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DISPOSAL OF  
HYPERGOLIC PROPELLANTS

Task 4 Report  
Disposal Pond Products

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by

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## PREFACE

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## 1. Abstract

The waste MMH scrubber liquor will consist of aqueous solutions containing small amounts of  $\text{CH}_4$ ,  $\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  as well as large amounts of  $\text{CH}_3\text{OH}$ . This waste is scheduled to be disposed of in stabilization ponds along with nitrate and nitrite salt solutions obtained as waste liquors from the  $\text{N}_2\text{O}_4$  scrubbers.

Task 4 is concerned with determining what possible hazardous materials can be generated by such combinations of items as described above as well as the finite lifetime of such materials in the stabilization ponds. The most useful analytical tool to investigate these problems is the Gas Liquid Chromatograph (GLC). This report is a compilation of data obtained to date which is necessary for performing the GLC analyses of the above materials as well as possible pond products. Also included in this report is a series of experiments designed to convert nitrate and nitrite salts to the environmentally innocuous  $\text{N}_2\text{O}$  and  $\text{N}_2$  using solar energy. These last experiments were designed to yield information which may be useful in 1) determining the final size and number of holding ponds required and 2) ameliorating the toxic effects of nitrate and nitrite on the pond biota.

## 2. Introduction

The Task 4 statement of work entitled "Disposal Pond Products" reads as follows:

"Investigate the various products which can be generated by hypergol waste disposal ponds, to determine safety and ecological effects and countermeasures. Define alternatives and compare results. Perform experimental procedures to verify concepts and to obtain reliable data for evaluation. Coordinate this task with Task 3 to maximize results from both tasks."

In order to investigate the various products which can be generated by hypergol disposal ponds, several analytical techniques must be employed. The most important of these is gas-liquid chromatography (GLC) which is used most often to determine concentrations of relatively volatile organic compounds. It is envisioned that if any of the hypergol wastes are added to the Disposal Pond (DP) and converted by sunlight or plant metabolism to toxic or carcinogenic materials, the presence of such products should be found upon GLC analyses of the pond water. GLC analyses can also be used to determine the concentrations of hypergol wastes remaining in the DP at the end of various time intervals. For example, it has been established that the products of the scrubbing reaction of MMH and NaOCl are  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CH}_4$ . All these products can be considered volatile and thus will evaporate in the DP. Therefore, it seems reasonable to suppose that these materials will not be present in appreciable concentrations after several days. Thus it is anticipated that the vast majority of these substances will be evaporated or incorporated into the plant life before the next load of hypergol waste from the scrubber is introduced into the DP. However, it is necessary to verify all this by proper experimentation and GLC analyses.

Also, a procedure for flushing MMH from tanks and pipelines has been in operation at KSC for many years. This procedure calls for the use of isopropyl alcohol (IPA) as the flushing agent. Information has been obtained that in the past MMH contaminated IPA has been dumped in various ponds at KSC with little thought as to the eventual environmental consequences of such action. Since the Shuttle operations will necessarily involve far more IPA flushing than has been used in the past, alternative disposal schemes must be studied, evaluated, and initiated. A previous study conducted by FIT has demonstrated the feasibility of recovering pure IPA from MMH contaminated IPA. This procedure would allow reuse of the IPA and conversion of MMH to an environmentally innocuous heterocycle. However, although this procedure has been found to work well on a laboratory scale, and has been found to be economically feasible, it has not been tested on a larger scale. Therefore, the possibility arises that at least some quantity of MMH contaminated IPA may be dumped into a disposal pond. Hence, it is necessary to develop analytical techniques for IPA in order know 1) at what concentration IPA is harmful to the plant and animal biota in the disposal pond and 2) the rate of evaporation of IPA from the pond. Thus, IPA was added to the prototype disposal pond (PDP) and GLC analyses were made at periodic intervals. Unfortunately, since our MMH addition procedure had not been approved by KSC at the time, we could not add MMH to the PDP.

### 3. GLC Standard Curves for MMH Waste Scrubber Liquor Products

In establishing the standard curves, it is known that the peak area drawn on the recorder is proportional to the concentration of the compound being ionized by the flame in the GLC. The peak area ( $\text{cm}^2$ ) is calculated by triangulation:

$$\frac{1}{2} \text{ Base (cm) } \times \text{ Height (cm) } = \text{ Area (cm}^2\text{)}$$

Once the concentration is known for two or more samples, a slope on a graph can be established, which can be used to measure an unknown concentration.

The conditions for the GLC analyses were as follows:

1. Instrument: Varian Aerograph 2400 with a Beckman 10" recorder
2. Column: Poropak Q, 80/100 S.S., 8'x1/8"
3. Temperature Settings: Injector 160°C  
Detector 250°C  
Column 145°C  
No temperature program
4. Flow rates: He 40 ml/min  
Air 400 ml/min  
H<sub>2</sub> 30 ml/min

Ethanol (EtOH) was used as an internal standard. The conditions were those established for C<sub>1</sub>-C<sub>6</sub> alcohols as presented in McNair and Bonnell's Basic Gas Chromatography (p. 62, 5th ed., Consolidated Printers, Berkeley, Calif., March 1969). Certain modifications were made for optimizing results in this laboratory.

The concentration of solvent is expressed as  $\mu\text{g/ml}$  in order to be directly proportional to the area under the peak.

The preparation of standards was accomplished by accurately weighing

out on analytical balance 100.0 mg of each standard into a volumetric flask. The initial addition of the alcohols (methanol, ethanol, and isopropanol) removes the insolubility problem of chloroform and methylene chloride in water. This solution is then diluted to a final volume of 10 mls with water. This provides a 10,000 ug/ml (ppm) solution of each of the five standards.

The working solutions used to prepare the standard curve were prepared from the 10,000 ug/ml stock solution by diluting as follows:

- a. 1 ml of stock solution diluted to 10 ml final volume with water = 1000 ug/ml.
- b. 5 ml of stock solution diluted to 100 ml final volume with water = 500 ug/ml.
- c. 1 ml of stock solution diluted to 100 ml final volume with water = 100 ug/ml.

Taking the sample peak for methanol from Run #631, test 4-5-20N, the peak area is calculated by triangulation to be 33.945 cm<sup>2</sup> at a range and attenuation of  $2 \times 10^{-12}$  at a known concentration of 100 ug/ml. If the range is not 1, concentration is divided by the range (2). 50 ug/ml is plotted versus 33.945 cm<sup>2</sup> on the graph.

These data points are used to establish the slope of the standard curve in the following manner. The median and mean are determined for the peak areas for samples of each material. The variant peak area for each sample point is determined. If the variant for a particular sample is very large, it is discarded until the mean approaches the median. The finalized average peak area per unit concentration then becomes the slope ratio. The slope ratio is then multiplied by three or more integers within the range of probable concentrations to derive the plotting points for the standard curve.

The GLC data used in plotting the standard curves are shown in Table 1. The calculations used in plotting the standard curves are shown on subsequent pages.

Table 1. Data Utilized in Establishing Standard Curves for MeOH, EtOH, CH<sub>2</sub>Cl<sub>2</sub>, IPA and CHCl<sub>3</sub>

Run	Test	Atten x 10 <sup>-12</sup>	Conc.ppm	Sample ID	Base cm	Ht cm	Area cm <sup>2</sup>
607	4-5-19A	16	1000	MeOH	4.9	21.9	53.655
				CHCl <sub>3</sub>	4.1	11.7	23.985
608	4-5-19B	16	1000	CHCl <sub>3</sub>	4.1	20.8	42.640
609	4-5-19C	16	1000	CHCl <sub>3</sub>	3.9	14.9	29.005
610	4-5-19D	32	1000	MeOH	1.1	15.1	8.305
611	4-5-19E	8	1000	CHCl <sub>3</sub>	4.1	24.7	50.635
612	4-5-19F	32	1000	MeOH	1.1	17.9	9.845
				CH <sub>2</sub> Cl <sub>2</sub>	1.6	31.1*	24.880
				CHCl <sub>3</sub>	5.1	7.8	19.890
613	4-5-19G	64	1000	MeOH	1.2	6.5	3.900
				EtOH	1.1	24.2	13.310
				CH <sub>2</sub> Cl <sub>2</sub>	1.7	12.2	10.370
				CHCl <sub>3</sub>	3.9	3.0	5.850
614	4-5-19H	128	1000	MeOH	1.1	4.0	2.200
				EtOH	1.0	16.5	8.250
				CH <sub>2</sub> Cl <sub>2</sub>	1.7	10.2	8.670
				IPA	1.8	19.8	17.820
				CHCl <sub>3</sub>	4.0	2.5	5.000
615	4-5-19I	64	1000	MeOH	1.2	6.6	3.960
				EtOH	1.2	26.0	15.600
				CH <sub>2</sub> Cl <sub>2</sub>	1.6	18.6	14.880
				CHCl <sub>3</sub>	3.7	4.8	8.880
617	4-5-19K	256	1000	MeOH	1.4	1.7	1.190
				EtOH	1.1	7.2	3.960
				CH <sub>2</sub> Cl <sub>2</sub>	1.6	4.7	3.760
				IPA	1.9	9.4	8.930
				CHCl <sub>3</sub>	3.5	1.1	1.925
618	4-5-20A	128	1000	MeOH	1.2	3.3	1.980
				EtOH	0.9	16.2	7.290
				CH <sub>2</sub> Cl <sub>2</sub>	1.8	7.7	6.9300
				IPA	1.8	19.4	17.460
				CHCl <sub>3</sub>	6.0	2.2	6.600
619	4-5-20B	128	500	MeOH	1.6	0.8	0.640
				EtOH	1.3	5.4	3.510
				CH <sub>2</sub> Cl <sub>2</sub>	1.6	3.9	3.120
				IPA	3.0	8.2	8.200
				CHCl <sub>3</sub>	3.3	0.9	1.485

Table 1 (cont.) Data Utilized in  
Establishing standard curves for  
MeOH, EtOH, CH<sub>2</sub>Cl<sub>2</sub>, IPA and CHCl<sub>3</sub>

Run	Test	Atten. x 10 <sup>-12</sup>	Conc. ppm	Sample ID	Base cm	Ht. cm	Area cm <sup>2</sup>
620	4-5-20C	64	500	MeOH	1.7	2.8	2.380
				EtOH	1.2	10.4	6.240
				CH <sub>2</sub> Cl <sub>2</sub>	1.1	7.5	4.125
				IPA	1.9	16.3	15.485
				CHCl <sub>3</sub>	4.0	2.0	4.000
621	4-5-20D	32	500	MeOH	1.7	16.8	14.280
				EtOH	1.4	20.5	14.350
				CH <sub>2</sub> Cl <sub>2</sub>	1.7	14.3	12.155
				CHCl <sub>3</sub>	4.4	13.5	17.700
622	4-5-20E	16	500	MeOH	1.3	13.0	8.450
				CH <sub>2</sub> Cl <sub>2</sub>	1.8	24.1	21.690
				CHCl <sub>3</sub>	4.4	6.2	13.640
623	4-5-20F	8	500	MeOH	1.4	25.9	18.130
				CHCl <sub>3</sub>	4.0	10.5	21.000
624	4-5-20G	4	500	CHCl <sub>3</sub>	4.3	19.9	42.785
625	4-5-20H	64	100	CH <sub>2</sub> Cl <sub>2</sub>	1.9	1.0	0.950
				IPA	3.3	1.8	2.970
626	4-5-20I	32	100	MeOH	1.5	3.6	2.700
				CH <sub>2</sub> Cl <sub>2</sub>	2.0	3.0	3.000
				IPA	3.5	3.4	5.950
627	4-5-20J	16	100	MeOH hidden			
				EtOH	4.7	3.7	8.695
				CH <sub>2</sub> Cl <sub>2</sub>	2.1	6.4	6.720
				IPA	3.5	7.3	12.775
629	4-5-20L	8	100	MeOH hidden			
				EtOH	4.4	4.8	10.560
				CH <sub>2</sub> Cl <sub>2</sub>	2.0	7.4	7.400
				IPA	3.3	11.9	19.635
630	4-5-20M	4	100	MeOH	3.6	9.5	17.100
				EtOH	5.5	11.2	30.800
				CH <sub>2</sub> Cl <sub>2</sub>	2.1	18.2	19.110
				IPA	3.1	29.1	45.105
				CHCl <sub>3</sub>	5.7	4.0	11.400
631	4-5-20N	2	100	MeOH	3.1	21.9	33.945
				EtOH	5.3	23.5	62.275
				CHCl <sub>3</sub>	7.3	10.9	39.785

a. Ethanol

Pertinent Calculations for GLC Standard Curves for Ethanol

Column retention time is 2.6 to 3.4 minutes

Molecular weight: 46.07

Density: 0.7893 x 95% strength = 0.7498

1. Peak Areas for Ethanol

<u>Conc (ppm)</u>	<u>Attenuation x Range</u>	<u>Area (cm<sup>2</sup>)</u>
100	2 x 10 <sup>-12</sup>	62.275
	4 x 10 <sup>-12</sup>	30.800
	8 x 10 <sup>-12</sup>	10.560
	16 x 10 <sup>-12</sup>	8.695
500	32 x 10 <sup>-12</sup>	14.350
	64 x 10 <sup>-12</sup>	6.240
	128 x 10 <sup>-12</sup>	3.510
1000	64 x 10 <sup>-12</sup>	13.310
	64 x 10 <sup>-12</sup>	15.600
	128 x 10 <sup>-12</sup>	7.290
	128 x 10 <sup>-12</sup>	8.250
	256 x 10 <sup>-12</sup>	3.960

2. Calculating ug at attenuation of 1

<u>Conc (ppm)</u>	<u>Conc (ug/ml)/Attenuation</u>	<u>Conc at Attenuation 1</u>	<u>Area (cm<sup>2</sup>)</u>
100	100/2	50.0	62.275
	100/4	25.0	30.800
	100/8	12.5	10.560
	100/16	6.3	8.695
500	500/32	15.6	14.350
	500/64	7.8	6.240
	500/128	3.9	3.510
1000	1000/64	15.6	13.310
	1000/64	15.6	15.600
	1000/128	7.8	7.290
	1000/128	7.8	8.250
	1000/256	3.9	3.960

3. Comparison of ug/ml to cm<sup>2</sup>

<u>ug/ml</u>	<u>cm<sup>2</sup></u>	<u>cm<sup>2</sup>/ug/ml</u>
3.9	3.960	1.015
3.9	3.510	.900
6.3	8.695	1.380
7.8	7.290	.935
7.8	8.250	1.058
7.8	6.240	.800
12.5	10.560	.845
15.6	15.600	1.000
15.6	13.310	.853
15.6	14.350	.920
25.0	30.800	1.232
50.0	62.275	1.246
		<u>12.184</u>
		12

4. Data Finalization for Plotting Slope

a. Summation

Number of samples (n) = 12

$$\Sigma \text{cm}^2/\text{ug/ml} = 12.184$$

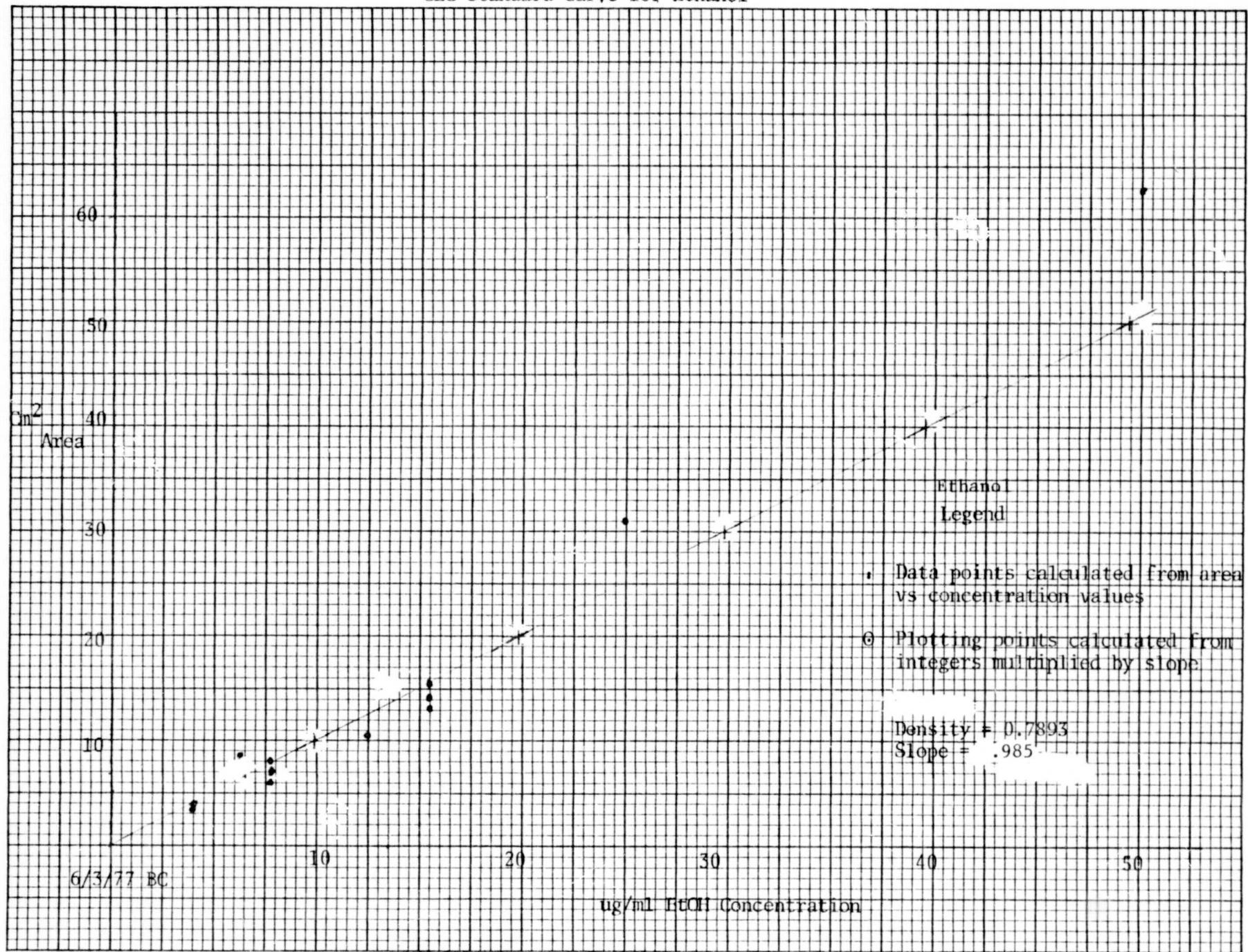
b. Slope n/Summation

$$\text{average cm}^2/\text{ug/ml} = .985$$

c. Plotting points. Area vs concentration

10 cm <sup>2</sup>	:	9.850 ug/ml
20	:	19.700
30	:	29.550
40	:	39.400
50	:	49.250

GLC Standard Curve for Ethanol



10.

Fig. 1

b. Isopropyl Alcohol (IPA)

Pertinent Calculation for GLC Standard Curves for IPA

Column retention time is 5.1 to 5.6 minutes

Molecular weight: 60.09

Density: 0.7954

1. Peak Areas for IPA

<u>Conc (ppm)</u>	<u>Attenuation x Range</u>	<u>Area (cm<sup>2</sup>)</u>
100	4 x 10 <sup>-12</sup>	45.105
	8 x 10 <sup>-12</sup>	19.635
	16 x 10 <sup>-12</sup>	12.775
	32 x 10 <sup>-12</sup>	5.950
	64 x 10 <sup>-12</sup>	2.970
500	64 x 10 <sup>-12</sup>	15.485
	128 x 10 <sup>-12</sup>	8.200
1000	128 x 10 <sup>-12</sup>	17.460
	128 x 10 <sup>-12</sup>	17.820
	256 x 10 <sup>-12</sup>	8.930

2. Calculating ug/ml at attenuation of 1

<u>Conc. ppm</u>	<u>Conc. (ug/ml)/Atten.</u>	<u>Conc. at Atten. 1</u>	<u>Area (cm<sup>2</sup>)</u>
100	100/4	25.0	45.105
	100/8	12.5	19.635
	100/16	6.3	12.775
	100/32	3.1	5.950
	100/64	1.6	2.970
500	500/64	7.8	15.485
	500/128	3.9	8.200
1000	1000/128	7.8	17.460
	1000/128	7.8	17.820
	1000/256	3.9	8.930

3. Comparison of ug/ml to cm<sup>2</sup>

<u>ug/ml</u>	<u>cm<sup>2</sup></u>	<u>cm<sup>2</sup>/ug/ml</u>
1.6	2.970	1.856
3.1	5.950	1.919
3.9	8.200	2.103
3.9	8.930	2.290
6.3	12.775	2.028
7.8	15.485	1.985
7.8	17.460	2.238
7.9	17.820	2.285
12.5	19.635	1.571
25.0	45.105	1.804

4. Data finalization for plotting slope

a. Summation:  $\text{cm}^2/\text{ug/ml} = 20.078$       Number of samples (n)=10

b. Slope: average  $\text{cm}^2/\text{ug/ml} = .498$

c. Plotting points. Area vs concentration

5 $\text{cm}^2$	:	2.490 ug/ml
10	:	4.980
20	:	9.960
25	:	12.450
30	:	14.940

c. Methanol

Pertinent Calculations for GLC Standard Curve for Methanol

Column retention time is 1.2 to 1.5 minutes

Molecular weight: 32.04      Density: 0.7928

1. Peak Areas for Methanol

<u>Conc (ppm)</u>	<u>Attenuation x Range</u>	<u>Area (<math>\text{cm}^2</math>)</u>
100	2 x $10^{-12}$	33.95
	4 x $10^{-12}$	17.100
	32 x $10^{-12}$	2.700
500	8 x $10^{-12}$	18.130
	16 x $10^{-12}$	8.450
	32 x $10^{-12}$	14.280
	64 x $10^{-12}$	2.380
	128 x $10^{-12}$	0.640
1000	16 x $10^{-12}$	53.655
	32 x $10^{-12}$	8.305
	32 x $10^{-12}$	9.845
	64 x $10^{-12}$	3.900
	64 x $10^{-12}$	3.960
	128 x $10^{-12}$	2.200
	128 x $10^{-12}$	1.980
256 x $10^{-12}$	1.190	

GLC Standard Curves for Isopropanol

cm<sup>2</sup>  
area

50  
40  
30  
20  
10

10 20 30

Isopropanol  
Legend

- Data points calculated from area vs concentration values
- ⊙ Plotting points calculated from integers multiplied by slope

Density = 0.785  
Slope = .498

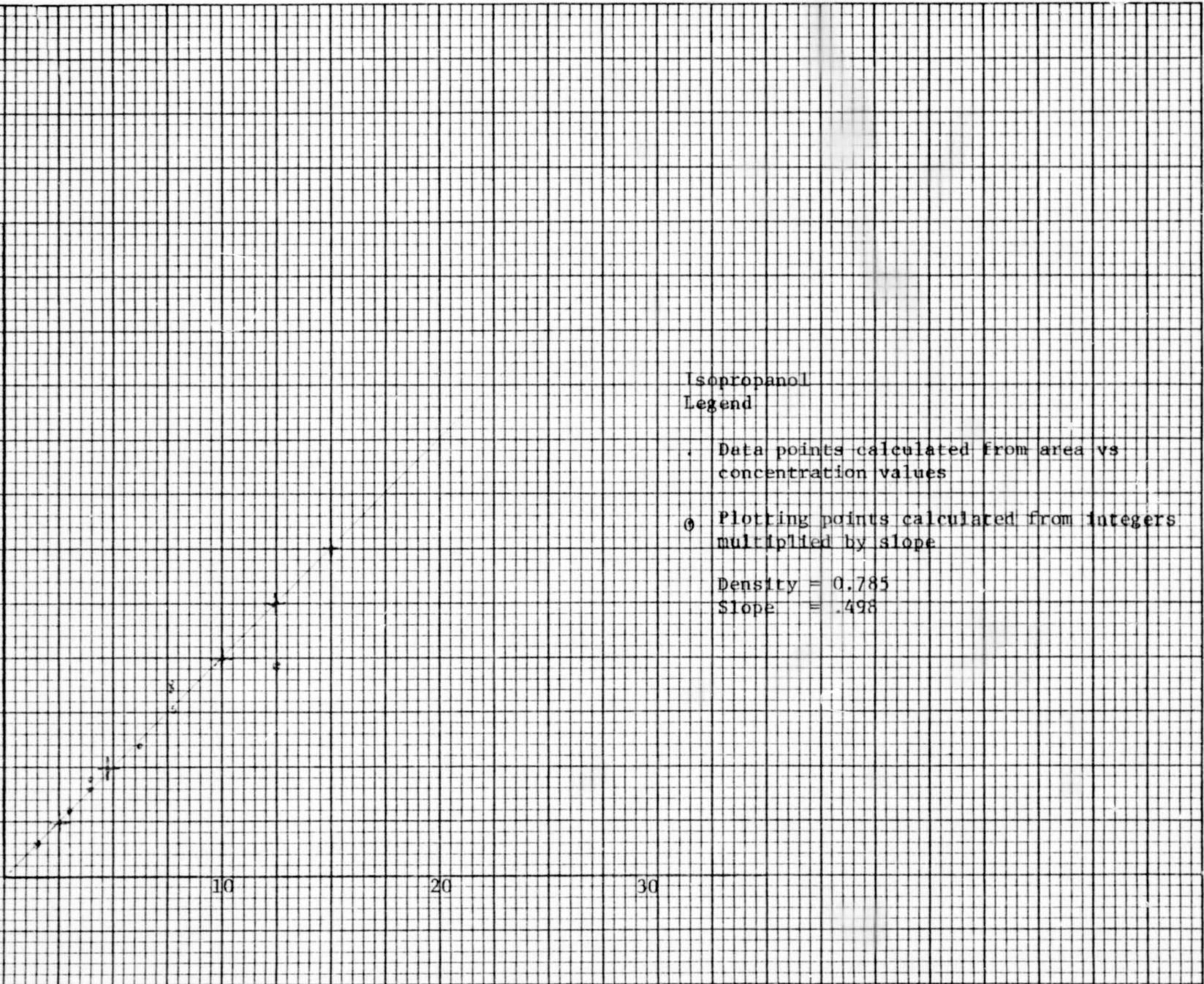


Fig. 2

2. Calculating ug at attention of 1

<u>Conc. (ppm)</u>	<u>Conc. (ug/ml/Atten.</u>	<u>Conc. at Atten. 1</u>	<u>Area (cm<sup>2</sup>)</u>
100	100/2	50.0	33.945
	100/4	25.0	17.100
	100/32	3.1	2.700
500	500/8	62.5	18.130
	500/16	31.3	8.450
	500/32	15.6	14.280
	500/64	7.8	2.380
	500/128	3.9	0.640
1000	1000/16	62.5	53.655
	1000/32	31.3	8.305
	1000/32	31.3	9.845
	1000/64	15.6	3.900
	1000/64	15.6	3.960
	1000/128	7.8	2.200
	1000/128	7.8	1.980
	1000/256	3.9	1.190

3. Comparison of ug/ml to cm<sup>2</sup>

<u>ug/ml</u>	<u>cm<sup>2</sup></u>	<u>cm<sup>2</sup>/ug/ml</u>
3.1	2.700	.871
3.9	0.640	.164
3.9	1.190	.305
7.8	2.200	.282
7.8	2.380	.305
7.8	1.980	.254
15.6	3.960	.254
15.6	3.900	.250
15.6	14.280	.915
25.0	17.100	.684
31.3	8.450	.270
31.3	8.305	.265
31.3	9.845	.315
50.0	33.945	.679
62.5	18.130	.290
62.5	53.655	.858

4. Data finalization for plotting slope

a. Summation:  $\Sigma \text{ cm}^2/\text{ug/ml} = 6.961$       Number of samples(n) = 16

b. Slope: median  $\text{cm}^2/\text{ug/ml} = 2.299$

c. Plotting points: Area vs concentration

5 cm <sup>2</sup>	: 11.495 ug/ml
10	: 22.990
15	: 34.485
20	: 45.980
25	: 57.475

### GLC Standard Curve for Methanol

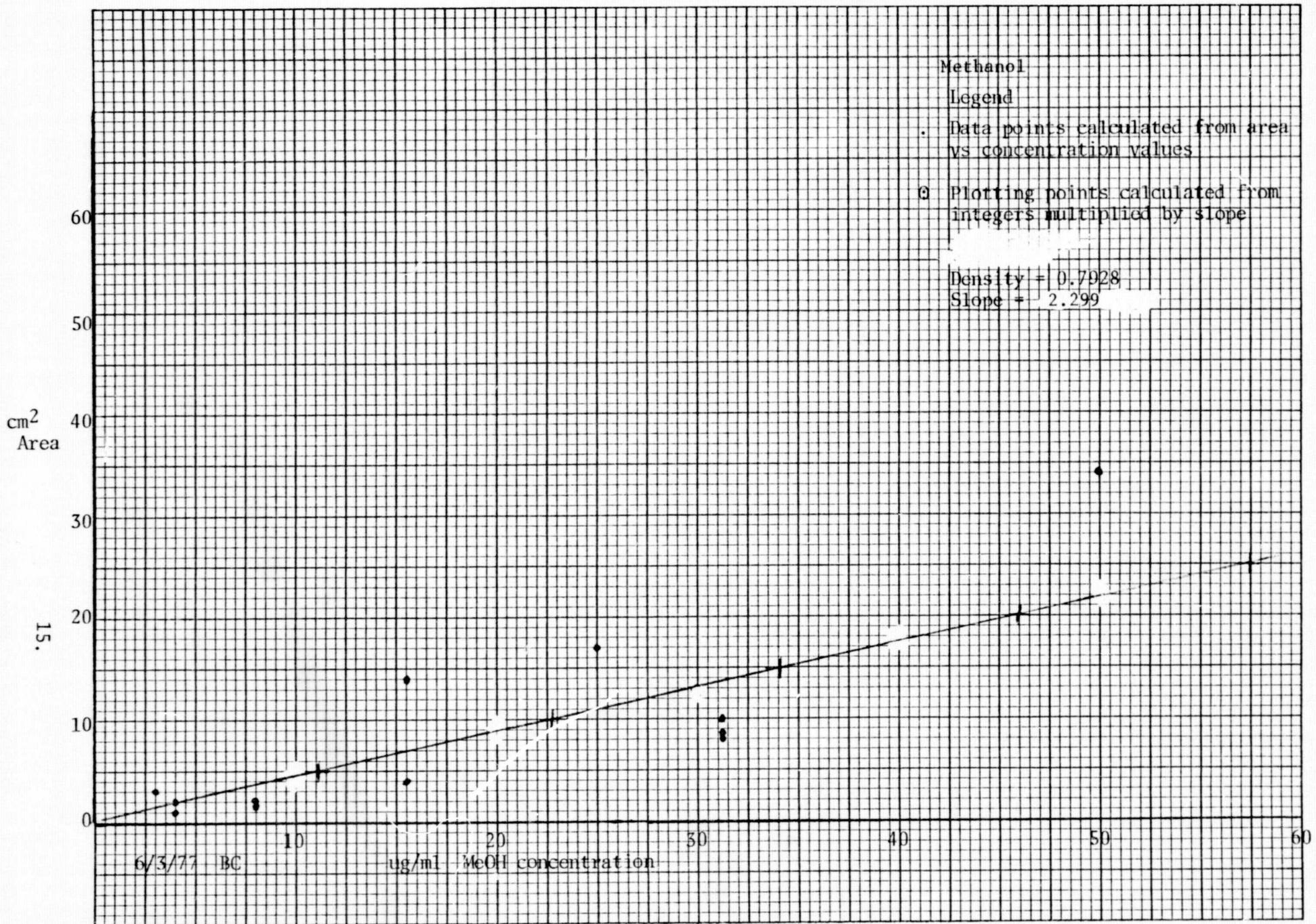


Fig. 3

d. Methylene Chloride

Pertinent Calculations for Standard Curve for Methylene Chloride

Column retention time is 4.5 to 4.7 minutes

Molecular weight: 84.94      Density: 1.336

1. Peak Areas for Methylene Chloride

<u>Conc (ppm)</u>	<u>Attenuation x Range</u>	<u>Area (cm<sup>2</sup>)</u>
100	4 x 10 <sup>-12</sup>	19.110
	8 x 10 <sup>-12</sup>	7.400
	16 x 10 <sup>-12</sup>	6.720
	32 x 10 <sup>-12</sup>	3.000
	64 x 10 <sup>-12</sup>	0.950
500	16 x 10 <sup>-12</sup>	21.690
	32 x 10 <sup>-12</sup>	12.155
	64 x 10 <sup>-12</sup>	4.125
	128 x 10 <sup>-12</sup>	3.120
1000	32 x 10 <sup>-12</sup>	24.880
	64 x 10 <sup>-12</sup>	10.370
	64 x 10 <sup>-12</sup>	14.880
	128 x 10 <sup>-12</sup>	6.930
	128 x 10 <sup>-12</sup>	8.670
	256 x 10 <sup>-12</sup>	3.760

2. Calculating ug at attenuation of 1

<u>Conc (ppm)</u>	<u>Conc (ug)/Attenuation</u>	<u>Conc at Attenuation 1</u>	<u>Area (cm<sup>2</sup>)</u>
100	100/4	25.0	19.110
	100/8	12.5	7.400
	100/16	6.3	6.720
	100/32	3.1	3.000
	100/64	1.6	0.950
500	500/16	31.3	21.690
	500/32	15.6	12.155
	500/64	7.8	4.125
	500/128	3.9	3.120
1000	1000/32	31.3	24.880
	1000/64	15.6	10.370
	1000/64	15.6	14.880
	1000/128	7.8	6.930
	1000/128	7.8	8.670
	1000/256	3.9	3.760

3. Comparison of ug/ml to cm<sup>2</sup>

<u>ug/ml</u>	<u>cm<sup>2</sup></u>	<u>cm<sup>2</sup>/ug</u>
1.6	0.950	.594
3.1	3.000	.968
3.9	3.760	.964
3.9	3.120	.800
6.3	6.720	1.067
7.8	8.670	1.112
7.8	6.930	.888
7.8	4.125	.529
12.5	7.400	.592
15.6	12.155	.779
15.6	10.370	.665
15.6	14.880	.954
25.0	19.110	.764
31.3	24.880	.795
31.3	21.690	.693

4. Data finalization for plotting slope

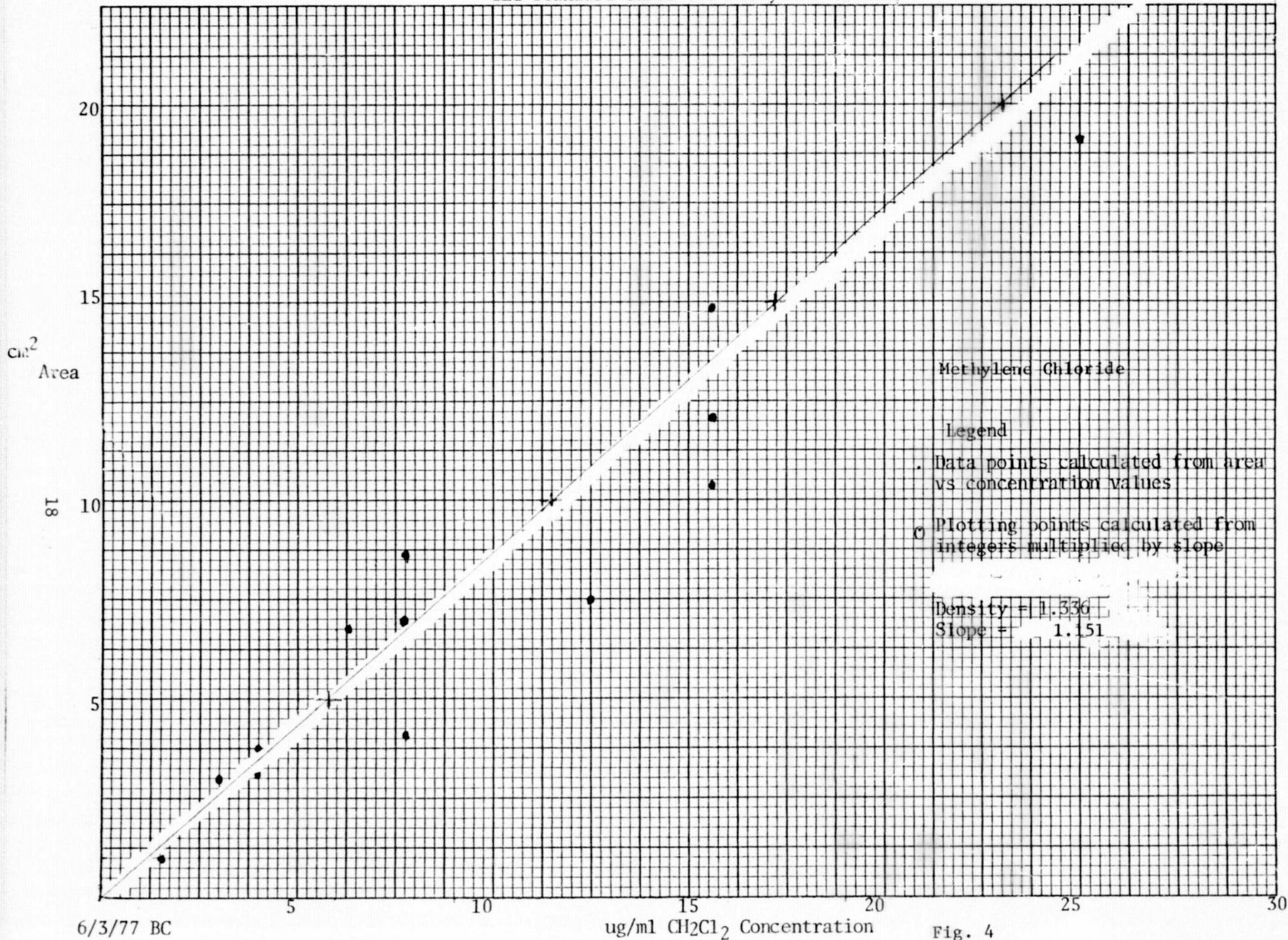
a. Summation:  $\Sigma \text{cm}^2/\text{ug/ml} = 12.164$       Number of samples (n) = 14

b. Slope: average  $\text{cm}^2/\text{ug/ml} = 1.151$

c. Plotting points. Area vs concentration

5 cm <sup>2</sup>	: 5.755 ug/ml
10	:11.510
19	:17.265
20	:23.020
29	:28.775

GLC Standard Curve for Methylene Chloride



c. Chloroform

Pertinent Calculations for GLC Standard Curve for Chloroform

Column retention time is 11.2 to 11.4 minutes

Molecular weight: 119.39      Density: 1.49845

1. Peak Areas for Chloroform

<u>Conc (ppm)</u>	<u>Attenuation x Range</u>	<u>Area (cm<sup>2</sup>)</u>
100	2 x 10 <sup>-12</sup>	39.785
	4 x 10 <sup>-12</sup>	11.400
500	4 x 10 <sup>-12</sup>	42.785
	8 x 10 <sup>-12</sup>	21.000
	16 x 10 <sup>-12</sup>	13.640
	32 x 10 <sup>-12</sup>	7.700
	64 x 10 <sup>-12</sup>	4.000
	128 x 10 <sup>-12</sup>	1.485
1000	8 x 10 <sup>-12</sup>	50.635
	16 x 10 <sup>-12</sup>	23.985
	16 x 10 <sup>-12</sup>	29.055
	16 x 10 <sup>-12</sup>	42.640
	32 x 10 <sup>-12</sup>	19.890
	64 x 10 <sup>-12</sup>	5.850
	64 x 10 <sup>-12</sup>	8.880
	128 x 10 <sup>-12</sup>	5.000
	128 x 10 <sup>-12</sup>	6.600
	256 x 10 <sup>-12</sup>	1.925

2. Calculating ug/ml at attenuation of 1

<u>Conc (ppm)</u>	<u>Conc (ug/ml/Atten.)</u>	<u>Conc at Atten. 1</u>	<u>Area (cm<sup>2</sup>)</u>
100	100/2	50.0	39.785
	100/4	25.0	11.400
500	500/4	125.0	42.795
	500/8	62.5	21.000
	500/16	31.3	13.640
	500/32	15.6	7.700
	500/64	7.8	4.000
	500/128	3.9	1.485
1000	1000/8	125.0	50.635
	1000/16	62.5	23.985
	1000/16	62.5	29.055
	1000/16	62.5	42.640
	1000/32	31.3	19.890
	1000/64	15.6	5.850
	1000/64	15.6	8.880
	1000/128	7.8	5.000
	1000/128	7.8	6.600
	1000/256	3.9	1.925

3. Comparison of ug/ml to cm<sup>2</sup>

<u>ug/ml</u>	<u>cm<sup>2</sup></u>	<u>cm<sup>2</sup>/ug/ml</u>
3.9	1.925	.494
3.9	1.485	.381
7.8	4.000	.513
7.8	5.000	.641
7.8	6.600	.846
15.6	8.800	.569
15.6	5.850	.375
15.6	7.700	.494
25.0	11.400	.456
31.3	13.640	.436
31.3	19.890	.635
50.0	11.400	.795
62.5	29.055	.465
62.5	23.985	.384
62.5	21.000	.336
62.5	42.785	.685
125.0	42.640	.341
125.0	50.635	.405

4. Data finalization for plotting slope

- Summation:  $\Sigma \text{ cm}^2/\text{ug/ml} = 9.251$       Number of samples(n) = 18
- Slope: Average  $\text{ cm}^2/\text{ug/ml} = 1.946$
- Plotting points. Area vs concentration

10cm <sup>2</sup>	: 19.46 ug/ml
20	: 38.92
30	: 58.38
40	: 77.84
50	: 97.30

GLC Standard Curve for Chloroform

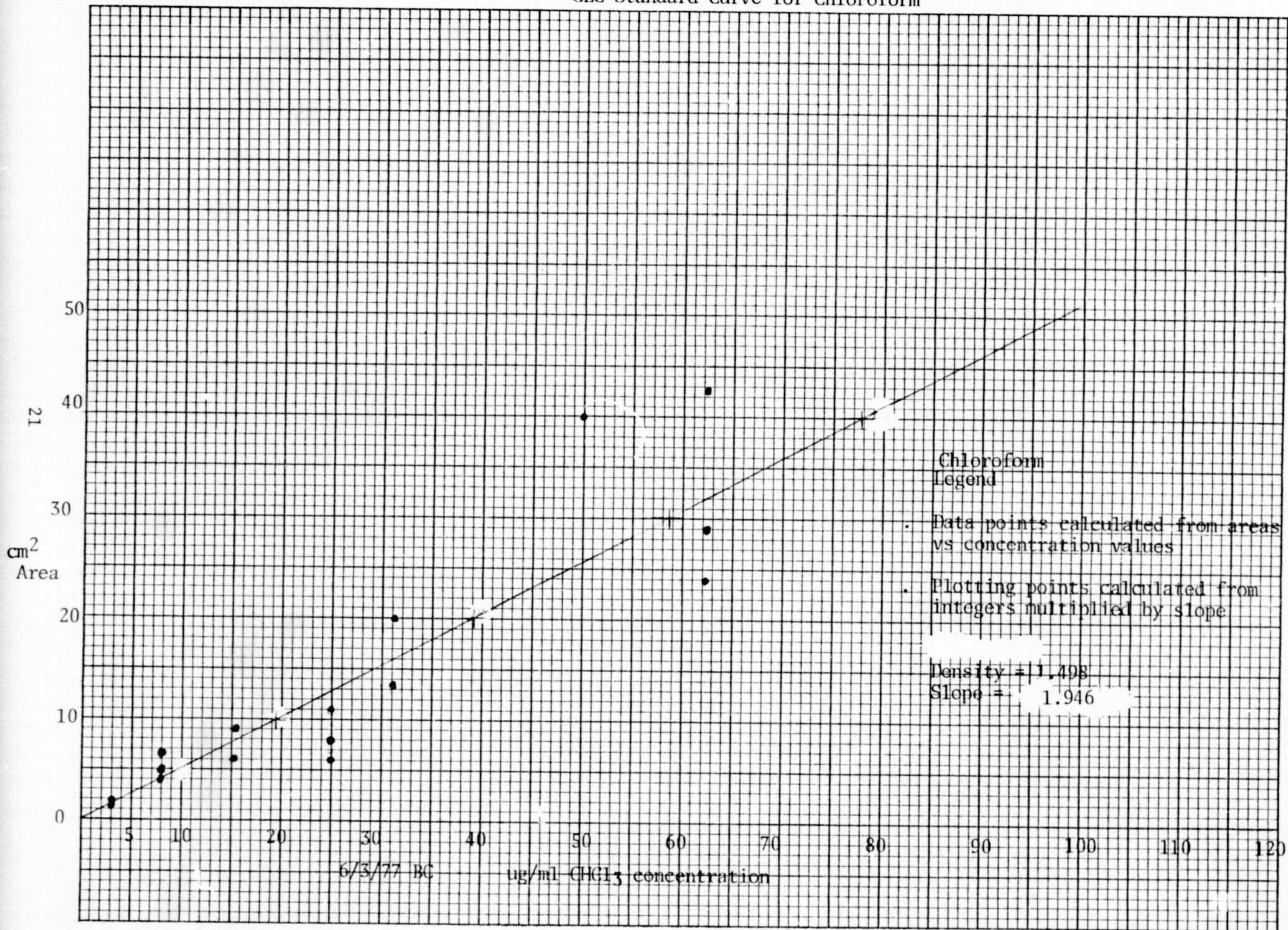


Fig. 5

f. Summary

IPA and MMH scrubber waste liquors can be analyzed using Gas Liquid Chromatography. The concentration and degradation rate of these materials in disposal ponds can be determined by using the standard curves delineated in this report.

### 3. Field Assays of IPA and MMH Scrubber Liquor Wastes

#### a. IPA

On April 27, 1977 a small amount of IPA was mixed into the PDP. An approximate calculation of the amount of IPA in the PDP which was based on an estimated volume of water in the pond was made. This estimate was 1000 ppm. A GLC assay was made of the pond water and it was determined that the concentration was 1070.6 ppm. A second sample taken on May 18, 1977 showed no trace of IPA present.

As discussed earlier, IPA may be a material designated to be disposed of in stabilization ponds. One advantage of IPA addition to the PDP or any disposal pond is that it provides a carbon source for water hyacinths and algae present in such ponds.

## b. MMH Scrubber Liquor Wastes

Experiments were initiated with an objective to study the evaporation rates of the reaction products of NaOCl degradation of MMH.

### Exp. No. 1

Five stainless steel pans of uniform dimension were placed on a platform. These pans (A, B, C, D, and E) all contained 500 ml of 5% NaOCl (250 mls H<sub>2</sub>O and 250 mls 10% NaOCl). To each pan was added the following:

- 1) 500 mls of 10% MMH (50 mls MMH and 450 mls H<sub>2</sub>O) to pan A.
- 2) 500 mls of 5% MMH (25 mls MMH and 475 mls H<sub>2</sub>O) to pan B.
- 3) 500 mls of 1% MMH (5 mls MMH and 495 mls H<sub>2</sub>O) to pan C.
- 4) 500 mls of 0.5% MMH (2.5 mls MMH and 297.5 mls H<sub>2</sub>O) to pan D.
- 5) 500 mls of 0.1% MMH (0.5 mls MMH and 499.5 mls H<sub>2</sub>O) to pan E.

When the combined solutions were prepared, the ambient temperature was 25°C. It was noted that upon mixing, a temperature change occurred in each of the pans. See Table 2.

Table 2.

Reaction Temperature of Various MMH Concentrations in 5% NaOCl

<u>Pan</u>	<u>Conc. of MMH</u>	<u>Time of Max. Temp.</u>	<u>Temperature</u>
A	10 %		40°C
B	5 %		38°C
C	1 %		36°C
D	0.5 %		28°C
E	0.1 %		24°C

A sample for assay was taken every 24 hours (except Saturday and Sunday), at which time two 1 ml samples of each concentration were drawn and stored for assay at a later time. The evaporation rates were determined using a spectrophotometric method to assay MMH concentration and GLC methods were used to determine levels of NaOCl reaction products. The operating conditions for the GLC were discussed in section

The results from the spectrophotometric assays for MMH levels in Exp. 1 are presented in Table 3.

Table 3.

Sample Date	A	B	C	D	E
6/3	11412.5	5602.5	*Negative	*Negative	200
6/4	5082.5	1650.0	807.5	* 2405.0	*61200.0
6/6	439.0	330.0	247.5	*1494900.0	*684750.0
6/7	82.5	*Negative	330.0	*71575.0	*4272500.0
6/8	60.0	*Negative	*Negative	*166000.0	*537250.0
6/9	Sample not taken due to complete evaporation				

\* Erroneous results caused by presence of Chlorine

Only the results from pan A were considered valid due to chlorine interference in absorbance readings of samples from the other pans. See Table 4.

Table 4

Degradation Rate of MMH in Pan A for Run 1

<u>Dates</u>	<u>Percent Degradation</u>
6/3-6/4	55.5
6/4-6/6	91.4
6/6-6/7	81.0
6/7-6/8	27.3

Total Degradation 99.5%

A second series of experiments was conducted which studied air and sunlight oxidation of MMH in solution with no Cl<sub>2</sub> source added. The results show that MMH is essentially totally degraded in about five days. The results for Exp. No. 2 are presented in Tables 5 and 6.

Table 5.

ppm MMH for Run 2 determined from Spectrophotometer Readings.

<u>Sample Date</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
6/9	91,300	39,425	12,850	8,500	415.0
6/10	23,850	14,100	7,365	5,395	92.5
6/13	Sample not taken due to complete evaporation				

Table 6

## Rates of Degradation of MMH for Run 2 in First Day

<u>Pan</u>	<u>Percent Degradation</u>
A	73.9
B	64.2
C	42.7
D	36.5
E	77.7

The GLC assays were conducted using conditions previously described. The only variables introduced in the tests on samples from Run 1 and 2 were sample size and attenuation. These modifications were used to optimize the peak height in order to more accurately measure the peak area. The peak area calculations were made by reducing sample size to 1 ul and multiplying by the attenuation. Then using the standard curve graphs from Section 3, the ug/ml (ppm) were calculated. The results are presented in Table 10.

Table 7

GLC Data Presenting Peak Area and Corresponding Concentration Values of  
Reaction Products for Exp. 1 and 2.

G<sub>1</sub>-1 (Run #1 on GLC, first day)

Sampled on 6/3 , Assayed on 6/4

Pan	Reaction Product ID	Area	Conc. (ug/ml)
A (10.0%)	CH <sub>3</sub> OH	41.862	96.241
	CH <sub>2</sub> Cl <sub>2</sub>	115.639	133.100
	CHCl <sub>3</sub>	4.652	9.053
B (5.0%)	CH <sub>3</sub> OH	74.325	170.873
	CH <sub>2</sub> Cl <sub>2</sub>	55.130	63.455
	CHCl <sub>3</sub>	2.337	4.458
C (1.0%)	CH <sub>3</sub> OH	5.155	11.851
	CH <sub>2</sub> Cl <sub>2</sub>	2.055	2.365
	CHCl <sub>3</sub>	.043	.084
D (0.5%)	CH <sub>3</sub> OH	3.311	7.612
	CH <sub>2</sub> Cl <sub>2</sub>	1.383	1.592
	CHCl <sub>3</sub>	.016	.031
E (0.1%)	CH <sub>3</sub> OH	2.513	5.777
	CH <sub>2</sub> Cl <sub>2</sub>	.447	.514
	CHCl <sub>3</sub>	.007	.014

Table 7 (cont.)

G<sub>1</sub>-4 (Run #1 on GLC, fourth day)

Sampled and Assayed on 6/6/77

Pan	Reaction Product ID	Area	Conc. (ug/ml)
A (10.0%)	CH <sub>3</sub> OH	.402	.924
	CH <sub>2</sub> Cl <sub>2</sub>	10.223	11.767
	CHCl <sub>3</sub>	.608	1.183
B (5.0%)	CH <sub>3</sub> OH	.487	1.120
	CH <sub>2</sub> Cl <sub>2</sub>	1.626	1.872
	CHCl <sub>3</sub>	.141	.274
C (1.0%)	CH <sub>3</sub> OH	.909	2.090
	CH <sub>2</sub> Cl <sub>2</sub>	.236	.272
	CHCl <sub>3</sub>	.021	.041
D (0.5%)	CH <sub>3</sub> OH	1.650	3.793
	CH <sub>2</sub> Cl <sub>2</sub>	.252	.240
	CHCl <sub>3</sub>	.007	.014
E (0.1%)	CH <sub>3</sub> OH	1.005	2.310
	CH <sub>2</sub> Cl <sub>2</sub>	.015	.017
	CHCl <sub>3</sub>	.003	.006

Table 7 (cont.)

G<sub>1</sub> 5 (Run #1 on GLC, fifth day)

Sampled and Assayed on 6/7/77

Pan	Reaction Product ID	Area	Conc. (ug/ml)
A (10.0%)	CH <sub>3</sub> OH	.240	.552
	CH <sub>2</sub> Cl <sub>2</sub>	4.024	4.632
	CHCl <sub>3</sub>	.324	.631
B (5.0%)	CH <sub>3</sub> OH	.459	1.055
	CH <sub>2</sub> Cl <sub>2</sub>	1.153	1.327
	CHCl <sub>3</sub>	.083	.162
C (1.0%)	CH <sub>3</sub> OH	.526	1.209
	CH <sub>2</sub> Cl <sub>2</sub>	.088	.101
	CHCl <sub>3</sub>	.013	.025
D (0.5%)	CH <sub>3</sub> OH	1.202	2.763
	CH <sub>2</sub> Cl <sub>2</sub>	.117	.135
	CHCl <sub>3</sub>	.004	.008
E (0.1%)	CH <sub>3</sub> OH	.853	1.961
	CH <sub>2</sub> Cl <sub>2</sub>	.007	.008
	CHCl <sub>3</sub>	.002	.004

Table 7 (cont.)

G<sub>1</sub>-6 (Run #1 on GLC, Sixth day)

Sampled and Assayed on 6/8/77

Pan	Reaction Product ID	Area	Conc.(ug/ml)
A (10.0%)	CH <sub>3</sub> OH	.155	.356
	CH <sub>2</sub> Cl <sub>2</sub>	2.785	3.206
	CHCl <sub>3</sub>	.162	.315
B (5.0%)	CH <sub>3</sub> OH	.192	.441
	CH <sub>2</sub> Cl <sub>2</sub>	.222	.256
	CHCl <sub>3</sub>	.057	.111
C (1.0%)	CH <sub>3</sub> OH	.316	.726
	CH <sub>2</sub> Cl <sub>2</sub>	.036	.041
	CHCl <sub>3</sub>	.011	.021
D (0.5%)	CH <sub>3</sub> OH	.859	1.975
	CH <sub>2</sub> Cl <sub>2</sub>	.048	.055
	CHCl <sub>3</sub>	.003	.006
E (0.1%)	CH <sub>3</sub> OH	.732	1.683
	CH <sub>2</sub> Cl <sub>2</sub>	*	*
	CHCl <sub>3</sub>	*	*

\*Concentration level below detection limits

Table 7 (cont.)

G<sub>2</sub>-1 (Run # 2 on GLC, first day)

Sampled on 6/9 , Assayed on 6/10

Pan	Reaction Product ID	Area	Conc. (ug/ml)
A (10.0%)	CH <sub>3</sub> OH	37.566	86.364
	CH <sub>2</sub> Cl <sub>2</sub>	109.342	125.853
	CHCl <sub>3</sub>	5.711	11.114
B (5.0%)	CH <sub>3</sub> OH	21.573	49.596
	CH <sub>2</sub> Cl <sub>2</sub>	50.450	58.068
	CHCl <sub>3</sub>	1.027	1.999
C (1.0%)	CH <sub>3</sub> OH	3.323	7.640
	CH <sub>2</sub> Cl <sub>2</sub>	1.130	1.301
	CHCl <sub>3</sub>	.056	.109
D (0.5%)	CH <sub>3</sub> OH	3.307	7.603
	CH <sub>2</sub> Cl <sub>2</sub>	1.552	1.786
	CHCl <sub>3</sub>	.012	.023
E (0.1%)	CH <sub>3</sub> OH	1.944	4.469
	CH <sub>2</sub> Cl <sub>2</sub>	.526	.605
	CHCl <sub>3</sub>	.009	.018

Table 7 (cont.)

G<sub>2</sub>-2 (Run #1 on GLC, second day)

Sampled on 6/10, Assayed on 6/11

Pan	Reaction Product ID	Area	Conc. (ug/ml)
A (10.0%)	CH <sub>3</sub> OH	23.396	53.787
	CH <sub>2</sub> Cl <sub>2</sub>	83.257	95.829
	CHCl <sub>3</sub>	3.222	6.270
B (5.0%)	CH <sub>3</sub> OH	14.937	34.340
	CH <sub>2</sub> Cl <sub>2</sub>	38.281	44.061
	CHCl <sub>3</sub>	.534	1.039
C (1.0%)	CH <sub>3</sub> OH	2.641	6.072
	CH <sub>2</sub> Cl <sub>2</sub>	.091	.105
	CHCl <sub>3</sub>	.044	.086
D (0.5%)	CH <sub>3</sub> OH	2.176	5.003
	CH <sub>2</sub> Cl <sub>2</sub>	.936	1.077
	CHCl <sub>3</sub>	.007	.014
E (0.1%)	CH <sub>3</sub> OH	1.274	2.929
	CH <sub>2</sub> Cl <sub>2</sub>	.420	.483
	CHCl <sub>3</sub>	.006	.012

Evaporation Rate of 10.0% MMH and 5% NaOCl Reaction Products

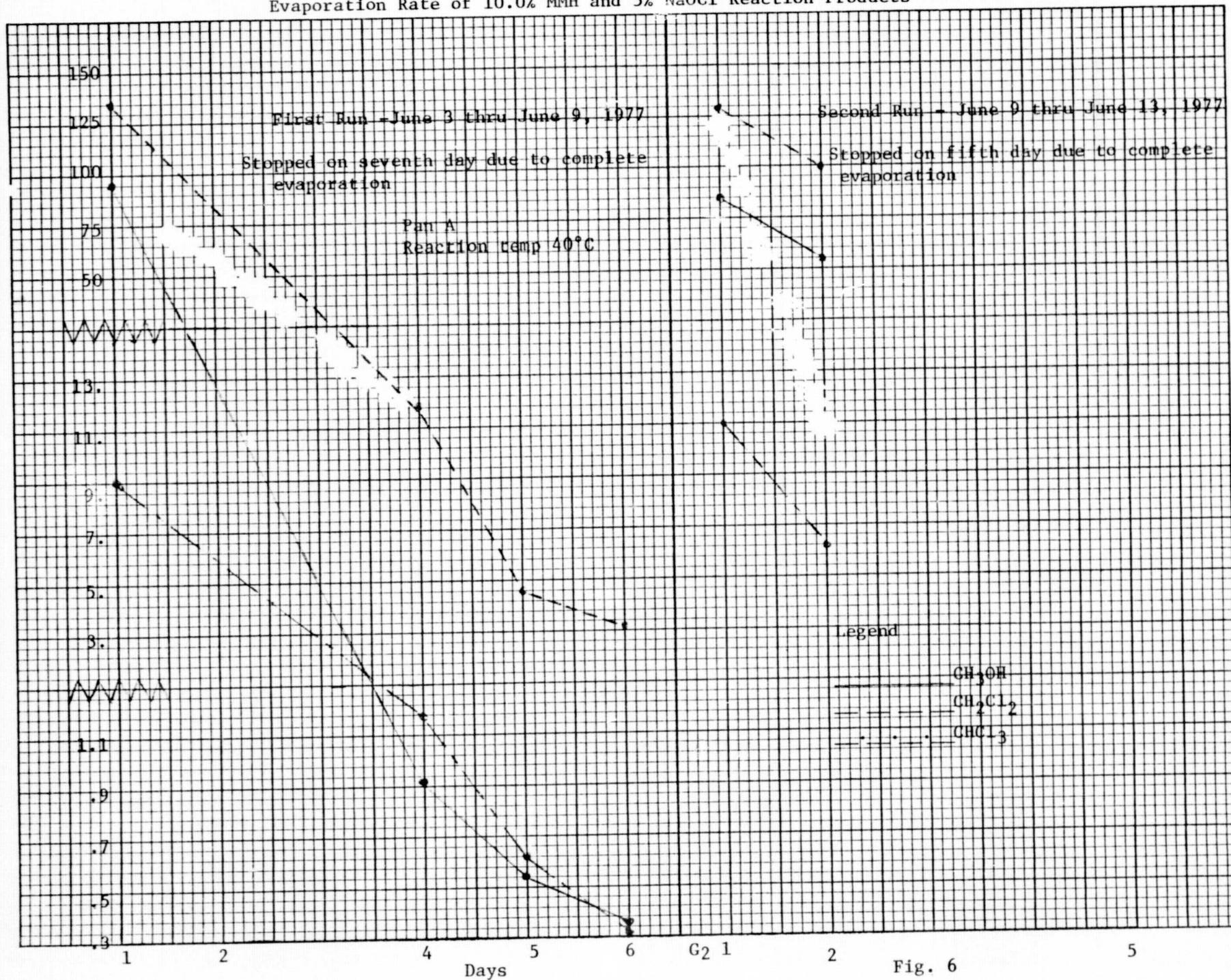
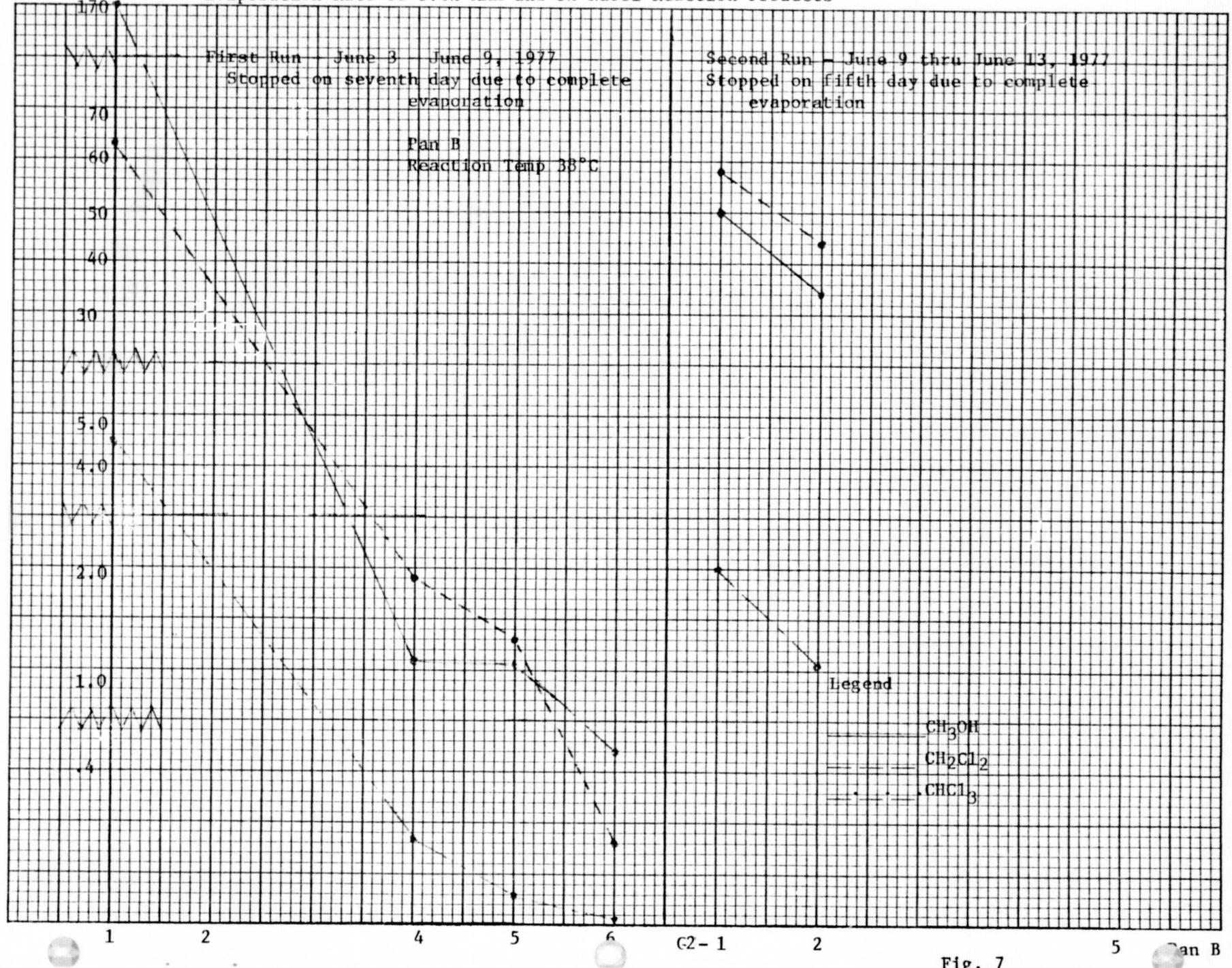


Fig. 6

Evaporation Rate of 5.0% MMH and 5% NaOCl Reaction Products



34

Fig. 7

5 Pan B

Evaporation Rate of 1.0% MMH and 5% NaOCl Reaction Products

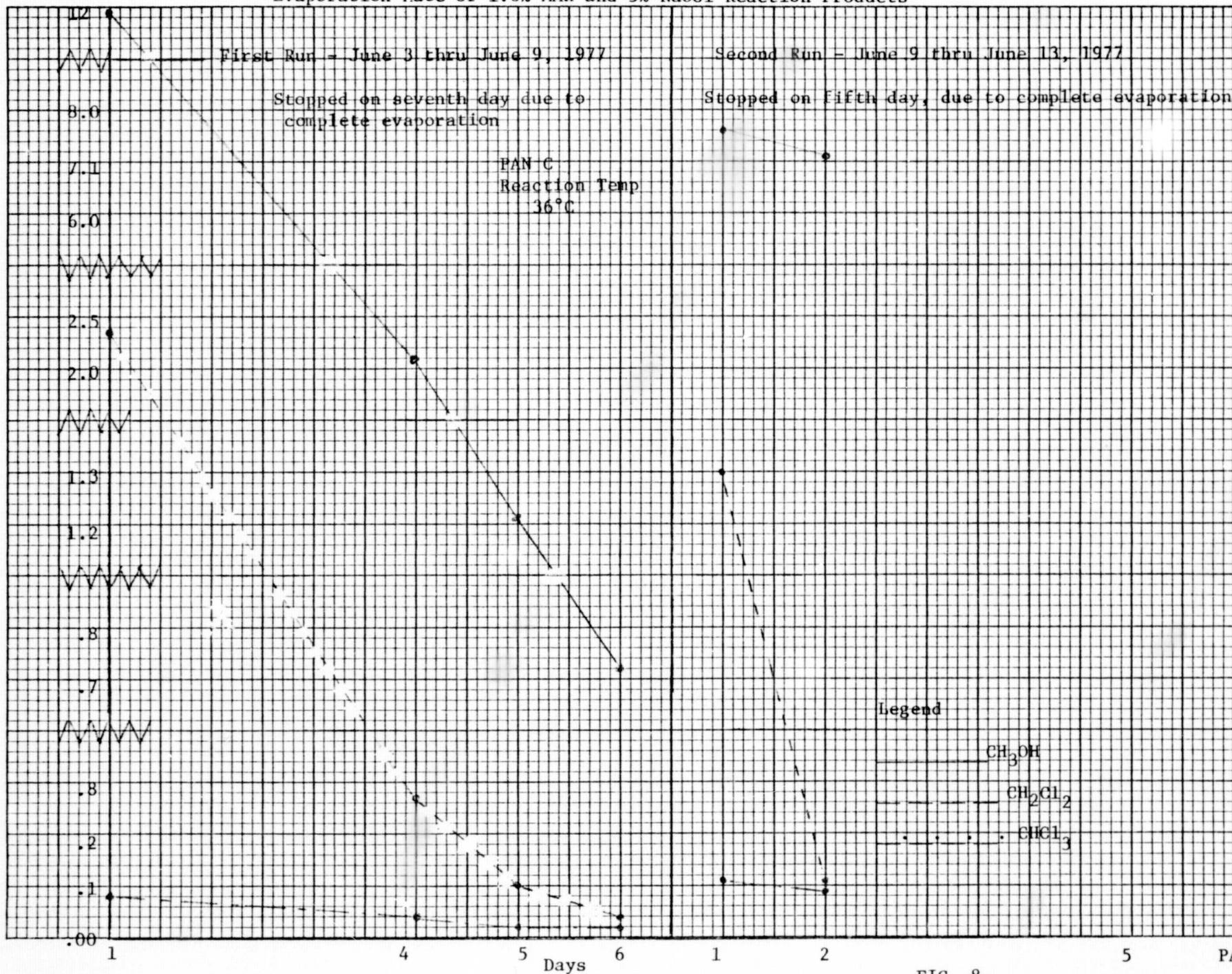
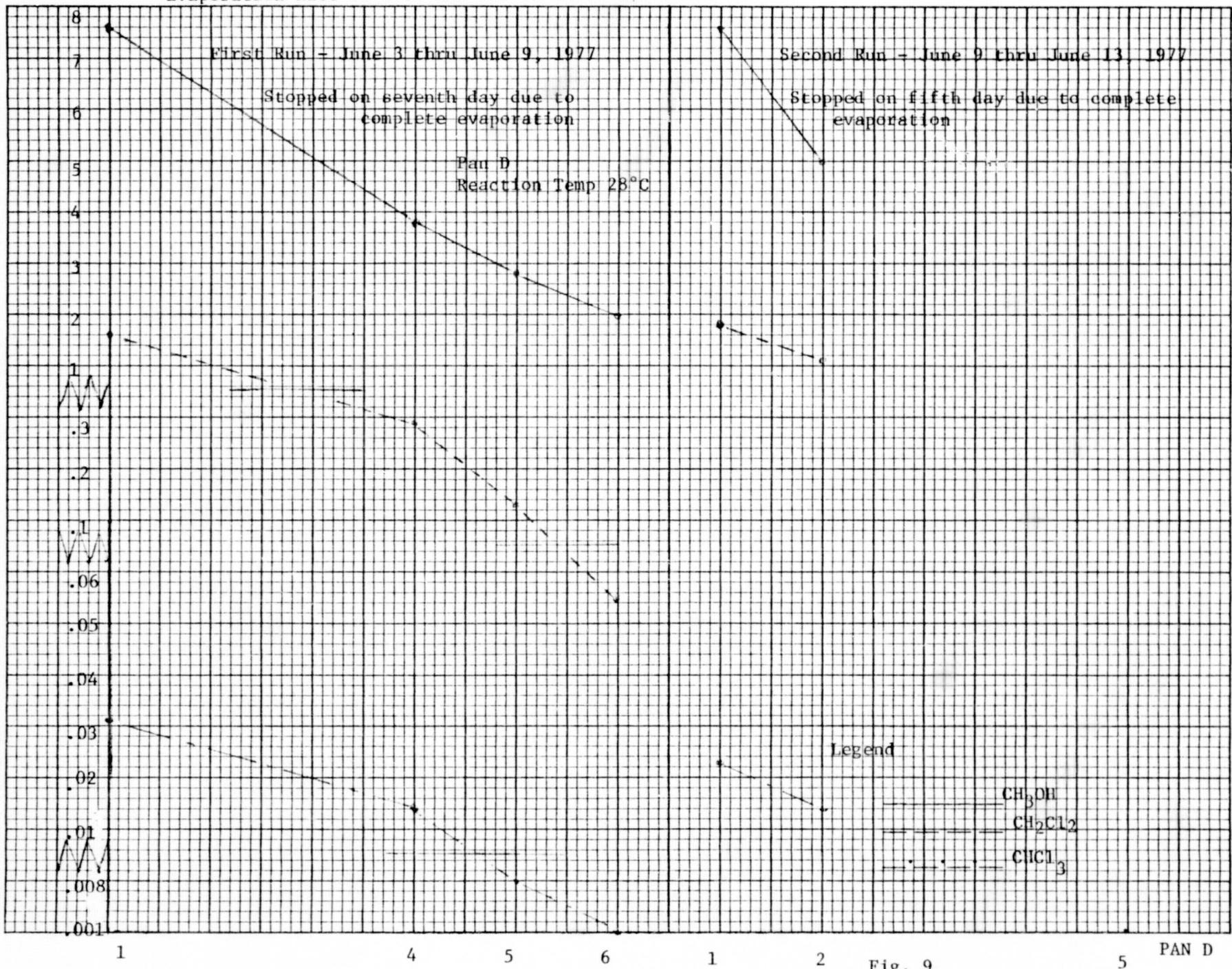


FIG. 8

Evaporation Rate of 0.5% MMH and 5% NaOCl Reaction Products



36

Fig. 9

5 PAN D

Evaporation Rate of 0.1% MMH and 5% NaOCl Reaction Products

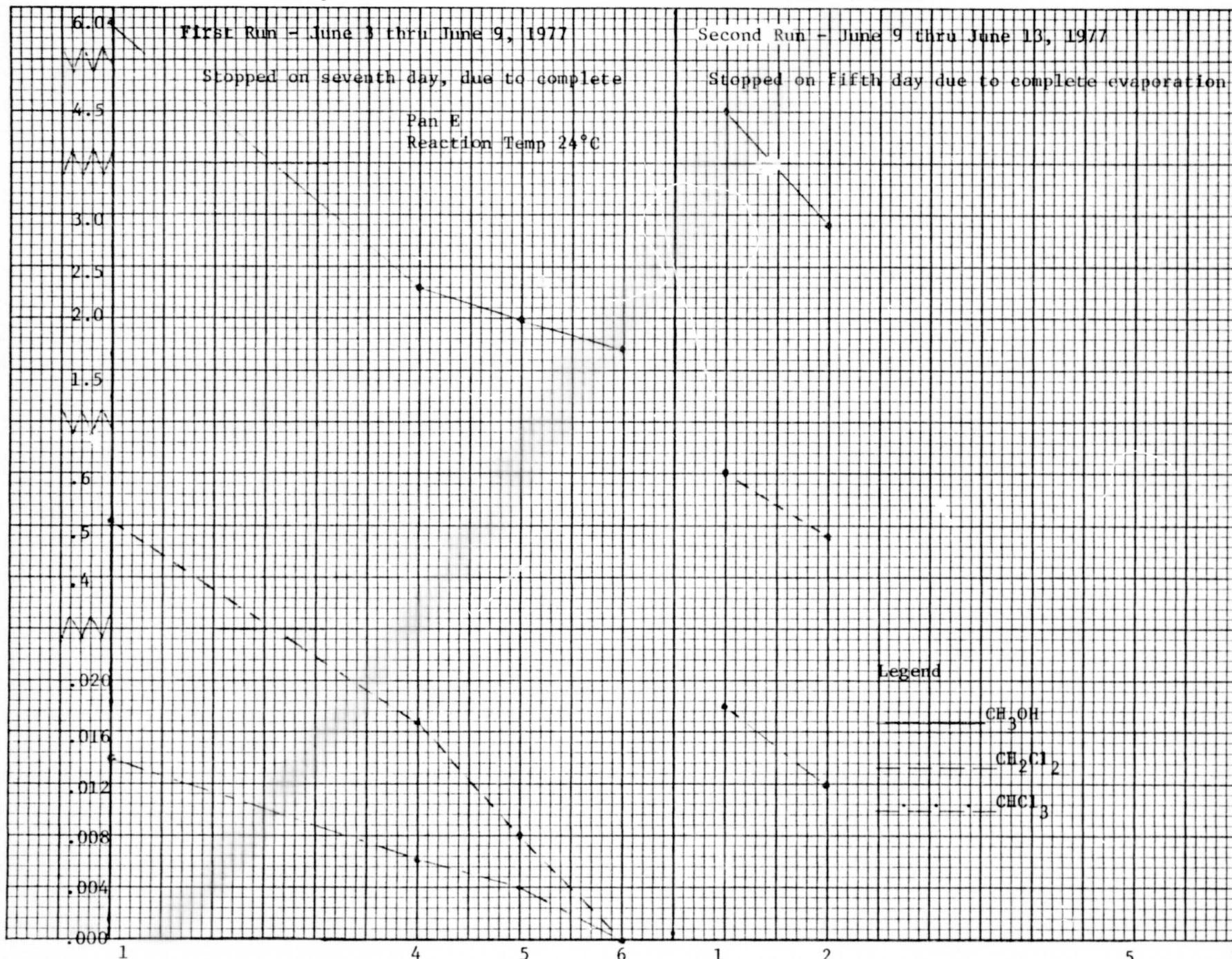


Fig. 10

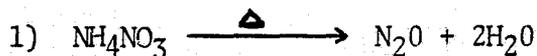
### C. Summary

The concentration of  $\text{CHCl}_3$  present in the reaction products of pan A was initially 9.05 ug/ml and in six days was reduced to .32 ug/ml (96.5%). The initial concentrations of  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{Cl}_2$  were in six days reduced 99.6% and 97.6% respectively. Lower concentrations of these materials initially present in the other pans evaporated at similar rates. The MMH degradation and oxidation also occurred at a similar rate.

The results also show the importance of heat evolved in the reaction of MMH and NaOCl. As more heat is evolved more  $\text{CHCl}_3$  is formed.

#### 4. Solar Conversion of Nitrate and Nitrite to Nitrous Oxide and Nitrogen

Another large problem involving pond products is concerned with the amount of sodium nitrate ( $\text{NaNO}_3$ ) and sodium nitrite ( $\text{NaNO}_2$ ) that is compatible with the pond biota, in particular water hyacinths. It is envisioned that scrubber liquor waste may amount to 1000 gallons of solution containing as much as 800 lbs. of  $\text{NaNO}_3$  and  $\text{NaNO}_2$ . This material must be diluted to a concentration of perhaps as low as 600 ppm in the disposal pond so as to not damage the biota. This would call for a 775 fold dilution of the scrubber wastes after entering the disposal pond. This is a relatively large amount of dilution. Thus if possible alternatives are available they should be investigated. One alternative involves conversion of nitrate and nitrite to environmentally innocuous materials. A series of pertinent reactions are shown below:



$\text{N}_2\text{O}$  nitrous oxide is considered environmentally innocuous as is, of course, nitrogen and water. Heating solutions of ammonium nitrate and nitrite is impractical but perhaps solar irradiation of the pond would provide enough energy to cause these reactions to proceed at significant rates. Therefore, a series of experiments were conducted in which ammonium chloride and sodium nitrate solutions were allowed to sit in the sun. The nitrate, nitrite and ammonium ion concentrations were then measured periodically to determine if reduction of nitrate and nitrite concentration was occurring. In experiment #1, a barrel 23 inches in diameter and 39 inches in height containing 20 gallons of water was placed in direct sunlight. To this was added the contents of one cylinder of  $\text{N}_2\text{O}_4$  and 4 lbs. of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and the pH was adjusted to 7.0. Analyses of nitrate, nitrite, and ammonium ion were taken over a 98 day period. The results are presented in Table 1.

TABLE 8

Solar Conversion of Nitrates and Nitrites  
To  $N_2O$  and  $N_2$  (Exp. No. 1)

Sample No	Water Height in Barrel (cm)	Date	Nitrate ppm	Nitrite ppm	Ammonia ppm
1	27	12-8-76	33,000	1320	8,296
2	27	12-12-76	26,400	3300	14,316
3	27	12-16-76	26,400	1403	
4	27	12-17-76	24,200	1320	7,930
5 *	31	1-3-77	20,900	1970	7,137
6 **	31	1-6-77	23,100	1650	13,420
7	31	1-13-77	22,440	1568	14,640
8	30.5	1-20-77	11,000	1865	10,370
9	30.5	1-25-77	14,080	2063	10,980
10	30.5	2-4-77	12,100	2558	10,736
11	30.5	2-14-77	9900	2310	7,686
12	29.5	2-22-77	12,100	1320	13,420
13	29.1	3-3-77	11,000	2178	12,078
14	27.3	3-16-77	12,320	2607	10,370

\* Added 2 lbs  $NH_4Cl$ . The pH was 6.0 at this point

\*\* pH 7.0

As seen from Table 1, after 98 days it appeared that the nitrate content had decreased to the point of diminishing returns. This was probably due to the blockage of large amounts of sunlight caused by the high walls of the barrel. It was reasoned that containers with lower walls which allowed greater access of sunlight would perhaps be more effective. Thus a portion of the barrel contents were placed in four stainless steel pans each measuring 10.5 inches x 7.25 inches x 6.25 inches. These pans were filled to a height of 10.5 cm with the above nitrate containing solution and were monitored for nitrate, nitrite, and ammonia as previously described (Exp. No 2). The amount of liquid was kept constant in this experiment. The results are described in Table 2.

Table 9

Solar Conversion of Nitrates and Nitrites to  $N_2O$  and  $N_2$  (Exp. No. 2)

Sample No.	Date	Total Nitrogen ppm	Nitrate ppm	Nitrite ppm	Ammonia ppm	pH
1	3-16-77	12,090	12,320	2,607	10,370	5.80
2	3-24-77	11,475	10,472	1,964	10,370	6.10
3	4-4-77	10,440	8,272	1,188	10,004	6.05
4	4-13-77	10,340	7,040	792	10,370	6.15
5	4-21-77	9,485	7,568	545	9,171	6.35
6	5-2-77	8,875	6,424	380	8,906	5.90
7	6-1-77	5,513	4,400	43	5,490	6.50

A third experiment (Exp. No. 3) was conducted in the following manner. A solution of neutralized  $N_2O_4$  was obtained from the barrel used in the first experiment and transferred to a shallow aluminum pan measuring 65.8" x 18.7" x 2.4". This shallow pan allowed maxim exposure to sunlight. The results are shown in Table 3.

TABLE 10

SOLAR CONVERSION OF NITRATES AND NITRITES TO  $N_2O$  and  $N_2$  (Exp. No. 3)

Sample No	Date	Nitrate ppm	Nitrite ppm	Ammonia ppm	Total Nitrogen	pH
1	4-2-77	11,968	561	10,004	11,090	5.5
2	4-28-77	9,504	495	7,930	8,810	5.9
3	5-9-77	11,264	165	7,930	9,110	6.1
4	5-17-77	8,360	69.3	7,930	8,421	6.0
5 *	6-1-77	3,432	19.8	2,928	3,186	6.9

\* No further samples could be taken due to overflow caused by rain

It is evident from the results that a pH approaching neutrality favors the reactions expressed in equations 1 and 2. At pH 8.0 a distinct smell of ammonia was noted. It is also evident that a greater exposure to sunlight allows greater rate of conversion of  $NO_3^\ominus$  and  $NO_2^\ominus$  to  $N_2O$  and  $N_2$  as demonstrated dramatically in these experiments.

a. Conclusion

The results obtained strongly indicate that solar conversion of high concentrations of  $\text{NaNO}_3$  and  $\text{NaNO}_2$  to  $\text{N}_2\text{O}$  and  $\text{N}_2$  is feasible. Therefore it may be desirable to plan for a second disposal pond to hold high concentrations of  $\text{NaNO}_3$  and  $\text{NaNO}_2$  in addition to the pond containing hyacinths already planned. Such an arrangement, involving the construction of two small ponds rather than one big one may be far more economical in construction costs and may also save on dilution water usage.