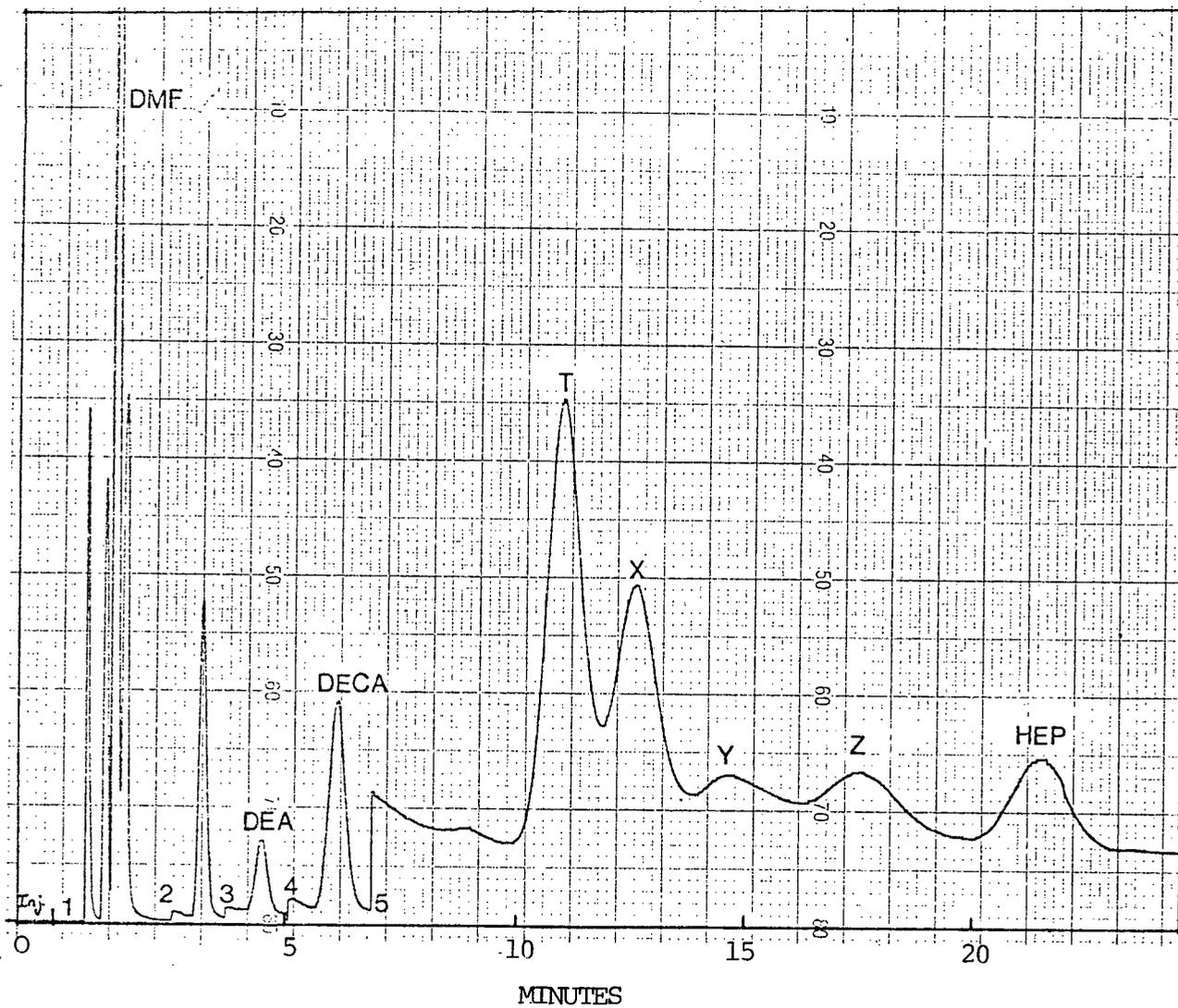
FIGURE E-1: Typical chromatogram of a DEA gas-treating sample obtained from industrial source. (Sensitivity: $1-512 \times 10^{-10}$ AFS; $2-32 \times 10^{-10}$ AFS; $3-8 \times 10^{-10}$ AFS; $4-32 \times 10^{-11}$ AFS; $5-32 \times 10^{-12}$ AFS. Condition as given in Table 10.)
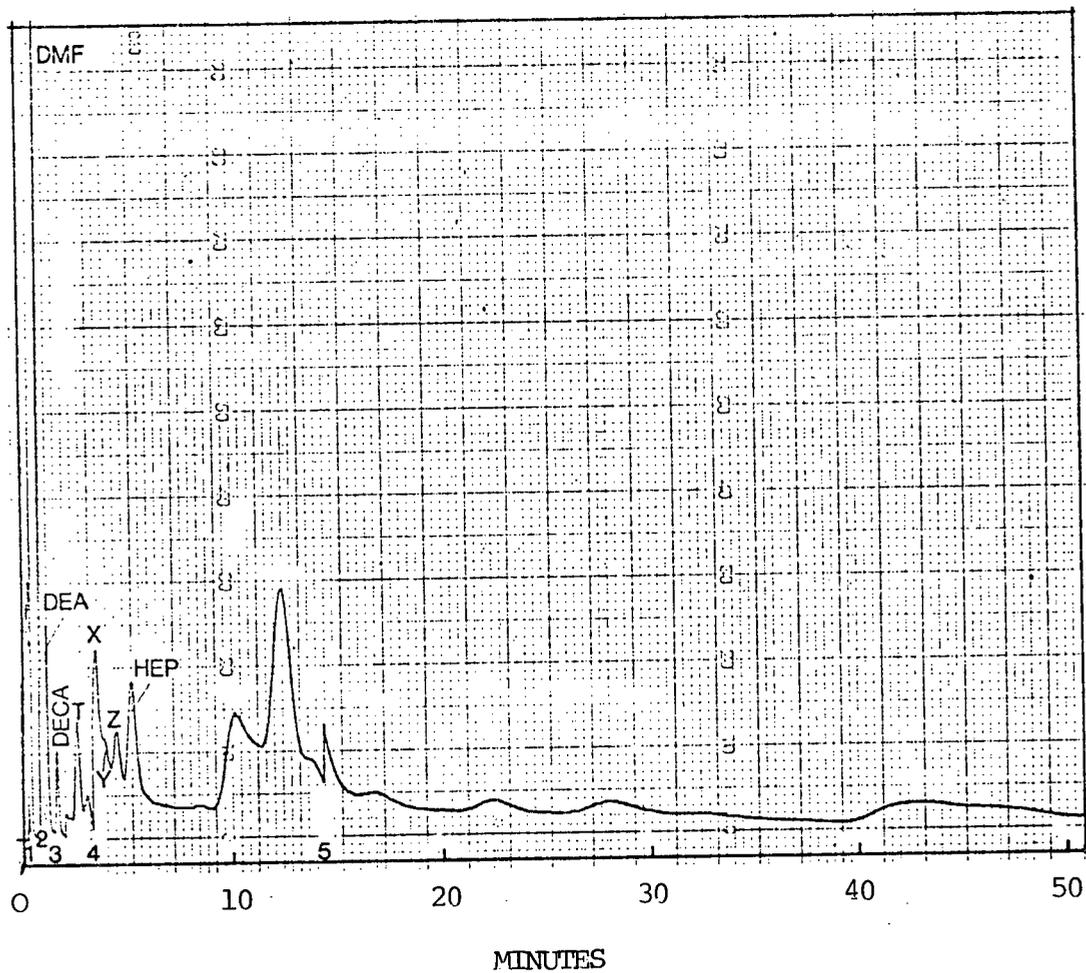
FIGURE E-2: Typical chromatogram of a DEA gas-treating sample obtained from an industrial source. (Sensitivity: $1-512 \times 10^{-10}$ AFS; $2-4 \times 10^{-10}$ AFS; $3-32 \times 10^{-11}$ AFS; $4-64 \times 10^{-12}$ AFS; $5-32 \times 10^{-12}$ AFS. Condition as given in Table 10 with the column temperature at 174° C.)

TABLE E-1: Analysis of industrial DEA gas-treating samples.

SAMPLE # PLANT	SOURCE	APPEAR-ANCE	ABSORBER TEMP °F / PRES PSIG	REGENERATOR TEMP °F / PRES PSIG / HEAT SOURCE	AMINE FILTER	CONCENTRATION DEA GMOLE/ML	HEP GMOLE/ML	T	X	Y	Z
1	BULK REMOVAL ABSORBER BL. PPT	CLEAR, YELLOW	250–875 / 255 950	47 / 55 PSIG / STEAM	PRECOAT TYPE OF DIATOMITE +ASBESTOS	0.00E-01	1.11E-04	2.5900	1.5200	0.0373	0.8100
2	BULK REMOVAL ABSORBER BL. PPT	CLEAR, YELLOW	250–875 / 255 950	47 / 55 PSIG / STEAM	PRECOAT TYPE OF DIATOMITE +ASBESTOS	3.13E-05	9.38E-05	1.2000	1.5300	0.0469	0.6200
3	FOLLOW UP TRIM ABSORBER BL. PPT	CLEAR, YELLOW	245–875 / 250 950	47 / 55 PSIG / STEAM	PRECOAT TYPE OF DIATOMITE +ASBESTOS	0.00E-01	1.11E-04	2.3500	1.0300	0.0117	0.5340
4	FOLLOW UP TRIM ABSORBER BL. PPT	CLEAR, GREEN	245–875 / 250 950	47 / 55 PSIG / STEAM	PRECOAT TYPE OF DIATOMITE +ASBESTOS	0.00E-01	1.04E-04	1.7900	0.8310	0.0209	0.6400
5		YELLOW	940 / 250 265	HOT OIL	CARTRIDGE FILTER + A.C. CARBON BED	0.00E-01	1.60E-05	0.5890	0.9310	0.0388	0.1750
6		CLEAR, GREEN–YELLOW	950,250 / 100 255	50 PSIG / STEAM	ASBESTOS + DIATOMACEOUS EARTH FILTER	1.44E-04	4.00E-06	3.1700	1.4100	0.0000	0.5060
7	FILTER DISCHAR BL. PPT GE OF #1 TRAIN	YELLOW, BL. PPT	117–1200,249 / 125 800 300	150–55 PSIG / 254 200 STEAM	LEAF FILTER	1.69E-04	7.50E-06	3.3400	1.5200	0.0421	0.2820
8	FILTER DISCHAR BL. PPT GE OF #2 TRAIN	YELLOW, BL. PPT	117–1200,249 / 125 600 300	150–55 PSIG / 254 200 STEAM	LEAF FILTER	2.00E-04	8.94E-06	2.8400	1.9600	0.0393	0.3930
9		CLEAR, YELLOW				2.31E-04	7.69E-06	2.3000	0.7170	0.0298	0.4840
10		CLEAR, YELLOW				8.13E-05	1.66E-05	2.5800	1.0100	0.0327	1.4900
11		CLEAR, BROWN–YELLOW				4.38E-05	5.75E-06	1.7600	0.6640	0.7400	1.9300

TABLE E-1: Analysis of industrial DEA gas-treating samples.   (continued)

12		*CLEAR, *BROWNISH*								*5.94E-04*	1.64E-05*	2.0200*	0.5580*	0.7240*	4.1500*
13		*CLEAR, *YELLOW								*2.52E-03*	1.38E-06*	3.4700*	0.3910*	0.0299*	0.0840*
14		*CLEAR, *YELLOW								*3.75E-05*	4.17E-05*	1.9600*	0.8090*	0.1330*	1.4300*
15		*YELLOW, *BL. PPT	*110*	910*	190*	12	*STEAM	*CELITE 545 *LEAF FILTER** *ACTIVATED *CARBON FILT.*	*1.44E-04*	2.58E-05*	2.2600*	0.6810*	0.0888*	0.2080*
16	*SALES *GAS FAC- *ILITY *STAGE 5	*CLOUDY, *YELLOW		950*	258- 265*		*65 PSIG *STEAM	*SOCK FILTER **CARBON *TREATING	*8.13E-05*	1.91E-04*	2.2700*	0.8370*	0.0156*	0.1200*
17	*FUEL GAS *TREATING *FACILITY	*CLEAR, *BROWN		*175- 210*	225*		*GAS	*PRECOAT * *DIA. EARTH+ *SOCK FILTER	*1.56E-05*	8.00E-06*	1.7000*	0.3520*	0.0214*	0.4340*
18	*H2S *STRIPPER *PET.REF.	*REDDISH- *YELLOW *BL. PPT							*1.83E-03*	3.75E-07*	0.6620*	0.0867*	0.1880*	0.6210*
19	*H2S *STRIPPER *PET.REF.	*REDDISH- *YELLOW *BL. PPT							*2.21E-03*	3.13E-07*	0.7790*	0.0900*	0.2750*	0.6070*
20	*STAGE II *EX FIL- *TER	*CLEAR, *GREEN- *YELLOW							*0.00E-01*	3.52E-05*	2.6700*	0.3640*	0.1940*	2.5400*
21	*STAGE II *EX SURGE *TANK	*CLEAR, *GREEN- *YELLOW							*4.38E-05*	3.21E-05*	3.4300*	0.7340*	0.3270*	1.6900*
22	*SURGE *TANK	*CLOUDY, *YELLOW, *BL. PPT							*3.13E-05*	2.59E-05*	1.7700*	0.4720*	0.1380*	1.0200*
23	*PLANT #1	*CLEAR, *YELLOW							*9.38E-05*	5.13E-06*	1.7800*	0.4930*	0.0105*	0.0415*
24	*PLANT #2	*CLEAR, *YELLOW, *BL. PPT							*8.75E-05*	1.63E-05*	1.2400*	0.2830*	0.0185*	1.0100*

TABLE E-1: Analysis of industrial DEA gas-treating samples. (continued)

25	*PLANT #1	*CLEAR, *DARK *BROWN	*118- * 165	*240- *1050*	*192-* 251*	14	*STEAM	*LEAF FILTER	*2.22E-03	*2.75E-06*	1.3400*	0.0905*	0.5910*	3.1200*
26	*PLANT #2	*CLEAR, *DARK *BROWN	*118- * 165	*240- *1050*	*192-* 251*	14	*STEAM	*LEAF FILTER	*2.29E-03	*5.81E-06*	3.1200*	0.1610*	0.4130*	3.2500*
27		*CLEAR, *BR.-YELL*							*6.88E-05	*5.19E-05*	2.9400*	1.2900*	0.0592*	0.4030*
28		*GREEN- *YELLOW, *BL. PPT	*150- * 950*	* 210*	14		*HOT OIL	*LEAF+CARBON *FILTER	*4.38E-05	*2.45E-05*	1.5100*	2.3600*	0.0000*	0.1460*
29		*BROWN- *YELLOW *BL. PPT	* 99- * 130*	*123- * 930*	*190- 244*	*11.5	*STEAM	*LEAF,CARBON *SOCK FILTER	*3.75E-05	*7.25E-06*	2.8200*	1.0600*	0.5680*	1.9500*
30	*MEA UNIT *PET.REF.	*GREEN- *YELLOW, *BL. PPT							*0.00E-01	*0.00E-01*	0.0000*	0.0000*	0.0000*	0.0000*
31	*MEA RE- *CLAIMER *PET.REF.	*GREEN- *HEAVY *BL. PPT							*0.00E-01	*0.00E-01*	0.0000*	0.0000*	0.0000*	0.0000*
32	*PET.REF.	*CLEAR, *GOLDEN- *YELLOW							*2.38E-04	*4.38E-07*	0.2520*	0.2600*	1.4400*	0.0790*
33	*REGENE- *RATOR *PET.REF.	*CLEAR, *YELLOW							*2.11E-03	*1.56E-06*	1.9000*	0.0395*	3.7500*	0.0372*
34		*CLEAR, *YELLOW	*100- * 106*	21- 500*	*231- 236*		*H2O+GLY- *COL	*SOCK FILTER	*1.88E-04	*1.06E-06*	1.1100*	0.9430*	0.9500*	0.0653*
35		*CLEAR	* 108*	090*	184- 202*	*10.5	*STEAM	*LEAF,CARBON *SOCK FILTER	*9.38E-05	*6.31E-06*	2.5200*	0.6820*	0.0314*	2.5200*
36		*CLOUDY *YELLOW							*1.90E-03	*1.56E-06*	0.5320*	0.5520*	0.0184*	0.1120*
37	*UOC LAB.	*YELLOW	* 365*	600*					*9.38E-05	*3.26E-05*	0.0000*	0.6350*	0.0740*	5.5900*

NOTE: CONCENTRATIONS OF T,X,Y,Z ARE EXPRESSED AS RATIO OF THEIR PEAK AREAS TO AREA OF DECANOLIC ACID INTERNAL STANDARD