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DISPOSAL OF
HYPERGOLIC PROPELLANTS

Task 4 Report

Disposal Pond Products

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by

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PREFACE

This study was conducted by Florida Institute of Technology under Contract NAS 10-8399, administered by the National Aeronautics and Space Administration, John F. Kennedy Space Center, Florida. The NASA Technical Representative for the contract was Mr. Harold H. Franks, DD-MDD, and the Alternate Technical Representative was Mr. Jimmy L. Dobson, DD-MDD. Florida Institute of Technology's study manager was Dr. Thomas E. Bowman, Mechanical Engineering Department.

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1. Abstract

The waste MMH scrubber liquor will consist of aqueous solutions containing small amounts of CH_4, Cl_2, CH_3Cl, CH_2Cl_2 and $CHCl_3$ as well as large amounts of CH_3OH. This waste is scheduled to be disposed of in stabilization ponds along with nitrate and nitrite salt solutions obtained as waste liquors from the N_2O_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 N_2O and 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 CH_3OH, CH_3Cl, CH_2Cl_2, $CHCl_3$ and 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 (cm^2) is calculated by triangulation:

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

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_2 30 ml/min

Ethanol (EtOH) was used as an internal standard. The conditions were those established for C_1-C_6 alcohols as presented in McNair and Bonnelli'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 ug/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^2 at a range and attenuation of $2x10^{-12}$ 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^2 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_2Cl_2, IPA and $CHCl_3$

Run	Test	Atten x 10^{-12}	Conc.ppm	Sample ID	Base cm	Ht cm	Area cm^2
607	4-5-19A	16	1000	MeOH	4.9	21.9	53.655
				$CHCl_3$	4.1	11.7	23.985
608	4-5-19B	16	1000	$CHCl_3$	4.1	20.8	42.640
609	4-5-19C	16	1000	$CHCl_3$	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	$CHCl_3$	4.1	24.7	50.635
612	4-5-19F	32	1000	MeOH	1.1	17.9	9.845
				CH_2Cl_2	1.6	31.1*	24.880
				$CHCl_3$	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_2Cl_2	1.7	12.2	10.370
				$CHCl_3$	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_2Cl_2	1.7	10.2	8.670
				IPA	1.8	19.8	17.820
				$CHCl_3$	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_2Cl_2	1.6	18.6	14.880
				$CHCl_3$	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_2Cl_2	1.6	4.7	3.760
				IPA	1.9	9.4	8.930
				$CHCl_3$	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_2Cl_2	1.8	7.7	6.9300
				IPA	1.8	19.4	17.460
				$CHCl_3$	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_2Cl_2	1.6	3.9	3.120
				IPA	3.0	8.2	8.200
				$CHCl_3$	3.3	0.9	1.485

Table 1 (cont.) Data Utilized in Establishing standard curves for MeOH, EtOH, CH_2Cl_2, IPA and $CHCl_3$

Run	Test	Atten, x 10^{-12}	Conc. ppm	Sample ID	Base cm	Ht. cm	Area cm^2
620	4-5-20C	64	500	MeOH	1.7	2.8	2.380
				EtOH	1.2	10.4	6.240
				CH_2Cl_2	1.1	7.5	4.125
				IPA	1.9	16.3	15.485
				$CHCl_3$	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_2Cl_2	1.7	14.3	12.155
				$CHCl_3$	4.4	3.5	7.700
622	4-5-20E	16	500	MeOH	1.3	13.0	8.450
				CH_2Cl_2	1.8	24.1	21.690
				$CHCl_3$	4.4	6.2	13.640
623	4-5-20F	8	500	MeOH	1.4	25.9	18.130
				$CHCl_3$	4.0	10.5	21.000
624	4-5-20G	4	500	$CHCl_3$	4.3	19.9	42.785
625	4-5-20H	64	100	CH_2Cl_2	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_2Cl_2	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_2Cl_2	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_2Cl_2	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_2Cl_2	2.1	18.2	19.110
				IPA	3.1	29.1	45.105
				$CHCl_3$	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
				$CHCl_3$	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

Conc (ppm)	Attenuation x Range	Area (cm^2)
100	2×10^{-12}	62.275
	4×10^{-12}	30.800
	8×10^{-12}	10.560
	16×10^{-12}	8.695
500	32×10^{-12}	14.350
	64×10^{-12}	6.240
	128×10^{-12}	3.510
1000	64×10^{-12}	13.310
	64×10^{-12}	15.600
	128×10^{-12}	7.290
	128×10^{-12}	8.250
	256×10^{-12}	3.960

2. Calculating ug at attenuation of 1

Conc (ppm)	Conc (ug/ml)/Attenuation	Conc at Attenuation 1	Area (cm^2)
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^2

ug/ml	cm^2	cm^2/ug/ml
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
		12.184
		12

4. Data Finalization for Plotting Slope

a. Summation — Number of samples (n) = 12

Σcm^2/us/ml = 12.184

b. Slope n/Summation

average cm^2/ug/ml = .985

c. Plotting points. Area vs concentration

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

GLC Standard Curve for Ethanol

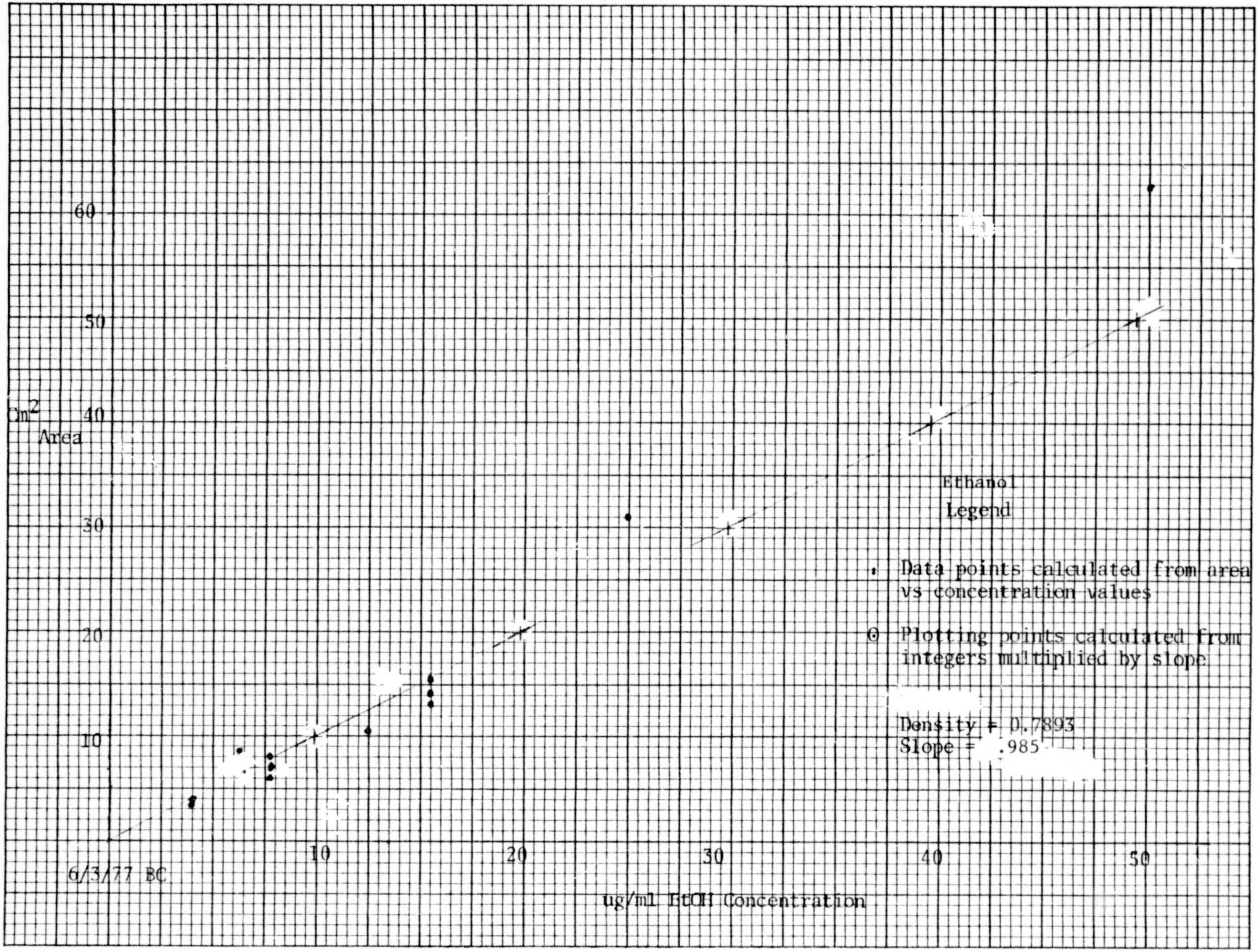

Fig. 1

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

Conc (ppm)	Attenuation x Range	Area (cm^2)
100	4×10^{-12}	45.105
	8×10^{-12}	19.635
	16×10^{-12}	12.775
	32×10^{-12}	5.950
	64×10^{-12}	2.970
500	64×10^{-12}	15.485
	128×10^{-12}	8.200
1000	128×10^{-12}	17.460
	128×10^{-12}	17.820
	256×10^{-12}	8.930

2. Calculating ug/ml at attenuation of 1

Conc. ppm	Conc. (ug/ml)/Atten.	Conc. at Atten. 1	Area (cm^2)
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^2

ug/ml	cm^2	cm^2/ug/ml
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: $cm^2/ug/ml$ = 20.078 Number of samples (n)=10

b. Slope: average $cm^2/ug/ml$= .498

c. Plotting points. Area vs concentration

5 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

Conc (ppm)	Attenuation x Range	Area (cm^2)
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

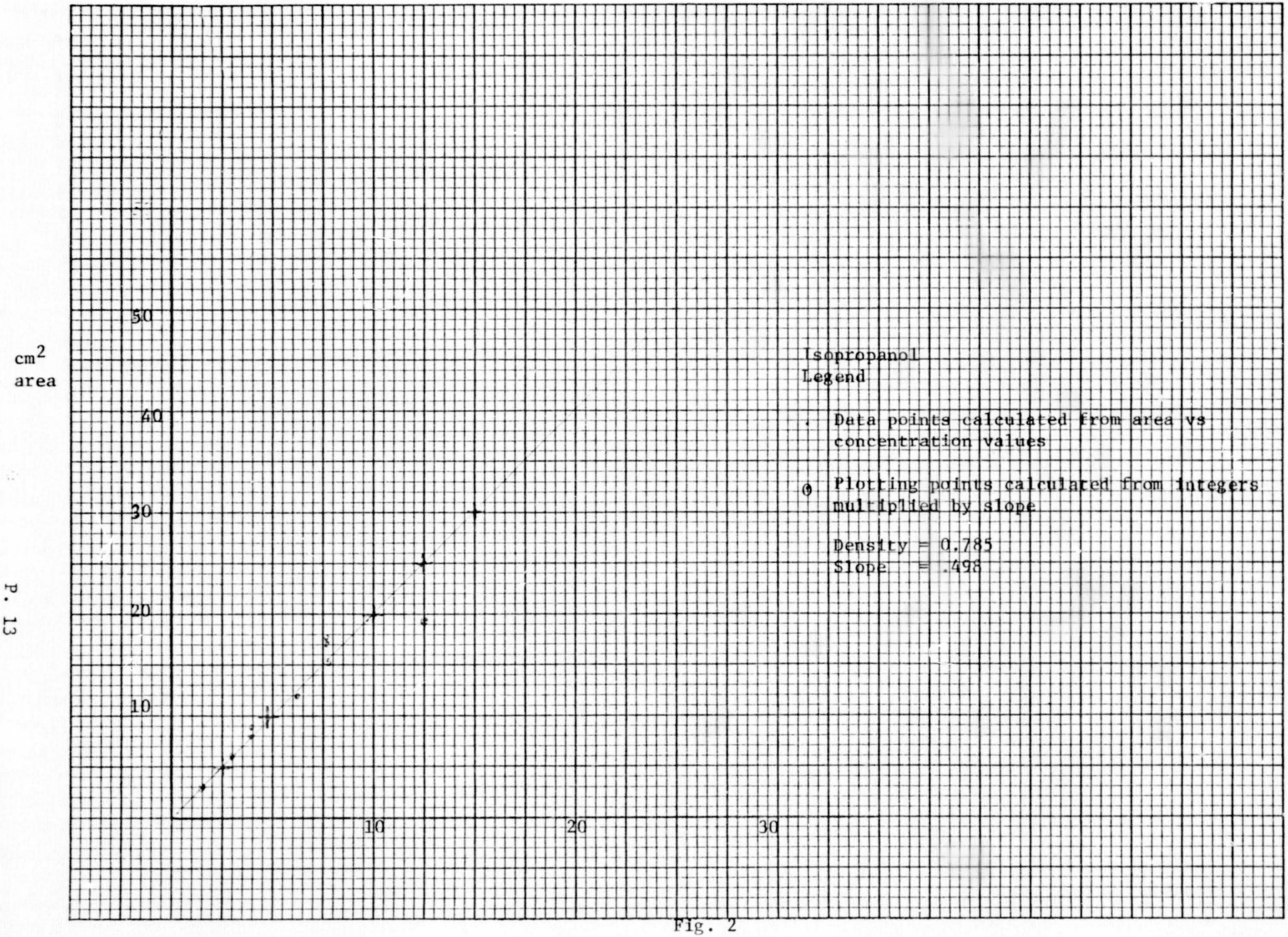

Fig. 2

2. Calculating ug at attention of 1

Conc. (ppm)	Conc.(ug/ml/Atten.	Conc. at Atten. 1	Area(cm^2)
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^2

ug/ml	cm^2	cm^2/ug/ml
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: Σ cm^2/ug/ml = 6.961 Number of samples(n) = 16

b. Slope: median cm^2/ug/ml = 2.299

c. Plotting points. Area vs concentration

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

GLC Standard Curve for Methanol

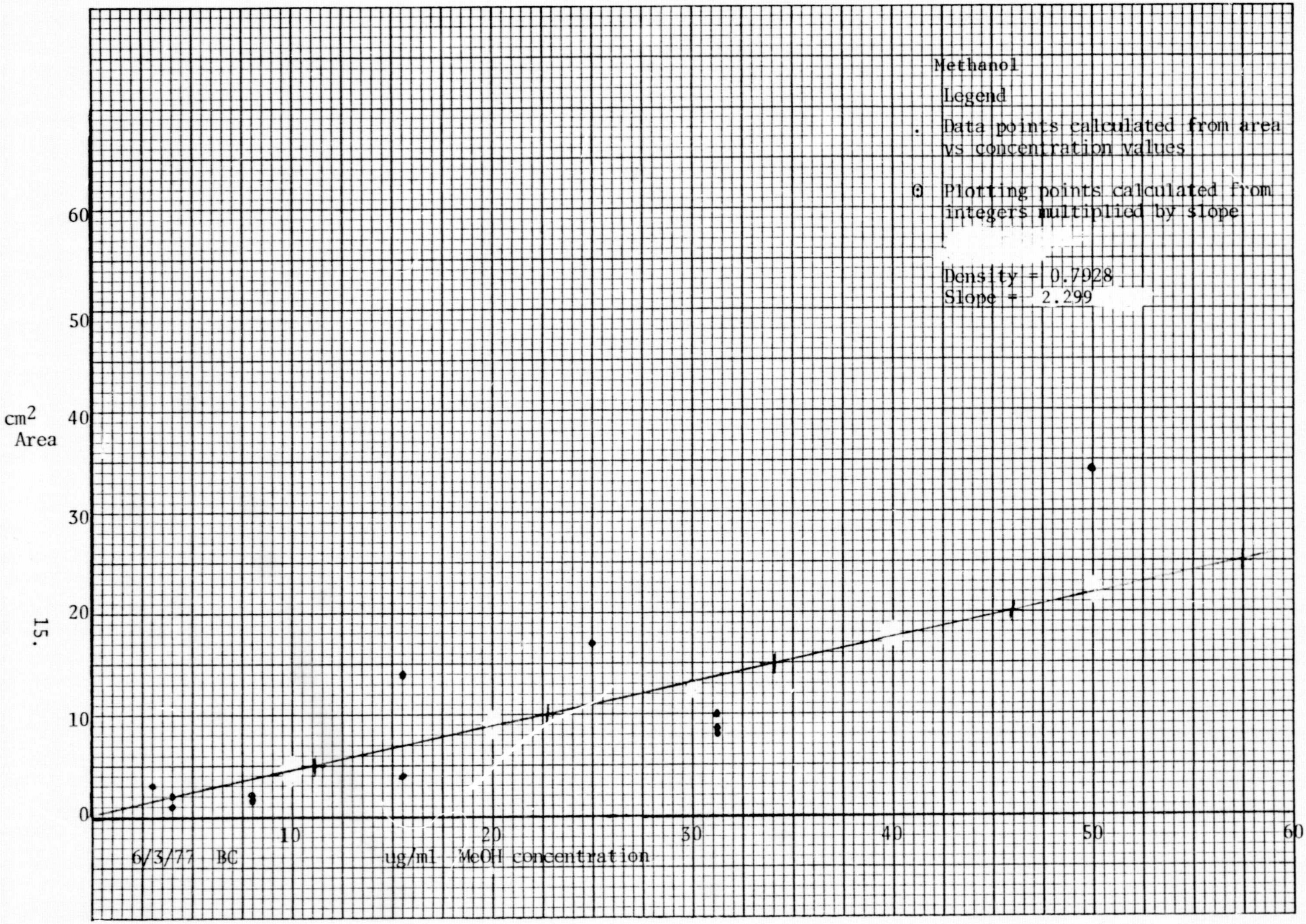

Fig. 3

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

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

2. Calculating ug at attenuation of 1

Conc (ppm)	Conc (ug)/Attenuation	Conc at Attenuation 1	Area (cm^2)
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^2

ug/ml	cm^2	cm^2/ug
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: Σ cm^2/ug/ml = 12.164 Number of samples (n) = 14

b. Slope: average cm^2/ug/ml = 1.151

c. Plotting points. Area vs concentration

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

GLC Standard Curve for Methylene Chloride

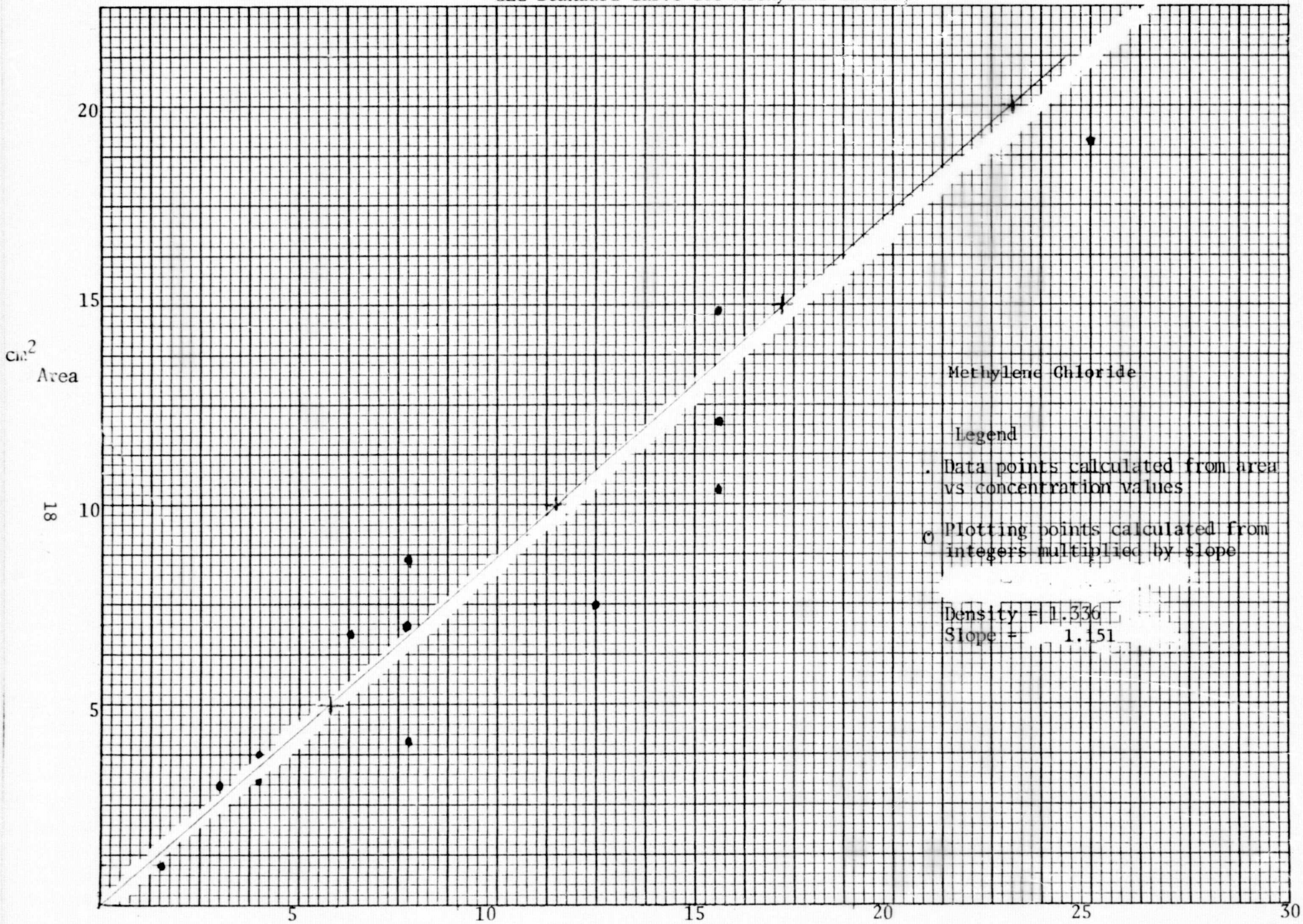

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Fig. 4

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

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

2. Calculating ug/ml at attenuation of 1

Conc (ppm)	Conc (ug/ml/Atten.	Conc at Atten. 1	Area (cm^2)
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^2

ug/ml	cm^2	cm^2/ug/ml
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

a. Summation: Σ cm^2/ug/ml = 9.251 Number of samples(n) = 18

b. Slope: Average cm^2/ug/ml = 1.946

c. Plotting points. Area vs concentration

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

GLC Standard Curve for Chloroform

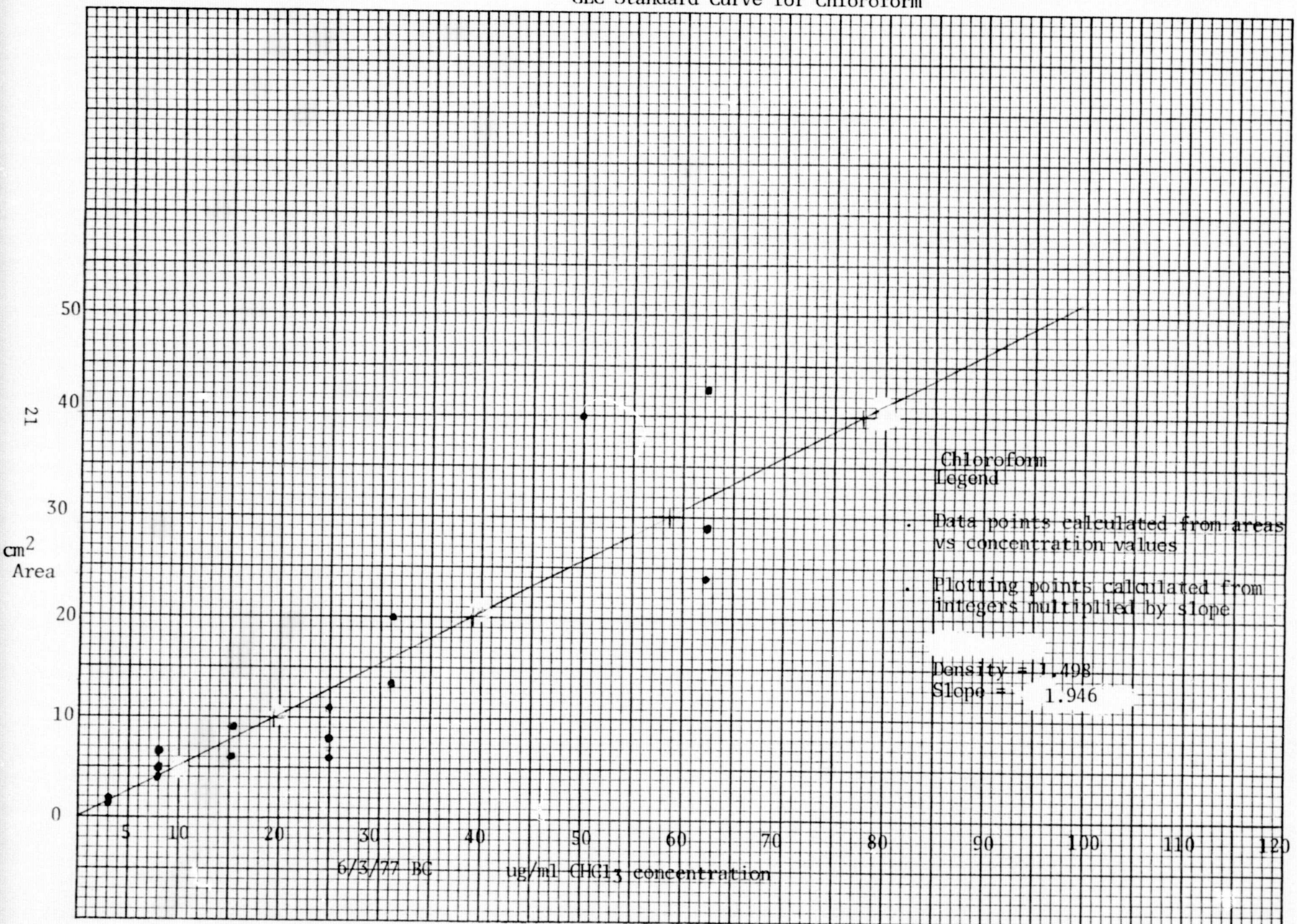

Fig. 5

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_2O 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_2O) to pan A.

2) 500 mls of 5% MMH (25 mls MMH and 475 mls H_2O) to pan B.

3) 500 mls of 1% MMH (5 mls MMH and 495 mls H_2O) to pan C.

4) 500 mls of 0.5% MMH (2.5 mls MMH and 297.5 mls H_2O) to pan D.

5. 500 mls of 0.1% MMH (0.5 mls MMH and 499.5 mls H_2O) to pan E.

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

Table 2.

Reaction Temperature of Various MMH Concentrations in 5% NaOCl

Pan	Conc. of MMH	Time of Max. Temp.	Temperature
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

Dates	Percent Degradation
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_2 source added. The results show that MMH is essentially totally degradeded 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.

Sample Date	A	B	C	D	E
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

Pan	Percent Degradation
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_1-1 (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_3OH	41.862	96.241
	CH_2Cl_2	115.639	133.100
	$CHCl_3$	4.652	9.053
B (5.0%)	CH_3OH	74.325	170.873
	CH_2Cl_2	55.130	63.455
	$CHCl_3$	2.337	4.458
C (1.0%)	CH_3OH	5.155	11.851
	CH_2Cl_2	2.055	2.365
	$CHCl_3$	.043	.084
D (0.5%)	CH_3OH	3.311	7.612
	CH_2Cl_2	1.383	1.592
	$CHCl_3$	.016	.031
E (0.1%)	CH_3OH	2.513	5.777
	CH_2Cl_2	.447	.514
	$CHCl_3$	.007	.014

Table 7 (cont.)

G_1-4 (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_3OH	.402	.924
	CH_2Cl_2	10.223	11.767
	$CHCl_3$	.608	1.183
B (5.0%)	CH_3OH	.487	1.120
	CH_2Cl_2	1.626	1.872
	$CHCl_3$	.141	.274
C (1.0%)	CH_3OH	.909	2.090
	CH_2Cl_2	.236	.272
	$CHCl_3$	.021	.041
D (0.5%)	CH_3OH	1.650	3.793
	CH_2Cl_2	.252	.240
	$CHCl_3$	.007	.014
E (0.1%)	CH_3OH	1.005	2.310
	CH_2Cl_2	.015	.017
	$CHCl_3$	.003	.006

Table 7 (cont.)

$G_1 \cdot 5$ (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_3OH	.240	.552
	CH_2Cl_2	4.024	4.632
	$CHCl_3$	.324	.631
B (5.0%)	CH_3OH	.459	1.055
	CH_2Cl_2	1.153	1.327
	$CHCl_3$	.083	.162
C (1.0%)	CH_3OH	.526	1.209
	CH_2Cl_2	.088	.101
	$CHCl_3$	.013	.025
D (0.5%)	CH_3OH	1.202	2.763
	CH_2Cl_2	.117	.135
	$CHCl_3$	.004	.008
E (0.1%)	CH_3OH	.853	1.961
	CH_2Cl_2	.007	.008
	$CHCl_3$	.002	.004

Table 7 (cont.)

G_1-6 (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_3OH	.155	.356
	CH_2Cl_2	2.785	3.206
	$CHCl_3$	.162	.315
B (5.0%)	CH_3OH	.192	.441
	CH_2Cl_2	.222	.256
	$CHCl_3$	.057	.111
C (1.0%)	CH_3OH	.316	.726
	CH_2Cl_2	.036	.041
	$CHCl_3$	.011	.021
D (0.5%)	CH_3OH	.859	1.975
	CH_2Cl_2	.048	.055
	$CHCl_3$	.003	.006
E (0.1%)	CH_3OH	.732	1.683
	CH_2Cl_2	*	*
	$CHCl_3$	*	*

*Concentration level below detection limits

Table 7 (cont.)

G_2-1 (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_3OH	37.566	86.364
	CH_2Cl_2	109.342	125.853
	$CHCl_3$	5.711	11.114
B (5.0%)	CH_3OH	21.573	49.596
	CH_2Cl_2	50.450	58.068
	$CHCl_3$	1.027	1.999
C (1.0%)	CH_3OH	3.323	7.640
	CH_2Cl_2	1.130	1.301
	$CHCl_3$	.056	.109
D (0.5%)	CH_3OH	3.307	7.603
	CH_2Cl_2	1.552	1.786
	$CHCl_3$	.012	.023
E (0.1%)	CH_3OH	1.944	4.469
	CH_2Cl_2	.526	.605
	$CHCl_3$	.009	.018

Table 7 (cont.)

G_2-2 (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_3OH	23.396	53.787
	CH_2Cl_2	83.257	95.829
	$CHCl_3$	3.222	6.270
B (5.0%)	CH_3OH	14.937	34.340
	CH_2Cl_2	38.281	44.061
	$CHCl_3$	.534	1.039
C (1.0%)	CH_3OH	2.641	6.072
	CH_2Cl_2	.091	.105
	$CHCl_3$	.044	.086
D (0.5%)	CH_3OH	2.176	5.003
	CH_2Cl_2	.936	1.077
	$CHCl_3$	.007	.014
E (0.1%)	CH_3OH	1.274	2.929
	CH_2Cl_2	.420	.483
	$CHCl_3$	.006	.012

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

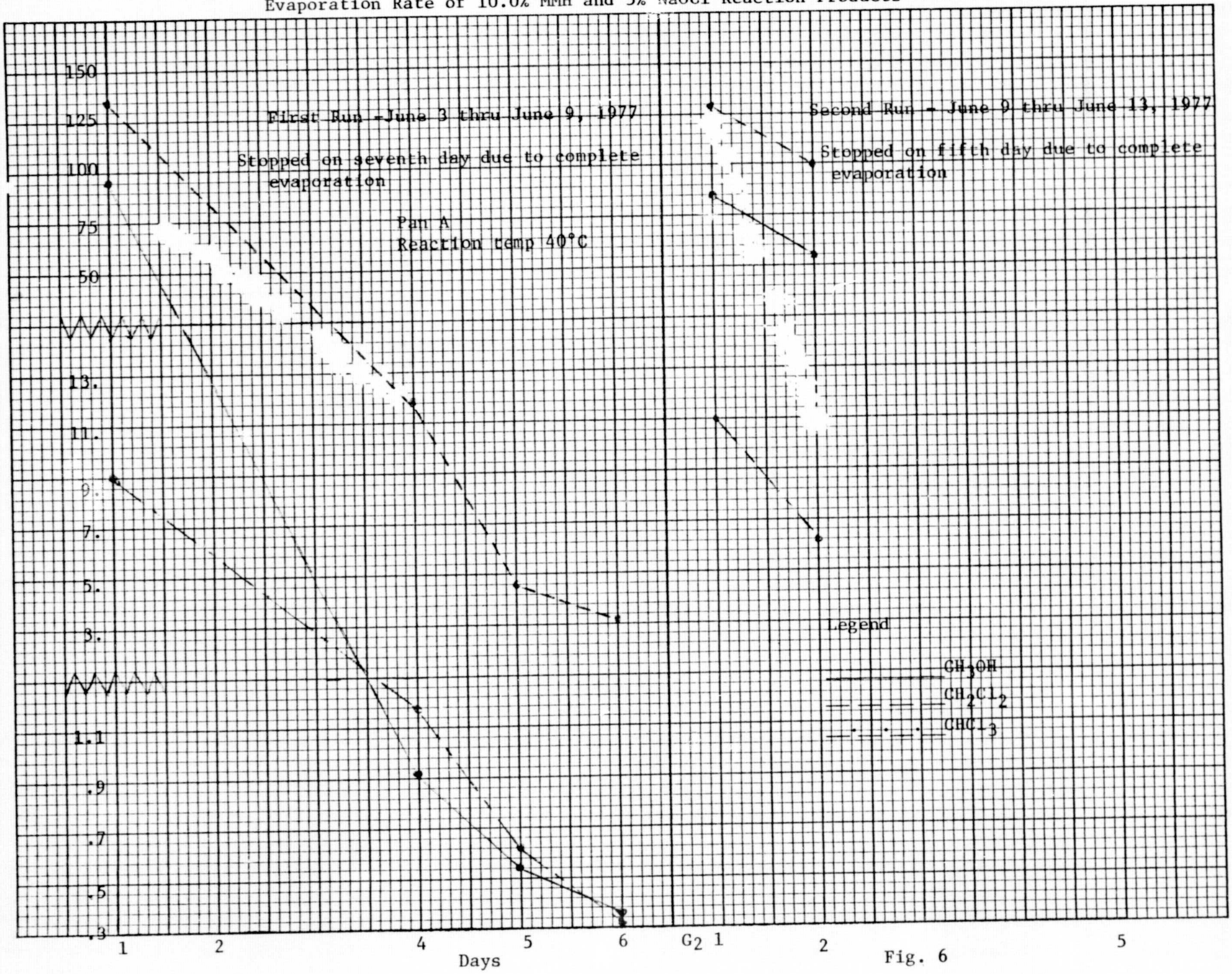

Fig. 6

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

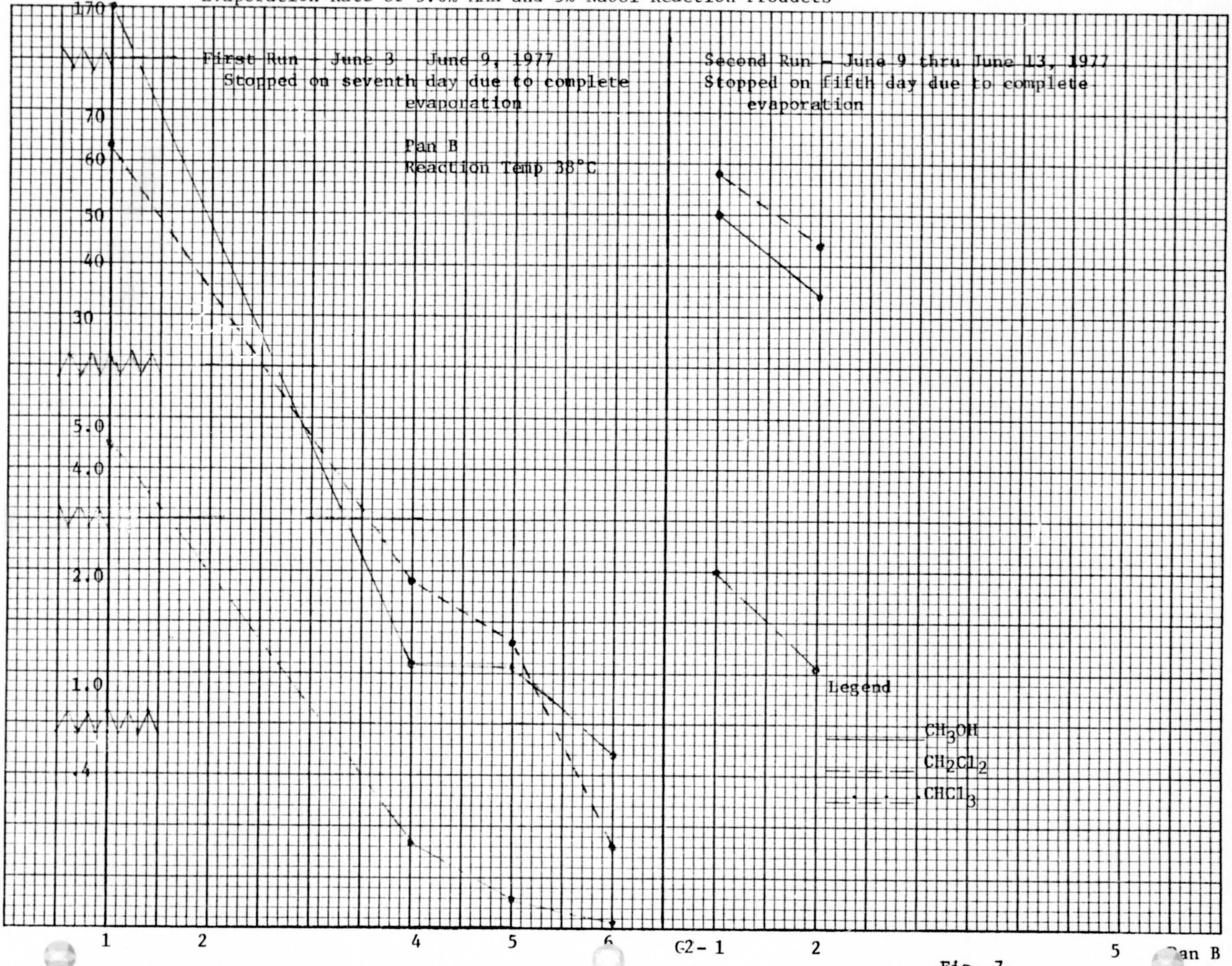

Fig. 7

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

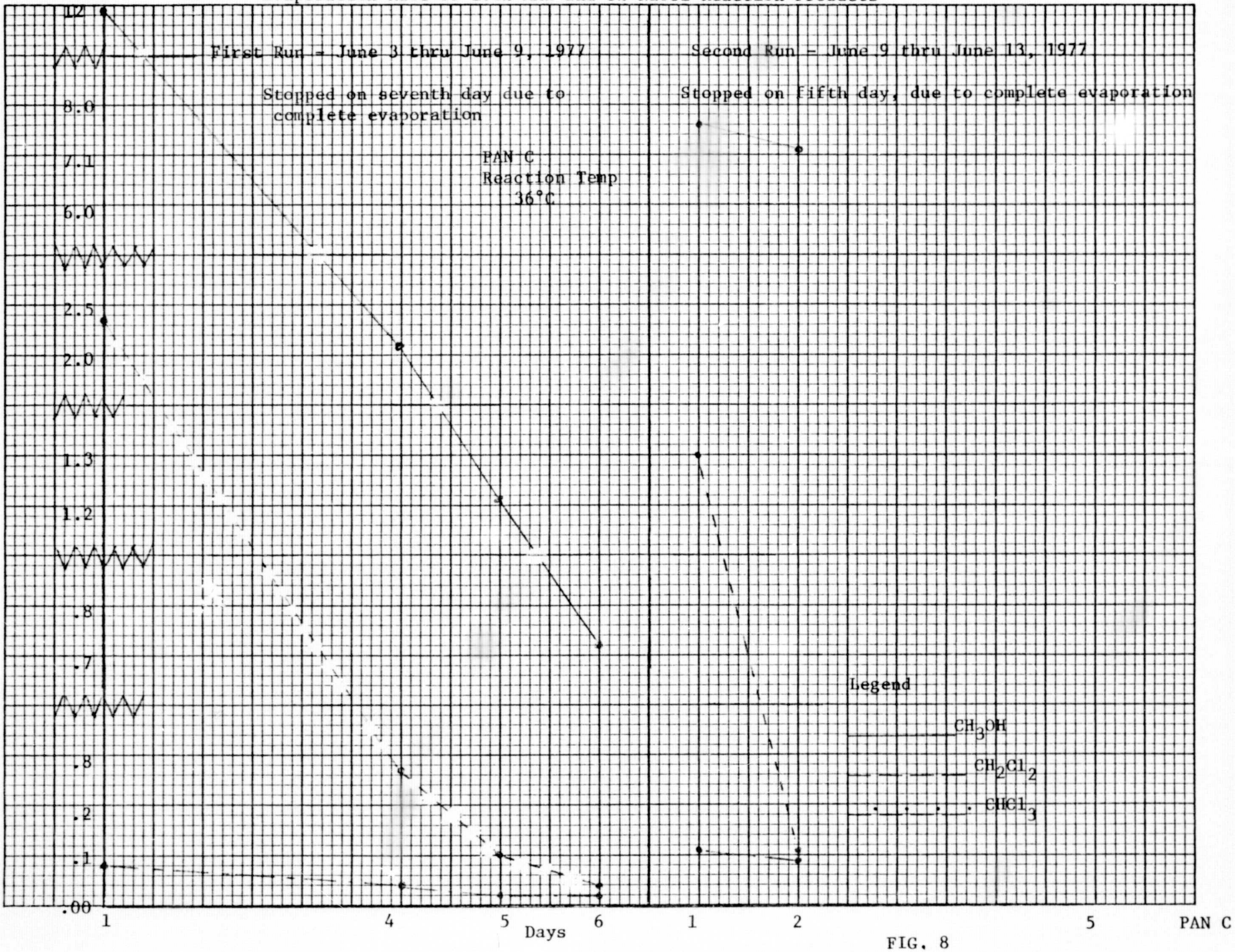

FIG. 8

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

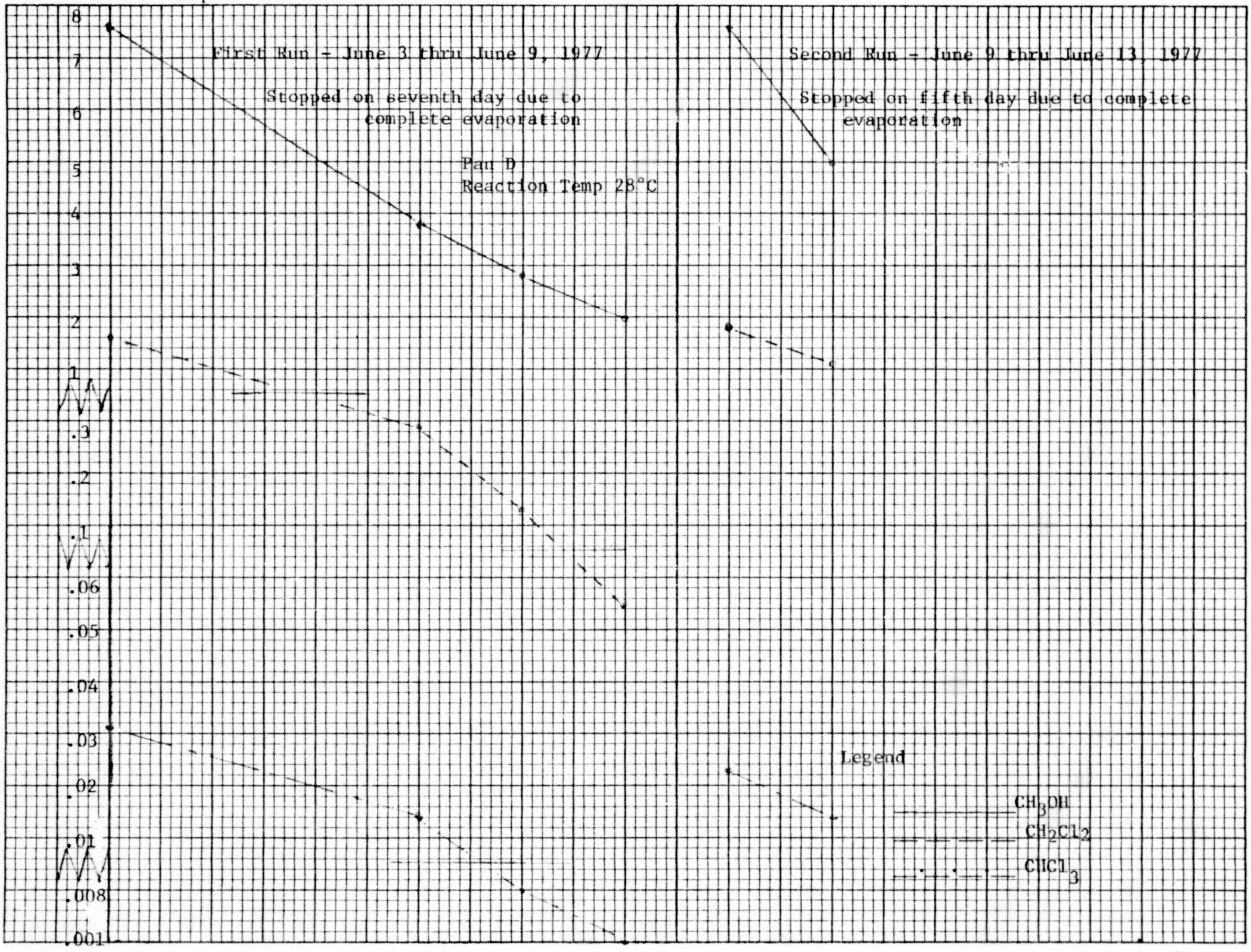

Fig. 9

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

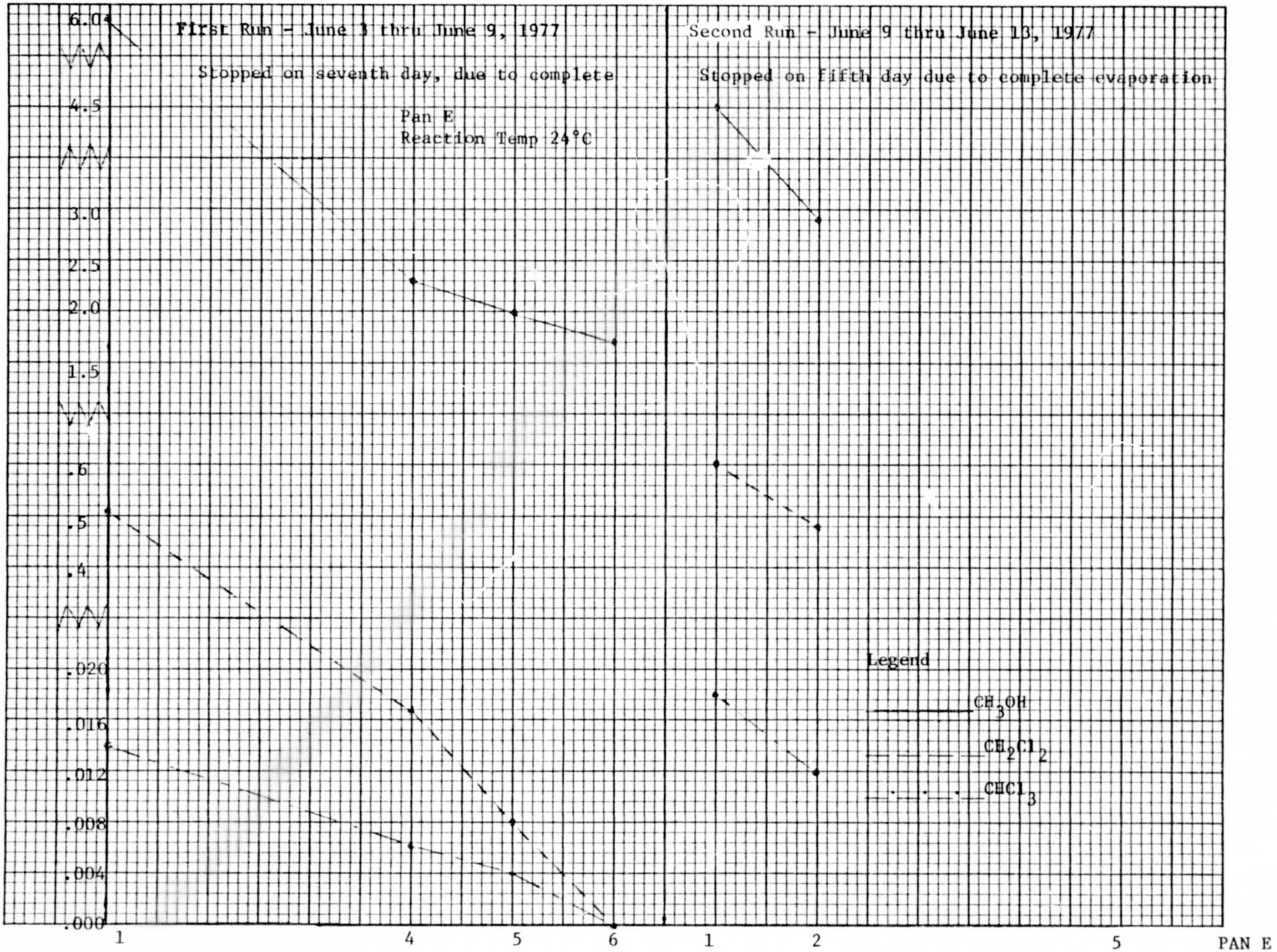

Fig. 10

C. Summary

The concentration of $CHCl_3$ 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 CH_3OH and CH_2Cl_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 $CHCl_3$ 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 ($NaNO_3$) and sodium nitrite ($NaNO_2$) 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 $NaNO_3$ and $NaNO_2$. 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:

1) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

2) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

N_2O 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 N_2O_4 and 4 lbs. of ammonium chloride (NH_4Cl) 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_20_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_20 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^{Θ} and NO_2^{Θ} to N_20 and N_2 as demonstrated dramatically in these experiments.

a. Conclusion

The results obtained strongly indicate that solar conversion of high concentrations of $NaNO_3$ and $NaNO_2$ to N_2O and N_2 is feasible. Therefore it may be desirable to plan for a second disposal pond to hold high concentrations of $NaNO_3$ and $NaNO_2$ 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.