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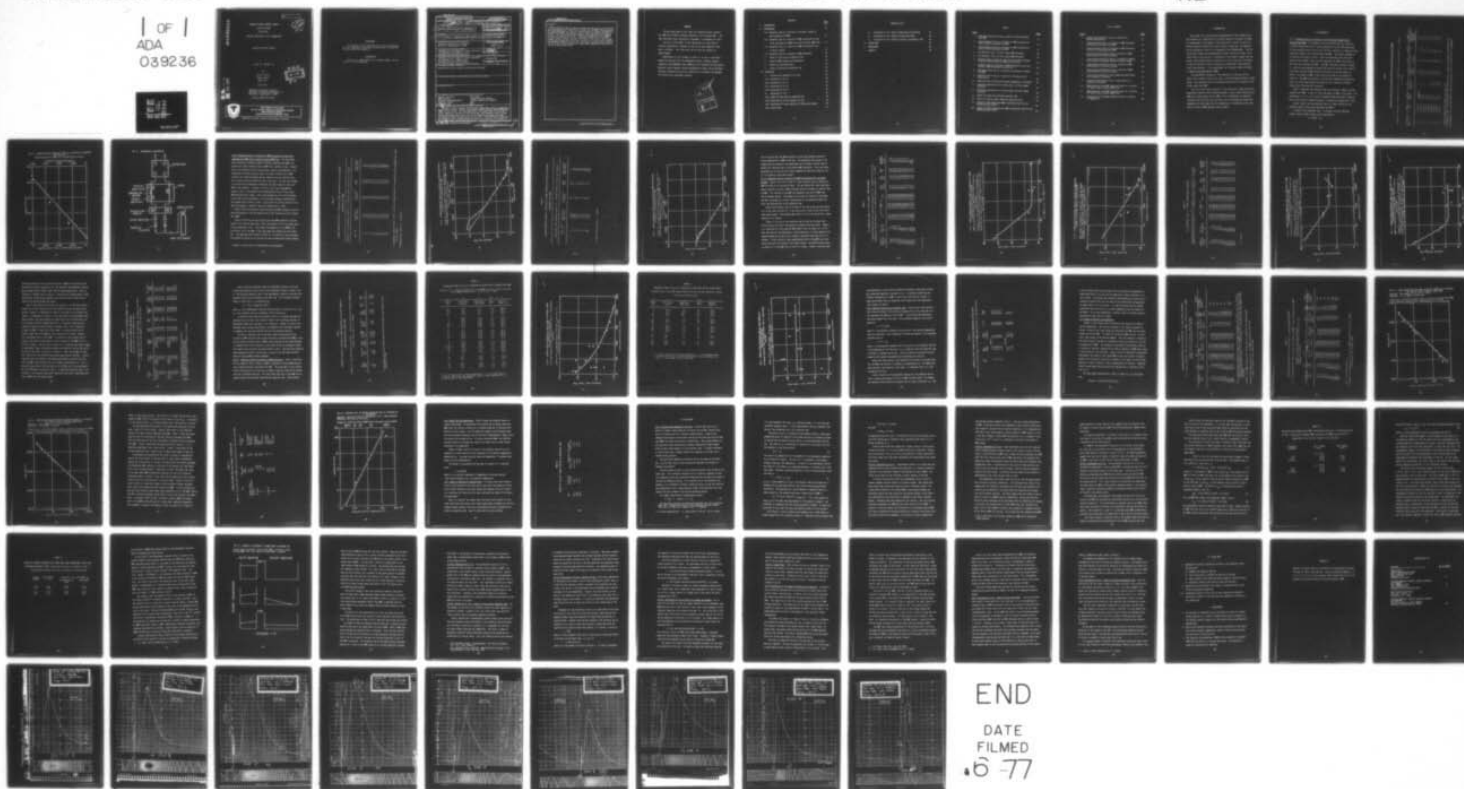
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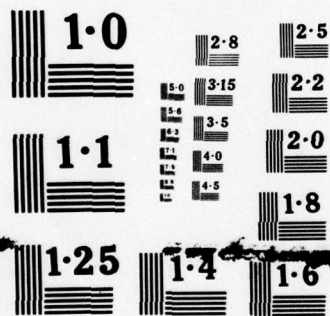
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RESIDUAL PROTECTIVE LIFE OF CARBON BEDS

Quarterly Progress Report

1 Sep. 76 - 30 Nov. 76

By

Alvin H. Weiss

Thomas Freund

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April 1977



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Retention times of weakly sorbed (probe) gases were used as a measure of the residual sorption capacity for strongly sorbed dimethyl methylphosphonate (DMMP) on ASC carbon. At room temperature, with space time of 3 sec and 12 cm/sec superficial velocity of He carrier gas, the retention time of carbon dioxide decreased from 4 to 0.3 min as the fractional length of the bed saturated with DMMP increased from zero to unity. Under different conditions the retention time of ethane decreased from 1.6 to 0.03 min as a mixture of He and DMMP vapors passed into the column.		

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→ The retention times of ethane and carbon dioxide as well as other probe gases were measured as a function of He flow rate and DMMP loading. Desorption experiments were carried out by passing pure He through a bed initially saturated with DMMP; the retention time of ethane was measured during the process. The rate of desorption of DMMP at room temperature was measured by successive weighings of a bed. To monitor movement of zone of DMMP through a zone of carbon, beds were fabricated in two parts: a section containing saturated carbon (inlet) and a section with a clean carbon (outlet). The movement of DMMP was monitored by the change in weight and in retention time of carbon dioxide through each tandem bed as DMMP moved from the first section to the second section.

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PREFACE

The work described in this report was authorized under Contract No. DAAA 15-76-C-0072, "Residual Protective Life of Carbon Beds". The work described covers the period of September 1 to November 30, 1976.

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I INTRODUCTION

Our concept for a non-destructive determination of the residual sorption capacity of a carbon bed for a strongly sorbed air pollutant is based on a measurement of the length of time required for a pulse of a gas in a flowing stream of another gas to pass through a carbon bed. The approach can be considered in terms of the language of gas chromatography. Thus the "carbon bed" becomes the chromatographic column; "the pulse of gas", hereafter known as the probe gas, is equivalent to the sample injected into the column; "the flowing stream of another gas" is the carrier gas; the length of time for the pulse of gas to traverse the carbon bed is the retention time of the probe gas. In our experiments the "strongly sorbed" pollutant is dimethyl methylphosphonate (DMMP).

The experimental procedure is the injection of a test gas such as ethane into a stream of carrier gas (e.g., air) which passes through a carbon column. The retention time of the probe gas varies with the loading of the carbon column with DMMP.

The rest of this report concerns (1) the search for a probe gas with an appropriate retention time difference between a carbon column saturated with DMMP and a carbon column free of DMMP, (2) an investigation of operating variables such as carrier gas flow rate, size of the probe gas sample, and temperature of the column, and (3) simulating, on a laboratory scale, movement of a zone of DMMP through a bed of carbon.

II EXPERIMENTAL

II-1-A Retention time as a function of the fractional length of bed saturated with DMMP: The retention time of the probe gas, CO_2 (0.25 cc), in helium carrier gas at $29 \pm 1^\circ\text{C}$ was determined on 2.00 g ASC carbon beds of cross-sectional area 0.164 cm^2 (1/4 inch O.D. tubing) as a function of the fractional length of the bed saturated with DMMP. The bed was composed of two sections of tubing in series. When a bed contained other than both sections free of DMMP or both sections saturated with DMMP, the section at the inlet side contained the DMMP. The DMMP "saturated" sections, columns 1-1' and 3-3', were prepared by passing 650 liters of helium, over a period of 39 hours, through a DMMP saturator and thence to the two columns in series. The weight of DMMP in each section was shown to be constant to within 2%. The DMMP-free sections of the bed were prepared by passing 635 liters of helium (used without purification) over a period of 39 hours through the as-received ASC carbon bed.

Table 1 summarizes the retention times and fractional length of column saturated with DMMP. Column III gives the weight of DMMP in the column. The uncertainty of $\pm 0.01 \text{ g}$ is a result of weighing before and after injections and not the intrinsic weighing accuracy. ΔP through the columns was < 1 torr.

Figure 1 shows that the retention time is a linear function of the fractional length of the column saturated with DMMP.

In terms of the retention time, t in minutes, and the fractional residual capacity (FRC) results can be expressed as:

$$t = 4(\text{FRC}) + 0.3$$

TABLE 1

Retention Time and Fractional Length of Column Saturated with DMMPProbe Gas 0.25cc CO₂, Temperature 29-30°C, 2.00g ASC Carbon, Carrier Gas He, V_s = 4.08 ccV_s = 4.08cc

I	II	III	IV	V	VI	VII.**	VIII
Expt. No.	Bed *	DMMP wt (g)	Fraction of Bed Sat.	Retention Time, t (min)	Vol. Flow, F (cc/min)	F t/V _s	Superficial ** velocity (cm/sec)
1	1-1/3-3'	0.68±0.01	1	0.34	76	5.7	7.5
2	1-1/3-3'	0.68	1	0.33	76	5.5	7.5
3	2-2/4-4'	0.00	0	4.43	78	76	7.7
4	1-1/3-3'	0.68	1	0.33	76	5.5	7.5
5	2-2/4-4'	0.00	0	4.20	78	72	7.7
6	1-1/4-4'	0.43	0.67	1.35	78	23	7.7
7	3-3/2-2'	0.22	0.33	2.73	76	46	7.5
8	1-1/4-4'	0.43	0.67	1.33	78	23	7.7
9	3-3/2-2'	0.22	0.33	2.70	76	45	7.5

* Inlet column/outlet column (see Figure A)

** Retention time divided by space time (space time = volume of the bed, V_s/flow rate, F)

*** Volumetric flow rate divided by the cross-sectional area of the bed (0.17 in diameter)

FIG 1: CARBON DIOXIDE RETENTION TIME AS A FUNCTION OF RESIDUAL
BED CAPACITY

Bed Prepared from DMMP-sat and DMMP-free sections.

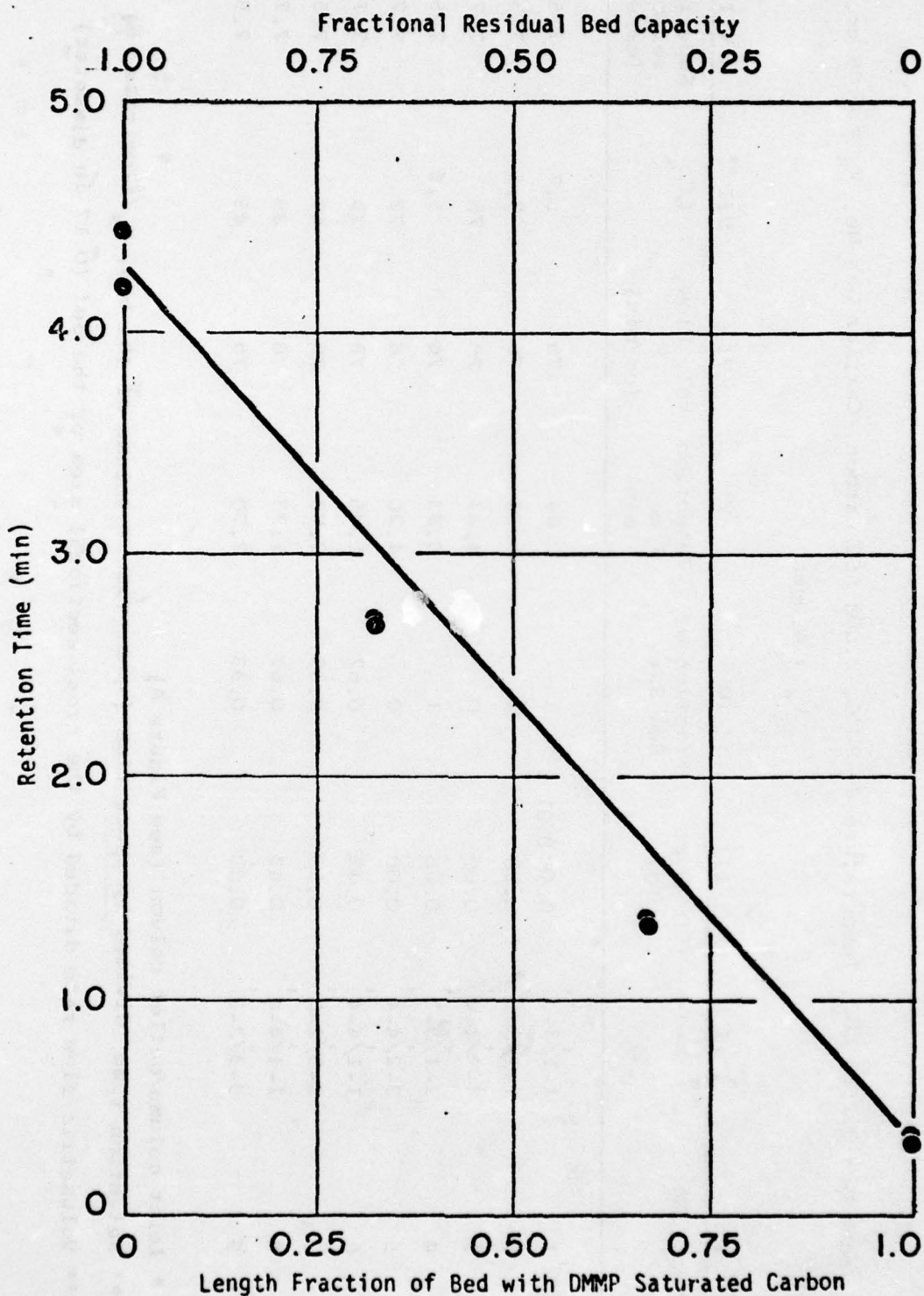
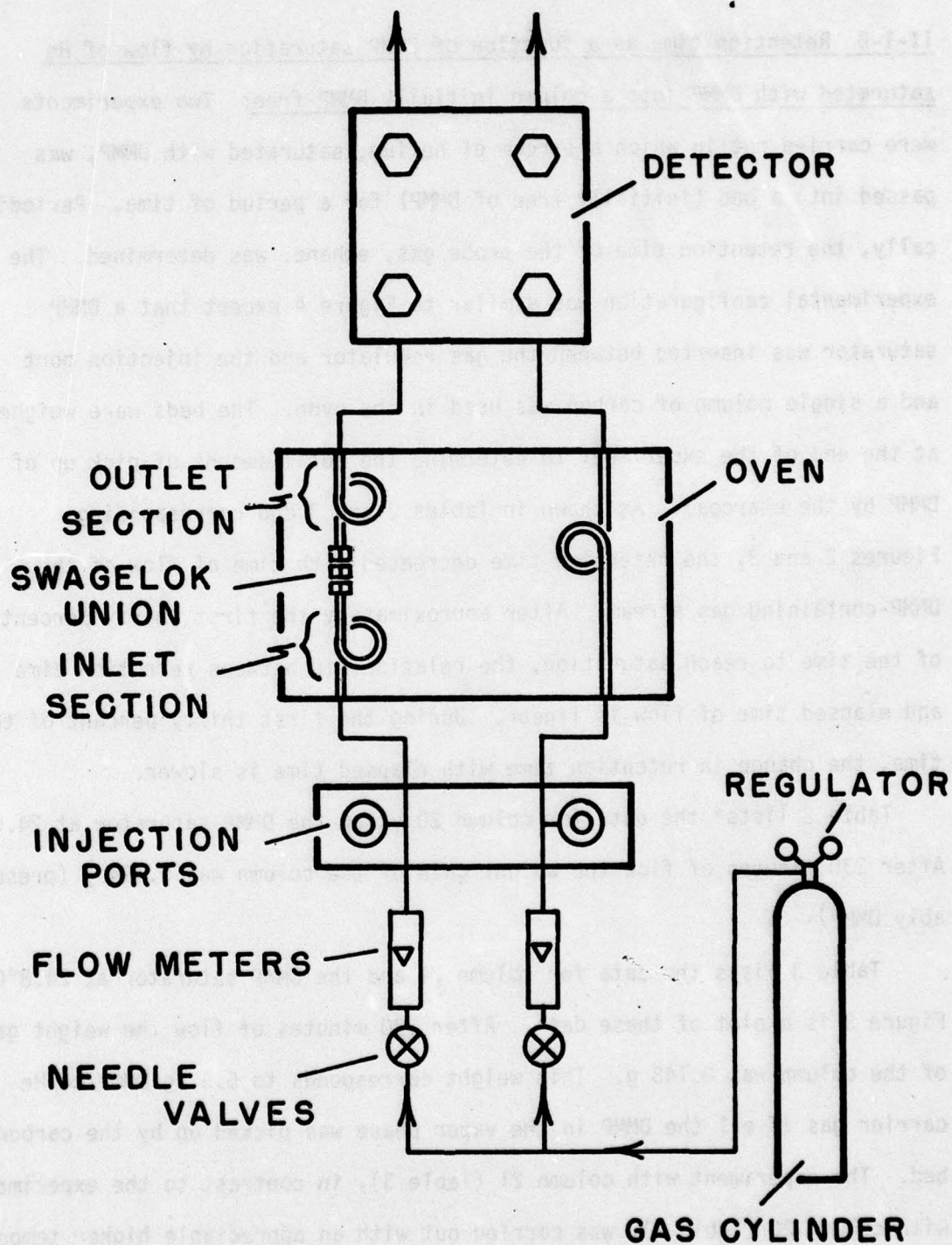


FIG. A: EXPERIMENTAL CONFIGURATION



II-1-B Retention time as a function of DMMP saturation by flow of He saturated with DMMP into a column initially DMMP-free: Two experiments were carried out in which a stream of helium, saturated with DMMP, was passed into a bed (initially free of DMMP) for a period of time. Periodically, the retention time of the probe gas, ethane, was determined. The experimental configuration was similar to Figure A except that a DMMP saturator was inserted between the gas regulator and the injection port and a single column of carbon was used in the oven. The beds were weighed at the end of the experiment to determine the total amount of pick up of DMMP by the charcoal. As shown in Tables 2 and 3 and corresponding Figures 2 and 3, the retention time decreased with time of flow of the DMMP-containing gas stream. After approximately the first thirty percent of the time to reach saturation, the relationship between retention time and elapsed time of flow is linear. During the first thirty percent of the time, the change in retention time with elapsed time is slower.

Table 2 lists* the data for column 20 using the DMMP saturator at 24.0°C. After 230 minutes of flow the weight gain of the column was 0.194 g (presumably DMMP).

Table 3 lists the data for column 21 and the DMMP saturator at 24.8°C. Figure 3 is a plot of these data. After 120 minutes of flow the weight gain of the column was 0.143 g. This weight corresponds to 5.5 µg DMMP/cc He carrier gas if all the DMMP in the vapor phase was picked up by the carbon bed. The experiment with column 21 (Table 3), in contrast to the experiment with column 20 (Table 2), was carried out with an appreciable higher tempera-

* Appendix A shows copies of representative chromatographs.

TABLE 2 *

ETHANE RETENTION TIME AS A FUNCTION OF DMMP SATURATION BY FLOW OF HELIUM

SATURATED WITH DMMP

Probe Gas : 0.4cc Ethane; Column 2 O: 0.50g ASC carbon; Carrier gas: Helium

Exp. No.	Retention Time, (min)	Flow rate ** (cc/min)	Temp. °C	Time of gas flow (min)
1	1.58	203	23.0	15
2	1.53	202	23.0	39
4	1.27	203	23.0	60
5	0.85	203	23.0	93
6	0.72	203	23.1	110
8	0.59	203	23.1	125
9	0.43	203	23.1	142
11	0.34	203	23.1	155
12	0.21	203	23.1	172
13	0.20	203	23.1	173
14	0.11	203	23.4	185
15	0.09	203	23.4	188
16	0.05	203	23.4	201
17	0.04	203	23.2	205
20	0.03	203	23.2	227

* Appendix A shows copies of the original chromatographs for representative determinations given in this Table.

** Superficial velocity - 21 cm/sec

FIG 2: ETHANE RETENTION TIME AS A FUNCTION OF DMMP SATURATION
BY FLOW OF He SATURATED WITH DMMP

Column 20, 0.50g ASC Carbon; Flow Rate: 200cc/min He; Probe Gas:
0.40cc Ethane; Temperature: 23.0-23.4°C; Weight DMMP: 0.00g at
0 min, 0.194g at 230 min.

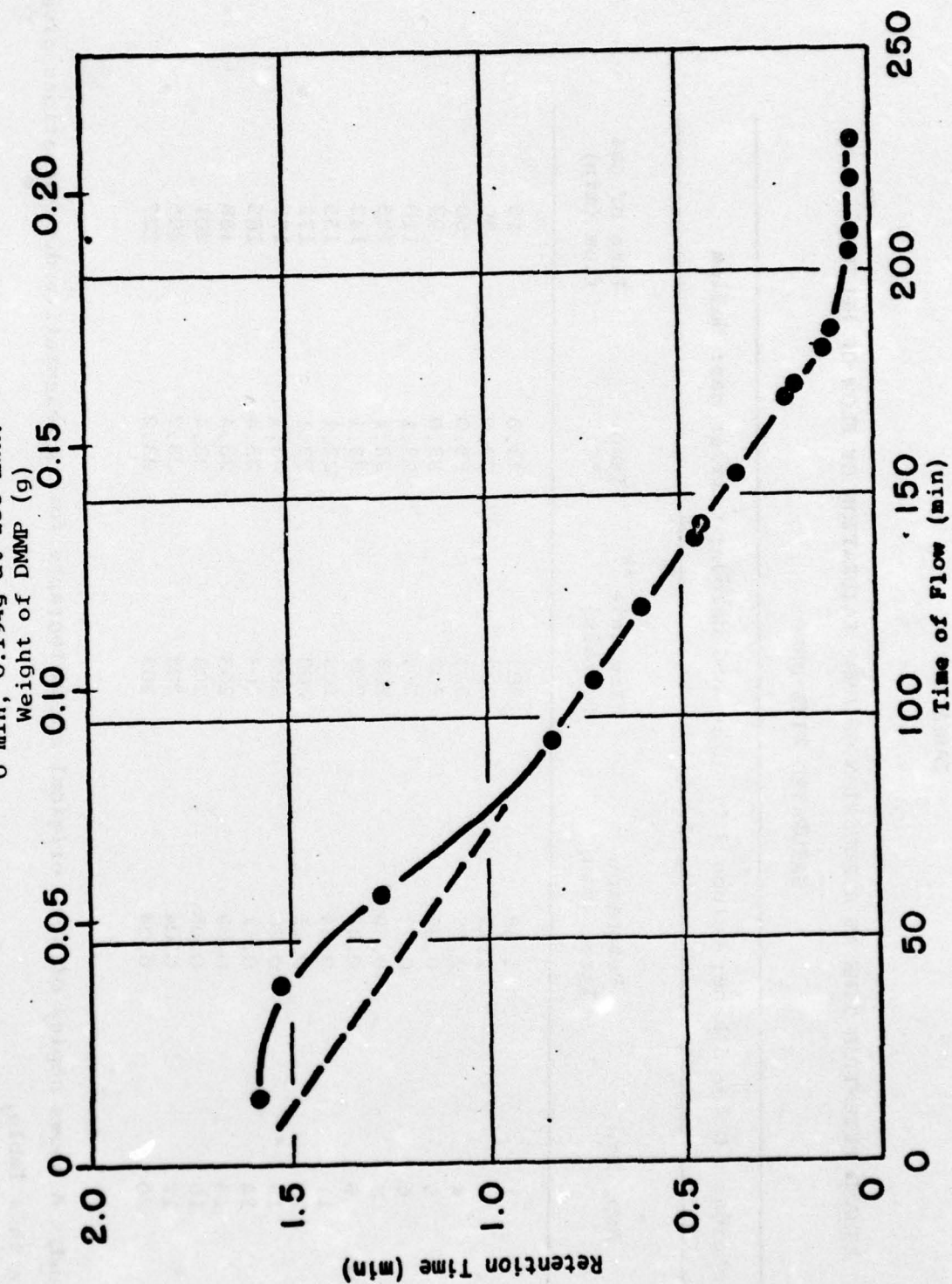


TABLE 3

ETHANE RETENTION TIME AS A FUNCTION OF DMMP SATURATION BY FLOW OF HELIUM

SATURATED WITH DMMP

Probe gas: 0.4cc Ethane; Column 2l: 0.50g ASC carbon; Carrier gas: Helium

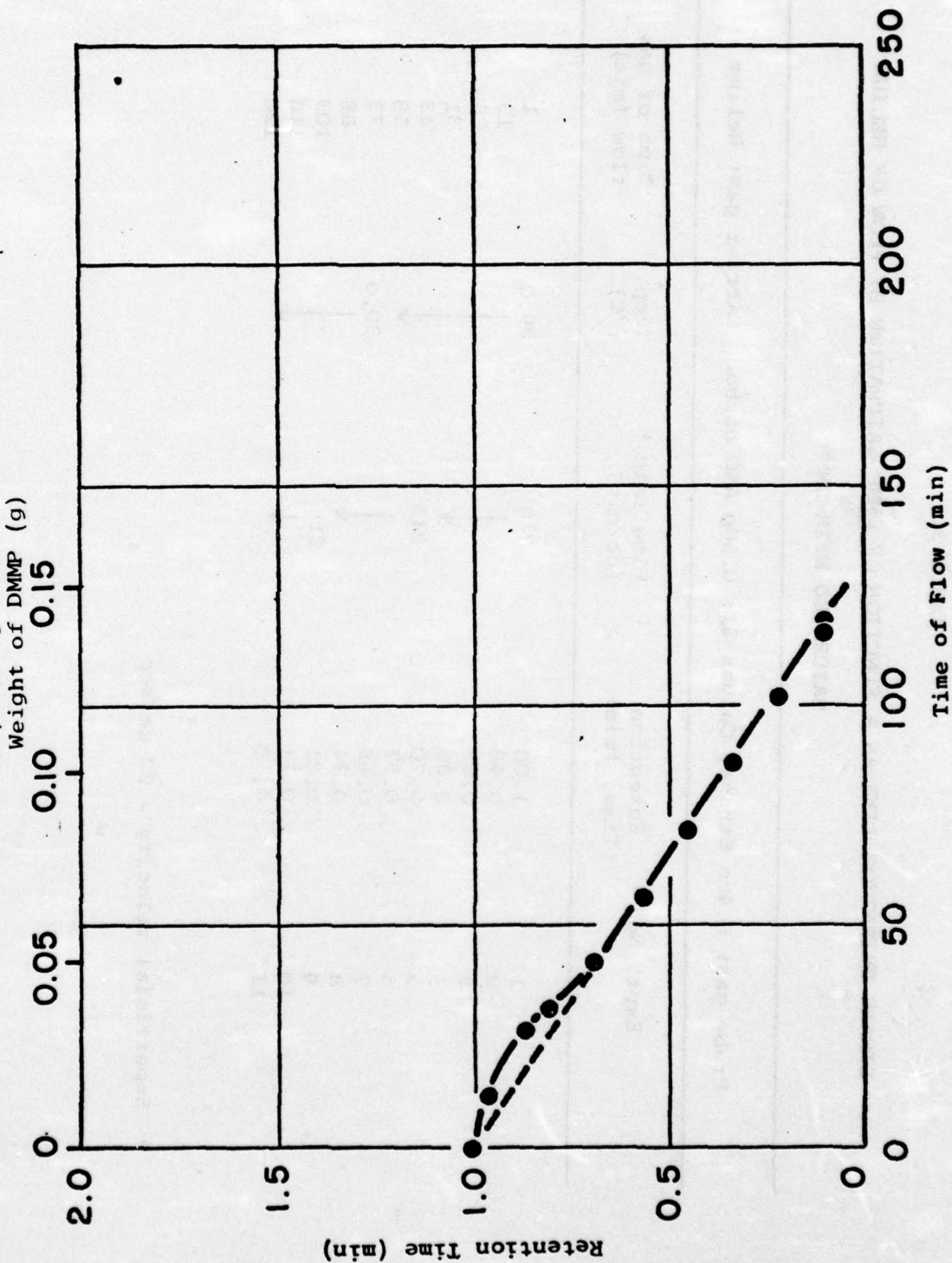
Expt. No.	Retention Time, (min)	Flow rate * (cc/min)	Temp. (°C)	Time of gas flow (min)
1	1.00	216	29.0	1
2	0.98	↓	↓	13
3	0.85	↓	↓	28
4	0.80	215	↓	31
5	0.70	↓	↓	43
6	0.57	↓	↓	58
7	0.45	216	30.0	73
8	0.34	↓	↓	88
9	0.21	↓	↓	103
10	0.11	↓	↓	118
11	0.10	↓	↓	120

* Superficial velocity - 22 cm/sec

Fig 3

FIG 3: ETHANE RETENTION TIME AS A FUNCTION OF DMMP SATURATION
BY FLOW OF He SATURATED WITH DMMP

Column 21, 0.50g ASC Carbon; Flow Rate: 215cc/min He; Probe Gas:
0.40cc Ethane; Temperature: 29-30°C; Weight DMMP: 0.000g at
0 min, 0.143g at 120 min



ture of the bed than the DMMP saturator to avoid any possible problem of liquid condensation of DMMP in the bed. The experiment with column 21 was stopped when the retention time approached zero to obtain a better idea of whether the retention went to zero before DMMP saturation. Also, the latter experiment was carried out at a higher temperature than with column 20, and all the retention times were shorter.

II-1-C Retention time as a function of DMMP distribution with in-series columns: Tables 4 and 5 and Figures 4-7 show retention time as function of DMMP distribution on two-section beds. The two-section ASC carbon beds were made by placing in series a DMMP-saturated section followed by a section free of DMMP. The location of the DMMP was changed by the flow of DMMP-free helium through the bed. The weights at the time of injection of the probe gas were calculated by a linear interpolation of the weighings before and after the determination of the retention time.

Table 4 and Figures 4 and 5 are data for the two-column bed with column 3-3' at the inlet end and 2-2' at the outlet end; a short column first and a long column second. The average space time is 2.4 sec and superficial linear velocity is 8.1 cm/sec.

Figure 5 is a plot of the retention time divided by the space time (Ft/V_s) versus the log of the volume of He passed into the column. Figure 4 is a linear-plot of Ft/V_s against DMMP weight ratio on column 3-3' to 2-2'. Over the course of the experiment, lasting 600 hours, 2.6 cubic meters of He passed through the columns with a change of retention time from 2.7 to 1.4 minutes. In this period of time, approximately half of the DMMP was transferred from the first column to the second column. The second column picked up almost all of the DMMP lost by the first column. Figure 4 indicates that

TABLE 4

CO₂ RETENTION TIME, 1/3 INLET LENGTH DMMP SATURATED

2.00g ASC Carbon Flow rate ~80cc/min Column 3-3' 2-2' Probe Gas 0.25 cc CO₂
 Temperature 29-30°C Column 3-3' = 0.6673g ASC Carbon, Column 2-2' = 1.3307g

Time of Gas Flow (hrs)	vol. of Gas Flow l	3-3'	2-2'	Total	Flow rate cc/min	Ret. time min	$\frac{F \cdot t}{V_s}$	$\frac{\text{wt 2-2'}}{\text{wt 3-3'}} \times 100$
0	0	0.2251	0.0000	0.2251				
0.68	3.1	0.2141	0.0115	0.2256	75.9	2.73	50.8	5.4
1.00	4.5	0.2090	0.0169	0.2259	75.9	2.70	50.2	8.09
7.30	34.8	0.1807	0.0478	0.2285	81.2	2.10	41.8	26.5
7.55	36.3	0.1796	0.0488	0.2283	81.2	2.10	41.8	27.2
10.00	47.5	0.1727	0.0580	0.2307	75.7	2.03	37.7	33.6
10.20	48.4	0.1721	0.0588	0.2309	75.7	2.05	38.0	34.2
78.8	380	0.1377	0.0871	0.2248	80.5	1.95	38.5	63.6
78.8	380	0.1377	0.0871	0.2248	80.5	1.88	37.1	63.6
103.6	492	0.1318	0.0888	0.2206	75.4	1.98	36.6	67.4
249.3	717	0.1105	0.1082	0.2187	73.2	1.90	34.1	97.9
249.3	717	0.1105	0.1082	0.2187	73.2	1.92	34.4	97.9
344.2	1289	0.0993	0.1103	0.2096	74.8	1.75	32.1	111
513.6	2158	(0.0891)	(0.1214)	(0.2105)	85.5	1.51	31.6	(136)
611.9	2648	0.0910	0.1122	0.2032	92.9	1.41	32.1	123

* $V_s = 4.08$

Fig 4

FIG 4: CARBON DIOXIDE RETENTION TIME AS A FUNCTION OF DMMP
DISTRIBUTION FOR IN-SERIES COLUMNS

DMMP Distribution given by DMMP weight ratio of inlet to
exit columns
Column 3-3', 0.67g ASC Carbon in Series with Column 2-2',
1.33g ASC Carbon; Flow Rate: 80cc/min He; Probe Gas: 0.25cc
Carbon Dioxide; Temperature 29-30°C; Column 3-3' at 0 min
sat. with DMMP

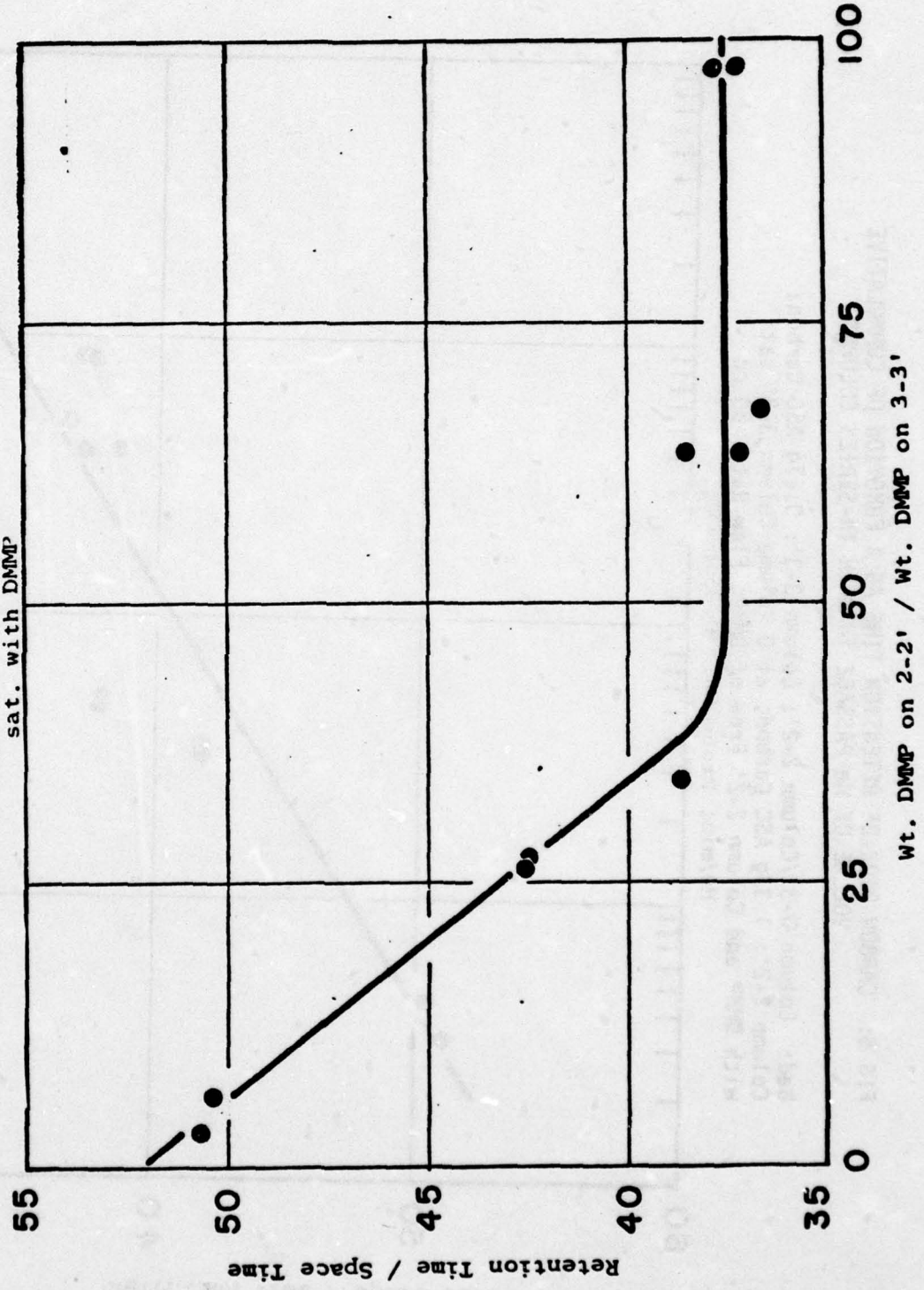


FIG 5: CARBON DIOXIDE RETENTION TIME AS A FUNCTION OF CUMULATIVE
VOLUME OF He PASSAGE THROUGH IN-SERIES COLUMNS

Bed: Column 3-3'/Column 2-2'; Column 3-3': 0.67g ASC Carbon;
Column 2-2': 1.33g ASC Carbon; at 0 Volume Column 3-3' sat
with DMMP and Column 2-2' Free of DMMP; Flow Rate: 80 cc
He/min; Probe Gas: 0.25cc CO₂

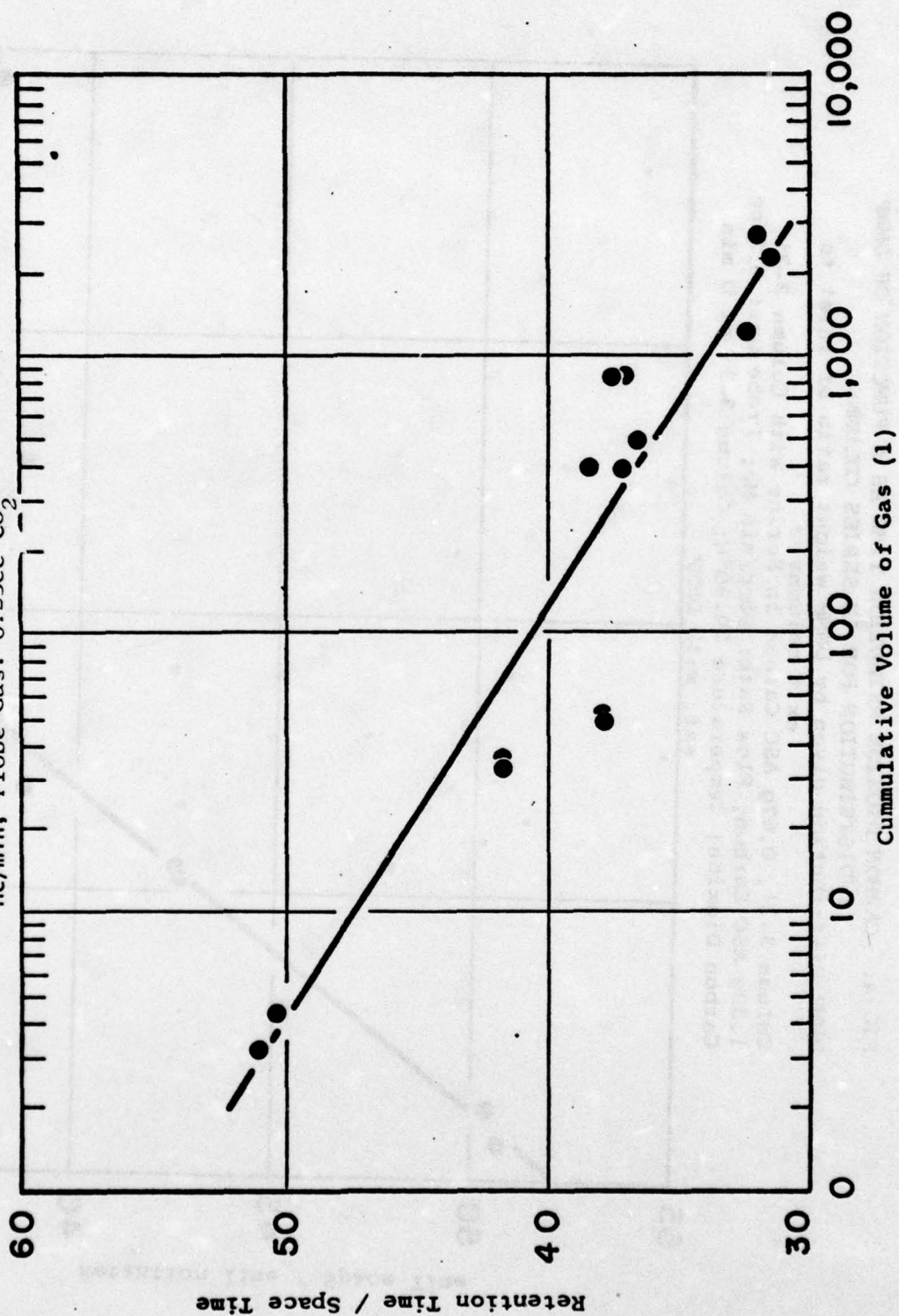


TABLE 5

CO₂ RETENTION TIME, 2/3 INLET LENGTH DMMP SATURATED

2.00g ASC Carbon; Flow Rate 80cc/min; Column 1-1'/4-4'; Probe Gas: 0.25 cc CO₂
 Temperature: 29-30°C; Column 1-1' : 1.3288g ASC Carbon, Column 4-4' : 0.6678g

Time of Gas Flow (hrs)	Vol of Gas Flow (l)	wts of DMMP (g)		Flow rate (cc/min)	Ret. time (min)	$\frac{F_t}{V_s}$	$\frac{wt\ 4-4'}{wt\ 1-1'} \times 100$
0	0	0.4425	0.0000	0.4425	0.4425	80.5	2.8
0.62	2.9	0.4298	0.0124	0.4422	1.35	26.6	4.1
0.90	4.3	0.4240	0.0181	0.4421	1.33	26.2	18.4
7.42	35.5	0.3727	0.0686	0.4413	0.91	17.8	18.7
7.67	36.7	0.3716	0.0695	0.4411	0.89	17.4	21.4
9.75	47.2	0.3614	0.0774	0.4388	0.90	17.1	21.7
9.93	48.0	0.3606	0.0781	0.4386	0.91	17.3	49.9
78.8	372	0.2878	0.1436	0.4314	0.78	14.9	49.9
78.8	372	0.2878	0.1436	0.4314	0.76	14.5	54.1
103.6	486	0.2766	0.1496	0.4262	0.68	12.8	69.5
249.3	1160	0.2367	0.1644	0.4251	0.63	12.1	69.5
249.3	1160	0.2367	0.1644	0.4251	0.65	12.4	70.5
344.2	1582	0.2167	0.1528	0.3695	0.73	13.2	73.6
513.6	2420	0.1945	0.1431	0.3376	0.74	14.9	67.1
611.9	2907	0.1980	0.1330	0.3310	0.71	15.8	

$V_s = 4.08\ cc$

FIG 6: CARBON DIOXIDE RETENTION TIME AS A FUNCTION OF DNMP
DISTRIBUTION FOR IN-SERIES COLUMNS

Retention Time vs. Log cumulative volume of He passed into
bed.

Column 1-1', 1.33g ASC Carbon in series with Column 4-4',
0.67g ASC Carbon; Flow Rate: 90cc/min He; Probe Gas 0.25cc
Carbon Dioxide; Temperature 29-30°C; Column 1-1' at 0 min
sat. with DNMP

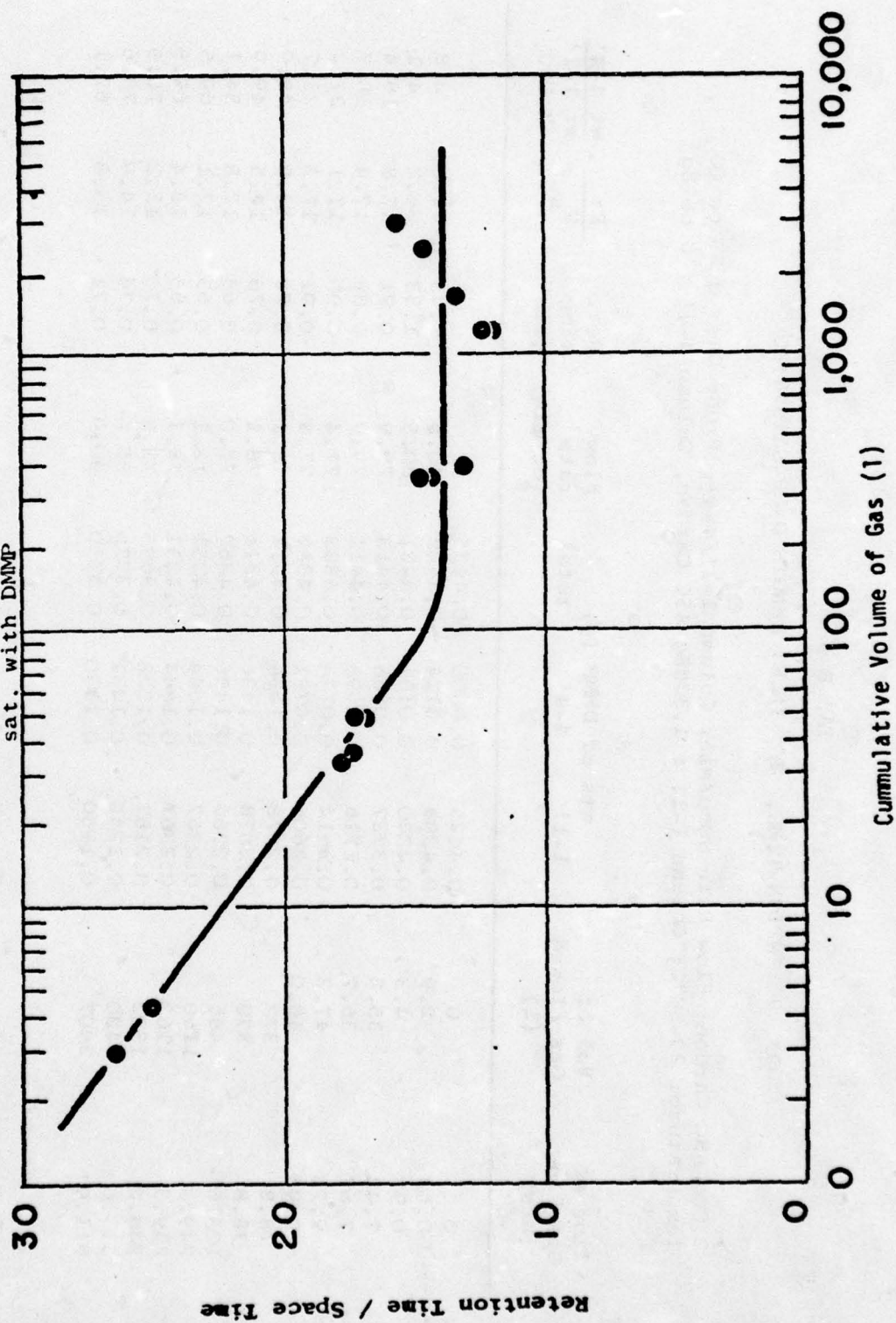
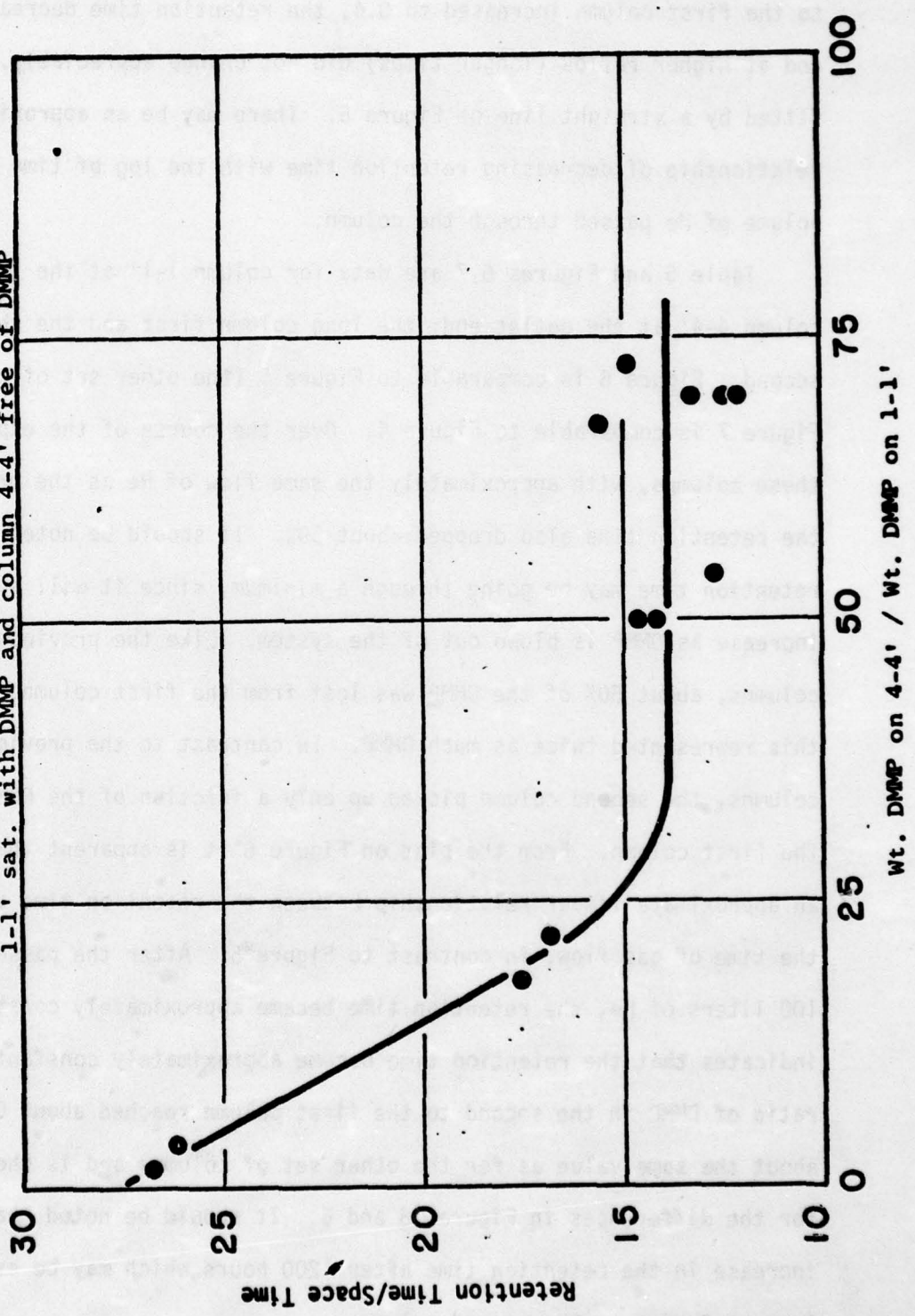


Fig 7

FIG 7: CARBON DIOXIDE RETENTION TIME AS A FUNCTION OF DMMP DISTRIBUTION FOR IN-SERIES COLUMNS
DMMP distribution given by DMMP weight ratio of inlet to exit columns

Column 1-1', 1.33g ASC Carbon in series with Column 4-4', 0.67g ASC Carbon; Flow Rate: 90cc/min He; Probe Gas: 0.25cc Carbon Dioxide; Temperature: 29-30°C; at time zero, column 1-1' sat. with DMMP and column 4-4' free of DMMP



during the period of time in which the ratio of DMMP on the second column to the first column increased to 0.4, the retention time decreased linearly, and at higher ratios (longer times) did not change appreciably. Data are fitted by a straight line on Figure 5. There may be an approximately linear relationship of decreasing retention time with the log of time of flow or volume of He passed through the column.

Table 5 and Figures 6,7 are data for column 1-1' at the inlet end and column 4-4' at the outlet end; the long column first and the short column second. Figure 6 is comparable to Figure 5 (the other set of columns) and Figure 7 is comparable to Figure 4. Over the course of the experiment with these columns, with approximately the same flow of He as the previous set, the retention time also dropped about 50%. It should be noted that the retention time may be going through a minimum, since it will eventually increase as DMMP is blown out of the system. Like the previous set of columns, about 50% of the DMMP was lost from the first column. However, this represented twice as much DMMP. In contrast to the previous set of columns, the second column picked up only a fraction of the DMMP lost by the first column. From the plot on Figure 6 it is apparent that there is not an approximate linear relationship between the retention time and the log of the time of gas flow, in contrast to Figure 5. After the passage of about 100 liters of He, the retention time became approximately constant. Figure 7 indicates that the retention time became approximately constant after the ratio of DMMP in the second to the first column reached about 0.4. This is about the same value as for the other set of columns and is the explanation for the differences in Figures 5 and 6. It should be noted that there is an increase in the retention time after 1200 hours which may be associated with loss of DMMP from the second column.

TABLE 6

RETENTION TIME OF INDIVIDUAL SECTIONS OF IN-SERIES COLUMNS AT END OF
REDISTRIBUTION OF DMMP BY HELIUM FLOW
(see last expt. at end of Tables 4 and 5)

Probe Gas : 0.25cc CO₂; Carrier Gas: He; Flow Rate: 90cc/min; Total Flow
of DMMP-free He into the columns: 2.5 m³ over 26 days

Column no	wt(s) carbon (g)	wt(s) DMMP (g)	Ret time min	$\frac{Ft}{V}$ s	total wt DMMP (g)	Flow rate cc/min	(cor) Ret * time (min)
3-3'/2-2' **	0.67/1.33	0.091/0.112	1.41	28.8	0.203	92.9	1.32
3-3'/2-2'	0.67/1.33	0.091/0.112	1.41	28.8	0.203	92.9	1.32
3-3'	0.67	0.091	0.20	12	0.091	92.9	0.15
3-3'	0.67	0.091	0.20	12	0.091	92.9	0.15
2-2'	1.33	0.112	1.20	36.4	0.112	91.5	1.11 a
2-2'	1.33	0.112	1.20	36.4	0.112	91.5	1.11 a
1-1'/4-4'	1.33/0.67	0.198/0.133	0.70	14.0	0.331	90.9	0.62
1-1'/4-4'	1.33/0.67	0.198/0.133	0.71	14.2	0.331	90.9	0.62
1-1'	1.33	0.198	0.43	13	0.198	90.9	0.36
1-1'	1.33	0.198	0.43	13	0.198	90.9	0.36
4-4'	0.67	0.133	0.19	11	0.133	90.6	0.14 b
4-4'	0.67	0.133	0.19	11	0.133	90.6	0.14 b

* (cor) Retention time see text for calculation

a) corrected to flow rate of 92.9cc/min

b) corrected to flow rate of 90.9cc/min

** Column 3-3' (inlet) connected to column 2-2' (outlet)

Table 6 shows the retention times for individual sections of the two-column beds measured at the finish of the experiments listed in Tables 4 and 5. The corrected retention time is the experimental retention time minus the retention time of He in nitrogen at the flow rate. The corrected retention time at a flow rate F_1 is calculated from

$$t'_1 = [t_2 - (F_A t_A / F_2)] (F_2 / F_1)$$

where t_2 is the experimental retention time for CO_2 at a flow rate of F_2 , and t_A is the retention time of He measured at the flow rate F_A .

It should be noted that the retention time of an in-series bed would be expected to be the sum of the retention times of the individual sections if they behave identically and there is no dispersion. However, the sum of the retention times (either uncorrected or corrected) of the individual sections is somewhat less than the retention time for the combined sections.

The drop in retention time of the dual columns associated with the transfer of DMMP from the inlet column (originally saturated with DMMP) to the outlet column (originally free of DMMP) can be ascribed to the large decrease in retention time of the originally clean column while the increase in retention time of the originally saturated column is small. Note that the retention time decreased for both in-series beds in spite of the fact that the total amount of sorbed DMMP decreased somewhat.

II-1-D Retention time as a function of DMMP desorption: Table 7 shows data for the retention time of ethane as DMMP is desorbed by flowing DMMP-free He into a column originally saturated with DMMP. The experiment in this section differs from section II-1-C by use of a higher linear gas velocity for desorption and a different probe gas. The Table shows that half of the DMMP can be removed without significantly affecting the retention time. Qualitatively,

TABLE 7
RETENTION TIME AS A FUNCTION OF DMMP DESORPTION BY He FLOW THROUGH A
DMMP SATURATED ASC CARBON BED

Column 20: 0.50g ASC Carbon; Flow Rate: 210cc/min; Carrier gas Helium; Temperature:
23-29°C; Probe Gas: 0.4 cc Ethane

Total Time (hr)	Gas Flow vol (l)	Flow Rate cc/min	wt DMMP on Bed (g)	Av Vap.* phase µg/cc	Ret. Time (min)	$\frac{F_t}{V_s}$	Temp °C
0	0	203	0.1944	0.03	0.03	5	23.2
140	1740	211	0.1432	0.06	0.04	8	29.5
193	2394	208	0.1050		0.07	13	29.0

* Calculated from column weight changes and the volume of gas flowing in the interval of time.

TABLE 8

RETENTION TIME OF CO₂ AS A FUNCTION OF FLOW RATE ON CARBON WITH DMMP

Column 12-13: 2.00g ASC Carbon with 0.67g DMMP; carrier gas He saturated with DMMP; Retention vol. of He in N₂ = 7.66cc

1	2	3	4*	5
Expt. No.	Flow Rate (cc/min)	Retention Time (min)	$\frac{F't'}{V_s}$	Column Temp. (°C)
34	9.5	2.4	3.3	28.0
35	9.5	2.4	3.3	28.0
42	9.8	2.4	3.1	29.0
43	9.8	2.4	3.1	29.0
1	20.8	0.73	1.6	30.0
2	20.8	0.80	2.0	30.0
4	21.4	0.50	0.7	35.0
5,6	21.4	0.80	2.1	35.0
18	21.3	0.85	2.3	30.0
19	23.0	0.90	2.9	29.5
16	42.5	0.40	2.0	32.0
36	45.6	0.43	2.6	28.0
37	45.6	0.48	3.1	28.0
44	45.0	0.40	2.3	29.0
45	45.0	0.40	2.3	29.0
9	90.4	0.18	1.9	34.0
23	93.0	0.20	2.4	30.0
24	93.0	0.19	2.2	30.0
25,26,27	93.0	0.19	2.2	29.0
28	93.0	0.19	2.2	28.5
30	93.0	0.20	2.4	30.0
31	93.0	0.20	2.4	30.0
12	129	0.12	1.7	32.0
40	143	0.10	1.5	29.0
41	143	0.10	1.5	29.0
14	169	0.08	1.3	32.0
49	214	0.06	1.1	29.0
50	214	0.06	1.1	29.0

* F' is the flow rate at column temperature, t' is the experimental retention time minus the retention time of a non-sorbed gas He, V_s is the volume of the carbon bed.

FIG 8: CARBON DIOXIDE RETENTION TIME ON DMP SATURATED CARBON
AS A FUNCTION OF FLOW RATE
Corrected Retention Time / Corrected Space Time vs. Uncorrected
Flow Rate

Column 14-15, 2.00g ASC Carbon; Probe Gas: 0.25cc CO₂; He
Carrier Gas; Temperature: 29-35°C

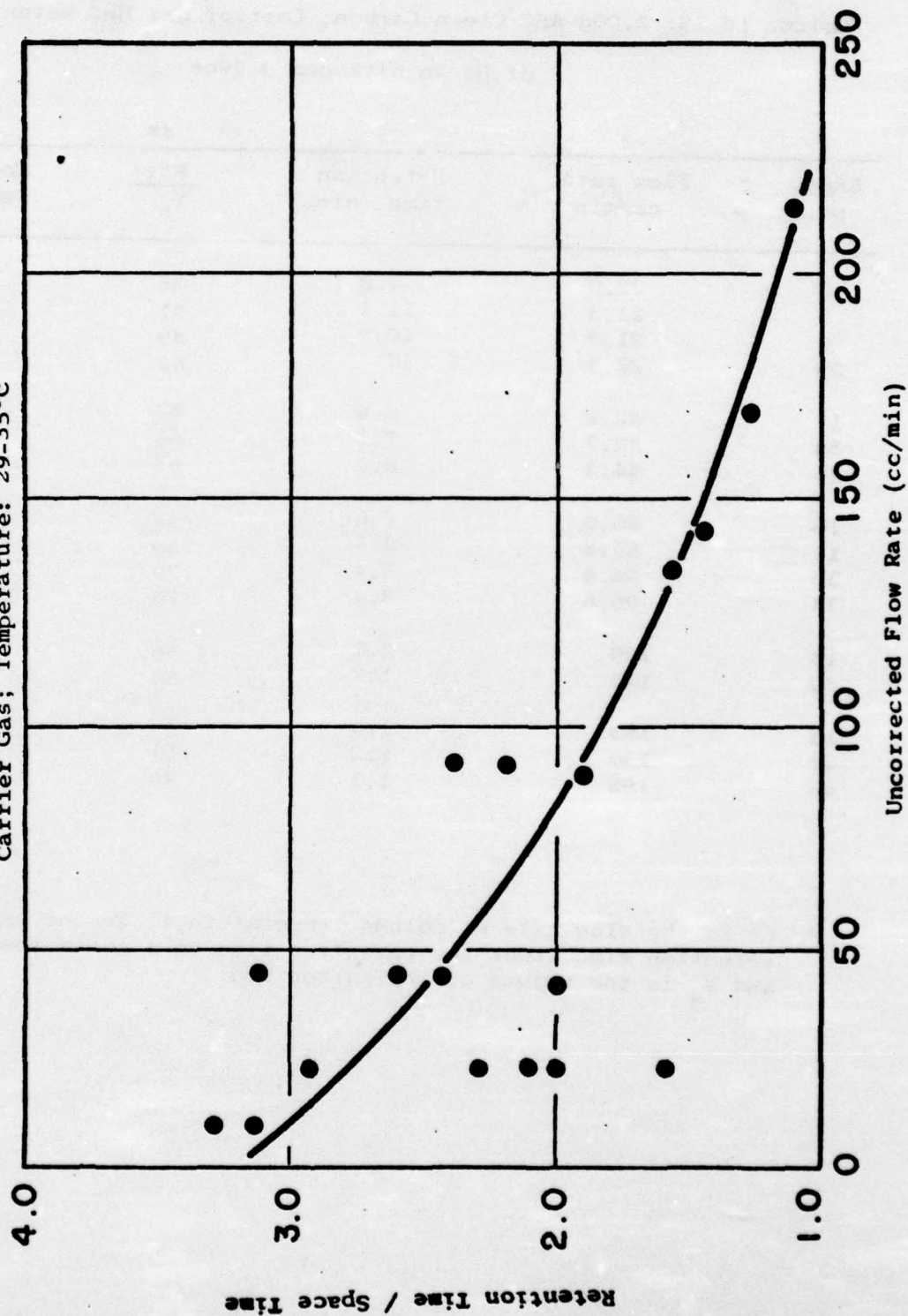


TABLE 9

RETENTION TIME OF CO_2 AS A FUNCTION OF FLOW RATE ON ASC CLEAN CARBON
 Column 14-15: 2.00g ASC Clean Carbon; Carrier gas He; Retention volume
 of He in nitrogen 9.29cc

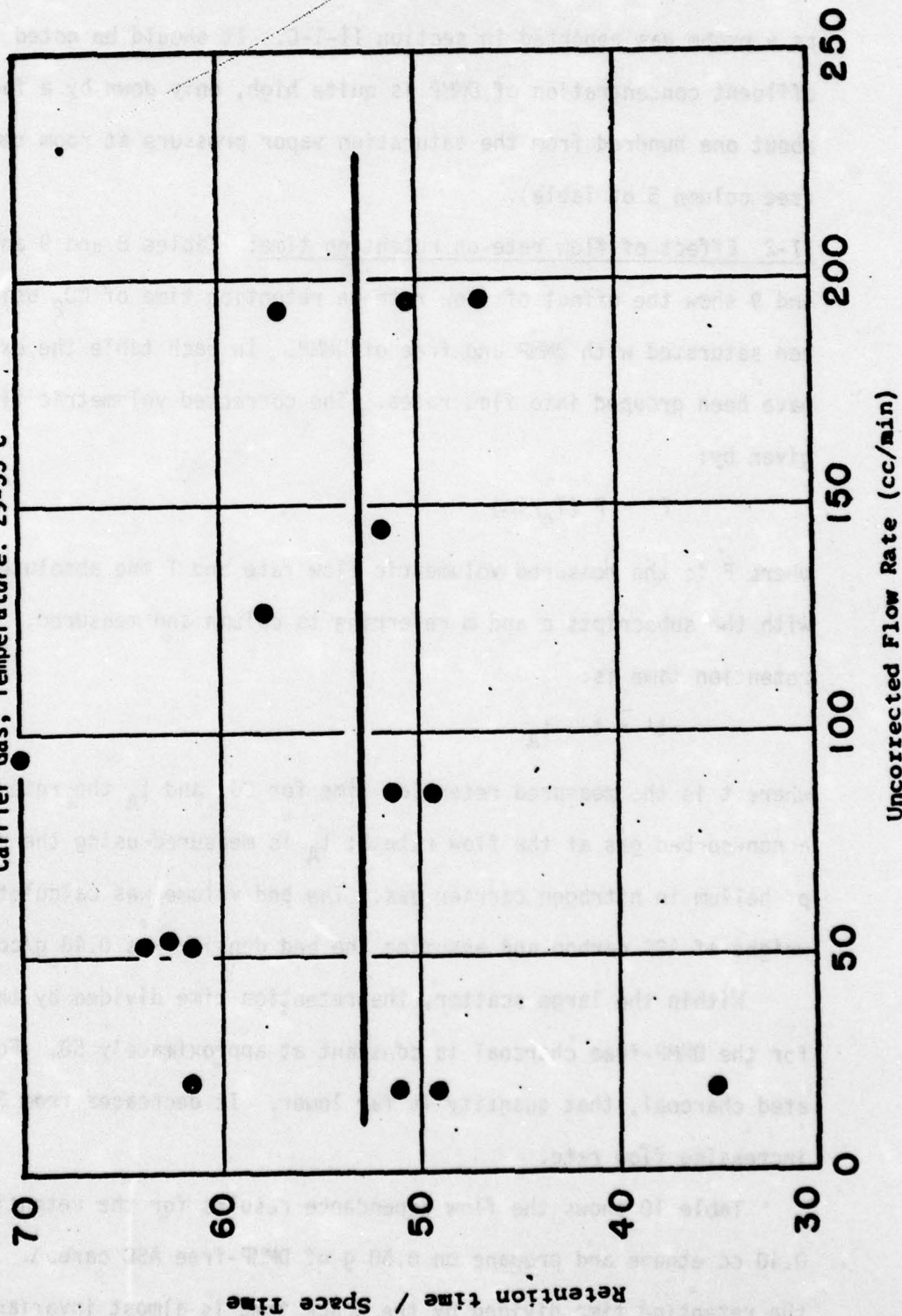
1	2	3	4*	5
Expt. no.	Flow rate, cc/min	Retention time, min.	$\frac{F't'}{V_s}$	Column temp. °C
3	22.0	7.8	36	30.0
7	21.3	11.1	51	35.0
8	21.3	10.9	49	35.0
20	22.3	13	62	30.0
17	42.2	6.9	62	32.0
38	42.7	7.1	65	28.0
46	44.3	6.7	63	29.0
10	86.8	2.8	52	34.0
11	86.8	2.7	50	34.0
32	96.6	3.4	70	29.0
33	96.6	3.4	70	30.0
13	129	2.1	58	31.5
39	145	1.7	52	29.0
15	193	1.4	57	32.0
47	196	1.2	51	29.0
48	196	1.1	46	29.0

* F' is the flow rate at column temperature, t' is the experimental retention time minus the retention time of a non-sorbed gas, He, and V_s is the volume of the carbon bed.

Fig 8

FIG 9: CARBON DIOXIDE RETENTION TIME ON CLEAN CARBON AS A
FUNCTION OF FLOW RATE
Corrected Retention Time / Corrected Space Time vs. Uncorrected
Flow Rate

Column 14-15, 2.00g ASC Carbon; Probe Gas: 0.25cc CO₂; He
Carrier Gas; Temperature: 29-35°C



the observations in this section confirm the findings using carbon dioxide as a probe gas reported in section II-1-C. It should be noted that the effluent concentration of DMMP is quite high, only down by a factor of about one hundred from the saturation vapor pressure at room temperature (see column 5 of Table).

II-2 Effect of flow rate on retention time: Tables 8 and 9 and Figures 8 and 9 show the effect of flow rate on retention time of CO_2 using ASC carbon saturated with DMMP and free of DMMP. In each table the experiments have been grouped into flow rates. The corrected volumetric flow rate is given by:

$$F' = F (T_c/T_m)$$

where F is the measured volumetric flow rate and T the absolute temperature with the subscripts c and m referring to column and measured. The corrected retention time is:

$$t' = t - t_A$$

where t is the measured retention time for CO_2 and t_A the retention time for a non-sorbed gas at the flow rate F ; t_A is measured using the retention time of helium in nitrogen carrier gas. The bed volume was calculated from the weight of ASC carbon and assuming the bed density was 0.48 g/cc.

Within the large scatter, the retention time divided by the space time for the DMMP-free charcoal is constant at approximately 50. For DMMP saturated charcoal, that quantity is far lower. It decreases from 3 to 1 with increasing flow rate.

Table 10 shows the flow dependence results for the retention time of 0.40 cc ethane and propane on 0.50 g of DMMP-free ASC carbon. For ethane, the retention time divided by the space time is almost invariant, i.e., con-

TABLE 10

RETENTION TIME OF ETHANE AND PROPANE DEPENDENCE ON FLOW RATE

Column 21-22 0.50g ASC Carbon free of DMPP; Probe Gas 0.40 cc, He Carrier Gas

Inj. no.	Ret. time (min)	Flow rate (cc/min)	Ft/V _s	Temp °C
Ethane				
1	3.10	101	324	24.0
2	3.15	101	329	24.1
3	6.30	50	324	24.2
4	1.50	204	318	24.3
5	3.10	101	328	24.3
6	1.11	270	312	24.3
Propane				
	14.4	23.7	328	44
	7.2	45.5	315	44
	3.3	90.1	286	44
	1.53	206.8	304	44

stant to within $\pm 3\%$, over the range of 50 to 270 cc/min corresponding to space times from 1.2 to 0.22 sec and superficial linear velocities of 5.1 to 27 cm/sec. For propane the retention time divided by the space time is constant to within $\pm 7\%$, over the range of 25 to 200 cc/min corresponding to space times of 2.4 to 0.29 sec. It should be noted that the propane experiments were carried out at a higher temperature than the ethane experiments. At the same temperature, retention times for propane would be considerably longer than for ethane.

II-3 Rates of Sorption and Desorption:

Tables 11 and 12 show rates of desorption and adsorption of DMMP on two ASC carbon beds. Each bed was composed of two columns connected in series; initially, the inlet column was saturated with DMMP and the outlet column was free of DMMP. The feed for the bed was DMMP-free He. Periodically, each column of the bed was weighed. Thus, the decrease in weight of the inlet column of the bed as a function of time was a measure of the rate of desorption of DMMP. The increase in the weight of the outlet column as a function of time was a measure of the rate of sorption of DMMP with a feed of the effluent of the inlet bed. Figures 10 and 11 describe the desorption experiments; the weight of the sorbed DMMP on the inlet column is plotted against the log (time of flow plus a constant); this manner of plotting was employed in order to obtain a linear representation of the data. Retention times of probe gases during the work was measured and is discussed in section II-1-C.

The vapor phase concentrations, shown in Column VII, are calculated from

$$C(\mu\text{g/cc}) = S/[(F)(60)(2.303(t+t_0))]$$

TABLE 11
DESORPTION-ADSORPTION FOR IN-SERIES BED, 1/3 INLET LENGTH SATURATED

e.c. Initial condition: inlet bed saturated with DMMP, outlet bed free of DMMP

Columns 3-3'/2-2'; He Flow ≈ 80 cc/min (av)
Column 2-2'=1.331g ASC Carbon, 3-3'=0.667g

I	II	III	IV	V	VI	VII*	VIII**
total gas vol (l)	total time (hrs)	wt DMMP col 3-3' (inlet)	col 2-2' (outlet)	deviation from mass bal	av. wt. loss rate of 3-3' mg/hr	conc DMMP Gas μ g/cc	% sorbed by second column
0	0	0.2251	0.0000		16.2	2.89	105
6.0	1.33	0.2036	0.0225	+0.0010	3.73	1.53	
13.2	2.83	0.1980	0.0301	+0.0030	4.09	1.00	116
24.3	5.08	0.1888	0.0408	+0.0045	3.75	0.65	
37.7	7.83	0.1785	0.0497	+0.0031	2.68	0.47	143
50.0	10.33	0.1718	0.0593	+0.0060	1.60	0.37	
70.8	14.83	0.1646	0.0628	+0.0023	0.42	0.27	90
380.1	78.83	0.1377	0.0871	-0.0003	0.24	0.054	
716.6	103.6	0.1318	0.0888	-0.0045	0.15	0.041	101
912.9	154.7	0.1240	0.0967	-0.0044	0.14	0.028	
1170	249.3	0.1105	0.1082	-0.0064	0.12	0.017	19
1289	344.2	0.0993	0.1103	-0.0155	0.06	0.013	108
2158	513.6	0.0891	0.1214	-0.0146	?	0.008	?
2648	611.9	0.0910	0.1122	-0.0219			

*VII concentration in effluent from first column estimated from Figure 10, i.e. based on $w = a \ln(t+t_0) + G$ where w is weight of DMMP on column 3-3' and a , t_0 , and G are fitting constants; and $dt = F dV$ where t is time of flow, F is flow rate and V the volume in the gas phase

**VIII % of DMMP leaving first column that is sorbed by the second column

*** Neg. value means not all of the DMMP desorbed by the first column is sorbed by the second column

TABLE 12

DESORPTION-ADSORPTION FOR IN-SERIES BED, 2/3 INLET LENGTH SATURATED

e.c. Initial condition: inlet section saturated with DMMP, outlet section free of DMMP

Columns 1-1'/4-4; He Flow $\approx$ 80cc/min

Column 1-1'=1.33g ASC carbon, column 4-4'=0.67g

Temperature 29-30°C

I	II	III	IV	V	VI	VII*	VIII*
total gas vol (l)	total time hrs	wt DMMP, g col 1-1' (inlet)	col 4-4' (outlet)	deviation from mass bal	av wt loss rate of 1-1' mg/hr	DMMP conc vap μ g/cc	% sorbed by second column
0	0	0.4425	0.000		20.6	5.4	+98
6.3	1.33	0.4151	0.0268	-0.0006	11.3	2.9	
13.6	2.83	0.3982	0.0462	+0.0019	6.48	1.9	+94
24.3	5.08	0.3836	0.0599	+0.0010	4.65	1.2	
37.5	7.83	0.3708	0.0701	-0.0016	4.52	0.87	+78
49.1	10.33	0.3595	0.0789	-0.0041	3.31	0.69	
71.8	14.83	0.3446	0.0945	-0.0034	0.89	0.50	+85
372	78.83	0.2878	0.1436	-0.0111	0.45	0.10	
486	103.6	0.2766	0.1496	-0.0163	0.31	0.078	+26
777	154.7	0.2607	0.1644	-0.0174	0.25	0.052	-10
1161	249.3	0.2367	0.1620	-0.0438	0.25	0.032	-46
1582.6	344.2	0.2167	0.1528	-0.0730	0.13	0.023	-44
2420	513.6	0.1945	0.1431	-0.1049	?		?
2907	611.9	0.1980	0.1330	-0.1115			

*VI see footnote Table 11

** Negative value means not all of the DMMP desorbed by the first column
is sorbed by the second column

FIG 10: DMMP DESORPTION FROM DMMP SATURATED CARBON AS A FUNCTION
OF TIME OF FLOW OF HELIUM (DMMP-FREE)

Abscissa: time (hours + 1.5) on log scale;

Ordinate: wt of DMMP on column (g)

Column 3-3': 0.67g ACS carbon; time 0: carbon saturated with DMMP

Flow rate: 80cc He/min; Temperature: $29.5 \pm 0.5^\circ\text{C}$

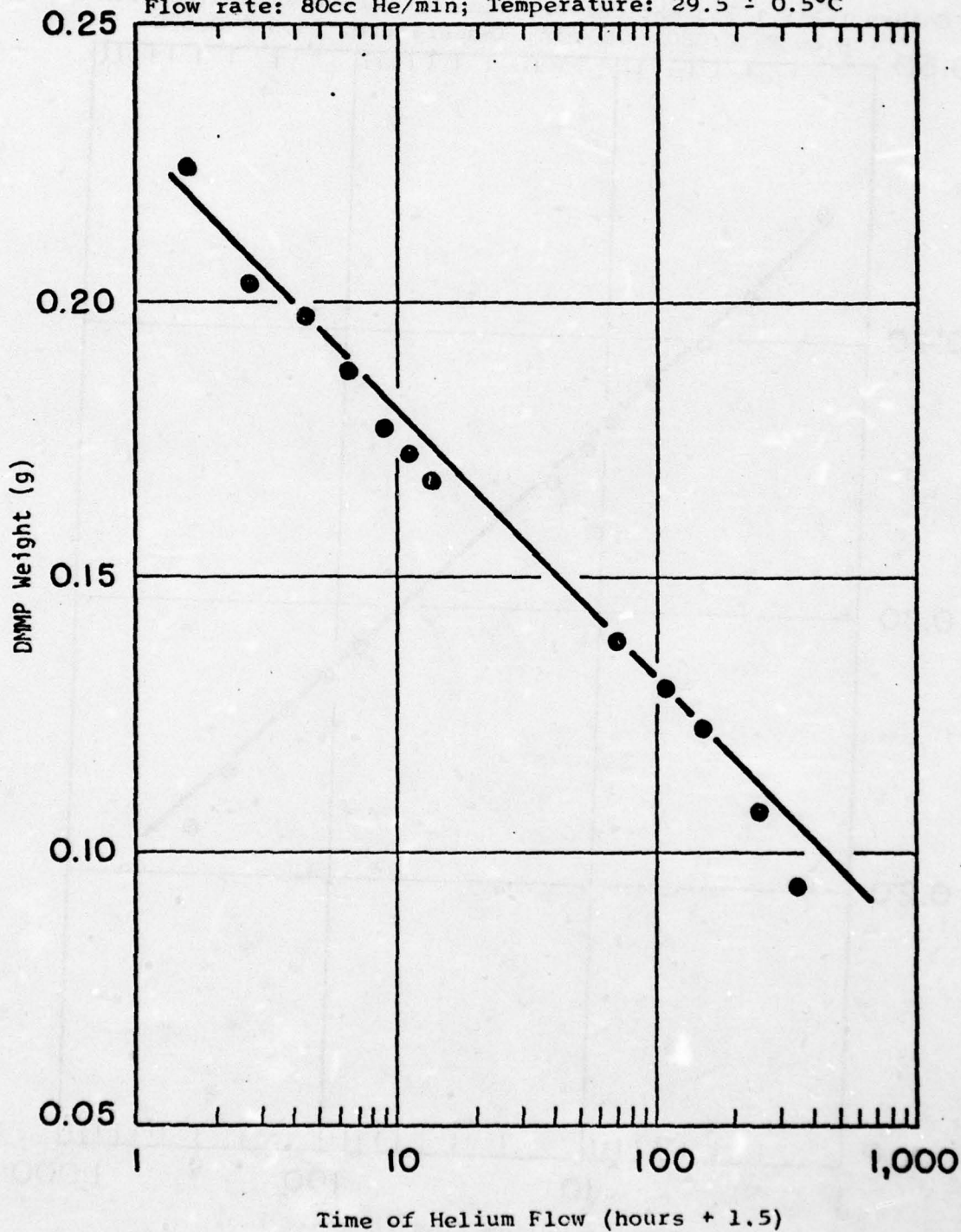


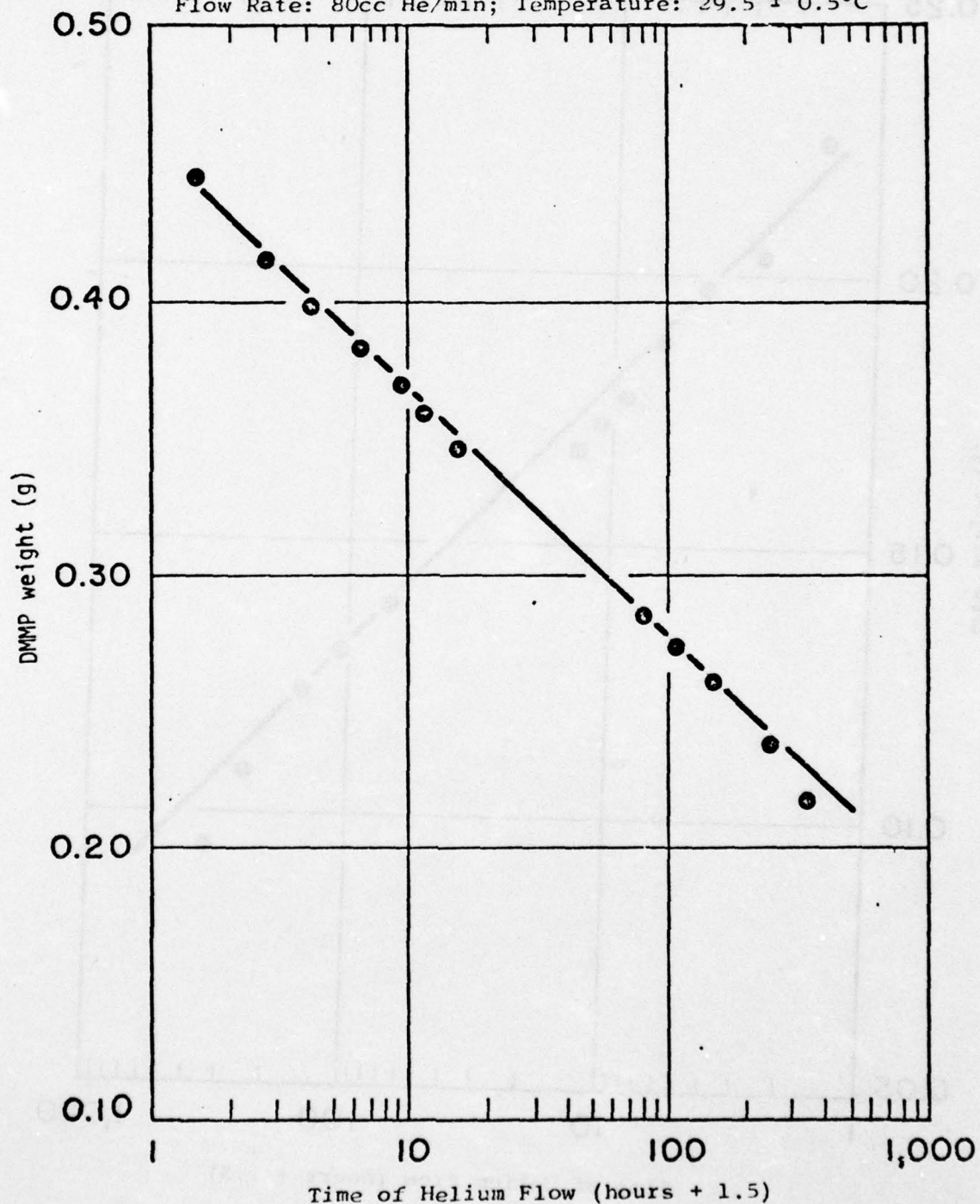
FIG 11: DMMP DESORPTION FROM DMMP SATURATED CARBON AS A FUNCTION OF TIME OF FLOW OF HELIUM (DMMP-FREE)

Abscissa: time (hours + 1.5) on log scale;

Ordinate: wt of DMMP on column

Column 1-1': 1.33g ASC carbon; time 0: carbon saturated with DMMP;

Flow Rate: 80cc He/min; Temperature: $29.5 \pm 0.5^\circ\text{C}$



where $S = dw/d [\log_{10} (t+t_0)]$. The value of S is taken from the plot of the weight of DMMP on the first section of the column vs $\log (t+t_0)$. The quantity t is the time of flow, t_0 a fitting constant, and F the flow rate in cc/min.

The two experiments both contain a two-section bed connected in series with a total of 2.0 g of carbon. However, they differ in the fractional length of the bed initially saturated with DMMP. Table 11 shows the experiment with the first one-third of the bed initially saturated with DMMP. Table 12 shows data for the first two-thirds of the bed initially saturated with DMMP. Figure 10 describes the desorption data of Table 11, i.e., a desorption experiment from a short column. Figure 11 (from Table 12) describes desorption from a column twice as long as that shown in Figure 10.

As indicated by the graphs and the values in column VI (average loss rate of the inlet section of the bed) and VII (vapor phase concentration leaving the inlet section of the bed), the desorption rate sharply decreases with decreasing DMMP loading, on the order of one hundred fold from saturation to half saturated carbon. Comparison of either the weight loss rates or the vapor-phase DMMP-concentration effluent from the first column at comparable times or volumes of flow, show that the desorption rate is almost twice as fast for the column which is twice as long. Except for the first value in Table 11, these two columns initially produce effluent concentrations close to the saturation vapor pressure of DMMP. It may be pointed out that the long initially-clean column sorbs essentially all of the DMMP leaving the short initially-saturated column (Table 11) over the course of the experiment. In contrast, after six days, the short initially DMMP-free column, which is fed DMMP by the effluent of a long column, showed net desorption. This statement is based on the negative values of column VIII in Table 12.

TABLE 13

SEARCH FOR PROBE GASES WITH SUITABLE RETENTION TIME

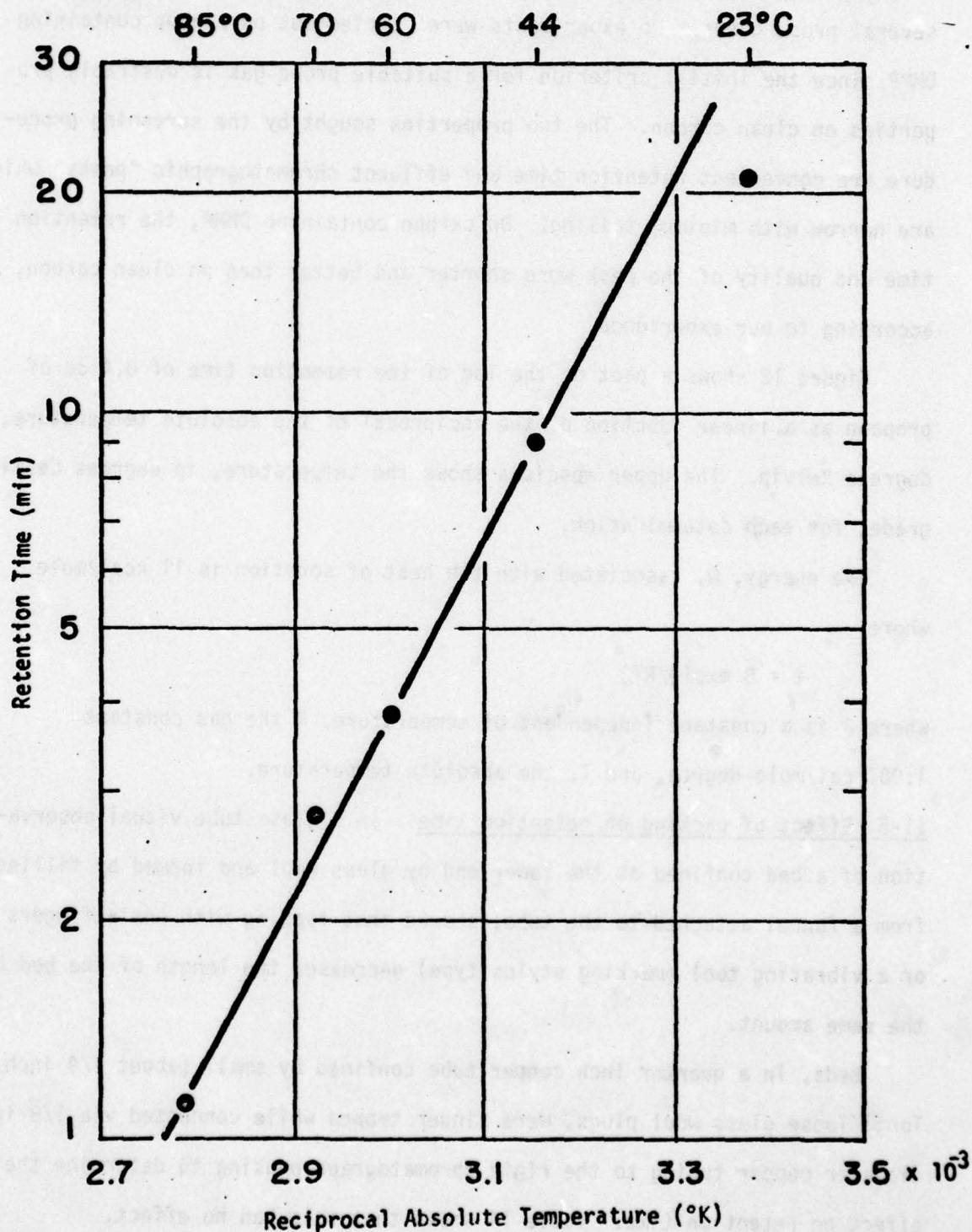
Column 21: 0.50g ASC carbon (DMMP free); He carrier Gas; Flow rate 207cc/min

Gas	Retention time (min)	Temp. (°C)	Quality of peak
diethyl ether	>30	44	not observed
methyl acetylene	>10	44	very poor
allene	>10	44	very poor
propane	1.30	85	excellent
	2.75	70	excellent
	3.80	60	good
	8.9	44	poor
	21	23	very poor
propane	9	44	very poor
	11		very poor
	6		poor
	8		poor
	12		very poor

FIG 12: ARRHENIUS PLOT OF PROPANE RETENTION TIME AS A FUNCTION OF TEMPERATURE

Abscissa: Reciprocal Absolute Temperature ($^{\circ}\text{K}$)⁻¹; Lower Ordinate: Retention Time (min) on log scale.

Column 21: 0.50g ASC Carbon (DMMP-free); Flow Rate: 20.7cc He/min



II-4 Search for new probe gases: Table 13 shows the retention times for several probe gases. No experiments were carried out on carbon containing DMMP since the initial criterion for a suitable probe gas is desirable properties on clean carbon. The two properties sought by the screening procedure are convenient retention time and effluent chromatographic "peaks" which are narrow with minimum tailing. On carbon containing DMMP, the retention time and quality of the peak were shorter and better than on clean carbon, according to our experience.

Figure 12 shows a plot of the log of the retention time of 0.4 cc of propane as a linear function of the reciprocal of the absolute temperature, degrees Kelvin. The upper abscissa shows the temperature, in degrees Centigrade, for each determination.

The energy, Q , associated with the heat of sorption is 11 kcal/mole where

$$t = B \exp(Q/RT)$$

where B is a constant independent of temperature, R the gas constant 1.987 cal/mole-degree, and T , the absolute temperature.

II-5 Effect of packing on retention time: In a glass tube visual observation of a bed confined at the lower end by glass wool and formed by filling from a funnel attached to the tube, showed that tapping with one's fingers or a vibrating tool (marking stylus type) decreased the length of the bed by the same amount.

Beds, in a quarter inch copper tube confined by small (about 1/4 inch long) loose glass wool plugs, were finger tapped while connected via 1/8 inch diameter copper tubing to the rigid chromatograph housing to determine the effect on retention time. Table 14 shows that this had no effect.

TABLE 14
EFFECT OF IN-SITU FINGER TAPPING ON RETENTION TIME

Gas	Flow Rate (cc/min)	Retention Time (min)	
		Before tap.	After tap.
CO ₂	88.2	0.65, 0.68	0.65
C ₂ H ₆	73.2	4.45	4.30
C ₂ H ₆	70.1	4.35	4.25

III DISCUSSION

III-1 Previous work compared to our work: We have shown the use of a pulse of a weakly sorbed probe gas to monitor the residual sorption capacity of a charcoal bed for a strongly sorbed material. Stamulis and Thompson* used decane as the sorbate and CO_2 as the probe gas while we have used DMMP and several probe gases, including CO_2 . They placed emphasis on the dispersion (peak spreading) and maximum concentration (peak height) while we have placed emphasis on the retention time. A further difference is that we have used a thermal conductivity detector, while they used a thermal-IR CO_2 detector.

Our most recent emphasis has been on the use of ethane as the probe gas. CO_2 has been found to have considerable problems with respect to humidity variations**.

The key reduced variable is the corrected retention time divided by the space time. The "corrected" retention time is directly a measure of sorption properties while the uncorrected retention time includes void volume in the bed and connecting tubing. For successful use of the retention time property, it is necessary to select a probe gas which, at the flow rate and bed configuration, has a large retention volume (long retention time) compared to the void volume of the bed and connecting tubing.

For simple "equilibrium" chromatographic theory:

$$F t' / V_s = C \quad \text{where } t' = t - t_A \quad (1)$$

* "The CO_2 Pulse Technique for Determining Residual Gas Life of Charcoal Beds, Part 1 Bench Scale Studies", Naval Research Laboratory Report 6793, Dec. 31, 1968, by A. Stamulis and J.K. Thompson

** Private Communication: L.A. Jonas Letter of 26 Oct. 76 to A. Weiss.

F is the volumetric flow rate, V_s is the bed volume, t' is the probe gas corrected retention time, t = total experimental probe gas retention time and t_A = non sorbed gas (e.g., He) retention time.

The value of $(t_A F)$ is essentially the gaseous volume or "dead space" between the point of injection of the probe gas which is located up stream of the bed and the detection device which is located downstream from the bed. The value of t_A is determined by injection of a gas such as He with the adsorbent in the bed container.

$$t_A F = C_G \quad (2)$$

The value of C_G depends only on the geometry of the experimental apparatus and the amount of sorbent. The value of C is dependent on the sorbent, sorbate, probe gas, and temperature. As shown in the experimental section, the value of C for ethane, to a good approximation, is constant over a wide flow range. Therefore, combining Equations 1 and 2, the experimental retention time is

$$t = (1/F)(C V_s + C_G) \quad (3)$$

If C_G is large compared to $(C V_s)$, the retention time of the probe gas is dominated by the dead space and will not reflect the probe gas/sorbent interaction. From Equation (3), the difference in retention time for a clean sorbent vs. the sorbent containing a sorbate such as DMMP is

$$\Delta t \approx 1/F V_s \Delta C \quad \text{where } \Delta C = C_{\text{clean col.}} - C_{\text{col. with sorbate}} \quad (4)$$

since C_G will be almost the same whether or not sorbate is present - the difference is presumably the pore volume occupied by sorbate. It should be noted that at very high flow rates the absolute value of Δt can be small.

From Figure 1, given by Stamulis and Thompson, for a clean carbon vs. carbon loaded with 0.18 g decane/g carbon at 1 liter/min, we can estimate that

$$(1/F) V_s \Delta C \approx 0.6 \text{ min}$$

and that

$$(1/F) C_G \approx 0.7 \text{ min}$$

The measured value of 0.6 min. is too small to use for an accurate correlation with loading and is especially poor considering that there is a 0.7 minute correction to it.

Since we have found that ethane has a higher value of ΔC than carbon dioxide we believe it is a more suitable choice for a probe gas. Propane has an even higher value of ΔC but at the superficial linear velocities of the filter shows very large peak dispersions and inconveniently long retention times.

III-2-A Discussion of II-1-A: Experimental section II-1-A shows that the retention time of carbon dioxide (the probe gas) is a linearly increasing function of the fractional length of the bed that is free of DMMP. The latter may be taken as the fractional residual capacity of the bed.

It should be pointed out that this experimental series differs in several respects from the large air filtration system. Bed lengths were about eight times longer than those of the air filtration system. The concentration gradient of the sorbed DMMP at the boundary between the saturated section and clean section of the bed was greater in the laboratory configuration than that which is expected in the large filtration system. Laboratory beds were composed of two sections: the inlet section previously saturated with DMMP and the outlet section free of DMMP. A large air filtration system, during exposure to a continuous feed of DMMP, will have a concentration gradient between the saturated inlet portion and the clean outlet portion dependent, in principle, on mass transport and

equilibrium sorption properties such as: inlet gas, phase concentration of DMMP, linear gas velocity, bed temperature, and diffusion coefficients. With respect to the equilibrium sorption properties, it is interesting to note that a very large change in partial pressure of DMMP results in only a very small change in sorbed DMMP concentration, e.g., a change in P/P_0^* from unity to 10^{-11} results in a decrease of only 50% in the amount of DMMP sorbed.

III-2-B Discussion of II-1-B: These experiments show that the retention time of ethane decreases, almost linearly, with time for a bed, initially clean, as the bed picks up DMMP from a stream of helium saturated with DMMP. After the first third of the time to DMMP saturation, the retention time obeyed the linear relationship; during the first third, the retention time changed more slowly. Extrapolation of the later 2/3 time period to zero time of flow (see straight lines of Figures 2 and 3) gives the retention time for the clean column. We believe this non-linear initial portion is experimentally real since we have found it twice.

The experiments with single columns 20 and 21, both the same lengths, were carried out slightly differently. The experiment with column 21 was stopped when the retention time became very low while the experiment with column 20 was continued for 30 minutes after the retention value became very low and almost constant. The total weight gains for columns 20 and 21 were 0.4 g and 0.3 g DMMP/g carbon, respectively. During the 30 minute period in which experiment 20 was continued after the retention time reached a low value, the concentration of sorbed DMMP might have increased from about 0.35 to 0.40 g DMMP/g C based on the assumption of complete sorption of the flow of DMMP into the bed. We conclude that the retention-time/DMMP-

* P/P_0 is the ratio of the partial pressure of DMMP to its saturation vapor pressure

weight behavior, at long times of flow, suggests that the retention time for ethane is close to zero at DMMP sorption concentrations somewhat below saturation.

An important experiment, to be done in the future, is to measure retention time as a function of the DMMP sorbed concentration for bed containing a lengthwise uniform concentration.

In summary, the experiments discussed in this section, using ethane as a test gas, are consistent with and supplementary to the experiments with carbon dioxide, discussed in section III-2-A. The ethane experiments suggest that the rate of change of retention time with sorbed concentration of DMMP is very small at both low and high concentrations of DMMP.

III-2-C Discussion of II-1-C: The experimental section II-1-C is a description of experiments in which sorbed DMMP is transferred from the inlet section to the outlet section in ASC carbon beds. (Initially the inlet section was saturated with DMMP and the outlet section was free of DMMP. Pure carrier gas was passed into the bed to move the DMMP from the first to the second section.) For a large fraction of the period of an experiment, the total amount of DMMP on both sections remained constant. The retention time of probe gas decreased as DMMP was transferred from the first section of the bed to the second section.

With both beds, the retention time dropped to about half the initial value as the DMMP was progressively transferred from the first to the second section of each bed. This large change in retention time as the DMMP moved down toward the outlet of the bed is an observation that may be valuable to exploit. One possibility is that it is associated with DMMP preferentially desorbing from large pores and readsorbing in small pores of the bare carbon.

The slight increase in retention time at the longest times (see Table 5) might be associated with the appreciable loss of DMMP from the total bed.

Table 6 shows the retention times for the individual sections of the bed at the end of the experiment. It is clear that the decrease in retention time of each of the two-section beds should be associated with the large decrease in retention time of the initially DMMP-free second sections.

The calculation given below shows that DMMP does not move as a plug and that retention time is not a linear function of homogeneous loading.

The calculation involves the change in retention time of the beds from the initial condition of a DMMP saturated inlet column and a DMMP-free outlet column to the end of the experiments in which both columns contain sorbed DMMP.

Table 15 lists the calculated and experimental changes in retention time at the flow rate of the in-series beds. The retention time, t , of a column at a flow rate F_1 is

$$t = (wt_1/wt_A) t_{DF_1} - [wt_C - (wt_1/wt_A)] t_{CF_1} \quad (6)$$

where wt_1 is the weight of DMMP on the column, wt_A is the weight ratio of DMMP to carbon at DMMP saturation, wt_C is the weight of the carbon in the column, t_{DF_1} is the retention time per gram of carbon saturated with DMMP at the flow rate, F_1 , and t_{CF_1} is the retention time per gram of carbon which is free of DMMP. The value of t_{DF_1} is calculated from Table 1, experiment numbers 1 and 2 by

$$t_{DF_1} = 0.335 (76/F_1)(1/2.00) = 0.13 \text{ min/g} \quad (7)$$

For the DMMP-free carbon, from experiment numbers 3 and 5,

$$t_{CF_1} = 4.3 (78/F_1)(1/2.00) = 1.81 \text{ min/g} \quad (8)$$

The experimental values of retention time given in Table 1 (before transfer of DMMP from the first to the second column) and in Table 6 (at the end of the DMMP transfer experiment) were corrected to the flow rate of the in-

TABLE 15

Retention Time Change when DMMP transferred from First to Second Sections
of Bed: Calculated assuming DMMP saturated and DMMP-free portions vs.

Experiment (see text for method of calculation)

Column(s) (numbers)	calc change (min)	expt change (min)
(F ₁ = 92.9)		
3-3'	+0.66	+0.11
2-2'	-0.57	-1.23
3-3'/2-2'	+0.09	-1.09
(F ₁ = 90.9)		
1-1'	+1.25	+0.24
4-4'	-0.67	-1.04
1-1'/4-4'	+0.56	-0.71

series bed listed in Table 6, thus, the flow-corrected experimental value

$$t_{F_1} = t_x (F_x/F_1) \quad (9)$$

where t_x is the experimental value at the measured flow rate F_x .

Thus the "calculated change" is the difference in the values of t , calculated by Equation 6, from the time of the first measurement on the in-series bed to last measurement on the bed; a positive value means that the retention time of the last measurement is longer than the first. The "experimental change" is the difference in the retention time corresponding to the time of the first measurement of the in-series bed to the experimentally determined last measurement on the bed. For the "experimental" and "calculated", the initial value is the same for the in-series bed and computed by Equation 6 for the individual sections.

The values of the "calculated change" for the in-series beds, 3-3'/2-2' and 1-1'/4-4', both increase because of a net loss of DMMP from both sections of the in-series beds. The loss of DMMP from 1-1'/4-4' is greater because the second section (originally free of DMMP) is half the length of 2-2'. The calculated retention time for each bed increases for the first section because of DMMP loss from the first section and decreases for the second section because of DMMP sorption on the second column. The experimental increase for the first sections is small in comparison to the expected increase calculated by the assumed model. The experimental decrease in retention time for the second sections is almost twice the expected value. Alternatively, on the same model, we can calculate the apparent weight of charcoal saturated with DMMP to account for the short retention time at the end of the experiment. Each section of both beds acts like sections composed of lengths too long in DMMP saturated charcoal

TABLE 16

WEIGHT OF CARBON SATURATED WITH DMMP WHEN DMMP TRANSFERRED FROM FIRST TO SECOND SECTIONS OF BED: Calculated on basis of retention times vs experimental weights (see text for method of calculation)

Column number	Total Carbon wt (g)	Carbon wt, sat with DMMP (g)	
		From Retention Time	From Weight
3-3'	0.67	0.60	0.27
2-2'	1.33	0.73	0.34
1-1'	1.33	1.19	0.59
4-4'	0.67	0.61	0.40

and too short in DMMP-free charcoal based on the experimental retention times of saturated and clean charcoal.

On the basis of the experimental retention time at the end of the transfer (Table 6) and retention time per gram for DMMP-free carbon and DMMP saturated carbon (Table 1), corrected to the same flow, the expected weight of carbon saturated with DMMP, wt_1/wt_A , was calculated from Equation (6) and is listed in Table 16 under "From Retention Time". The next column, "From Weight", is calculated by dividing the weight of DMMP on the column by the weight of DMMP per weight of carbon at DMMP saturation. The ratio of the value "From Retention Time" to the value "From Weight" is approximately 2:1 indicating that after redistribution of the DMMP, each column acts with respect to retention time, like a column with twice the length of a DMMP saturated portion.

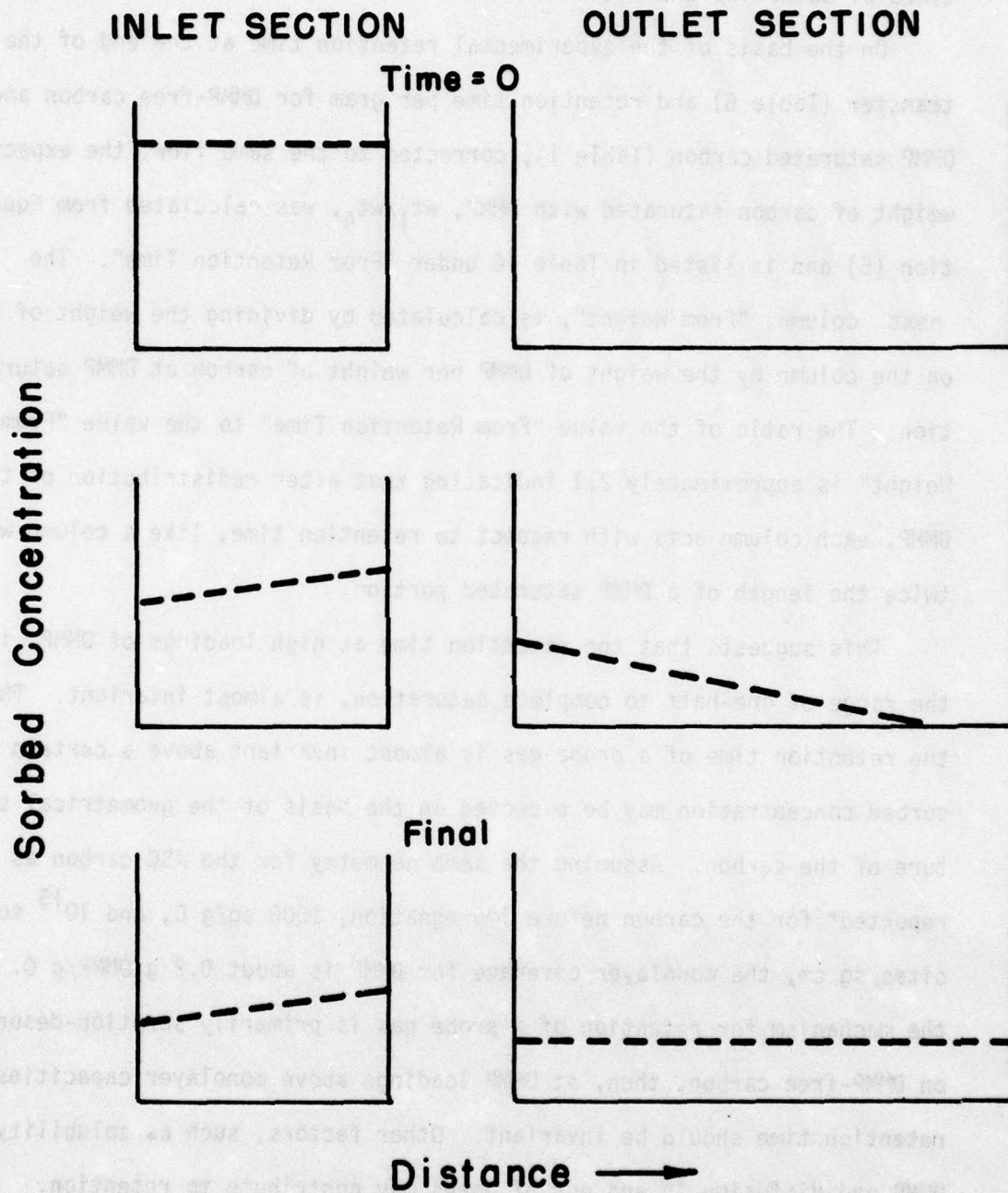
This suggests that the retention time at high loadings of DMMP, in the range of one-half to complete saturation, is almost invariant. That the retention time of a probe gas is almost invariant above a certain DMMP sorbed concentration may be expected on the basis of the geometrical structure of the carbon. Assuming the same geometry for the ASC carbon as that reported* for the carbon before impregnation, 1000 sq/g C, and 10^{15} sorption sites/sq cm, the monolayer coverage for DMMP is about 0.2 g DMMP/g C. If the mechanism for retention of a probe gas is primarily sorption-desorption on DMMP-free carbon, then, at DMMP loadings above monolayer capacities, the retention time should be invariant. Other factors, such as solubility in DMMP and diffusion in and out of pores may contribute to retention.

Figure B qualitatively shows a model for three sorbed concentration profiles for each section of the bed at progressively increasing elapsed

* L.A. Jonas, private communication to T. Freund

FIG. B: SCHEMATIC FOR MOVEMENT OF SORBED DMMP IN CHARCOAL BED

Pure He feed; Initially, inlet section DMMP - saturated, outlet section DMMP-free; Total amount of sorbed DMMP - constant.



time of flow of DMMP-free gas into the first section. Shown are the postulated profiles for bed 3-3' $\frac{1}{2}$ -2', which initially contained at the inlet section 0.67 g carbon saturated with DMMP and at the outlet section 1.33 g carbon free of DMMP. The area under a profile is proportional to the total weight of DMMP sorbed on a column. The features that the profiles are intended to show include: (1) a total loss of about 50% of the DMMP from the first section, (2) a sorption on the second section of somewhat less than that lost from the first section, (3) a small increase in the retention time of the first column and (4) a large decrease in retention time of the second column (about equivalent to half the length acting like DMMP saturated carbon).

The profile changes in the inlet section are based on the experimental finding that a DMMP-saturated column roughly desorbs at a weight rate proportional to its length (see Tables 11 and 12, columns VI or VII). This column-length dependence implies that DMMP is desorbed from the whole length of the column and suggests that the profile should not have a sharp edge.

The profile for the second section is, also, not sharp since some of the DMMP leaving the first section is not picked up by the second section. The weight data for bed 1-1' $\frac{1}{4}$ ' show this result even more clearly.

Our model is that the retention time of probe gas is primarily determined by the area of the carbon which is free of DMMP. Above a DMMP monolayer coverage the retention time is invariant. Thus, the first section has all except the first portion at or above monolayer coverage with the result that the retention time does not increase appreciably as half of the DMMP is desorbed. The retention time of the second section decreases because all or most of the DMMP sorbed is at or below monolayer coverage.

From Table 4, the decrease in the quantity, retention time divided by space time, is approximately proportional to the weight of DMMP sorbed on the second section.

III-2-D Discussion of II-1-D: The experimental section II-1-D is a description of the increase in retention time of ethane as DMMP is desorbed from a short carbon column at high linear gas velocity. Approximately half of the DMMP was removed during the course of the experiment starting with a saturated carbon bed. The increase in retention time, in the absolute sense, was very small. This experiment confirms our finding with CO₂ on longer columns at lower linear gas velocities, that the retention time is almost constant above DMMP sorbed concentrations of one-half saturation. Therefore, this experiment supports our previous supposition that retention of a probe gas is primarily associated with the DMMP-free area of the carbon.

III-3-A Discussion of II-2: Effect of flow rate on retention time: For the purposes of scaling up the laboratory results by either empirical or theoretical methods, volumetric flow rate (space time) and superficial linear velocity must be considered important variables.

Simple "equilibrium" chromatographic theory* leads to the conclusion that the retention volume (the product of the retention time and volumetric flow rate), should be a constant, i.e., independent of flow rate, for given column, probe gas and temperature. The notion is based on assigning a constant relating the amount sorbed on the column and the concentration in the gas phase. Thus, the volume of carrier gas necessary

* Erich Heftmann, Editor, "Chromatography", 2nd Edition, Reinhold, N.Y., N.Y., 1976, Chapter 9

D.A. Leathard and B.C. Shurlock, "Identification Techniques in Gas Chromatography", Wiley, New York, 1970

to transport any particular sorbed gas is invariant. When mass transport rate processes become important the assigned constant and the retention volume are no longer invariant with flow. Extension of the "equilibrium" theory to account for the size of the bed shows that the retention volume divided by the bed volume should be invariant. The retention volume divided by the bed volume is the same as the retention time divided by the space time.

III-3-B Discussion of II-2-A: Results for CO₂: While these experiments, as indicated by the Figures 8 and 9, have considerable scatter, there is a trend for the retention volume to decrease with increasing flow rate. In part, the scatter in the experiments may be accounted for by the non-constancy of the bed temperature. However, we do not believe, on the basis of the temperature coefficient of the retention time, that this is the major cause of the scatter. It should be noted that the experiments were carried out over an eight day period with gas flowing most of the time.

Presumably for the laboratory results to be applicable to the large scale 4'x4'x4' air filter the linear gas velocity, space time and bed geometry effects should be measured or we should have the ability to calculate them. Studies involving the volumetric flow variation can be thought of as a study of either gas velocity or space time since the superficial (or piston) linear flow velocity, v in cm/sec, is given by:

$$v = (F)/A$$

where F is the volumetric flow rate in cc/sec and A is the cross-section of the bed, and the space time, τ in sec, is

$$\tau = (wt)(1/\rho)(1/F)$$

where wt is the weight of the bed of density ρ . In order to reproduce

the superficial velocity and space time of the filter simultaneously, the laboratory experiment must have the same bed depth as the filter.

The filter operates at a space time of 0.3 sec and a superficial linear velocity of 9.5 cm/sec. Our experiments with CO₂, at 200 cc/min, our fastest volumetric flow rate, corresponded to a space time of

$$\tau = (2.0 \text{ g})(1/0.48 \text{ g/cc})(1/200 \text{ cc/min})(60 \text{ sec/min}) = 1.25 \text{ sec}$$

We did include in our experimental range the filter's superficial velocity, 93 cc/min corresponds to 9.5 cm/sec

$$v = (93 \text{ cc/min})(1/60 \text{ min/sec})/[\pi(0.216)^2 \text{ cm}^2] = 9.5 \text{ cm/sec}$$

Therefore, we believe, except for lateral spreading irregularities in a large filter, that a laboratory scale experiment of a bed of carbon in a 1/4 O.D. copper tube of 3 cm length with a flow rate of 93 cc/min reproduces the filter.

III-3-C Discussion of II-2-B results for ethane and propane: Our results for the effect of flow for ethane obtained on a six centimeter long DMMP-free bed, over a short period of time, show a good constancy for the retention volume per unit volume of the bed, i.e., 312 to 329 over a flow range of 50 to 270 cc/min which corresponds to space times of 1.2 to 0.15 sec and superficial velocities of 5 to 27 cm/sec. At a space time of 0.3 sec (corresponding to the conditions of the 4x4x4 ft large filter) the retention time is:

$$t = (0.3 \text{ sec})(1/60 \text{ min/sec})(320) = 1.6 \text{ min.}$$

This value of 1.6 min for DMMP-free carbon makes ethane a reasonable choice for the practical system of the filter. Probably a slightly higher value would be preferable but we have not found such a probe gas.

Our results for propane also show reasonable constancy for the retention volume with flow rate. It should be noted that these were obtained

at 44°C and therefore are not directly applicable to room temperature. However, under certain conditions propane may prove to be useful probe gas for the residual capacity of a bed.

III-3-D Future Plans: Since we have not done a systematic study of the effect of the length of the bed, we expect to simulate the large scale filter by using a small diameter tube with same length and superficial velocity as the filter. Therefore, we will use a 1/4 O.D. tube with a bed length of 3 cm and flow rate of 93 cm/min. We expect to use air instead of helium

III-4 Discussion of II-3 Rates of Desorption and Sorption: Experiments were carried out gravimetrically and consisted of flowing high purity helium through a two-part bed. Initially, the first section contained ASC carbon saturated with DMMP and the second section carbon free of DMMP. The weight loss of the first section measured the loss of DMMP through desorption. The weight gain of the second section measured the sorption by carbon of low concentrations of DMMP in the gas phase. Two experiments were carried out simultaneously in the same dual column chromatograph.

As evident from column V of Tables 11 and 12, initially, reasonable mass balance was obtained between the loss in weight of the first section and gain in weight of the second section until longer times. At longer times, the second column did not pick up all the DMMP desorbed from the first column. The lack of complete DMMP pick up by the second column has serious implication for a protection system.

The rates of desorption from the first sections of the two beds should be compared. The rate of desorption from column 1-1' (16 cm long) is approximately twice as fast as from column 3-3' (8 cm long). This

result, the total rate of desorption approximately proportional to the length of column, is evidence of the importance of mass transport at this linear gas velocity. The implication is that the gas phase picks up DMMP throughout the length of the column. At much lower gas velocities it might be expected that gas at the inlet portion of the first section would become saturated with DMMP and no pickup by the gas phase would occur from the rest of the column since the gas phase concentration of DMMP would be high enough to equal vapor pressure of DMMP from the carbon saturated with DMMP. Our results imply that, at this gas velocity, the DMMP does not move down the column as a sample band or wave as described by Klotz*.

The rate of loss of DMMP, from the initially saturated column, as a function of average DMMP loading is not proportional to the vapor pressure of the sorbed DMMP as calculated from the DMMP isotherm** assuming homogeneous loading. At a loading of 50% of saturation, the vapor pressure of sorbed DMMP should be down by a factor of 10^{11} . Our results, given in column VII of Tables 11 and 12, show that at 50% average loading the effluent gas phase concentration is down by only a factor of about 100 from the saturation vapor pressure. The implication of this finding is that there is a lengthwise distribution of the DMMP loading. Toward the outlet end the sorbed concentration is much higher than the average loading.

The DMMP vapor phase concentration of the effluent from an initially saturated bed can be estimated since there is a linear relationship between the weight of DMMP on the column and the log of the quantity: time of flow plus a constant, as shown on Figures 10 and 11.

* I.M. Klotz, Chem. Rev., 39, 244 (1946)

** L.A. Jonas, private communication to T. Freund

Even at low inlet vapor phase concentrations of DMMP on a partially loaded bed there are circumstances in which the bed will loose more DMMP than it will sorb. An illustration of such a circumstance is shown in column VIII of Table 12. The percent of effluent from the first column sorbed by the second column, for long times, is negative; the meaning of a negative value is that the effluent concentration from the second column is higher than inlet concentration to the second column. This circumstance occurs at an average loading of about 50% of saturation and an inlet concentration of about 1/100 of the saturation vapor pressure of DMMP.

This last finding emphasizes the need for knowing both the average loading and the distribution of DMMP on the bed for an adequate protection system.

III-5 Discussion of II-4: Search for New Probe Gases: We use the following criteria in the search for a new probe gas: (1) at room temperature a retention time on DMMP-free carbon of two to four minutes at the space time and superficial linear velocity of the large scale filter, and (2) a good chromatographic "peak". We use DMMP-free carbon in our screening procedure since all probe gases investigated so far give shorter retention times on carbon containing DMMP; the time on DMMP saturated carbon is usually below 0.1 minute. Therefore, we can expect a good range of retention times with respect to residual bed capacity. For estimating the retention time at large scale filter conditions from other flow conditions and bed sizes we assume that the retention time divided by the space time is a constant. By a "good" chromatographic peak we mean one which has: (1) a high ratio of peak height to half width (maximum signal to the difference in time of the signal at half maximum signal at the increasing and decreasing portions of the signal)

and (2) a symmetrical signal (small "tailing").

The temperature dependence of the retention time of propane energy corresponds to the heat of sorption of propane on carbon. The energies which have been reported in the previous quarterly for hydrocarbons and carbon dioxide are 11 kcal/mol-degree or lower. We expect the heat of sorption of DMMP to be greater than the heat of vaporization of DMMP, which is reported to be 14 kcal/mol-degree.

III-6 Discussion of II-5: Effect of Packing on Retention Time: Since the particles of ASC are large, irregular in shape, and have a size distribution, we investigated the effect of packing in a 0.17 inch inner diameter tube. Jonas* has successfully packed larger diameter columns by use of a free-fall method involving dropping the particles through four feet of air. We found this inconvenient and carried two types of experiments, visual in a glass tube, and measuring the effects on the retention time of agitating a column.

From the visual experiments conducted in a glass tube, we found that the linear length of the bed, as filled by "free-fall" of a few inches from a funnel connected to the glass tube by plastic tubing, did decrease either by tapping with fingers or by use of a vibrator (a marking stylus type). The resulting length of the bed by either method of agitation was indistinguishable.

We had hoped to find a method of making the end of the bed flat and perpendicular to the length of the tube. We tried several method of placing the glass wool plugs in the tube but concluded that the definition of the end of the bed is probably no better than about 2 mm.

The in situ attempts to agitate a bed confined by glass wool plugs, about 1/4 inch long, showed no significant experimental effect on the retention time

* L. Jonas, private communication to F. Freund

IV FUTURE WORK

- I. Determine the effect of operating variable on the retention time of the probe gas:
 - 1) diameter and length of the bed
 - 2) size of the pulse in relation to the size of the bed.
 - 3) water content of the carbon and water content of the carrier gas.
 - 4) substances sorbed on ASC from air other than moisture.
- II. Determine the best detector with respect to reproducibility, sensitivity and operating conditions.
- III. Theoretical analysis of the roles of mass transport and sorption equilibria in terms of flow conditions and geometrical structure of the sorbent bed.

V CONCLUSIONS

1. The principle of retention time (or hold-up) of a pulse of a weakly sorbed probe gas in a stream of flowing carrier gas as a measure of the residual sorption capacity for ASC carbon has been experimentally demonstrated.
2. Many of the operating variables have been investigated at the laboratory state including: temperature, chemical nature of the test gas, and flow rate of the carrier gas.
3. The adsorption and desorption of DMMP and the migration of adsorbed DMMP down the length of a bed have been shown. The probe gas is capable of detecting this migration.

APPENDIX A

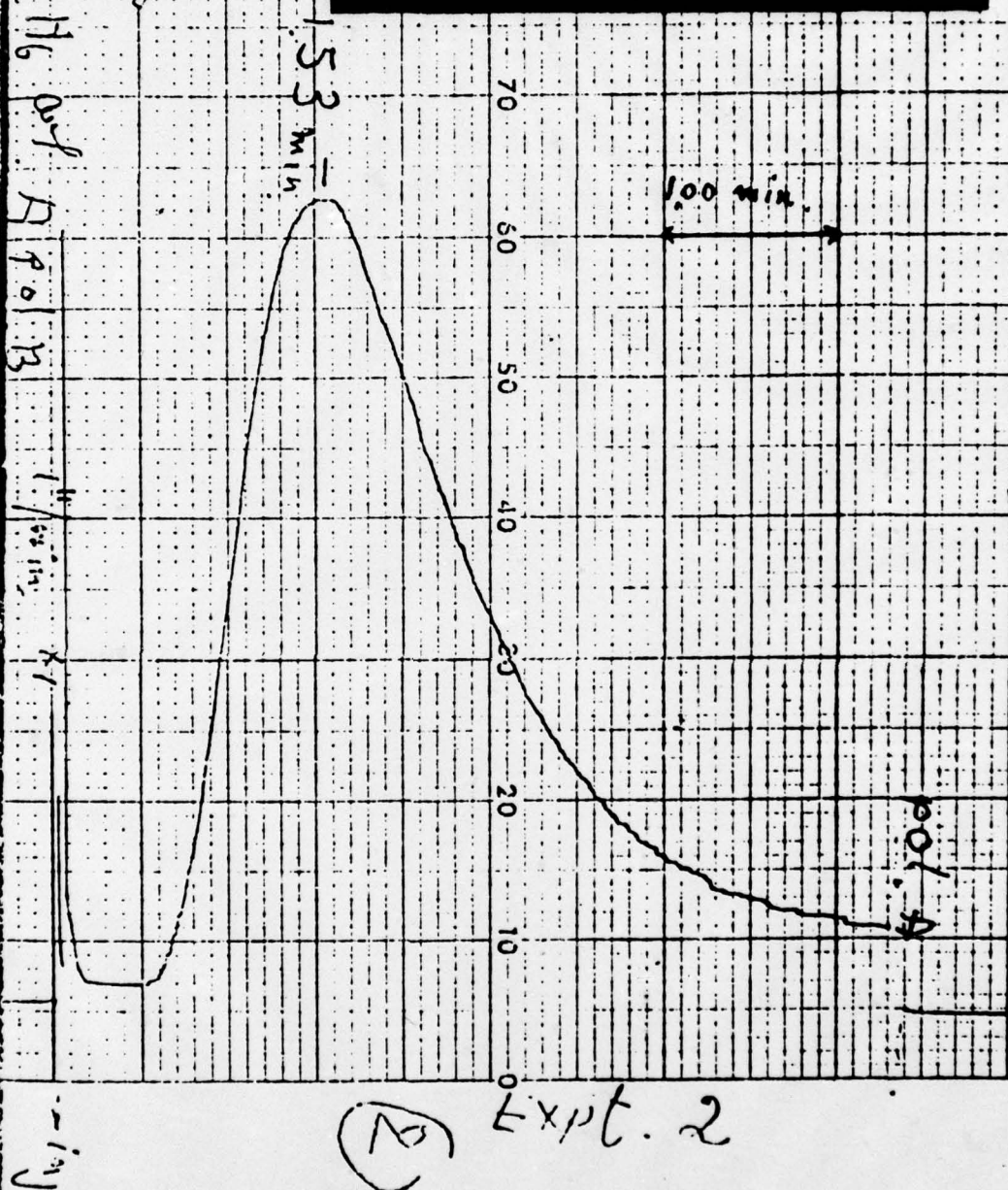
Appendix A contains copies of representative chromatographs from which the data for Table 2 was compiled. Shown are Experiment Numbers 2, 4, 5, 6, 8, 9, 11, 14, 17, with retention times ranging from 1.53 to 0.04 minutes as the column picked up increasing amounts of DMMP.

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Director-Commander, Chemical Systems Laboratory USA ARRADCOM Attn: Dr. Leonard A. Jonas, DRDAR-CL Aberdeen Proving Ground, MD 21010	20

Chromatogram for Experiment 2

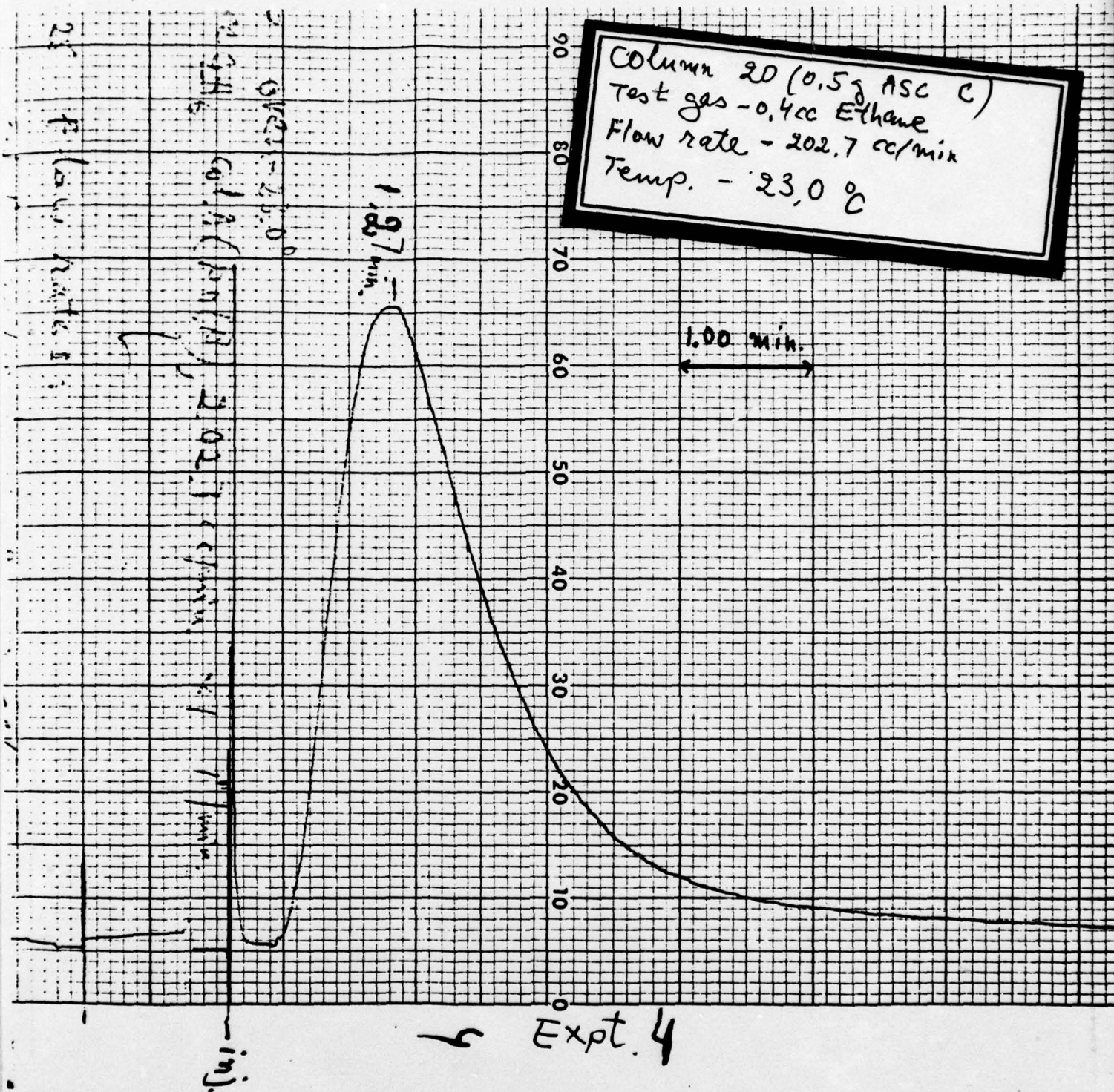
Column 20 (0.5 g Asc C)
Test gas - Ethane
Flow rate - 202 cc/min.
Temp. 23.0°



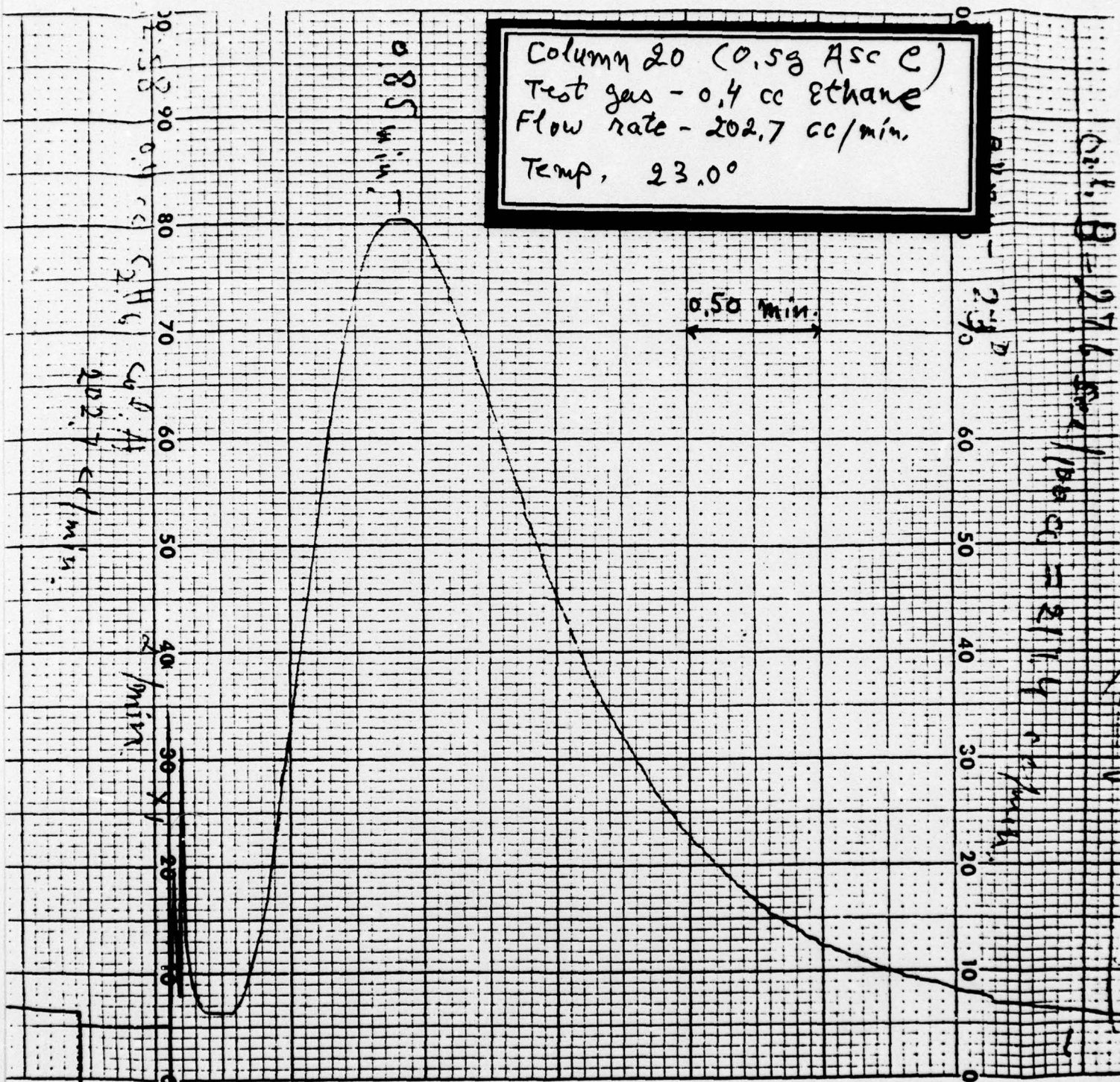
(10) Expt. 2



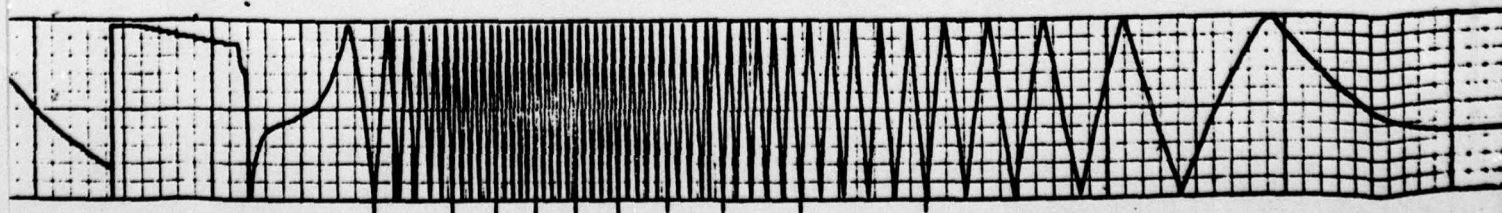
Column 20 (0.5 μ ASC C)
 Test gas - 0.4cc Ethane
 Flow rate - 202.7 cc/min
 Temp. - 23.0 $^{\circ}$ C



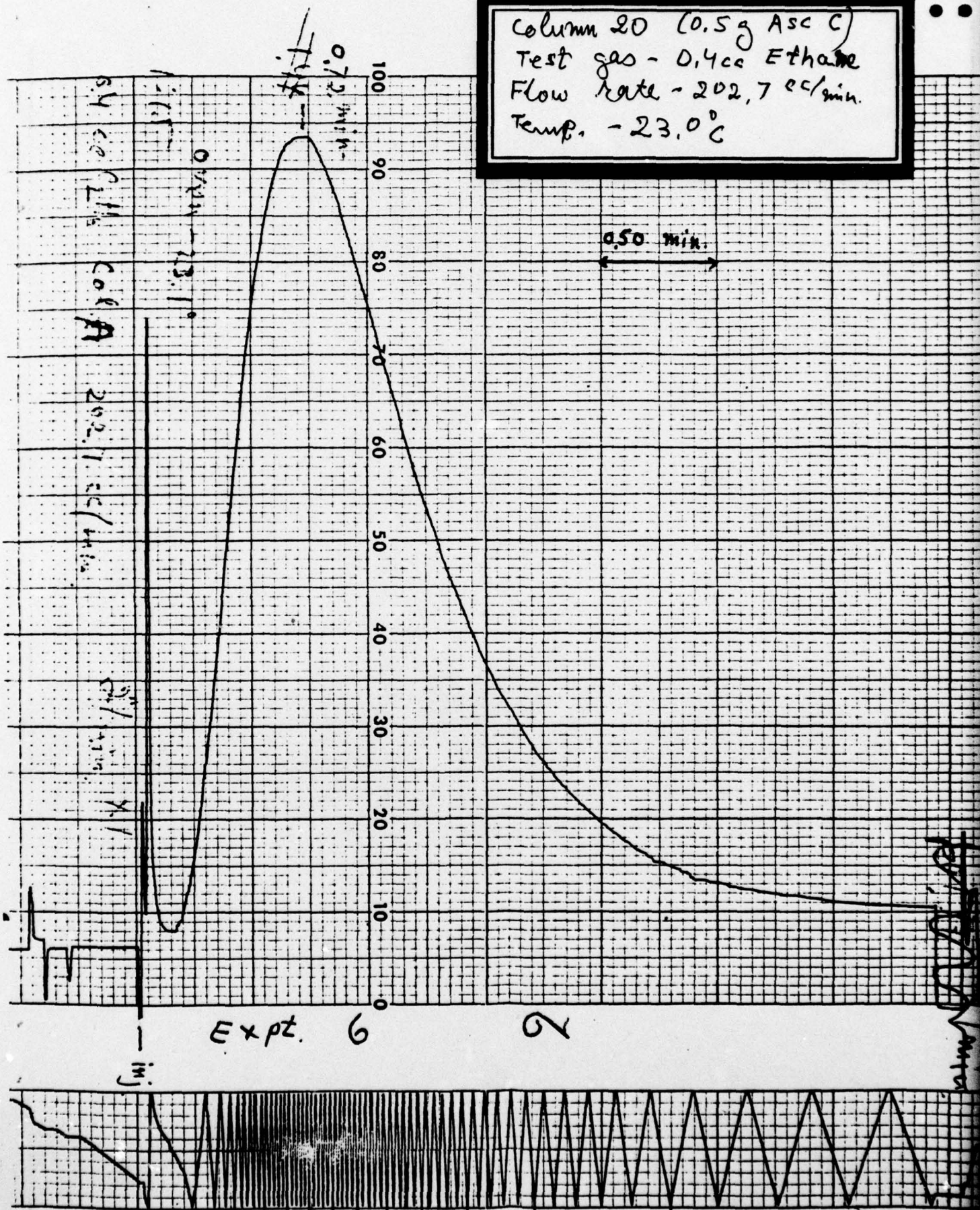
Column 20 (0.5g Asc C)
 Test gas - 0.4 cc ethane
 Flow rate - 202.7 cc/min.
 Temp, 23.0°



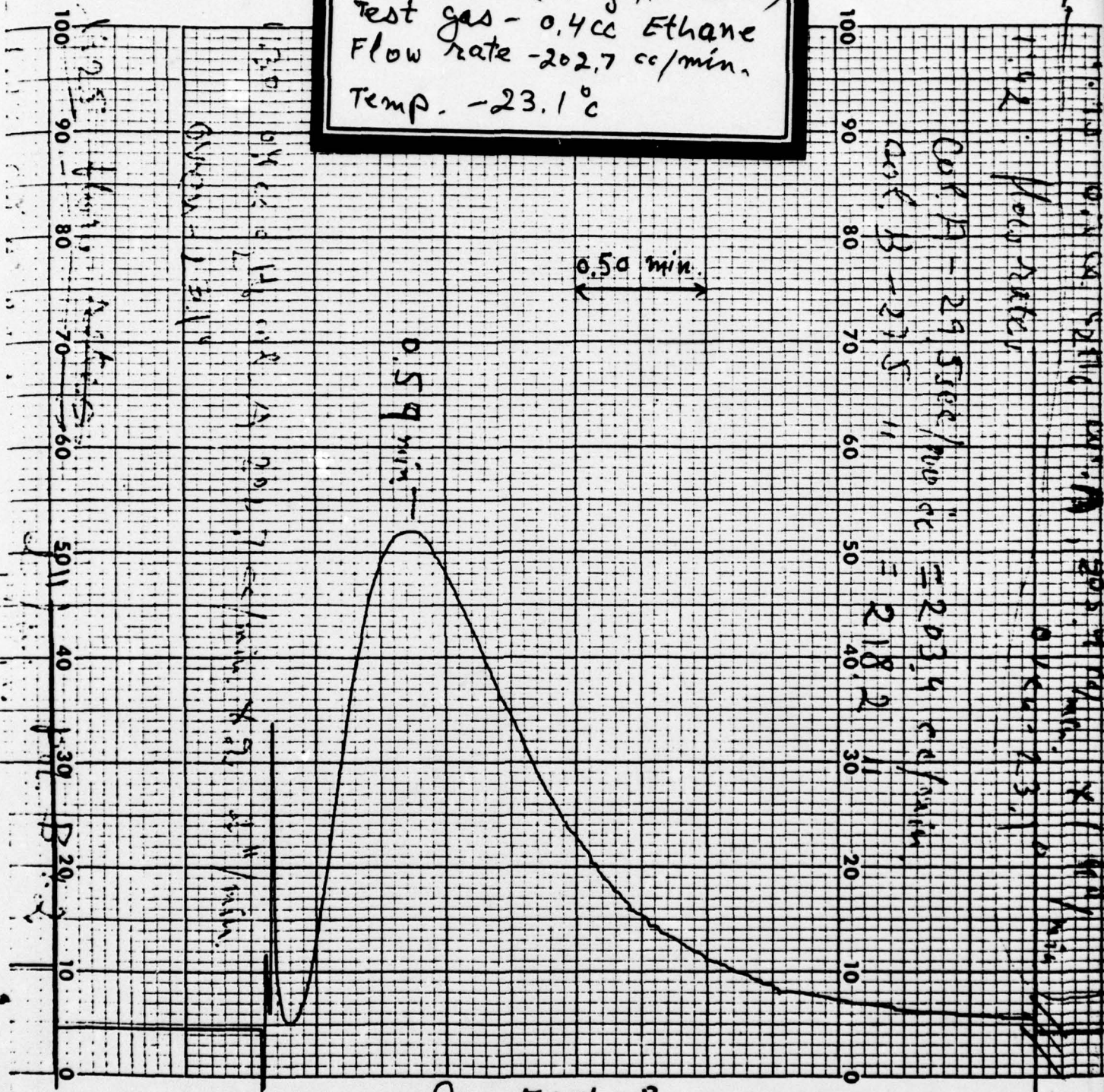
Expt. 5 9



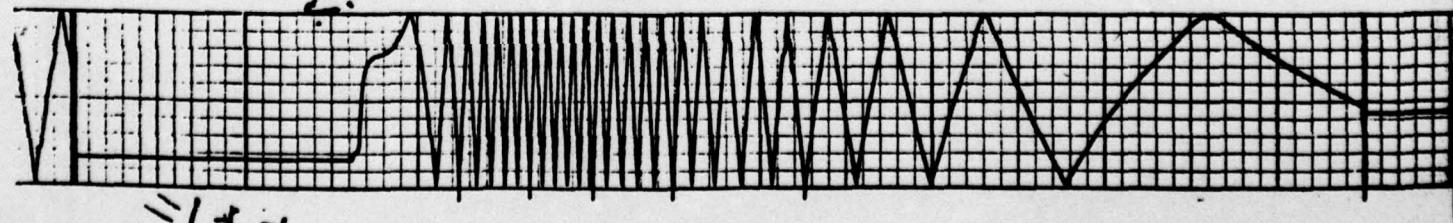
Column 20 (0.5 g Asc C)
 Test gas - 0.4 cc Ethane
 Flow rate - 202.7 cc/min.
 Temp. - 23.0°C



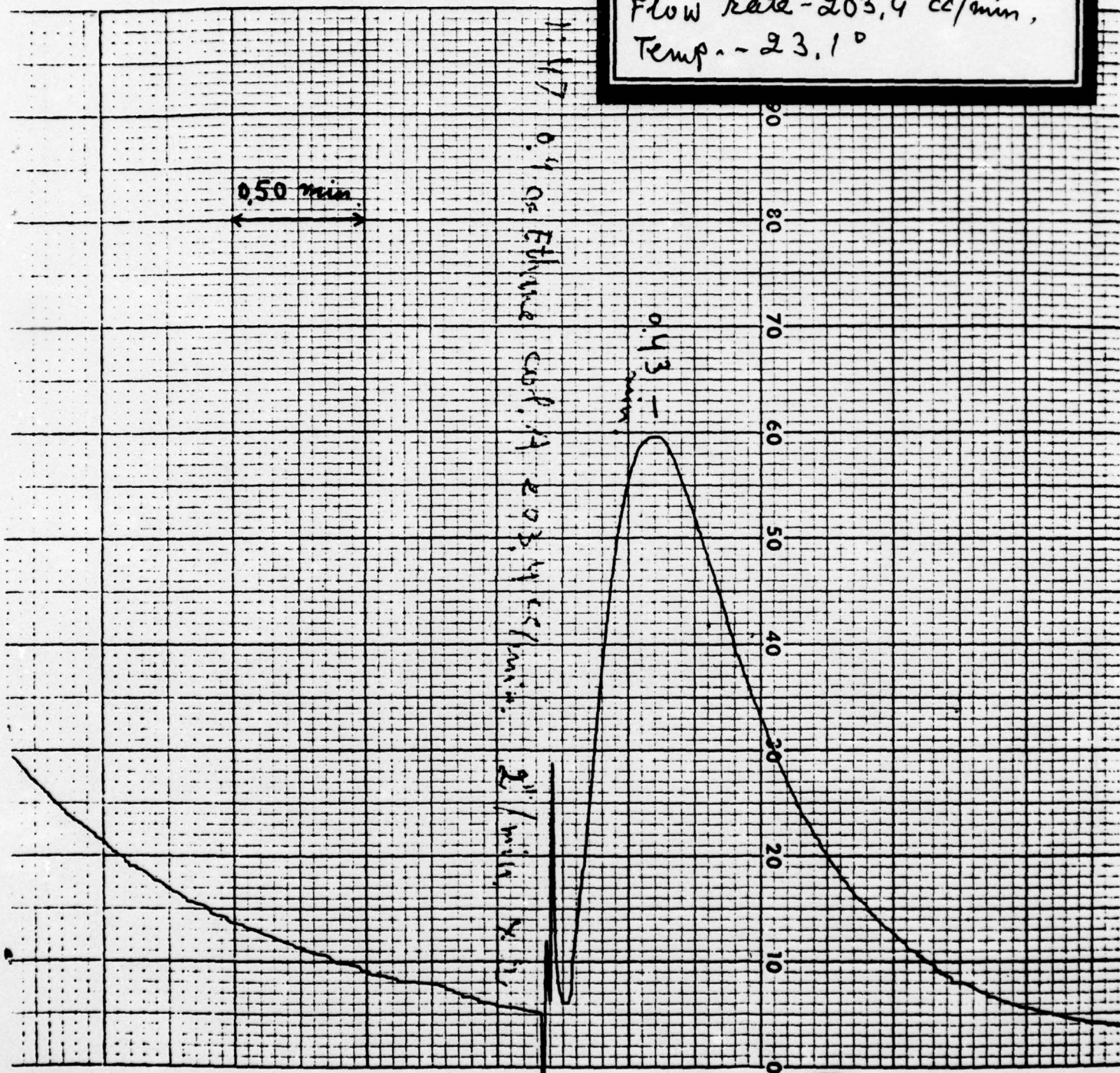
Column 20 (0.5g Asc Carbon)
 Test gas - 0.4cc Ethane
 Flow rate - 202.7 cc/min.
 Temp. - 23.1 °C



8 Expt. 8



Column 20 (0.5, ASC C)
Test gas - 0.4 cc Ethane
Flow rate - 203.4 cc/min,
Temp. - 23.1°



Expt. 9

(9)



Column 20 (0.5 g ASC C)
 Test gas - 0.4 cc Ethane
 Flow rate - 203.4 cc/min.
 Temp. - 23.1°C

cc C₂H₆ col. A, 203.4 cc/min.

0.4 cc/min - 23.1°C

X 2, 4" / min.

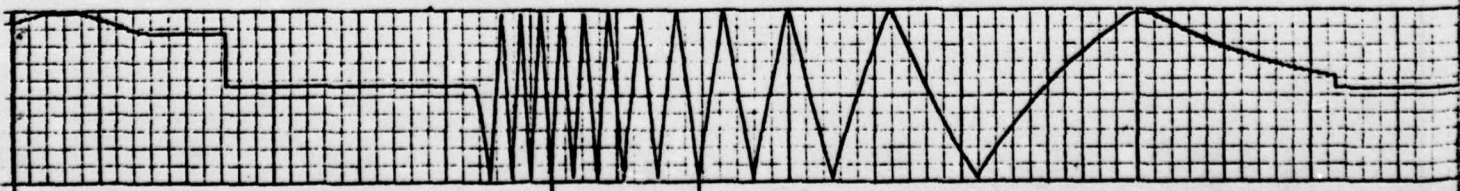
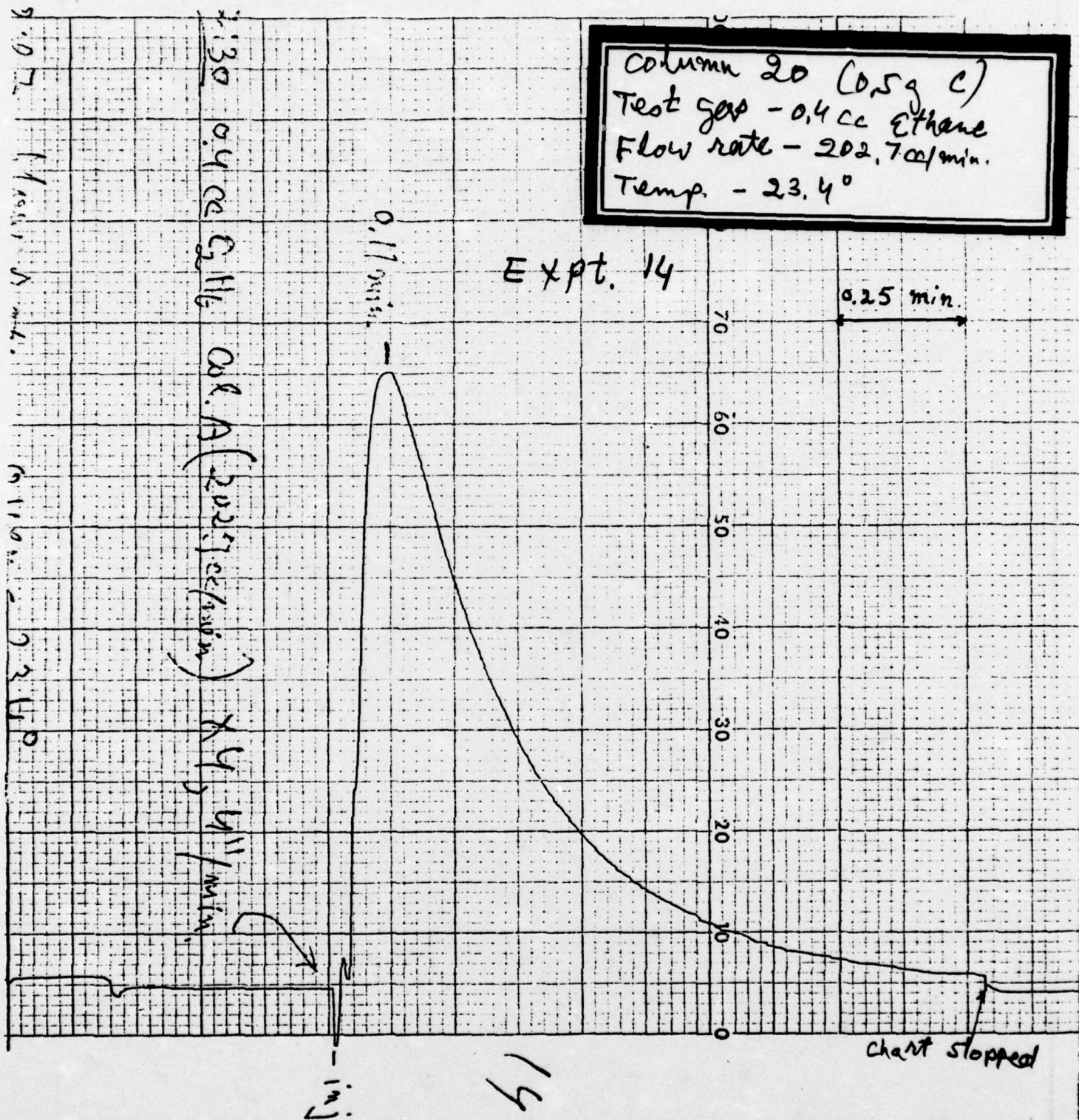
0.34 min.

0.25 min.

EXPT. II

Column 20 (0.5 g C)
 Test gas - 0.4 cc Ethane
 Flow rate - 202.7 cc/min.
 Temp. - 23.4°

Expt. 14



Column 20 (0.5g Carbon, ASC)
 Test gas - 0.4 cc Ethane
 Flow rate - 202.7 cc/min.
 Temp. - 23.2 °C

