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**INVESTIGATION OF THE EXTRACTION OF HYDROCARBONS
FROM SHALE ORE
USING SUPERCRITICAL CARBON DIOXIDE**

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TABLE OF CONTENTS

	PAGE
1.0 Introduction	1
2.0 Experimental Program.....	3
2.1 Design and Construction of Test Apparatus....	3
2.2 Extraction Vessel.....	7
2.3 Compressor.....	9
2.4 Oil Collection Tube.....	10
3.0 Test Program.....	14
3.1 Test Procedure.....	14
3.2 Data Collection and Reduction.....	17
4.0 Results.....	18
4.1 Data Summary.....	21
4.2 Calculations of Relevant Parameters.....	21
4.3 Time Dependence of Oil and Water Yields.....	24
4.4 Dependence of Oil Extract on Particle Size.....	34
4.5 Conditions of the Run.....	36
4.6 Temperature.....	36
4.7 Density.....	36
4.8 Shale Pretreatment.....	43
4.9 Solvent Gas.....	44
5.0 Conclusions.....	45
Appendix A Equipment Purchase and Specifications for Shale Oil Extraction Apparatus	
Appendix B Cambridge Analytical Associates Analysis Report-GC/MS of Shale Oil	
Appendix C Experimental Run Data Sheets	
Appendix D Curve Fitting Calculations for Oil and Water Extracts as a Function of Density and Temperature	

LIST OF FIGURES AND TABLES

FIGURES		PAGE
Figure 1	Diagram of Test Apparatus.....	4
Figure 2	Photograph of Test Apparatus.....	6
Figure 3	Durolok Vessel.....	8
Figure 4	Diagram of Condenser.....	11
Figure 5	Photograph of Condenser.....	12
Figure 6	Thermodynamic Properties of Carbon Dioxide.....	25
Figure 7a	Effect of Time on Oil Yield.....	27
Figure 7b	Effect of Time on Water Yield.....	28
Figure 8	Process Efficiency VS Length of Run.....	35
Figure 9	Extract Yield VS Particle Size.....	37
Figure 10	Oil Extract Fraction VS Temperature.....	39
Figure 11	Water Extract Fraction VS Temperature.....	40
Figure 12	Oil Extract Fraction VS Density.....	41
Figure 13	Water Extract Fraction VS Density.....	42

TABLES		PAGE
Table 1	Test Program Matrix.....	15
Table 2	Fischer Assay Results for Fresh and CO ₂ Processed Shale.....	19
Table 3	Carbon, Hydrogen, Nitrogen Analysis of Extracted Liquids.....	19
Table 4	Carbon, Hydrogen, Nitrogen Analysis of Bitumen and Kerogen.....	20
Table 5	Experimental Data.....	22
Table 6	Reduced Data Flow.....	23
Table 7	Data for Time Dependence Correlations.....	29
Table 8	Statistical Calculations for Oil Extract Correlation With Time.....	30
Table 9	t Distribution for Statistical Analysis.....	31
Table 10	Statistical Calculations for Water Extract Correlation with Time.....	32
Table 11	Reduced Data.....	38

1.0 INTRODUCTION

The U.S. shale reserves are a huge potential source of domestically produced liquid fuels. Conservative estimates of shale oil supply, considering only the highest energy content shales, place the recoverable supply at 200 billion barrels of oil equivalent. At these quantities, shale oil is the most promising source of unconventional, domestically produced oil for the United States. Conventional methods of producing synthetic oils from shale are, however, both expensive and environmentally problematical. The difficulty in producing useful liquid fuels from shale comes from the physical and chemical characteristics of the organic matter in the shale. The organic matter is a solid material called kerogen. The kerogen, imbedded in layers of sedimentary rock, must be removed and converted into a liquid product before it can be sent to an oil refinery and then sold to the public.

Present technology to recover the kerogen involves retorting the ore, a high temperature process which decomposes the kerogen into crude shale oil. This process to remove the kerogen from the rock and to convert it to a liquid fuel is not commercially economical at the present time. In addition to the large capital expense of retorting technology, there is a large fuel cost due to thermal inefficiency. Heating the shale to pyrolytic temperatures (800-1000°F) requires that 30 - 40% of the hydrocarbons contained in the ore be burned. The major problems with this technology include the following:

- 1) Low oil yield due to thermal inefficiency;
- 2) High equipment costs for large heat transfer vessels;
- 3) Possible degradation of pyrolytic oil quality due to oxidation of hydrocarbons in high temperature combustion gases; and
- 4) Huge water requirements for the cooling of the retort products (in an area where water resources are scarce).

In spite of the problems with shale oil recovery, interest in shale will continue as long as imported oils are expensive and their supply is unreliable. In light of both the interest in shale oil and the problems

associated with conventional shale oil production, there is a need for the development of new and different technologies to produce shale oil. In this research effort, an extraction method was investigated as an alternative method to remove organic matter from the shale. Using supercritical carbon dioxide as a solvent, hydrocarbons were extracted from the shale at low temperatures under moderate pressure. The process investigated is a cycle. The first step in this cycle is the pressurized extraction step. Dense carbon dioxide passes through the shale under moderate pressure causing organic matter to dissolve into the CO₂. In the second step the CO₂, dissolved hydrocarbons, and water pass into a low-pressure chamber where CO₂ returns to a gaseous state and the hydrocarbons and water collected from the shale are condensed and collected.

The investigation of the process to extract hydrocarbons from oil shale using supercritical carbon dioxide is based on evidence that carbon dioxide is a good solvent of organic materials at conditions above its critical point. The critical point of a fluid is the condition at which all intrinsic properties of the liquid and vapor are identical. For CO₂, this occurs at 88°F and 1069 psi, where the critical density is 28.91 lbs./cu.ft. With supercritical fluids, small changes in pressure can produce large changes in density. It is this change in density which most effects the solvent power of the CO₂. A cycle of extraction and precipitation can be achieved, with little expenditure of work, as small changes in pressure increase and decrease the solvent power of CO₂. This extraction process was studied experimentally. Organic matter was dissolved out of the shale into dense CO₂ in one chamber and the solute (hydrocarbons and water) was collected from the CO₂ in a low pressure chamber down-stream of the extraction vessel.

In this experimental program, the operational variables which affect the extraction process (temperature, pressure, time of extraction, shale particle size, pretreatment) were studied. One goal of the program was to discover which variables significantly affected extraction, in terms of both extract volume and composition. The second objective of the work was assessing the feasibility of the process in light of the laboratory results obtained in the parametric studies.

2.0 EXPERIMENTAL PROGRAM

The experimental program was divided into the following basic tasks:

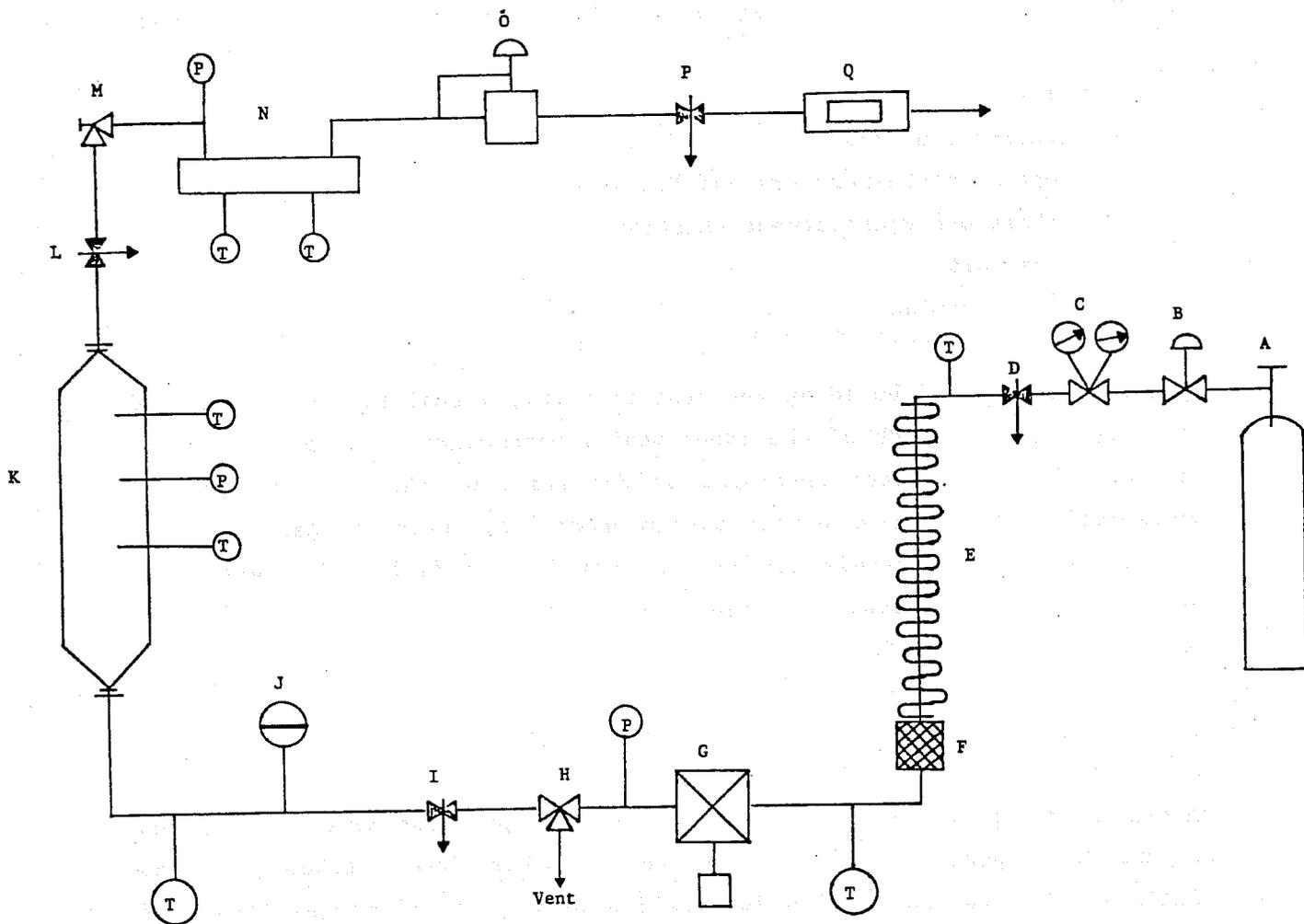
- o Design and Construction of Test Apparatus.
- o Experimental Studies: Effect of Following Variables on Extract Volume and Composition
 - Particle Size
 - Extraction Time
 - Operating Temperature and Pressure
 - Shale Ore Pretreatment (Heating)
- o Data Analysis
- o Report Generation

After designing and building the test facility, a test plan was developed to gather data on each of the experimental parameters. The procedures to collect these data were developed at the start of the test program and were refined by experience with system operation. Data was gathered once the system was adequately tested and considered reliable. The apparatus design and construction, test plan, test procedures, and data collection are described in the following sections.

2.1 Design and Construction of Test Apparatus

A diagram and photograph of the entire testing apparatus appear in Figures 1 and 2, respectively. The flow through this system takes place as follows. The carbon dioxide is supplied by a pressurized gas tank. The gas is heated slightly and compressed to the desired pressure. This high pressure (dense CO₂) then passes through the extraction vessel where the ground shale is contained. It is in this vessel that the hydrocarbon extraction takes place. The gas (plus extract) passes out of the vessel through an expansion valve and into a low pressure vessel filled with metal chips on which the oil condenses. A back-pressure regulator controls the pressure in the condenser vessel. A mass flow meter at the exit of the system measures the flow of the CO₂ (and extract gases) through the apparatus.

FIGURE 1
DIAGRAM OF TEST APPARATUS

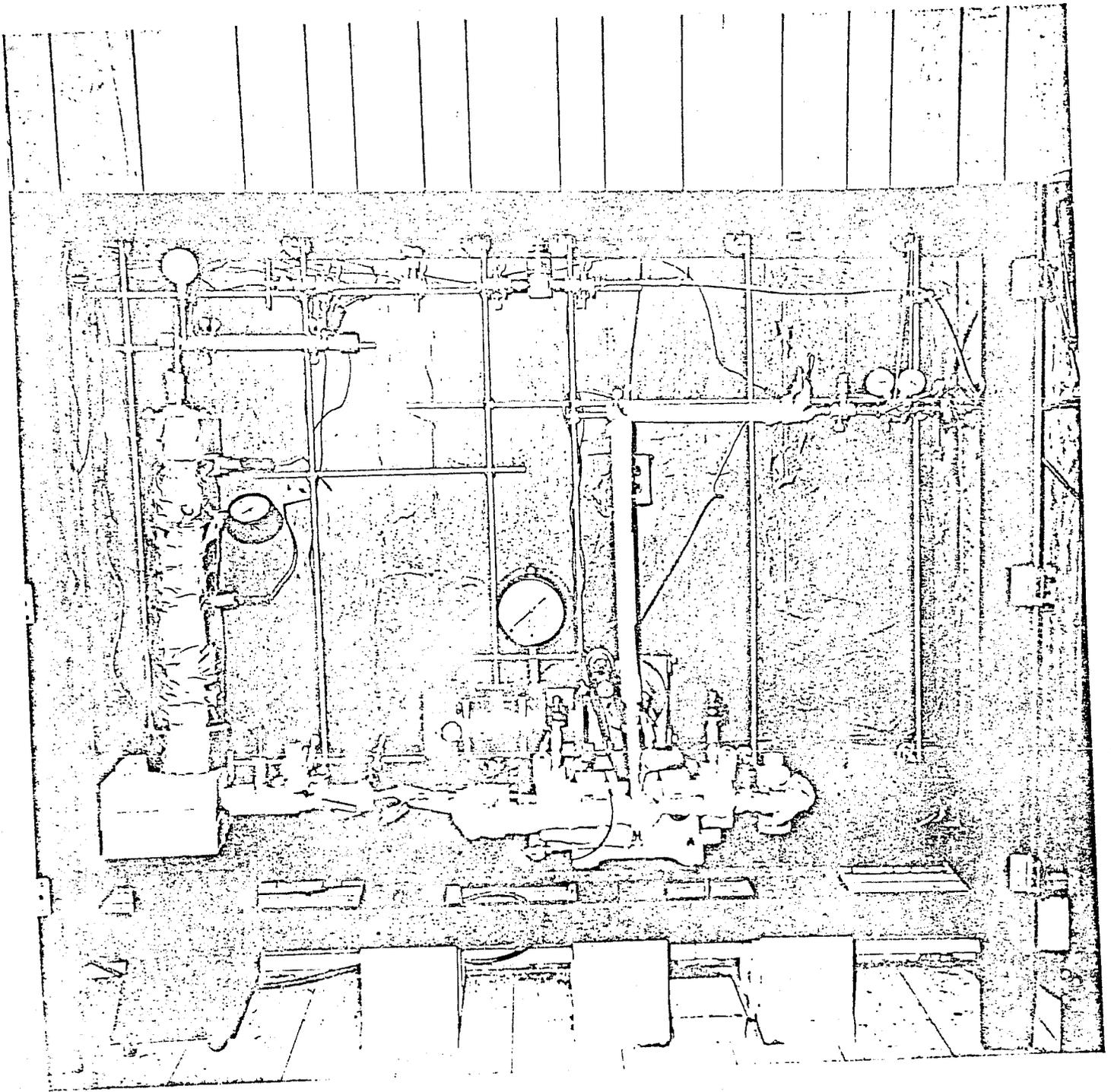


Index To Figure 1

A	CO ₂ Cylinder
B	Flow Limit Shut Off Valve
C	Pressure Regulator
D	Needle Valve
E	Heating Tape
F	5 mm Filter
G	Compressor
H	3 Way Ball Valve
I	Needle Valve
J	Rupture Disk
K	Extraction Chamber (with heating tape & insulation)
L	Needle Valve
M	Angle Micro Metering Valve
N	Condenser Tube
O	Back Pressure Regulator
P	Needle Valve
Q	Mass Flow Meter

Note: Pressure and temperature indicators are marked as (P) & (T) respectively.

FIGURE 2
PHOTOGRAPH OF TEST APPARATUS



The three key pieces of equipment in the test apparatus that required particular attention in their design were the extraction vessel, the compressor, and the condensor vessel. Each piece is discussed below in terms of important considerations that went into its design and/or purchase.

2.2 Extraction Vessel

To size the extraction vessel, the following assumptions were made:

- 1) In initial runs, the ratio of oil extracted to oil present in the run would be ten percent (10%);
- 2) A volume of at least 50 cubic centimeters of oil is needed to run the proposed tests on extracted hydrocarbons;
- 3) A maximum pressure in the vessel will be 4500 psi ($P_r = 4$); and
- 4) A maximum temperature in the vessel will be 400°F ($T_r = 4.5$).

Other design considerations are as follows:

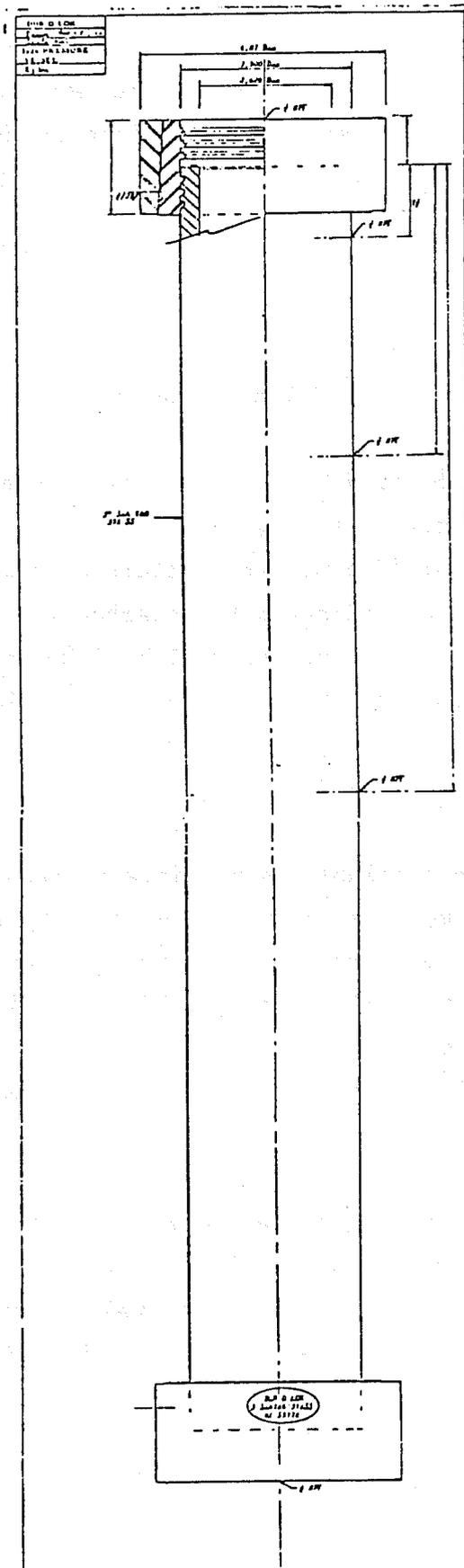
- 1) The vessel must be as simple as possible to open and close;
- 2) The sealing rings must be compatible with a CO₂ environment;
- 3) The flow through the vessel must be vertical so that solvent can percolate through the bed of shale. (The vessel, therefore, must have an inlet and outlet port); and
- 4) Shale to be used in the test runs will contain between 30-35 gallons of oil per ton of shale.

Approximately 2.2 liters of ground shale are required to extract 50 grams of oil from shale rock given a 10% extraction rate. A sample size of 50 grams was considered desirable for capture and analysis considerations. The required size of the extraction vessel was thus determined to be 2 1/4 liters in volume.

A DUROLOK vessel, shown in Figure 3, was selected. The clamp arrangement on both ends of the vessel allows easy opening and closure. The O-ring

FIGURE 3

DURALOK VESSEL



ensures a seal between the lid and the vessel body. The vessel, made of 3 inch diameter schedule 160 316 stainless steel pipe, has three 1/4" taps in the walls and one in each end to allow connection of gauges, thermocouples, and tubing.

An O-ring made of silicon rubber was selected for use with this vessel. Other common O-ring materials, such as viton or teflon, could not be used because CO₂ is soluble in the material and because the materials cannot be used at high temperature. Researchers of supercritical fluid extraction systems at Arthur D. Little, in Cambridge, Massachusetts, found silicon O-rings to be acceptable in a high temperature CO₂ environment. On the basis of these studies, silicon O-rings were used in our studies.

2.3 Compressor

Because little is known about the solubility of kerogen in CO₂, it was not possible to accurately calculate a required CO₂ flow rate that would extract 50 cubic centimeters of organic matter from the shale over the course of a test run.

After consulting with research groups studying supercritical systems, it was learned that extraction fluid flow rate was often the limiting factor that determined the speed of a test run. Thus, a double-ended, single stage compressor was selected for use. The double-ended machine has a larger flow capacity than other, less expensive models. A Superpressure diaphragm-type, double-ended, motor-driven compressor (Model No. 46-13421) was selected. The maximum working pressure of the compressor is 10,000 psi. The maximum pressure ratio is 14, which requires that the CO₂ leaves the cylinders at relatively high pressure in order to reach this limit.

The compressor was controlled with a contact relay assembly that connected to a pressure indicator at point I in the line (See Figure 1). The contact relay could be adjusted to establish two pressure limits, one low and one high, at which the compressor would turn on or turn off, respectively. The control box and electrical contacts were also Superpressure products (Model No. 324-2060 and 1603-146).

2.4 Oil Collection Tube

The tube in which the extracted organic matter would condense was designed according to the following criteria. The tube had to:

1. Be light in weight relative to the fluids caught inside it, so that determination of the quantity of oil extracted by the supercritical process could be made by weighing the tube plus extracted products.
2. Be able to withstand a maximum pressure of 1200 psi (safety factor for potential "water hammer" effects included).
3. Have adequate heat transfer characteristics to allow temperature control of the condensation process.
4. Be easily detachable from the rest of the experimental set-up.
5. Have a simple opening and closing mechanism.
6. Allow simple and complete cleaning between runs.

The vessel was a one inch diameter aluminum tube with brass caps on either end and a diagram and photograph of the condenser are shown in Figures 4 and 5.

The tube was filled with material on which the extracted oils and water could condense. It was known from other extraction investigations that finding the correct condenser material is important for the complete capture of the extract. Over the course of the experimental program, we used both metal chips and glass beads. The advantages and disadvantages of each are discussed in the section of experimental results.

Other components of the system were ordered on the basis of standard engineering methods and judgement. A list of all the equipment purchased, the manufacturers, the specifications, and the costs are presented in Appendix A.

The shale used in this experiment came from the U.S. Department of Energy, Laramie Energy Technology Center, Laramie, Wyoming. The material was mined from the Anvil Points Mine near Rifle, Colorado. This is Mahogany Zone

FIGURE 4
DIAGRAM OF CONDENSER

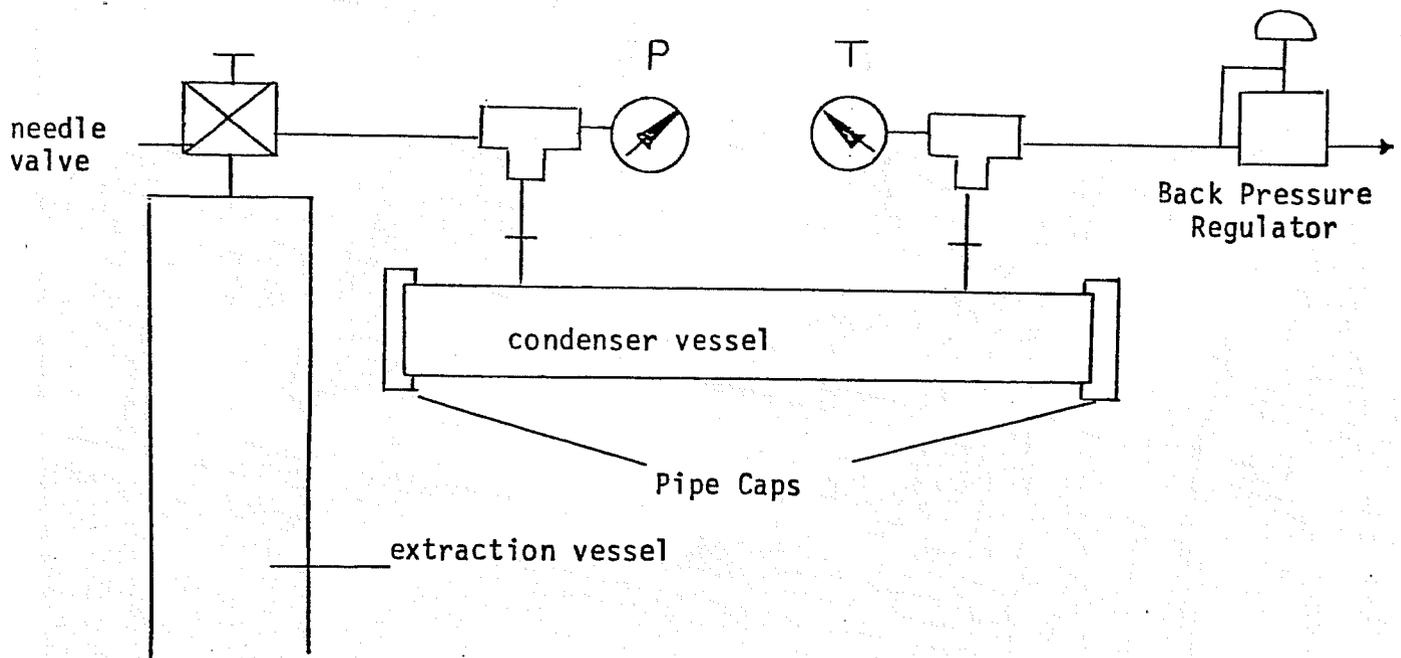
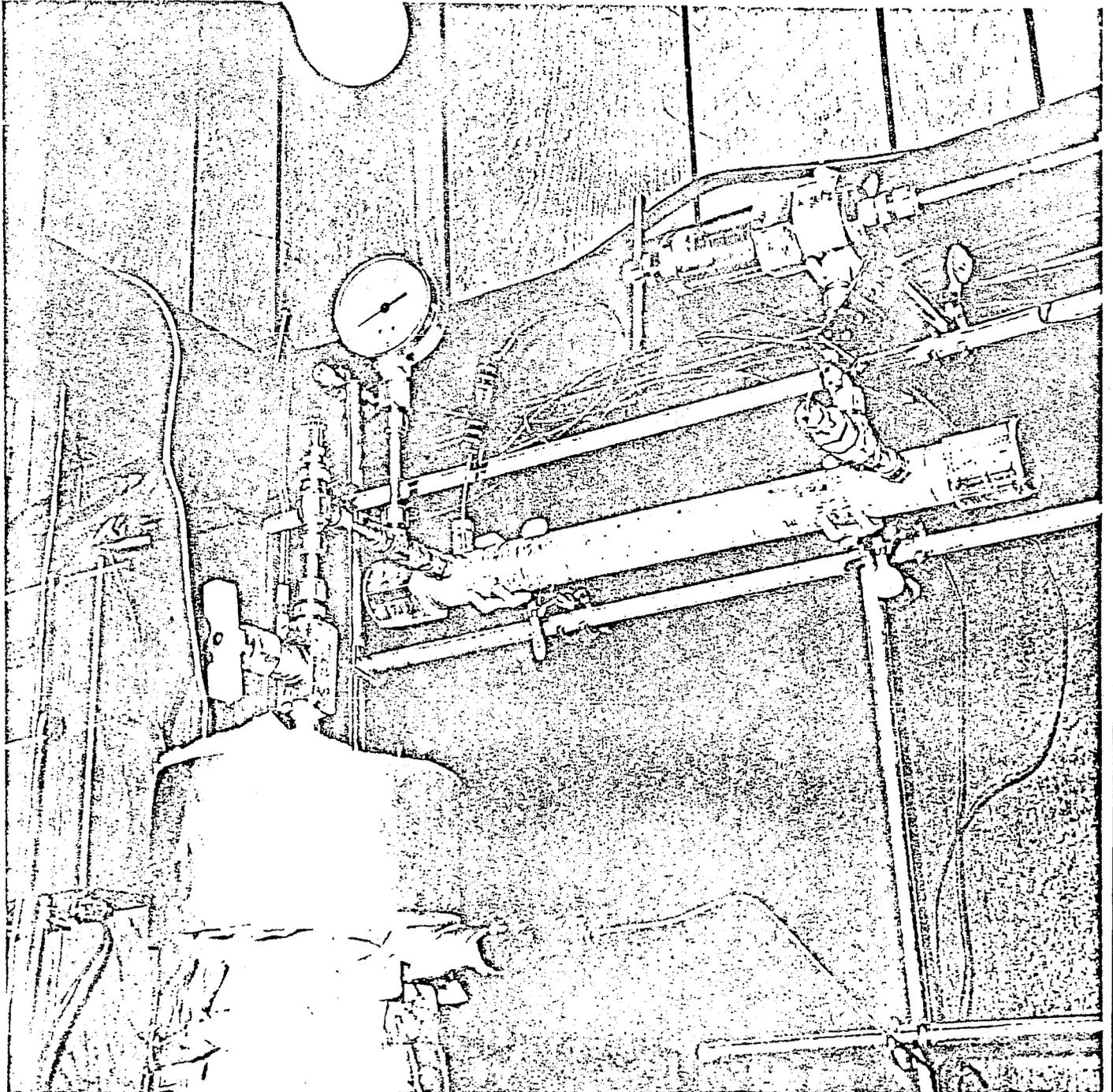


FIGURE 5
PHOTOGRAPH OF CONDENSER



shale from the Piceance Basin which contains approximately 60 gallons of oil per ton of rock. (The oil content is greater than was expected. Designs of system components are therefore conservative.) There is very little gas in this shale.

In the packaging and delivery of this shale, attempts were made to find shale with unoxidized surfaces. The shale was placed in plastic lined barrels and sealed to prevent additional oxidation from occurring. Three quarters of a ton of shale were delivered for use on this project.

3.0 TEST PROGRAM

Table 1 presents the set of runs which were performed to investigate the influence of particle size, time of extraction, and temperature and pressure on the volume and composition of extracted hydrocarbons.

In this test matrix, Runs 1 through 3 are to investigate the effect of particle size on extract volume and composition. Runs 1, 4 and 5 are performed to obtain time dependence data. The last runs, 6 through 12, map out extraction as a function of temperature, pressure and density of the carbon dioxide solvent.

In the second part of the test program, two other factors were investigated: preheat treatment of the shale and the use of another gas (ethylene) as the solvent.

3.1 Test Procedure

The experimental procedure used in the operation of this apparatus was as follows:

The shale vessel was cleaned from the previous run and filled with shale of the desired particle size. The volume of shale was weighed, and the weight was recorded. The shale was packed in the vessel between glass wool and sintered metal discs which cover both the inlet and outlet ports of the vessel. The primary purpose of the sintered disc at the bottom (inlet) of the vessel was to distribute the CO₂ throughout the shale. It was intended that the filter disc would prevent the incoming CO₂ from simply boring through the shale along the axis of the vessel and thus miss contact with most of the shale. The glass wool and sintered disc at the top of the vessel (the outlet port) was primarily to prevent pieces of the rock from escaping the vessel and damaging down stream components.

The condenser tube was cleaned with methylene chloride and filled with stainless steel chips. The chips served as added surface area for the hy-

TABLE 1

TEST PROGRAM MATRIX

Run #	T (°F)	P (psi)	Size(um)	Time (hrs)	
1	140	1800	1500	3	*
2	140	1800	1000	3	*
3	140	1800	500	3	*
4	140	1800	1500	1	*
5	140	1800	1500	8	*
6	150	2000	1500	3	*
7	170	2150	1500	3	*
8	180	2300	1500	3	*
9	200	2500	1500	3	*
10	200	3000	1500	3	
11	250	3200	1500	3	*
12	250	2500	1500	3	

* indicates that the density of the fluid is that of the density at the critical point.

drocarbons to condense on. These chips were also cleaned with methylene chloride at the start of each run. The weight of the chamber and chips was taken and recorded at the start of each run.

The shale vessel, wrapped in heating tape and covered with fiberglass insulation, and the condensing chamber, wrapped in cold packs and covered with fiberglass insulation, were put back in the apparatus. Variac controlled heat tape around the CO₂ tubing upstream of the shale vessel and the heat tape around the vessel itself were used to achieve and maintain the desired temperature of extraction.

To start the run, the valve at the outlet of the shale vessel was shut. CO₂ was allowed to flow through the compressor and into the vessel. The lines were heated and the carbon dioxide was pumped until the temperature and pressure of the shale/CO₂ mixture in the extraction vessel were at the desired levels. When the run pressure and temperature were achieved, the metering valve at the top of the vessel was opened. CO₂ was allowed to leave the vessel at the rate that it entered, thus keeping a stable pressure in the vessel itself as the solvent flowed through. Constant temperature in the vessel was maintained by periodically adding heat to the vessel to compensate for heat lost out the sides of the vessel and with the hot, exiting CO₂.

Constant temperature in the condenser tube was maintained by covering the tube with ice packs and insulating the system. Most of the temperature drop of the gas occurred from the pressure drop across the metering valve, and not by cooling by the ice packs. The ice packs were changed regularly as they warmed up over the course of the run. Constant pressure (400psi) in the chamber was maintained with a back pressure regulator. The 400 psi pressure was selected as a compromise pressure. The pressure had to be below the critical pressure of the gas, so that the CO₂ would lose its solvent power and drop the dissolved materials. But too great a pressure drop caused a freezing problem in the metering valve, as the CO₂ changed phase with the pressure drop. At 400 psi, a length of heating tape kept the metering valve reasonably ice free.

To determine whether any oil escaped the condensing chamber and exited the system with the used CO₂, the exhaust gas line had a cotton wad attached to the end of it . This cotton was checked periodically throughout the run.

The run was thus allowed to continue for the duration of the desired run time. The flow rate of the CO₂ was recorded systematically, as were the temperature and pressure of important components in the system. The cold packs on the condensing tube were occasionally changed to maintain the tube at around 40°F. When the run was completed, the compressor was shut off and the CO₂ (and extract) was allowed to bleed into the condensor tube until the extraction vessel pressure dropped below 1070 psi. The run was then over, and the condensor tube was weighed. The condensor tube was stored in a vertical orientation overnight to allow the liquids to drip into the end cap. The following day the liquids were removed from the cap with a syringe. The apparent water fraction was separated from the oil fraction with a syringe. The water fraction was weighed and its volume was measured in a graduated cylinder. The shale rock was weighed before and after each run.

3.2 Data Collection and Reduction

The total weight of extracted liquids was calculated by subtracting the initial from the final weight of the condensor tube. It was assumed that all of the water fraction of the extract drained out of the chamber because water is nonviscous and flows easily. Thus the weight of the water fraction which was weighed separately is reasonably accurate. Some of the extract, however, did stick to the walls of the condensor tube and the metal chips. It was assumed that this material was part of the oil fraction. The weight of the oils captured was calculated as the difference between the total weight of extracted liquids and the weight of the water fraction. Selected samples of the extract were sent out for carbon, hydrogen and nitrogen (C,H,N) analysis and Gas Chromatograph/Mass Spectrometer analysis. Samples of the shale rock from before and after these selected runs were sent out for C,H,N analysis.

4.0 RESULTS

The average amount of oil removed from the shale corresponds to about 1 percent of the organic matter in the ore. The maximum oil yield obtained from a run corresponds to 0.73 gallons of oil per ton of shale. The shale used contains 60 gallons per ton of oil. Thus the maximum yield was about 1.3 percent. Water was extracted from the shale in greater amounts than was oil. A Fisher assay done on the shale before and often the extraction process showed that more than half of the water in the rock was removed by the carbon dioxide extraction process.

The material removed from the shale was a liquid composed of three separate layers. A clear, nonviscous liquid was at the bottom of the sample bottle after removal from the condensor tube. This substance was water with some dissolved hydrocarbons in it. Its density was about 0.98 g/cc, and the carbon content was less than 1 percent by weight. On top of the water were two oily layers, the top layer being slightly more yellow in color than the bottom layer. The oil often had a slightly green tinge to it. The color was probably due to extraction of metals, such as copper or nickel, from the shale rock. The oil layers were small in volume (about 2 mls) and were difficult to separate from each other for analysis. All the liquid extract and the exhaust gas from the system were characterized by a strong musty smell. The smell was strongest in the liquid sample, slightly lighter in the exhaust gas and just evident in the shale rock. The more ground the rock, the stronger its smell.

The results of the Fischer Assays conducted on fresh shale and post extraction shale are shown in the table below. Given the extra gas plus losses in the post extraction shale, the oil yield changed very little from the fresh shale. From this run, 0.53 gallons/ton of oil were collected.

TABLE 2
FISCHER ASSAY RESULTS FOR FRESH AND CO₂ PROCESSED SHALE

<u>Sample</u>	<u>Oil(gal/ton)</u>	<u>Water (gal/ton)</u>	<u>Gas+Loss(%)</u>
Fresh	60.0	10.6	2
Post CO ₂ Extraction	57.4	4.8	4.3

Analysis of the oil and water fractions collected from the runs were performed. In the first set of tests, a carbon, hydrogen, nitrogen (C,H,N) analysis was conducted on both the extract and the shale rock itself.

The results of the C,H,N analysis on both the oil, water and shale rock samples of an early run are presented below. The analysis was done on extract which had been removed at 140°F and 1800psi. The shale particle size was 500 microns.

TABLE 3
CARBON, HYDROGEN, NITROGEN ANALYSIS OF EXTRACTED LIQUIDS

Sample Description	%C	%H	%N
Oil Fraction	84.92	12.84	0.11
Water Fraction	0.62	11.08	0.07
Fresh Shale Rock	28.58	3.41	0.85
Used Shale Rock	29.18*	3.43	0.86

* The used shale rock has a slightly higher carbon content than the fresh rock, because carbon dioxide dissolves into the rock and forms calcium carbonate over the course of the run.

The oil fraction composition is more similar to the composition of bitumen than that of kerogen. The weight percents of raw kerogen and bitumen are shown below.

TABLE 4
CARBON, HYDROGEN, NITROGEN ANALYSIS OF BITUMEN AND KEROGEN

Sample Description	%C	%H	%N
Kerogen	80.52	10.30	2.39
Bitumen	82-84	9-11	.3-.5

It is reasonable that the bitumen fraction would be extracted since it is a conventionally soluble compound. This is in contrast to the kerogen which is relatively insoluble in conventional solvents.

In addition to the CHN weight percent analyses which were performed, a gas chromatograph/mass spectrometer analysis was performed on samples of the oil extract. From this analysis we found that the oil contains primarily saturated and unsaturated hydrocarbons (alkanes, cyclo-alkanes and alkenes) with boiling points ranging from 150 to 500°C. The two predominant components are both alkanes: nonadecane (nC19) and eicosane (nC20). Several non-alkane compounds including xylene, a pyrrole dione, primethyl tetrahydrofuran and nitrogen heterocyclic were found in the oil. The complete GC/MS report is included in Appendix B in the back of this report.

Even though the total amount of oil collected was small, the parameters that most affected the quantity of extracted material were still studied. These parameters are time, particle size, temperature and pressure of CO₂, shale pretreatment, and gas composition. The results of these parametric

studies are presented in the following sections. The complete tabulation of experimental results is shown in Table 5. Reduced data and selected data for specific analysis are presented afterwards.

4.1 Data Summary

Data for all the runs performed are presented in Table 5. The full data sheets for the runs from which this table was derived are included in Appendix C. The run numbers listed correspond to the order in which the experiments were conducted. These numbers do not match the run numbers in the test program section because equipment and experimental considerations altered the test schedule somewhat.

Oil and water extract weights are normalized with respect to the weight of the input shale. This parameter is referred to as the 'extract fraction'. The oil extract fraction is, in turn, normalized with respect to the total amount of CO₂ pumped per run. This parameter, extract fraction per liter CO₂, gives an indication of the efficiency of extraction for each test condition.

Table 6 shows the oil and water extract fractions and extract fractions per liter of solvent (CO₂), as well as the reduced temperature, pressure and density of the test runs.

4.2 Calculations of Relevant Parameters

The procedure used to calculate the parameters in Table 6 are as follows:

Run #3	Oil Extract 1.2 grams	Shale Weight 1794.5 gms
	Water Extract 1.8 gms	
	$\frac{\text{Oil Extract}}{\text{Shale Extract}} = \frac{1.2}{1794.5}$	$\frac{\text{Water Extract}}{\text{Shale Extract}} = \frac{1.8}{1784.5}$
	= 6.7×10^4 gm/gm	= 10.0×10^4 gm/gm

TABLE 5
EXPERIMENTAL DATA

Run #	Shale Input (gm)	Temp. (°F)	Pressure (psi)	Time (hr)	Size (um)	Water Extract (gm)	Oil Extract (gm)	Total Extract (gm)	Flow Rate (lpm)	Average Heated Temperature (°F)
1	1609.5	91	1100	3	1000	2.5	.1	2.6	5.0*	-
2	1700.0	140	1800	3	500	7.0*	2.0*	9.0	6.4	-
3	1794.5	142	1635	1	1500	1.8	1.2	3.0	4.9	-
4	1770.5	146	1801	2.75	1500	7.6	2.1	9.7	6.4	-
5	1749.8	139	1837	8	1500	11.0	4.3	15.3	5.5	-
9	1784.6	139	1831	3	1500	5.7	1.5	7.2	6.7	-
10	1790.5	140	1744	3	1500	4.3	1.8	6.1	5.0	-
12	1759.3	203	2454	3	1500	7.8	2.5	10.3	3.4	-
13	1784.6	200	3000	3	1500	6.0	4.8	10.8	3.2	-
15	1818.9	170	1329	3	1500	4.6	1.1	5.7	5.9	358
16	1708.5	224	2115	3	1000	13.5	4.8	18.3	4.9	372
17	1761.8	267	2409	2.5	1000	13.9	5.0	18.9	4.8	213
18	1550.7	251	2283	3	500	13.1	3.2	16.3	5.7	205
20	1705.9	144	1812	3	1000	3.8	2.1	5.9	4.6	-
21	1797.7	202	2004	3	1500	8.7	4.0	12.7	5.6	-

* Approximated

TABLE 6
REDUCED DATA FLOW

Run #	Size (um)	Time (hr)	Pressure (MPa)	Temp. (°K)	Oil Extract Amt. Shale (x10 ⁴)	Average Flow Rate of CO ₂ (lpm)	Water Extract Amt. Shale (x10 ⁴)	Oil Extract Amt. Shale/Flow Rate (gm/g.l)x10 ⁶	Density (Kg/m ³)	Comments
1	1000	3	7.5	306	0.60	5.0	15.5	.06	285	
2	500	3	12.5	342	11.8	6.4	41.0	1.00	330	
3	1500	1	11.3	334	6.7	4.9	10.0	2.29	345	time
4	1500	2.75	12.4	336	11.9	6.4	42.9	1.13	400	time
5	1500	8	12.7	332	24.6	5.5	62.9	0.09	435	time
9	1500	3	12.6	332	8.4	6.7	31.9	0.67	435	time
10	1500	3	12.0	333	10.1	5.0	24.0	1.12	400	time
12	1500	3	16.9	368	14.2	3.4	44.3	2.33	360	
13	1500	3	20.7	366	26.9	3.2	33.1	4.65	555	
15	1500	3	9.2	350	6.0	5.9	25.3	.55	200	heating to 358of
16	1000	3	14.6	380	28.1	4.9	79.0	3.16	280	Heating to 372of
17	1000	2.5	16.6	404	28.4	4.8	78.9	3.91	250	heating to 213of
18	500	3	15.7	395	20.6	5.7	84.5	2.00	250	heating to 205of
20	1000	3	12.5	335	12.3	4.6	22.3	1.47	415	
21	1500	3	13.8	367	22.3	5.6	48.4	2.23	310	

The oil extract per flow rate is calculated in the following way:

Run #3 Flow rate 4.9 gpm Run 1 hour

Oil Extract/Shale Weight = 6.7×10^4

Extraction Rate = $6.7 \times 10^{-4} / 60 = 1.12 \times 10^{-5}$ gm oil/gm shale per minute

Oil Extract /
Shale Weight/Flow Rate = $1.12 \times 10^{-5} / 4.9 = 2.286 \times 10^{-6}$

From Figure 6, the density of CO₂ at the temperature and pressure of the run is obtained.

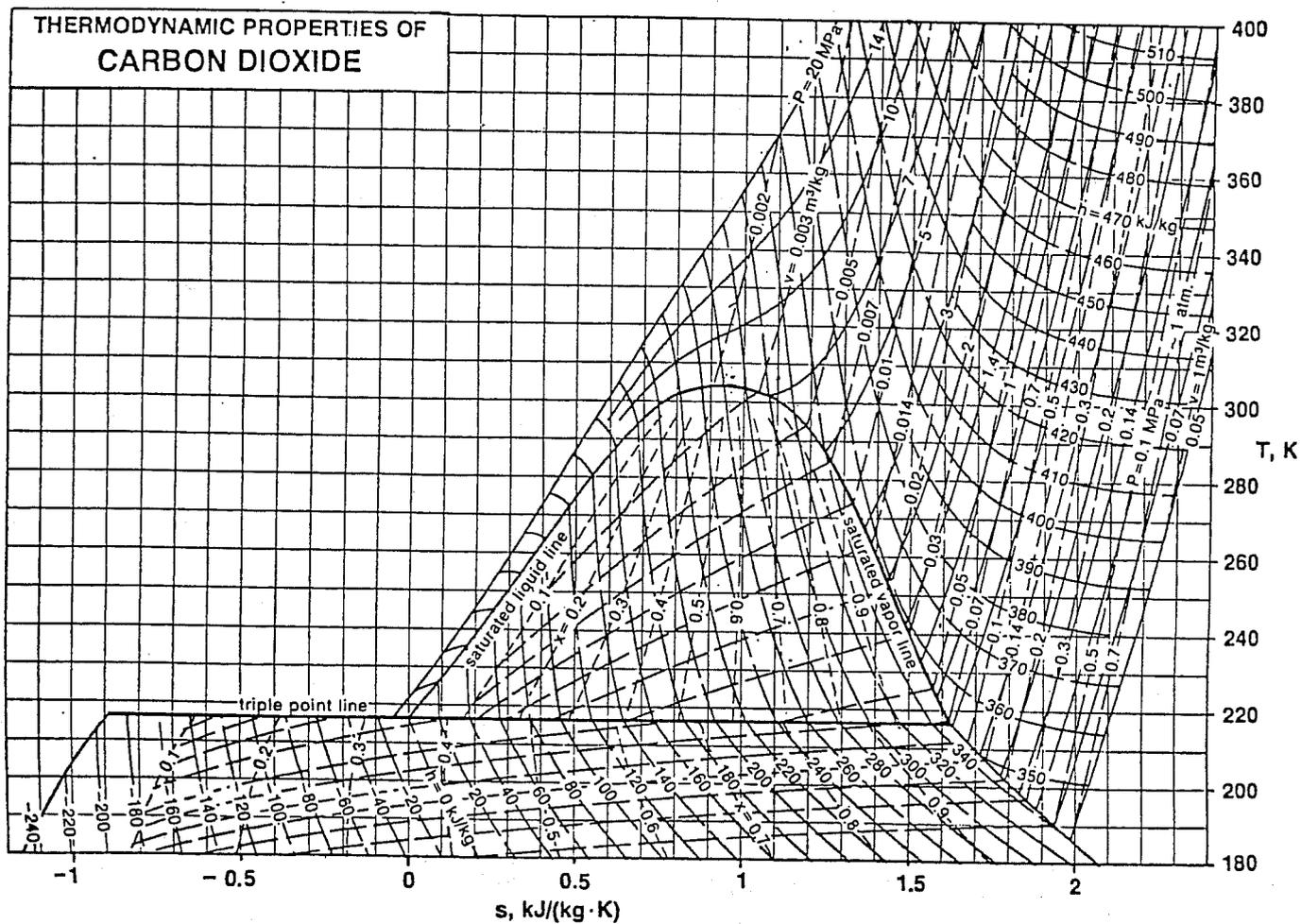
A series of runs were conducted in which the shale was preheated prior to the extraction process. It was hoped that mild thermal degradation of the organic matter would improve extraction efficiency. The temperature to which the batches of shale were heated is listed in the "comments" column of Table 6.

Analysis of the data showed that the amount of oil extracted is a strong function of time of extraction and temperature of extraction. Oil extract is a weak function of particle size and density of CO₂. Preheating the shale before the extraction run served to greatly increase the amount of water collected, but this preheating had little effect on oil yield. In the following paragraphs, the effect of time, temperature, density, particle size, and pretreatment on both oil and water extract are discussed.

4.3 Time Dependence of Oil and Water Yields

Both oil and water yield vary directly with time of extraction. Runs of 1, 3 and 8 hours were performed at the same temperature, pressure, and shale

FIGURE 6
THERMODYNAMIC PROPERTIES OF CARBON DIOXIDE



particle size. As can be seen in Figure 7, both oil and water extract have a linear dependence on extraction time.

A statistical analysis of the significance of the apparent correlation of extract weight and run duration is shown in the following calculations. As is shown, both oil extract and water extract have a statistically significant variation with duration of run. Table 7 displays the data for Runs 3, 4, 5, and 10 which were used to study time dependence.

A regression and correlation were used for investigation of the relationship between oil and water extract and the duration of the run. Tables 8 and 10 present the calculation of the least-square regression line and the correlation coefficient.

The following calculations show the statistical significance of the oil extract versus time correlation.

$$\text{Slope } b = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sum (x-\bar{x})^2}$$

$$= 109.196/38.0521$$

$$= 2.87$$

$$\text{Intercept, } a = \bar{y} - b\bar{x}$$

$$= 10.3 - (2.87)(2.96)$$

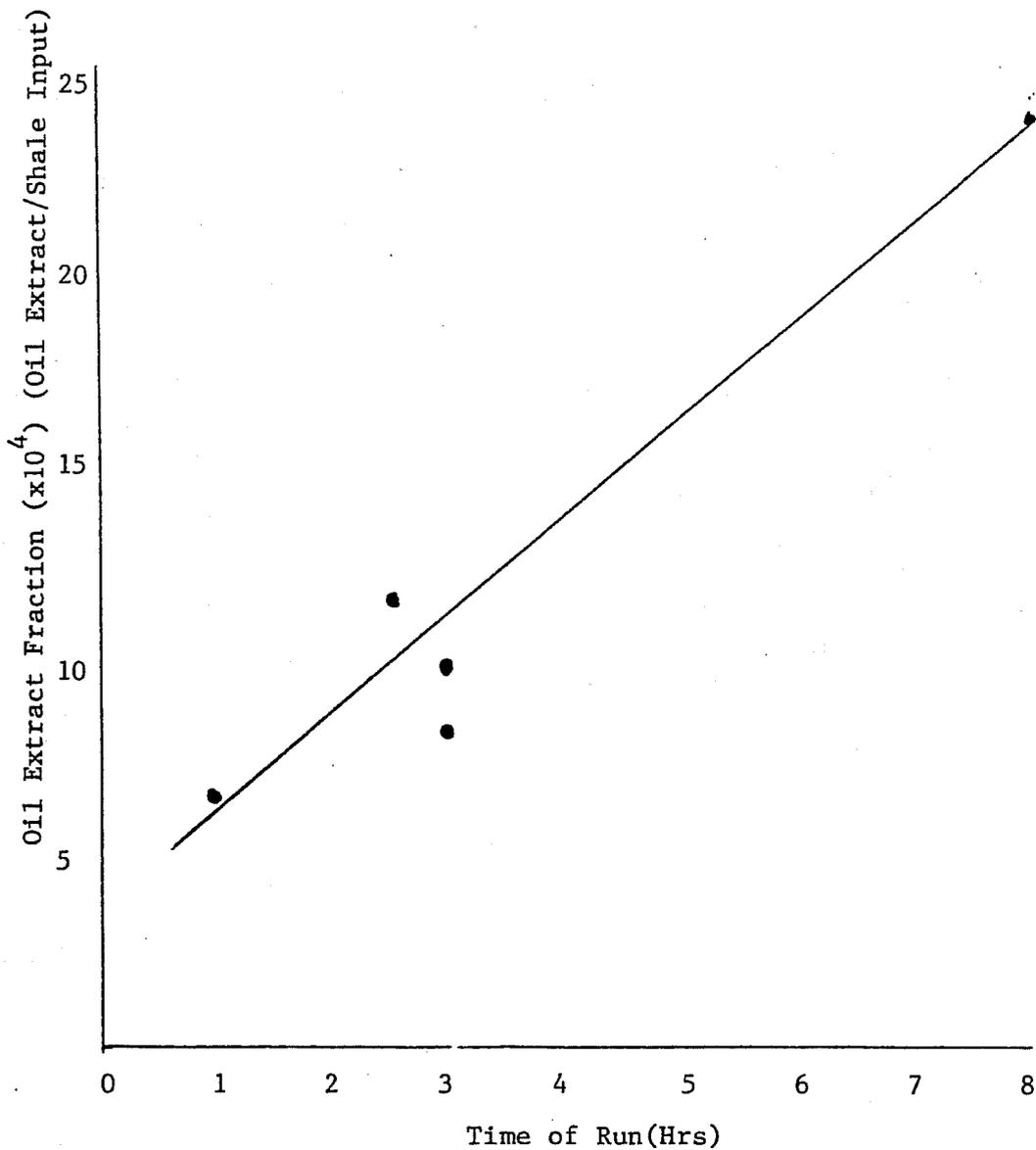
$$= 1.8048$$

$$\text{Coefficient of Correlation, } r = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

$$= \frac{109.196}{(38.0521)(329.75)}$$

$$= 0.97$$

FIGURE 7a
EFFECT OF TIME ON OIL YIELD



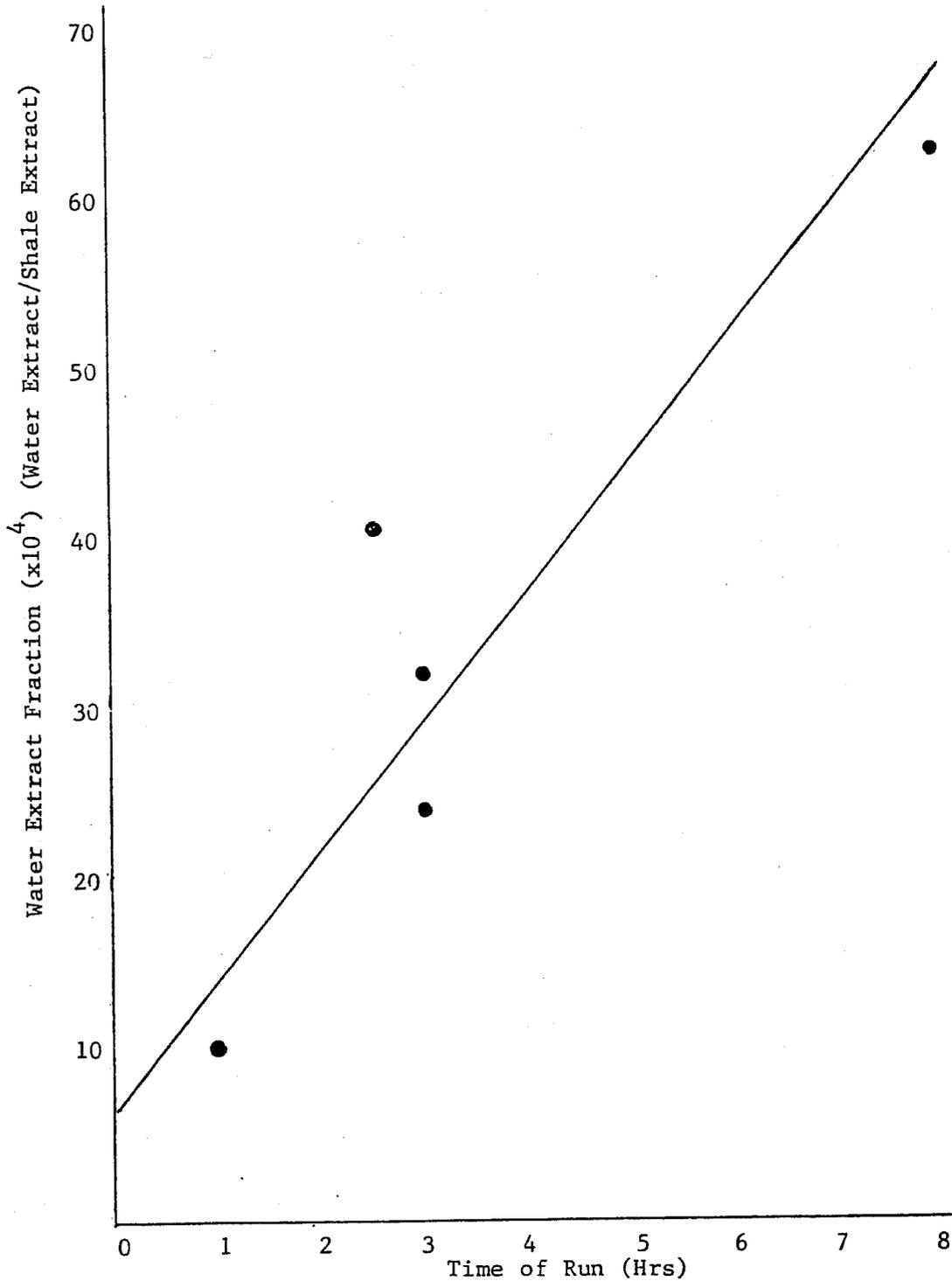
Conditions of Run:

T = 332-336^oK

P = 11.3 - 12.7 MPa

Size = 1500um

FIGURE 7b
EFFECT OF TIME ON WATER YIELD



Condition of Runs:

T = 332-336°K
P = 11.3 - 12.7 Mpa
Size = 1500um

TABLE 7

DATA FOR TIME DEPENDENCE CORRELATIONS

Run #	3	4	5	9	10
(<u>Oil Extract</u> Amount of Shale) 10^4	6.7	11.9	24.6	8.4	10.1
(<u>Water Extract</u> Amount of Shale) 10^4	10.0	42.9	62.9	31.9	24.0
Duration of Run, hrs.	1	2.75	8	3	3
Pressure, MPa	11.3	12.4	12.7	12.6	12.0
Temperature, °K	334	336	332	332	333
Size, μm	1500	1500	1500	1500	1500

A regression and correlation are used for investigation of the relationship between the extract and the duration of the run. Tables 4 and 6 present calculations of the least square regression line and the correlation coefficient.

TABLE 8

STATISTICAL CALCULATIONS FOR OIL EXTRACT CORRELATION WITH TIME

Duration of Run, x (hrs)	Mean \bar{x}	Oil Extract, y	Mean y	$x - \bar{x}$	$y - \bar{y}$	$(x - \bar{x})^2$	$(y - \bar{y})^2$	$(x - \bar{x})(y - \bar{y})$
0		0		-2.96	-10.3	8.7616	106.09	30.4880
1		6.7		-1.96	-3.6	3.8416	12.96	7.0560
2.75	2.96	11.9	10.3	-0.21	1.6	0.0441	2.56	-0.3360
8		24.6		5.04	14.3	25.4016	204.49	72.0720
3		8.4		0.04	-1.9	0.0016	3.61	-0.0760
3		10.1		0.04	-0.2	0.0016	0.04	-0.0080
						38.0521	329.75	109.196

TABLE 9

t DISTRIBUTION FOR STATISTICAL ANALYSIS

(This table gives the values of t for differing df that cut off specified proportions of the area in one and in two tails of the t distribution)

df	Area in two tails				
	.10	.05	.02	.01	.001
	Area in one tail				
	.05	.025	.01	.005	.0005
1	6.314	12.706	31.821	63.657	636.619
2	2.920	4.303	6.965	9.925	31.598
3	2.353	3.182	4.541	5.841	12.941
4	2.132	2.776	3.747	4.604	8.610
5	2.015	2.571	3.365	4.032	6.859
6	1.943	2.447	3.143	3.707	5.959
7	1.895	2.365	2.998	3.499	5.405
8	1.860	2.306	2.896	3.355	5.041
9	1.833	2.262	2.821	3.250	4.781
10	1.812	2.228	2.764	3.169	4.587
11	1.796	2.201	2.718	3.106	4.437
12	1.782	2.179	2.681	3.055	4.318
13	1.771	2.160	2.650	3.012	4.221
14	1.761	2.145	2.624	2.977	4.140
15	1.753	2.131	2.602	2.947	4.073
16	1.746	2.120	2.583	2.921	4.015
17	1.740	2.110	2.567	2.898	3.965
18	1.734	2.101	2.552	2.878	3.922
19	1.729	2.093	2.539	2.861	3.883
20	1.725	2.086	2.528	2.845	3.850
21	1.721	2.080	2.518	2.831	3.819
22	1.717	2.074	2.508	2.819	3.792
23	1.714	2.069	2.500	2.807	3.767
24	1.711	2.064	2.492	2.797	3.745
25	1.708	2.060	2.485	2.787	3.725
26	1.706	2.056	2.479	2.779	3.707
27	1.703	2.052	2.473	2.771	3.690
28	1.701	2.048	2.467	2.763	3.674
29	1.699	2.045	2.462	2.756	3.659
30	1.697	2.042	2.457	2.750	3.646
40	1.684	2.021	2.423	2.704	3.551
60	1.671	2.000	2.390	2.660	3.460
120	1.658	1.980	2.358	2.617	3.373
∞	1.645	1.960	2.326	2.576	3.291

TABLE 10

STATISTICAL CALCULATIONS FOR WATER EXTRACT CORRELATION WITH TIME

Duration of Run, x (hours)	Mean \bar{x}	Water Extract, y	Mean \bar{y}	$x - \bar{x}$	$(x - \bar{x})^2$	$y - \bar{y}$	$(y - \bar{y})^2$	$(x - \bar{x})(y - \bar{y})$
0				-2.96	8.7616	-28.62	819.10	84.7152
1		10.0		-1.96	3.8416	-18.62	346.70	36.4952
2.75	2.96	42.9	28.62	-0.21	0.0441	14.28	203.92	2.9988
8		62.9		5.04	25.4016	34.28	1175.12	172.7712
3		31.9		0.04	0.0016	3.28	10.76	0.1312
3		24.0		0.04	0.0016	-4.62	21.34	-0.1848
					38.0521		2576.94	296.9268

A test of the null hypothesis $\rho = 0$ is

$$t_{n-2} = r / \sqrt{1-r^2} \sqrt{n-2}$$

By following the t
distribution with n-2df

$$t_{6-2} = 0.97 / \sqrt{1-(0.97)^2} \sqrt{6-2}$$

$$= 7.98$$

which gives P less than 0.01 (obtained from t distribution, Table 9). Thus, if there were no correlation, these experimental results would occur by chance alone less than one time in a hundred. One can conclude that there is a statistically significant correlation between oil extract and the duration of the run.

A similar type of statistical analysis is presented below for the correlation between water extract and duration of the run.

Slope b

$$= \frac{\sum (x-\bar{x})(y-\bar{y})}{\sum (x-\bar{x})^2}$$

$$= 296.9268 / 38.0521$$

$$= 7.80$$

Intercept, a

$$= \bar{y} - b\bar{x}$$

$$= 28.62 - (7.80)(2.96)$$

$$= 5.5226$$

Coefficient of Correlation, r

$$= \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

$$= \frac{296.9268}{\sqrt{(38.0521)(2576.94)}}$$

$$= \frac{296.9268}{\sqrt{(38.0521)(2576.94)}}$$

$$= 0.95$$

A test of the null hypothesis $\rho = 0$ is

$$t_{n-2} = p / \sqrt{1-r^2} \sqrt{n-2}$$

By following the t distribution with n-2df

$$t_{6-2} = 0.95 / \sqrt{1-(0.95)^2} \sqrt{6-2}$$

$$= 6.08$$

which gives $p < 0.01$. Thus, there is a statistically significant correlation.

Though it was shown that increasing the length of run also increased the amount of oil collected, it was found that this was taking place at a cost of process efficiency. Plotted below is a graph of extract fraction (grams oil/grams shale) per liter CO₂ as a function of run duration.

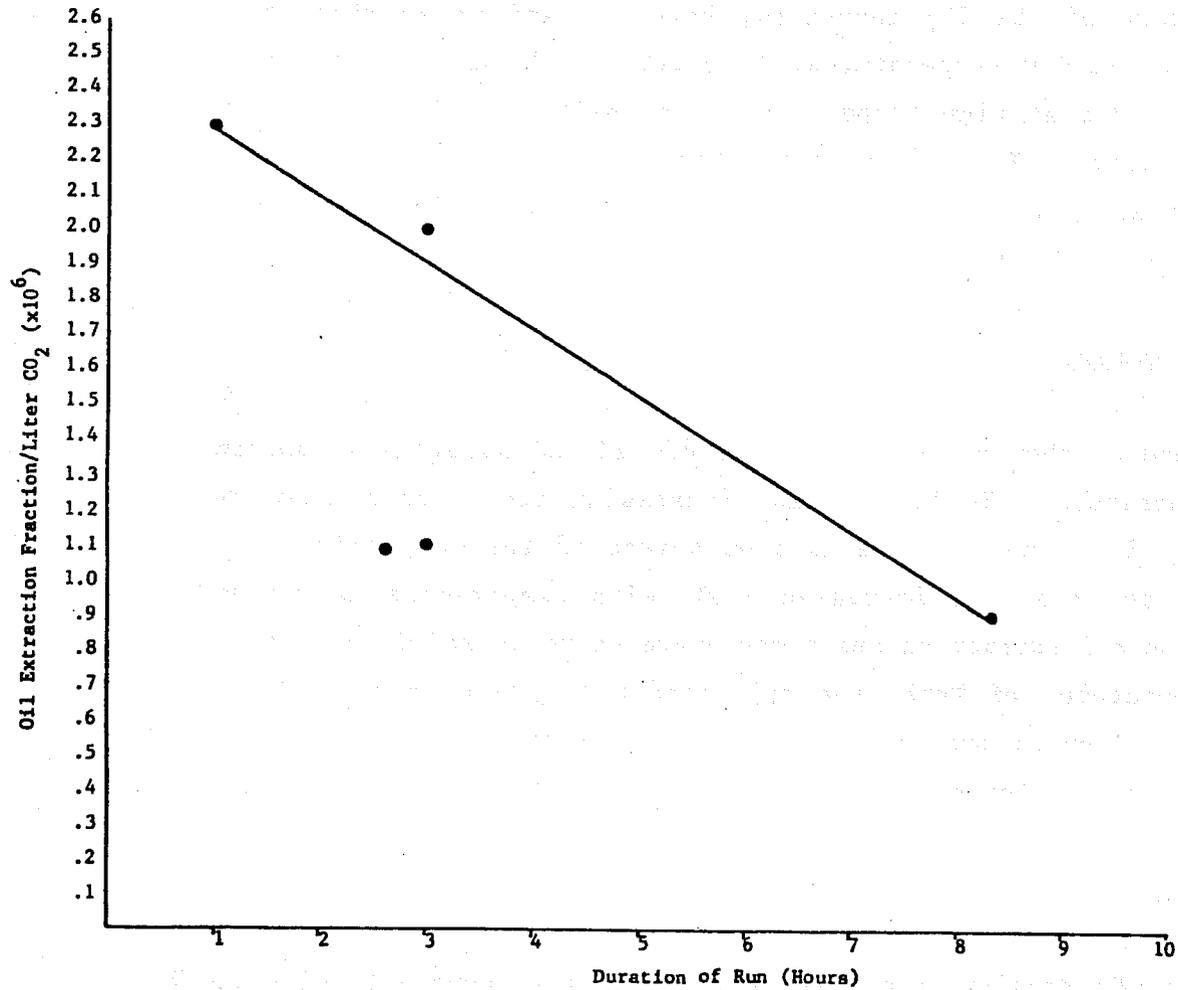
It shows that the extract fraction per unit of CO₂ varies inversely with the length of the run. The extract fraction per liter of CO₂ is 0.9×10^{-6} grams oil/(grams shale liter CO₂) for the 8 hour run. For the one hour run, this figure is 2.29×10^{-6} grams oil/(grams shale liter CO₂). More oil was extracted in the longer runs, but the efficiency of collection (oil wt/CO₂ weight) was also lower for these runs.

4.4 Dependence of Extract Yield on Particle Size

In the size range studied, for 500 to 1500 microns, particle size is not a very important determinant of oil yield. There is, however, an inverse relationship between shale particle size and the water yield from the run. The graphs below show water and oil yields as a function of shale particle size. In these runs the conditions of extraction, time, temperature and pressure, were held constant at 3 hours, 140°F and 1800 psi respectively. As can be seen, the weight of water extracted decreases with increasing particle size. The oil yield remains about constant. The data for these graphs come from runs 2, 9, 10 and 20.

FIGURE 8

PROCESS EFFICIENCY VERSUS LENGTH OF RUN

(1500 μ M particle; $T_r \approx 1.1$; $\rho_r \approx 1.6$)

4.5 Conditions of the Run

The conditions of the run, temperature, pressure and density of the CO₂, were varied to determine their effect on oil and water extraction yields. Temperature is the most important variable determining extract quantity. As the temperature of the CO₂ increases, both oil and water yield increase dramatically. At low temperatures, an effect of density of extract yield can be seen. But at high temperatures, the effect of density on extract yield is not clear. Table 11 displays the oil and water extract fractions for each run along with the reduced temperature, pressure and density of the CO₂ used in each run.

4.6 Temperature

Figures 10 and 11 show extract fractions of oil and water as a function of reduced temperature. In both cases, increasing temperature dramatically increased yields. Though there is some spread of the data points at each temperature, the trend of increased yield with temperature is definitely apparent. The oil extract versus temperature curve is fairly linear. At a reduced temperature of $T_r=1$, the oil extract is almost zero. The water yield does not drop to zero as quickly as the oil yield. The plot of water yield versus reduced temperature fell off with an exponential decay.

4.7 Density

The effect of CO₂ density on oil and water yields is apparent only when T_r is low and the temperature does not determine extract volume. Figures 12 and 13 show oil and water yield, respectively, as a function of reduced density. As can be seen in these graphs, extract yield increases slightly with increased density at low temperatures ($T_r = 1.1$). At high temperatures, however, any relationship between ρ_r and yield is not clear.

Appendix D shows a series of calculations performed to find a relationship between oil yield (and water yield) and both density and temperature. The

FIGURE 9
EXTRACT YIELD VERSUS PARTICLE SIZE

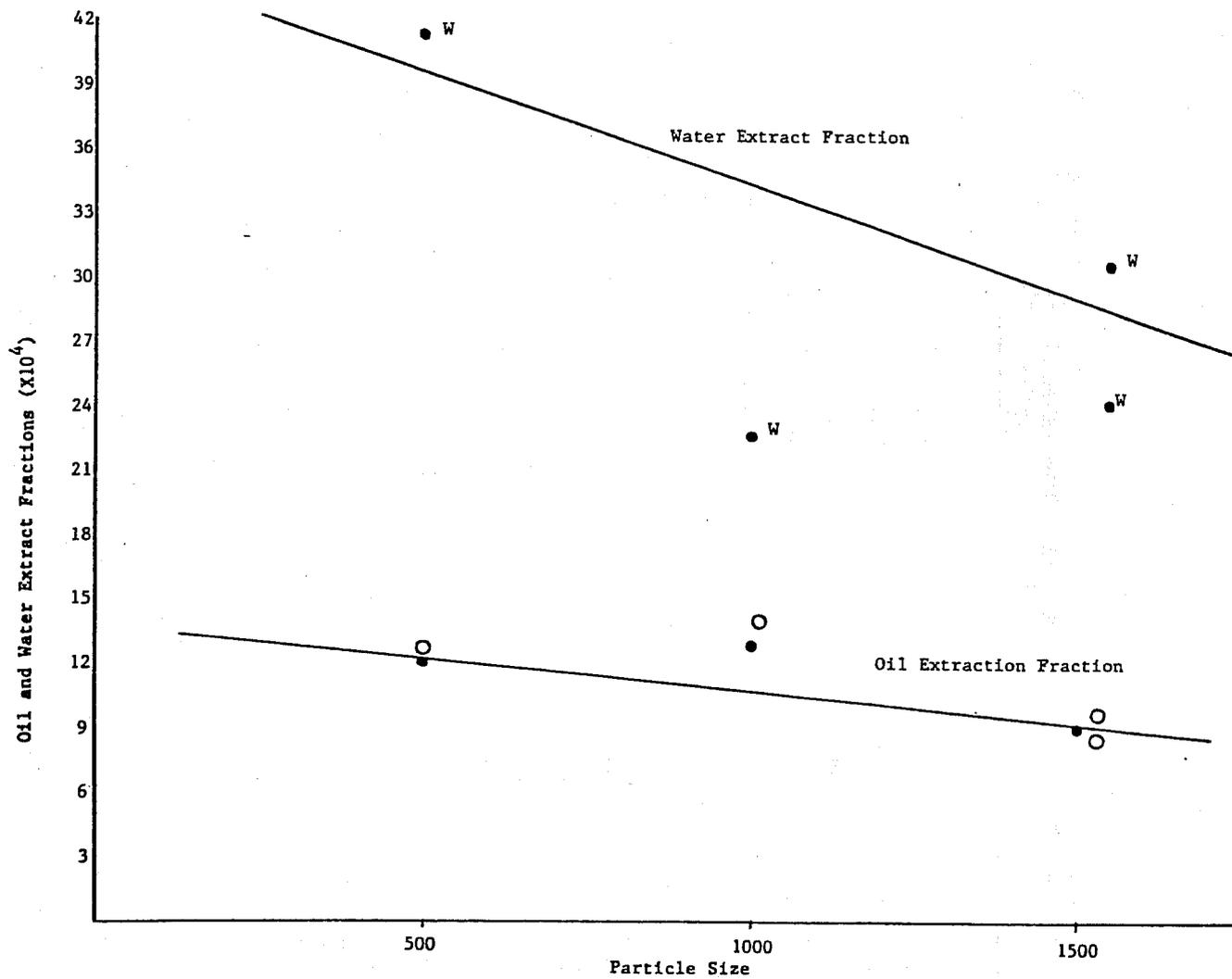


TABLE 11
REDUCED DATA

Run #	Size (um)	Reduced Density r	Reduced Pressure r	Reduced Temperature Tr	Oil Extracted Amnt of Shale ($\times 10^4$)	Water Extracted Amnt of Shale ($\times 10^4$)	Oil Extract/Amt of Shale Flow Rate CO_2 $g/g.1 \times 10^6$	Comments
9	1500	0.94	1.7	1.09	8.4	31.9	0.67	Time 3 hours
10	1500	0.86	1.6	1.10	10.1	24.0	1.12	t = 3 hrs
12	1500	0.77	2.3	1.21	14.2	44.3	2.33	t = 3 hrs
13	1500	1.20	2.8	1.20	17.4	43.1	4.65	t = 3 hrs
15	1500	0.43	1.2	1.15	6.0	25.3	.55	t = 3 hrs
21	1500	0.67	1.9	1.21	22.3	48.4	2.23	t = 3 hrs
16	1000	0.60	2.0	1.30	28.1	79.0	3.16	t = 3 hrs
17	1000	0.54	2.2	1.30	28.4	78.9	3.91	t = 2.5 hrs
20	1000	0.90	1.7	1.10	12.3	22.3	1.47	t = 3 hrs
1	1000	1.00	1.0	1.00	0.6	15.5	0.06	
18	500	0.54	2.1	1.30	20.6	84.5	2.00	t = 3 hrs
3	1500	0.74	1.5	1.10	6.7	10.0	2.29	t = 1 hr
4	1500	0.86	1.7	1.10	11.9	42.9	1.13	t = 2.75 hrs
5	1500	0.94	1.7	1.10	24.6	62.9	.09	t = 8 hrs.

Notes:

Critical Parameters of CO_2 : $P_c = 7.4 MP_a$ $T_c = 304^\circ K$ $\rho_c = 463.1 Kg/m^3$

FIGURE 10

OIL EXTRACT FRACTION VERSUS TEMPERATURE
(Time = 3 Hours)

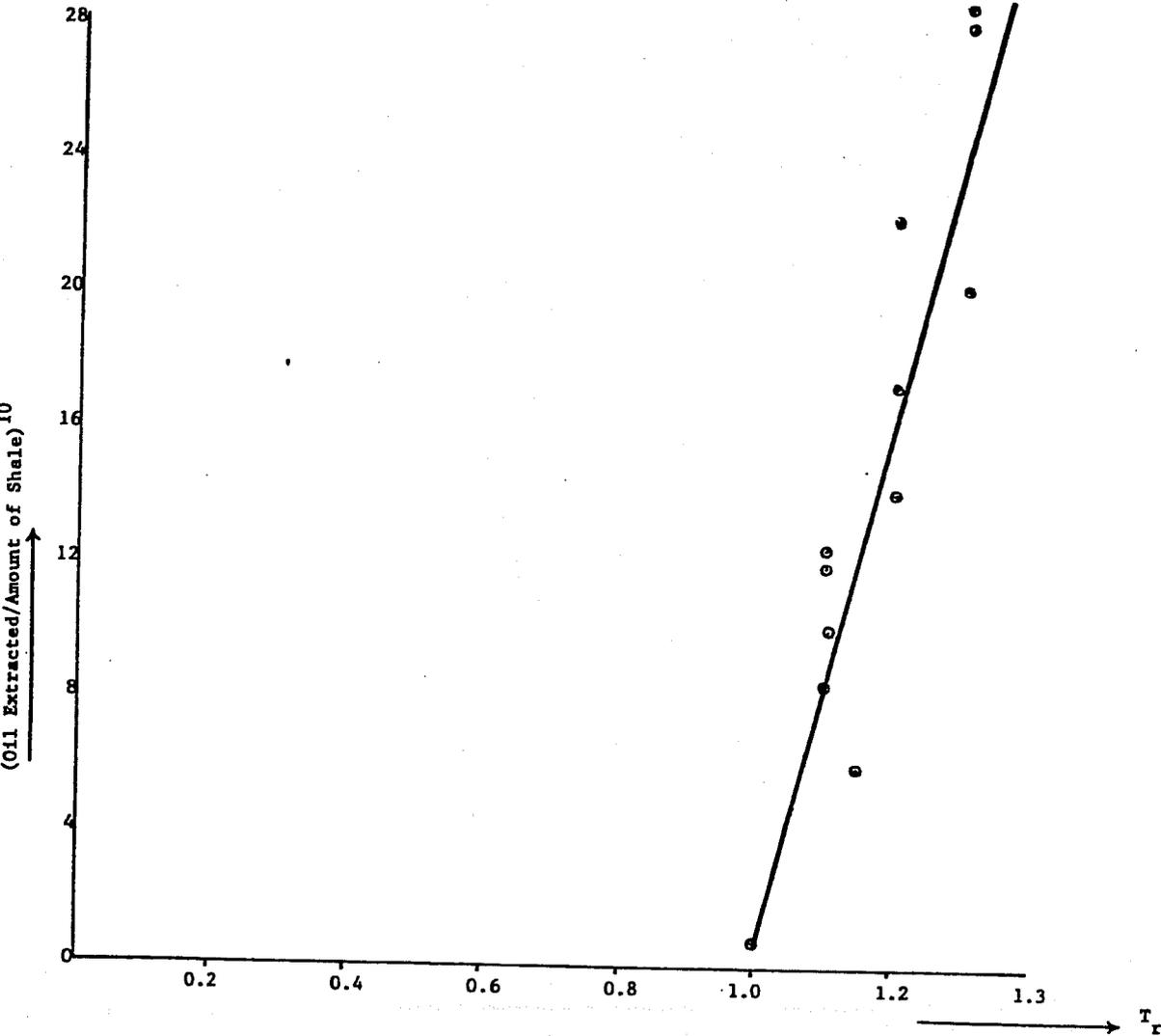


FIGURE 11

WATER EXTRACT FRACTION VERSUS TEMPERATURE
(Time = 3 Hours)

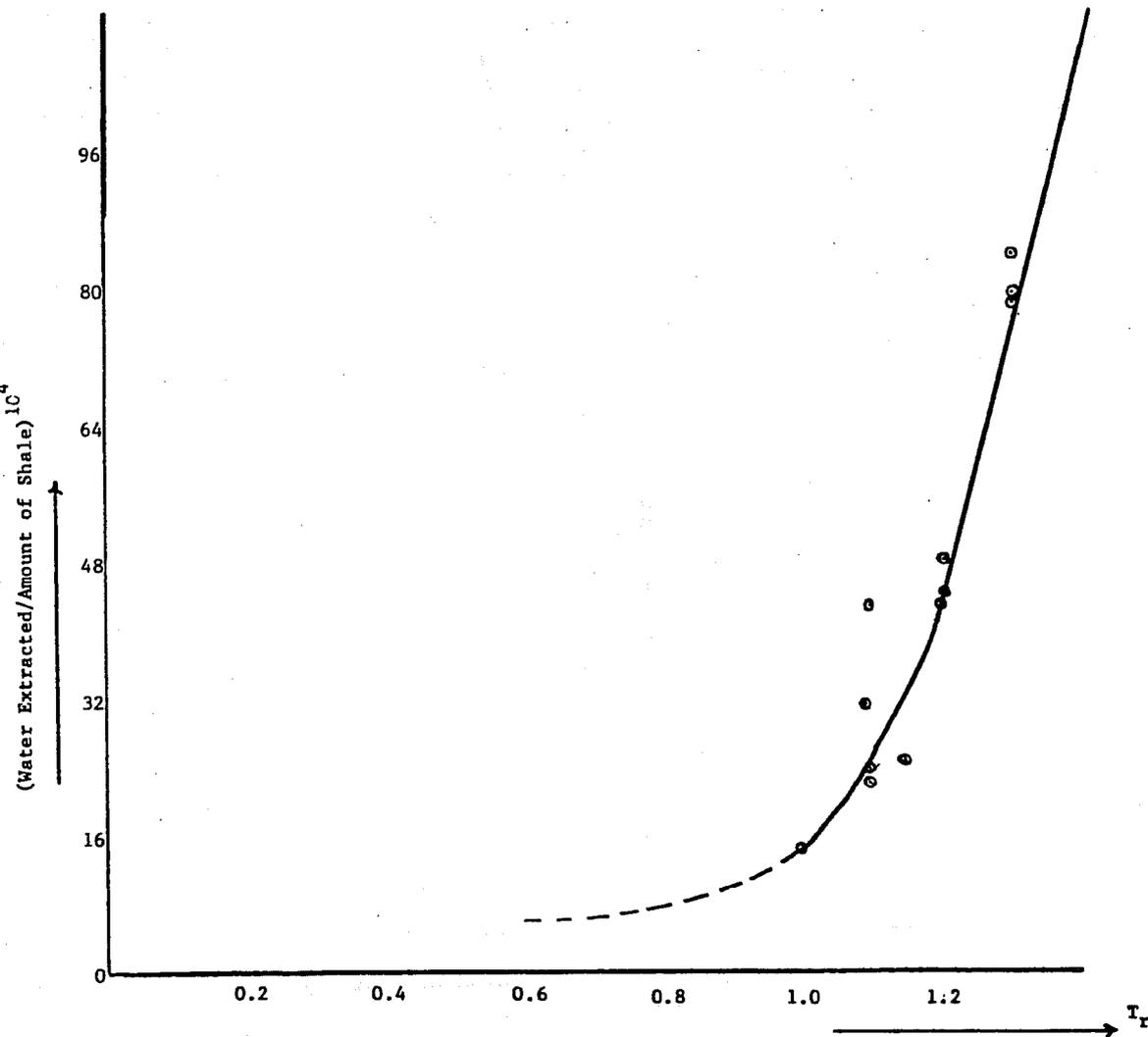


FIGURE 12

OIL EXTRACT FRACTION VERSUS DENSITY
(Time = 3 Hours)

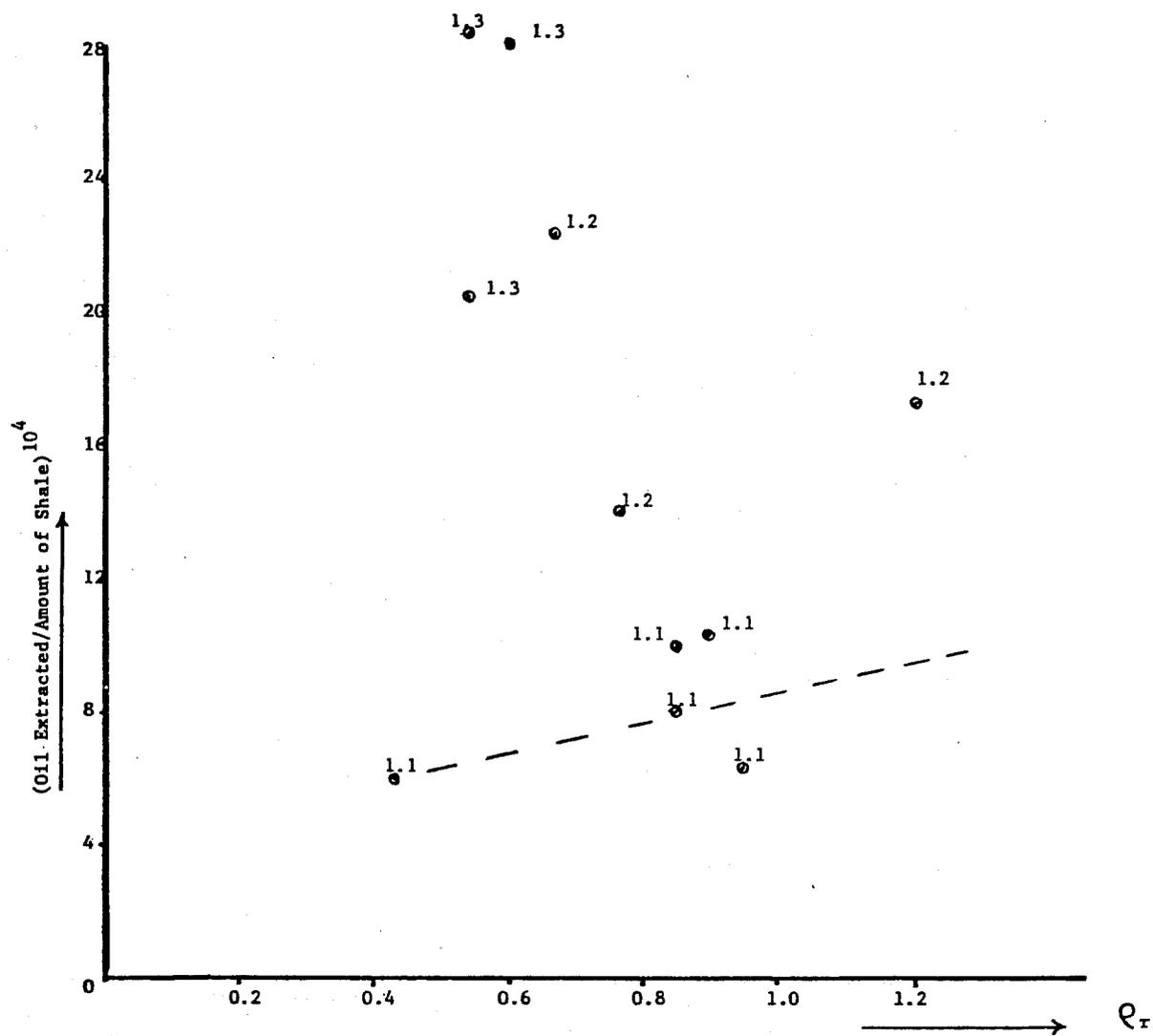
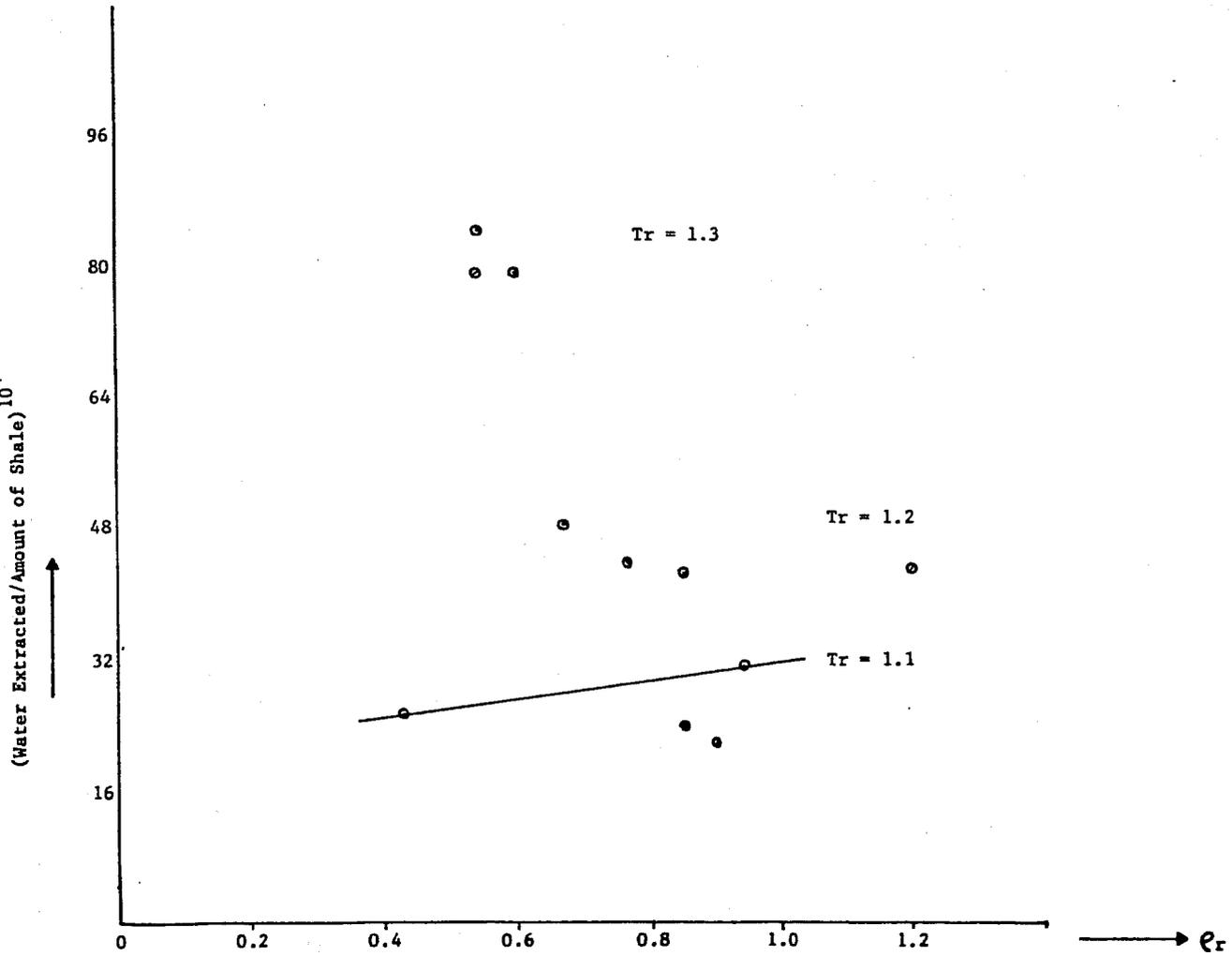


FIGURE 13
WATER EXTRACT FRACTION VERSUS DENSITY
(Time = 3 Hours)



calculations are a curve fitting procedure. The resultant equations of yield vs reduced temperature and density are as follows:

For oil yield

$$Y_o = 7.44 \rho_r + 0.90 T_r^{12}$$

For water yield

$$Y_w = 98.75 \rho_r - 124.53 T_r^{-7.5}$$

Where:

Y_o = oil yield/shale input

Y_w = water yield/shale input

ρ_r = reduced density

T_r = reduced temperature

As mentioned above, the complete calculations that determined these equations are included in Appendix D.

4.8 Shale Pretreatment

For some runs, the shale was heated prior to the introduction of carbon dioxide flow into the extraction vessel. The shale was heated in an attempt to mildly degrade the kerogen. It was anticipated that smaller hydrocarbon compounds, broken down from the larger kerogen molecule, would dissolve better into the carbon dioxide.

The shale was preheated at temperatures up to 370°F for one hour. The amount of oil extracted during these runs was slightly higher than the yields of the standard runs of comparable temperatures. Water yields from the preheated runs were quite high. The amount of water collected per gram of shale input was almost triple the amount of water collected in a standard run. The preheating may have driven water out of the pores of the shale, while standard runs extracted only surface water from the shale

rock. The preheated experiments are Runs 15, 16, 17, 18. The yields of these runs compared to other runs are illustrated in Table 6.

4.9 Solvent Gas

Given the low extract yields of CO₂ extraction runs, it was desired to try another solvent in the extraction process. An experiment was performed with ethylene at its critical point. It was hoped that ethylene would serve as a hydrogen donor and augment the breakdown of kerogen into soluble hydrocarbon fractions. Results of the test, however were not promising. No oil or water was extracted with the ethylene. One problem may have been the low operating temperature of the run. Operating temperatures and pressures were not raised above the critical condition because of safety restrictions.

5.0 CONCLUSIONS

Extraction of hydrocarbons from shale rock with supercritical CO₂ at temperatures below 400°F does not produce high enough yields for the process to be commercially viable. It could be, however, that at higher temperatures the yield may sharply increase. It was shown that yield is increased with smaller particle size, increased time of extraction, increased temperature, and increased density of the solvent. Experiments with more powerful solvents, such as toluene, for example, may result in higher yields than runs with carbon dioxide. The high extract fraction of water from the shale by carbon dioxide may be useful for some dehydration processes where thermal processes are not possible.

CONFIDENTIAL

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[The remainder of the text is illegible due to extreme blurriness.]

Appendix A

**EQUIPMENT PURCHASE AND SPECIFICATIONS
FOR SHALE OIL EXTRACTION APPARATUS**

Equipment Name	Manufacturer & Model	Pressure Rating (PSI)	Temp. Rating °F	Additional Information	Cost Per Unit	# Purchased	TOTAL Including Tax & Deliv.
Pressure Regulator	Veriflo HPR 802	5000	-----	Flow coeff. Cv=.044	\$179.00	2	\$370.13
Back Pressure Regulator	Veriflo BPR-50-2	2000	-----	316 stainless Cv=.5	\$175.00	1	\$433.09
Flow Limit Shut-off Valve	Veriflo FLV-110 SV 500T	3000	-40° to 300°F	Valve set to shut off flow greater than 40 liters per minute	\$255.00	1	
Thermocouples	Pyromation, Inc. Thermocouple Wire	10000	1400°F	Type J Thermocouples in MGO insulated sheath. Compression fitting to attach to fitting.	\$ 18.00 \$.304./ft	5 70	\$117.26
Temperature Readouts	Precision Digital Meters, PD 720 PD 120 enclosure	-----	274 - 1340	Accuracy ± .9°F in 5 to 960°F range Multi-channel encl.	\$295.00 \$130.00	1 1	\$446.25
Pressure Gauges	Ametek 5841 3½" 3½" 6"	1500 5000 10000		Accuracy 1-1½-1% of span	\$ 58.00 \$ 58.00 \$115.00	1 1 1	\$247.03
Filters	Ametek P1535 2½"	1500 10000		Accuracy 1% of span To protect gauges from pressure surges	\$ 5.70	1	
Valves	Marsh Needle Valve	10000	-40-500°F	Flow coeff. Cv=.4	\$ 16.90	4	\$ 68.29
Tubing	Superpressure 45-11020.	65000		½" OD 3/32 ID 304 stainless	\$ 4.40/ft less	30	\$135.00
Mass Flow Meter	Teledyne Hastings Raydist	250 tested to 500	212°F	2% accuracy	\$1,175.00	2	\$2,360.61
Compressor	Superpressure	10000 psi		Single stage, double ended 58 strokes/minute volumetric displacement .26 in ³ /stroke	\$5,796.00	1	\$6,085.80
Compressor Controller Contact Relay	Superpressure			Electric contact relay to control starter motor of compressor to maintain pressure between 2 set points	\$ 678.50	1	\$712.43
Condensor Tube	Stainless Pipe and Fitting	2000	300°F	Weight .68 lbs	\$ 22.30	1	\$ 22.30
Extraction Vessel	DUROLOK	4500	450°F	Silicon o-rings in closures; 3" diameter schedule 160, 316 stainless steel (U.T.S. 88000 psi)	\$1,335.00	1	\$1,335.50

Appendix B

CAMBRIDGE ANALYTICAL ASSOCIATES ANALYSIS REPORT

GC/MS OF SHALE OIL



Cambridge Analytical Associates

222 Arsenal Street / Watertown, Massachusetts 02172 / (617)923-9376

FORMAL REPORT OF ANALYSIS

PREPARED FOR: Energy and Environmental
Engineers, Inc.
P.O. Box 215
Cambridge, MA 02141

CUSTOMER ORDER NUMBER:

CAMBRIDGE ANALYTICAL ASSOCIATES, INC.

REPORT NUMBER: 83-521

DATE PREPARED: November 21, 1983

PREPARED BY: David L. Fiest



TABLE OF CONTENTS

1. INTRODUCTION

2. ANALYTICAL METHODS

3. RESULTS

4. QUALITY ASSURANCE DOCUMENTATION

Certification

1. INTRODUCTION

This report summarizes results of chemical analyses performed on samples received by CAA in June, 1983. Analytical methods employed for these analyses are described in Section 2 and results are presented in Section 3. The last section contains certifications supporting the analytical results.

2. ANALYTICAL METHODS

Analytical methods utilized for sample analysis are summarized below. Ten milliliters of the water/oil mixture provided by E3I was extracted with dichloromethane to isolate organic compounds. The extract was dried with sodium sulfate, concentrated by rotary evaporation and analyzed by fused silica capillary gas chromatography/mass spectrometry. Analytical conditions are summarized in Figure 1.

3. RESULTS

Results of analyses are presented in Table 1 and Figures 2 - 15. Figures 3 and 4 are plots of masses 55 and 69, 57 and 71 which are indicative of alkene and cycloalkane, and alkane compounds, respectively. The similarity of the total ion chromatogram (labelled TIC) with the selected ion chromatograms (labelled 55, 69, 57 and 71) indicates that the majority of the compounds in the sample are alkanes, alkenes, and cycloalkanes. A few peaks in the total ion chromatogram did not have corresponding peaks in the selected ion chromatograms. The mass spectra of these peaks were evaluated to identify their chemical structure. Figures 5 through 15 are computer library matched spectra for the major peaks in the sample. They show the most likely compound identifications for peaks in the sample.

In summary, the oil sample contains primarily saturated (alkane) and unsaturated (alkene) hydrocarbons with boiling points ranging from 150 to 500°C. The two predominant components are both alkanes, nonadecane (nC19) and eicosane (nC20). Several non-alkane compounds including xylene, a pyrrole dione, trimethyl tetrahydrofuran and a nitrogen heterocyclic were found in the oil.

Figure 1

ANALYTICAL CONDITIONS FOR
GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSIS

Instrument: Finnigan 1020/OWA Gas Chromatography/Mass Spectrometer

Features: Sigma 3 Gas Chromatograph
Nova 4 Microcomputer, Perkin Elmer 10 megabyte disk

Inlet: Splitless - GROB

Column: 0.25 mm i.d. x 30 m length
0.25 μ m coating thickness
DB5 fused silica capillary
(J & W Scientific)

Interface: Direct insertion of the column into the source

Detector: Mass Spectrometer

Ionization Voltage: 70eV
Electron Multiplier: 2KV
Scan Rate: 400 amu/sec (41-450)

Carrier Gas: Helium (2 ml/min.)

Temperatures: Injection Port: 250^oC
Transfer Oven: 300^oC
Column Oven: 30^oC for 4 minutes, 8^oC/min to 300^oC

Table 1
Results of GC/MS Analysis

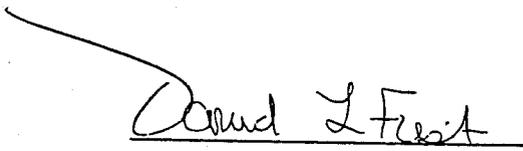
Scan Number	Identification
354	C_9H_{18} Trimethyl Cyclohexane
397	Xylene
519	$C_{10}H_{20}$ Dimethyl Cyclooctane
539	$C_{10}H_{20}$ Dimethyl Cyclooctane
647	$C_{11}H_{22}$ Cycloalkane
865	3-ethyl-4-methyl-1H-pyrrole-2,5,-dione
961	Trimethyl tetrahydronaphthalene
998	Nitrogen heterocyclic
1228	$nC_{19}H_{40}$ Nonadecane
1306	$nC_{20}H_{42}$ Eicosane
1698	$nC_{26}H_{54}$ Hexacosane

4. QUALITY ASSURANCE DOCUMENTATION

Certification

This work has been checked for accuracy by the following staff personnel:

Director, Organic
Chemistry Laboratory



David L. Fiest

David L. Fiest

KIL
07/26/83 22:05:00
SAMPLE: 8305414

7421553.

E³I

83-521

FIGURE 2

TOTAL ION CHROMATOGRAM
OF THE SHALE OIL SAMPLE

56

Pyrimidyl

cyclohexane

CH₃ cyclohexane

(319 MS)

354 (54.4)

(519 MS)

(54.4) (519 MS)

647 (616.4)

*for branched alkyls
C₁₈-C₂₀*

C₁₉
-C₂₀

*retention
times
X
methyl
ethyl
propyl
butyl
pentyl
hexyl
heptyl
octyl
nonyl
decyl
undecyl
dodecyl
tridecyl
tetradecyl
pentadecyl
hexadecyl
heptadecyl
octadecyl*

196

NC₂₆

100.0

RIC

3000 SCAN
50:00 TIME

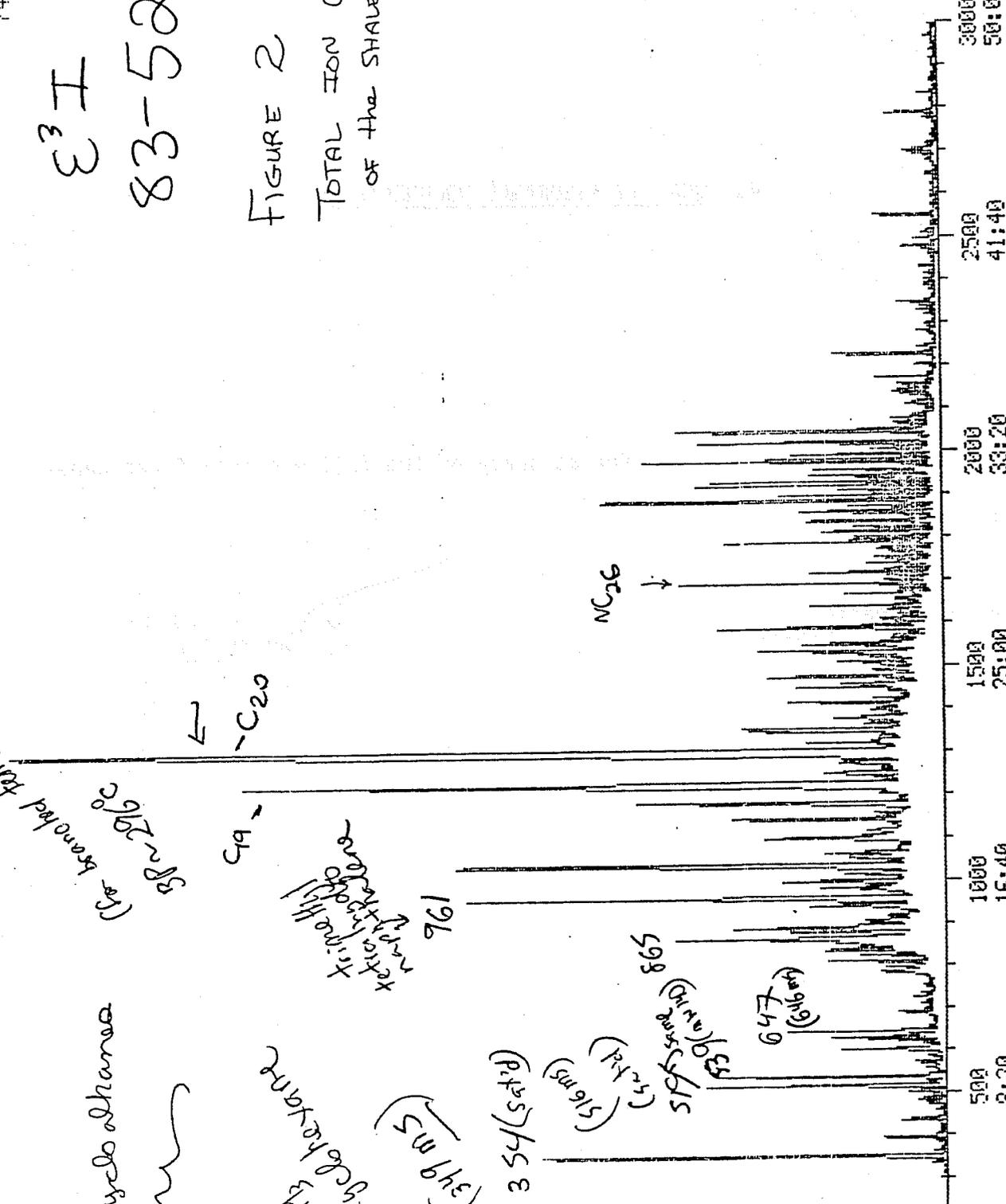
2500
41:40

2000
33:20

1500
25:00

1000
16:40

500
8:20

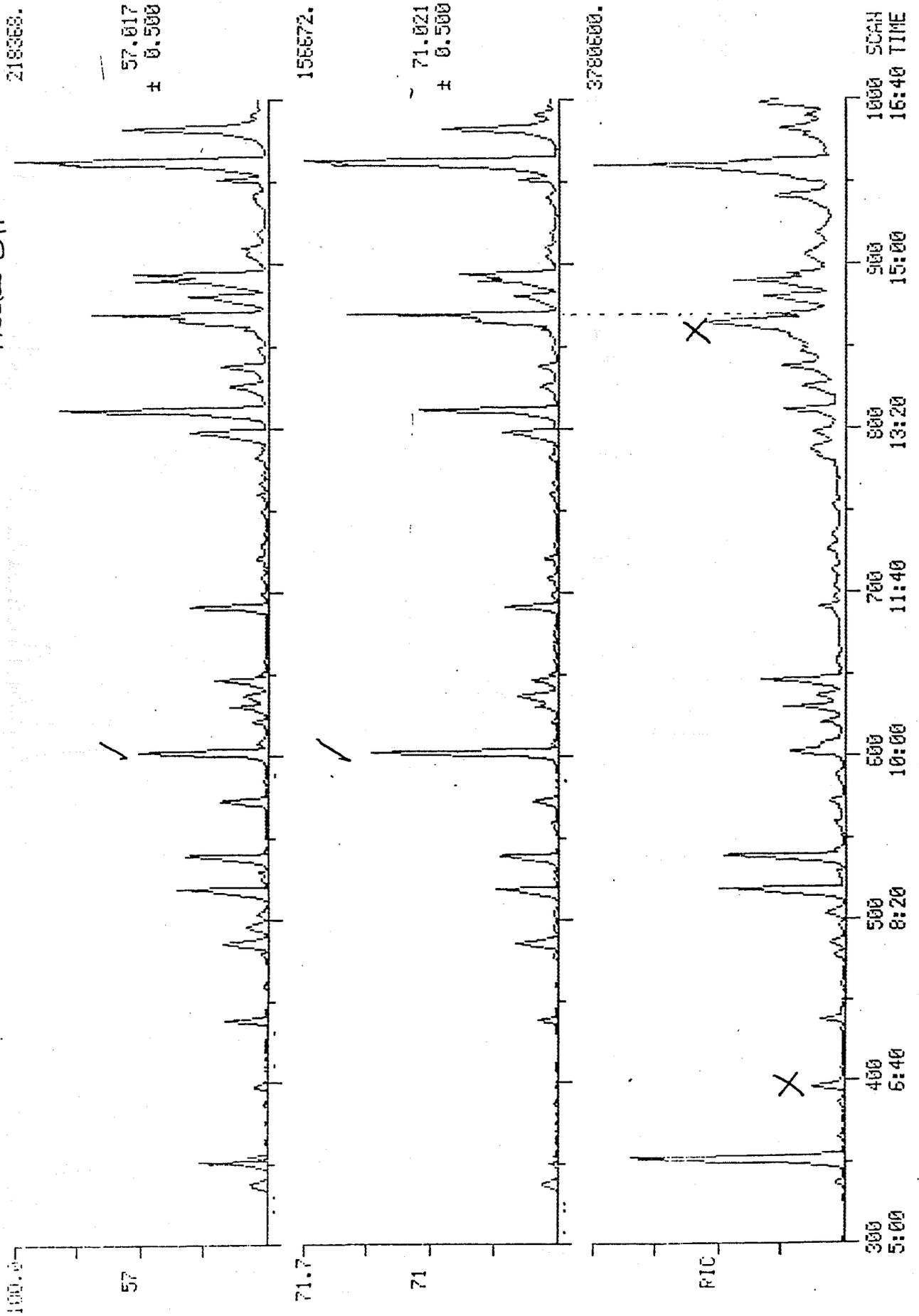


RIC + MASS CHROMATOGRAMS
07/25/83 22:05:00
SAMPLE: 8305414

DATA: ABN126

SCANS 300 TO 1000

Figure 3A



RIC 1700 SCAN
07/26/88 22:05:00
SAMPLE: 8305414

Figure 3B

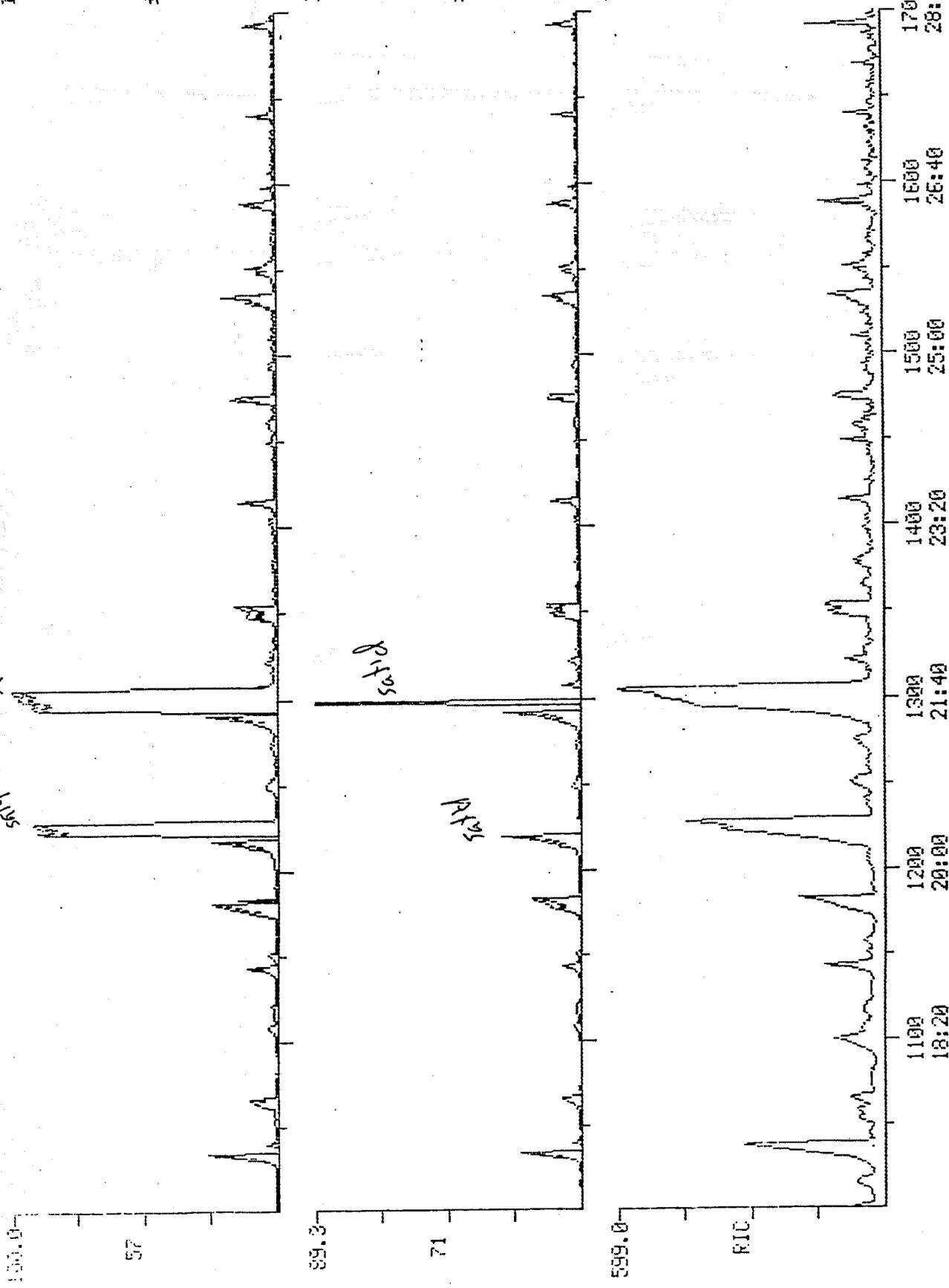
1239030.

57.017
± 0.500

1105910.

71.021 58
± 0.500

7421950.



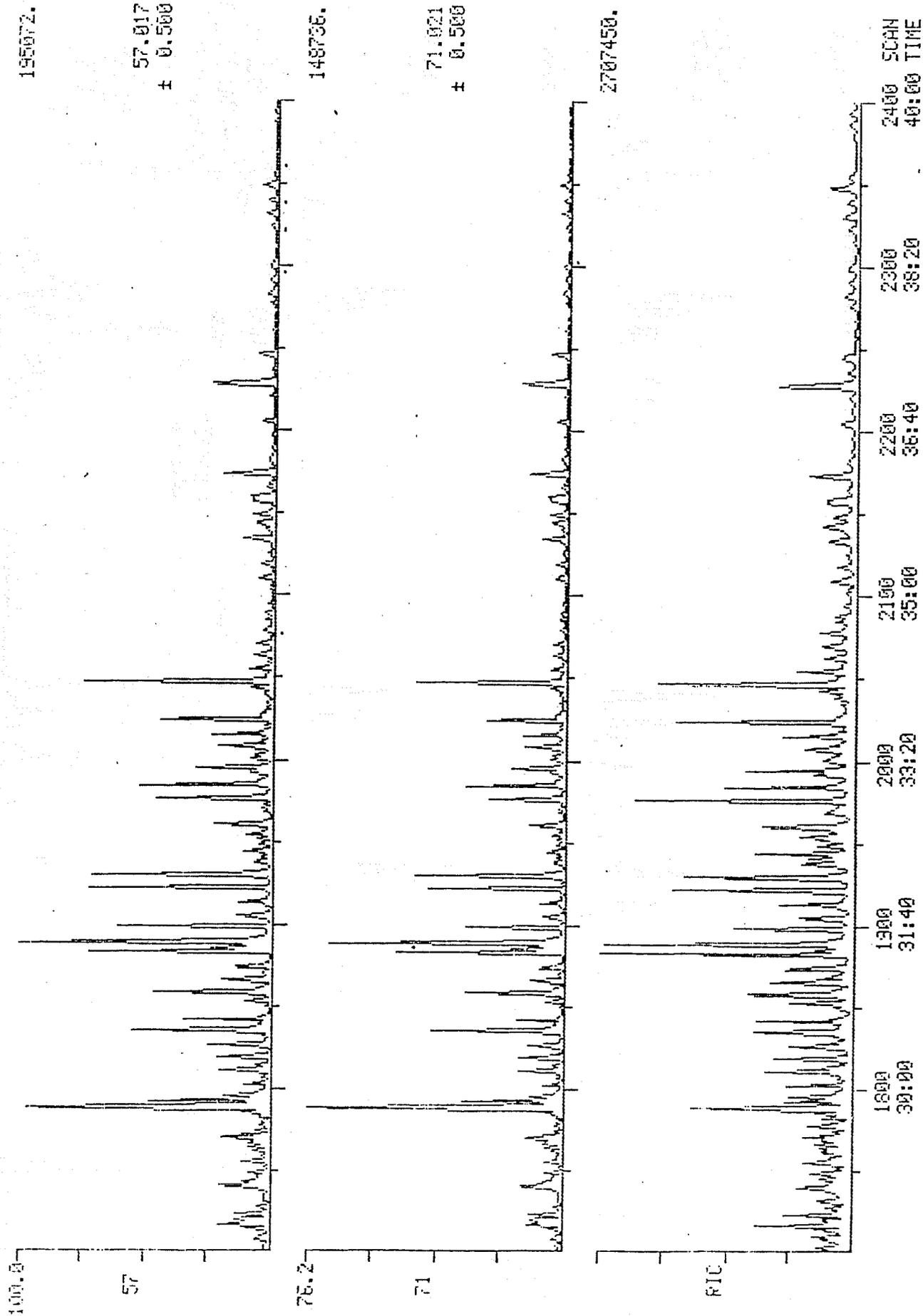
1700 SCAN
28:20 TIME

RIC + MASS CHROMATOGRAMS
07/26/83 22:05:00
SAMPLE: 8305414

DATA: ABN126

SCANS 1701 TO 2400

Figure 3C



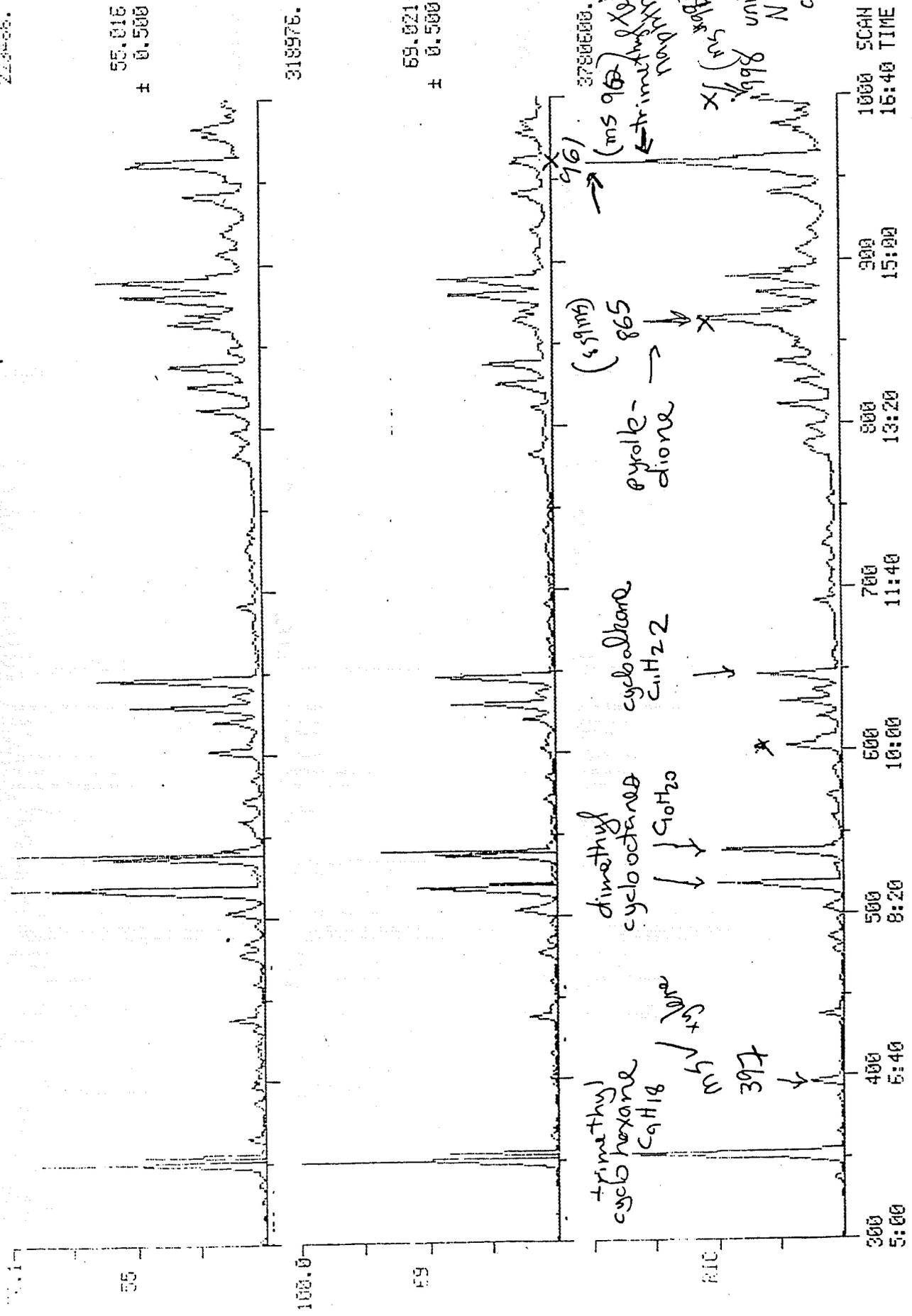
RIC + MPES CHROMATOGRAMS
 07/25/83 23:05:00
 SAMPLE: 8995414

DATA: AENLIZ

SCANS 300 TO 1000

FIGURE 4A

223456.



RIC + MASS CHROMATOGRAMS
07/25/83 22:05:00
SAMPLE: 8305414

DATA: ABN126

SCANS 1001 TO 1700

FIGURE 4B

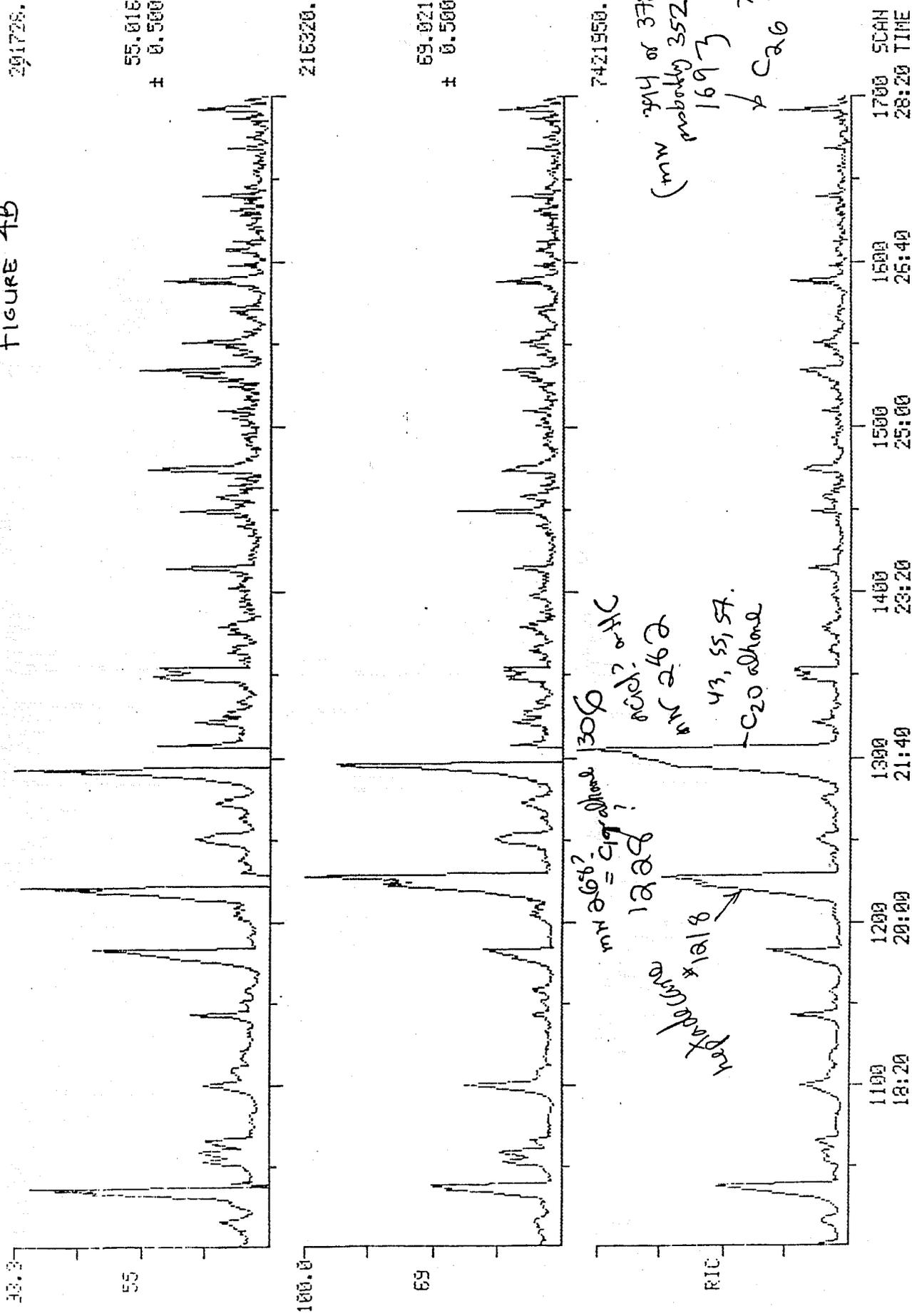
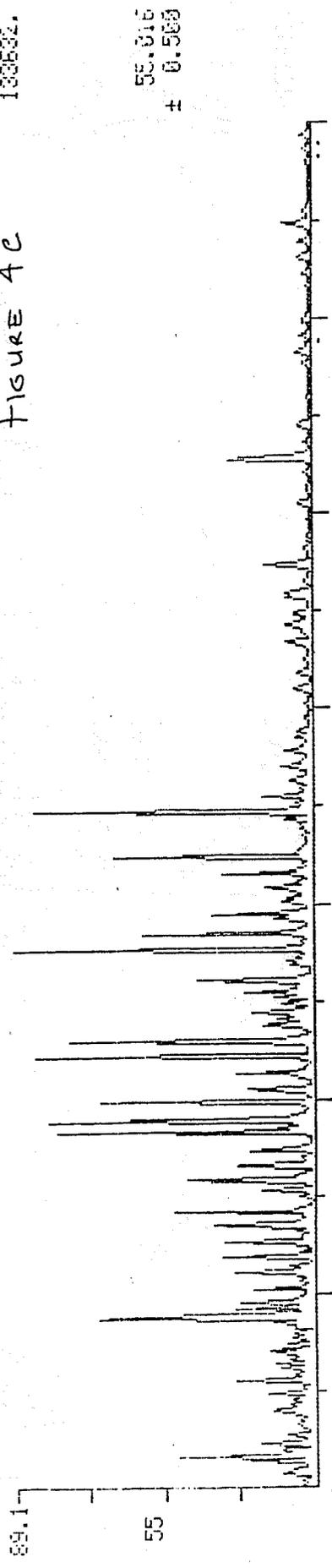
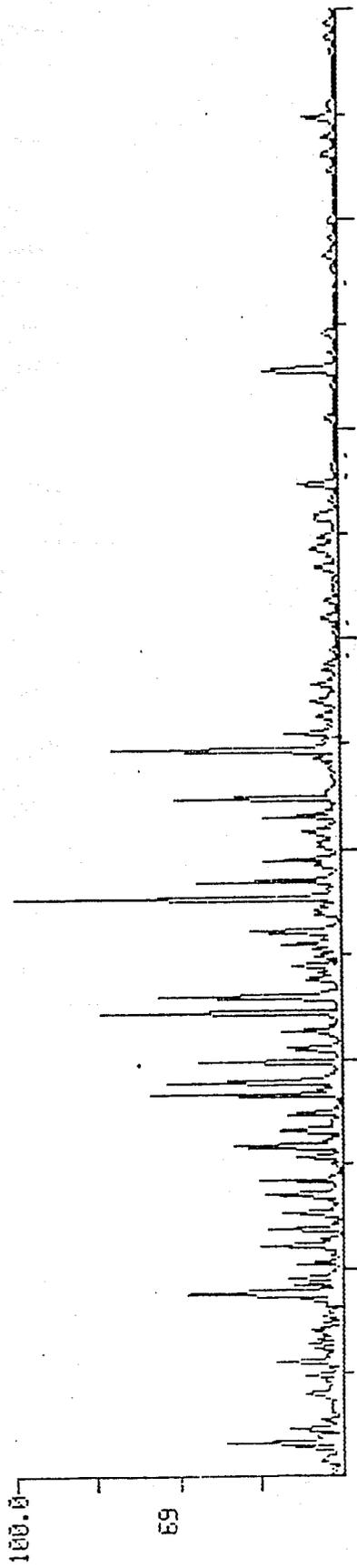


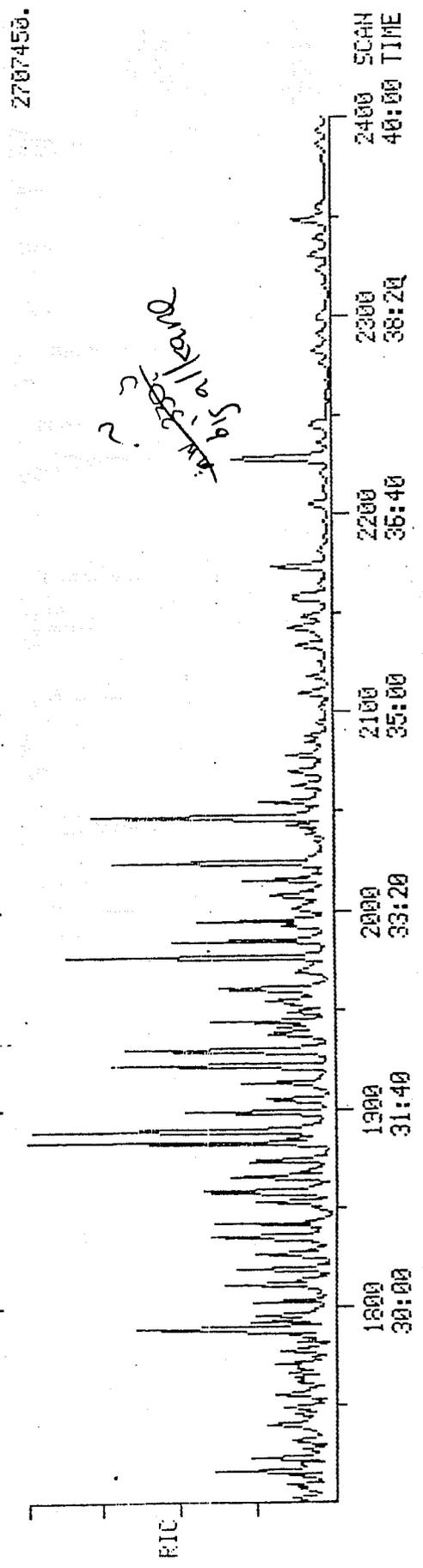
FIGURE 4c 130532.



62
69.021
± 0.500



Handwritten note:
2
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400

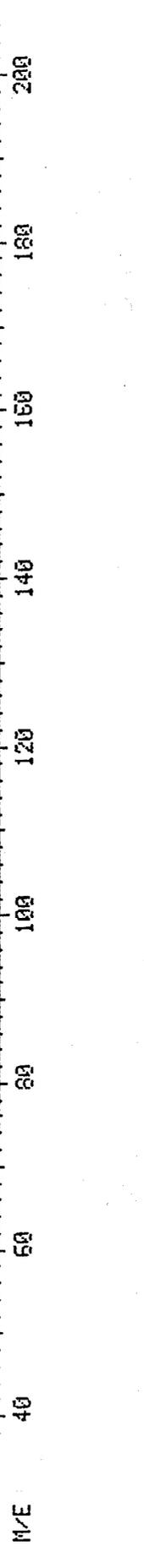
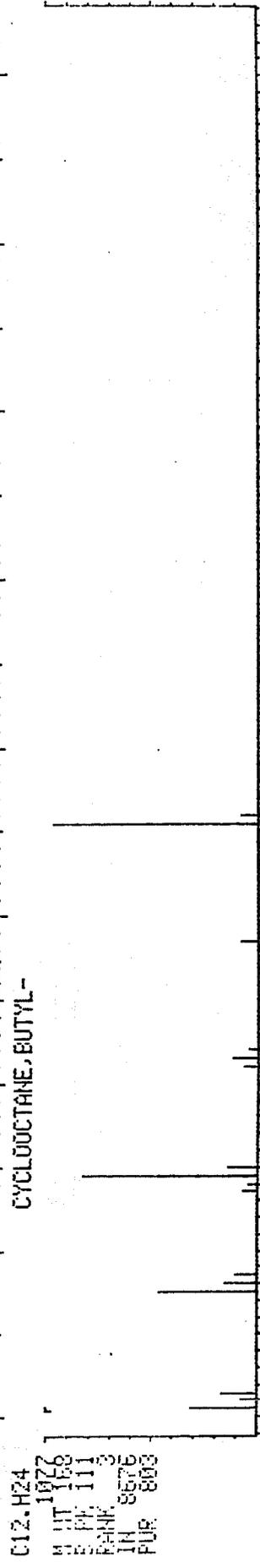
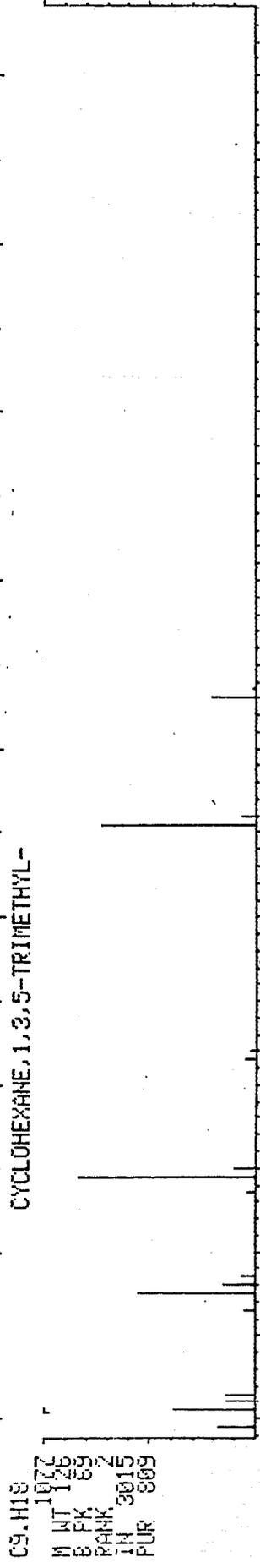
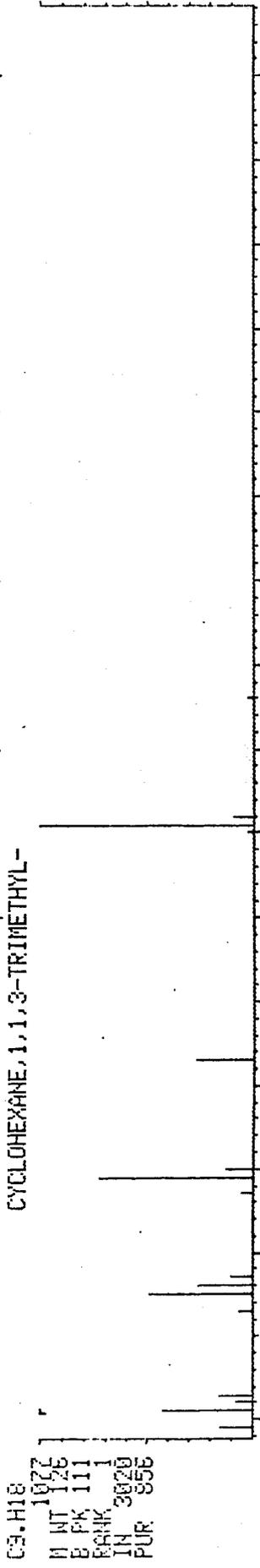
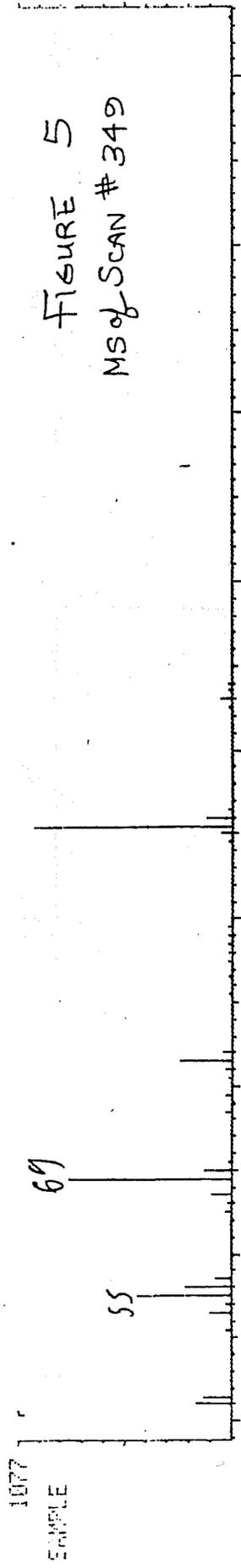


LIBRARY SEARCH
07/26/83 22:05:00 + 5:49
SAMPLE: 8305414

DATA: ABN126 # 349

BASE.M/E: 111
RIC: 644095.

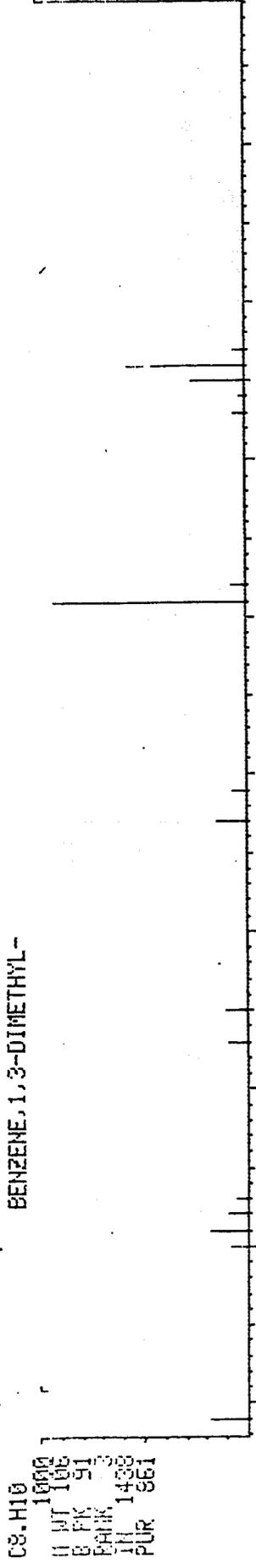
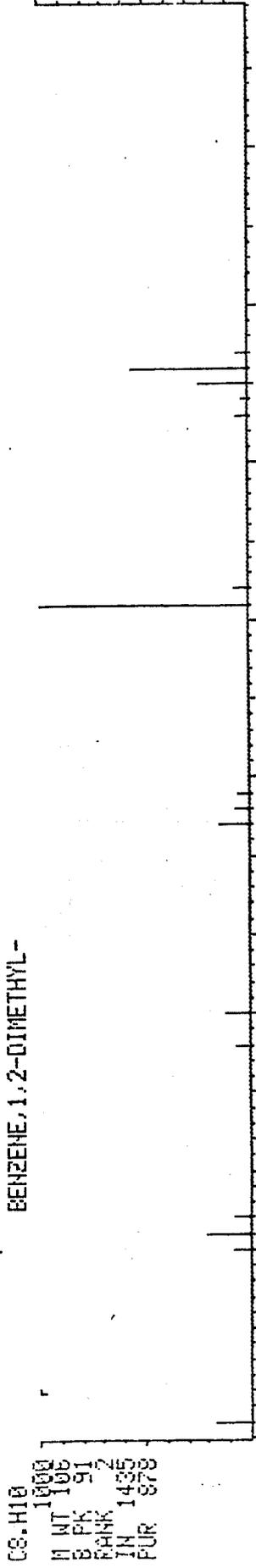
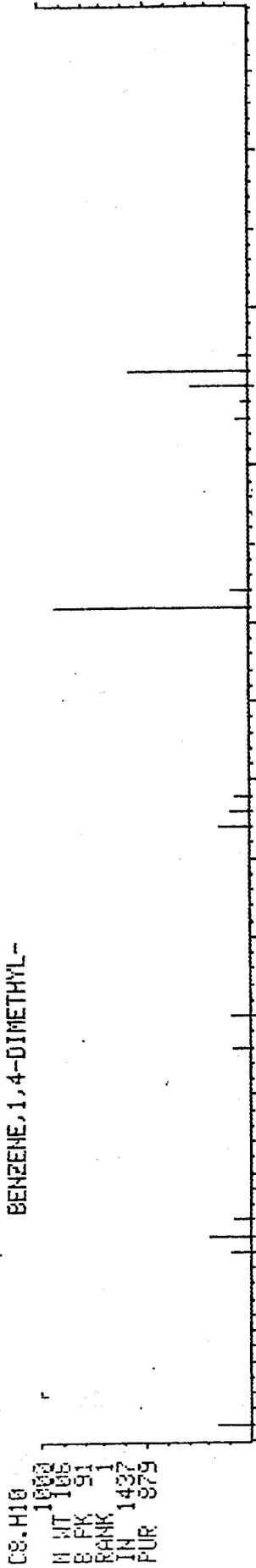
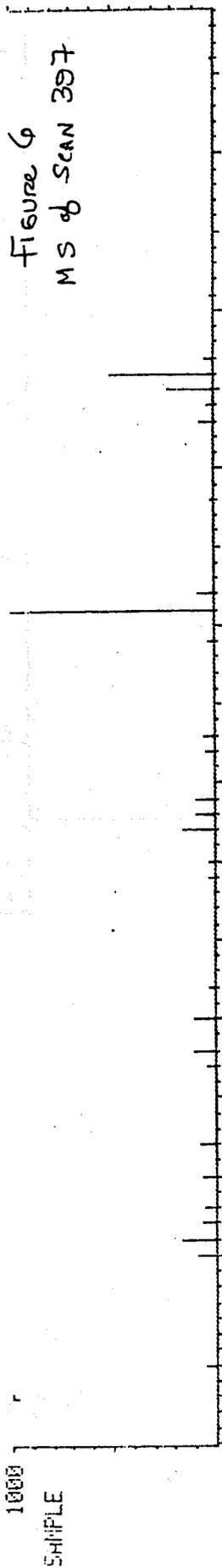
FIGURE 5
MS of SCAN # 349



LIBRARY SEARCH
07/25/83 22:05:00 + 6:37
SAMPLE: 8305414
ENHANCED (S 15B 2N 0T)

DATA: ABN125 # 397

BASE M/E: 91
RIC: 416255.

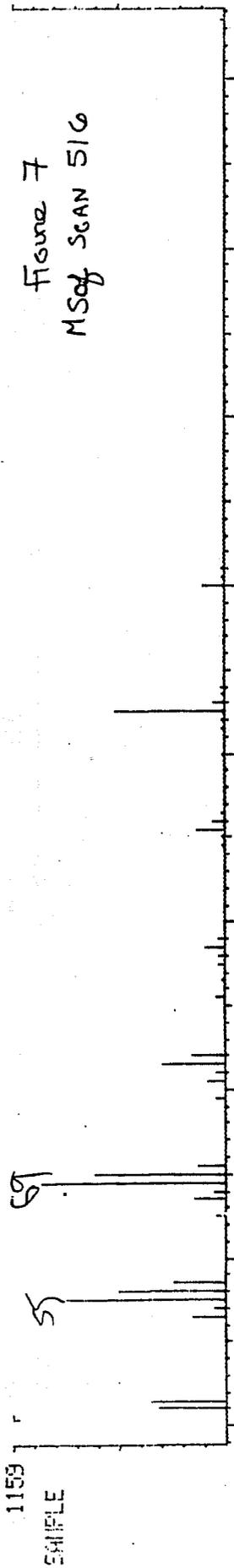


M/E

LIBRARY SEARCH
07/26/83 22:05:00 + 8:36
SAMPLE: 8305414

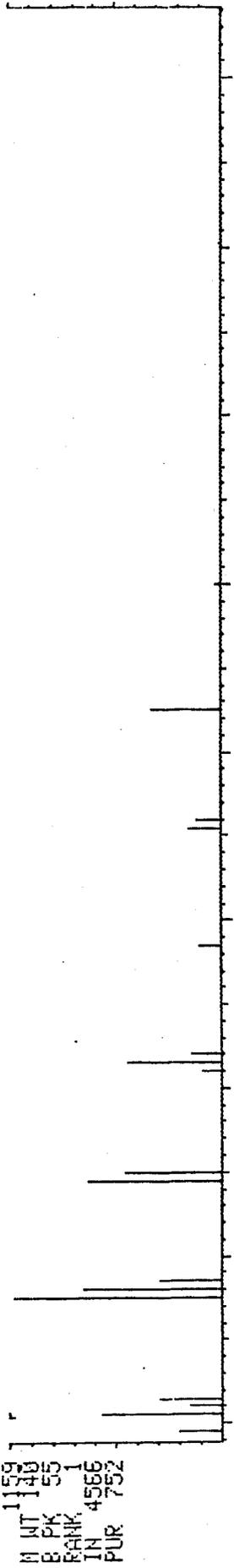
DATA: ABN126 # 516

BASE M/E: 69
RIC: 820223.



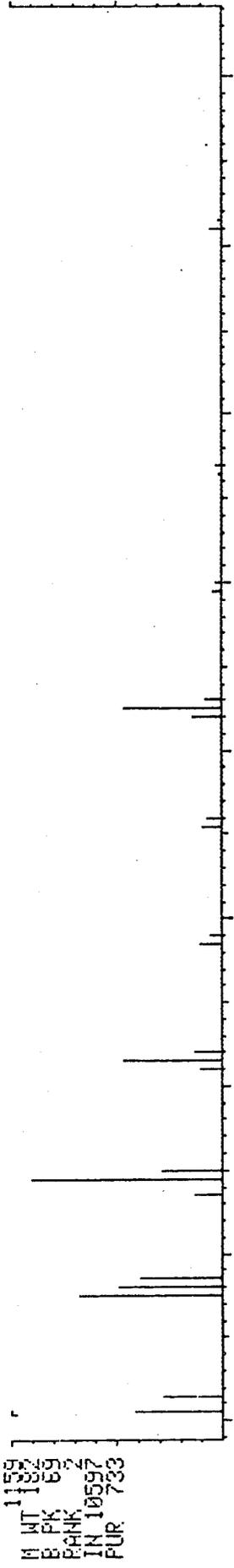
CYCLOOCTANE, 1,4-DIMETHYL-, TRAN

C10.H20
M WT 1159
B PK 57
RANK 1
IN 4566
PUR 752



CYCLOPENTANE, 1,2-DIBUTYL-

C13.H26
M WT 1159
B PK 69
RANK 2
IN 10597
PUR 733



CYCLOPENTANE, 1-BUTYL-2-PROPYL-

C12.H24
M WT 1159
B PK 69
RANK 3
IN 8702
PUR 728

M/E

DATE: 01/14/69
TIME: 10:45 AM

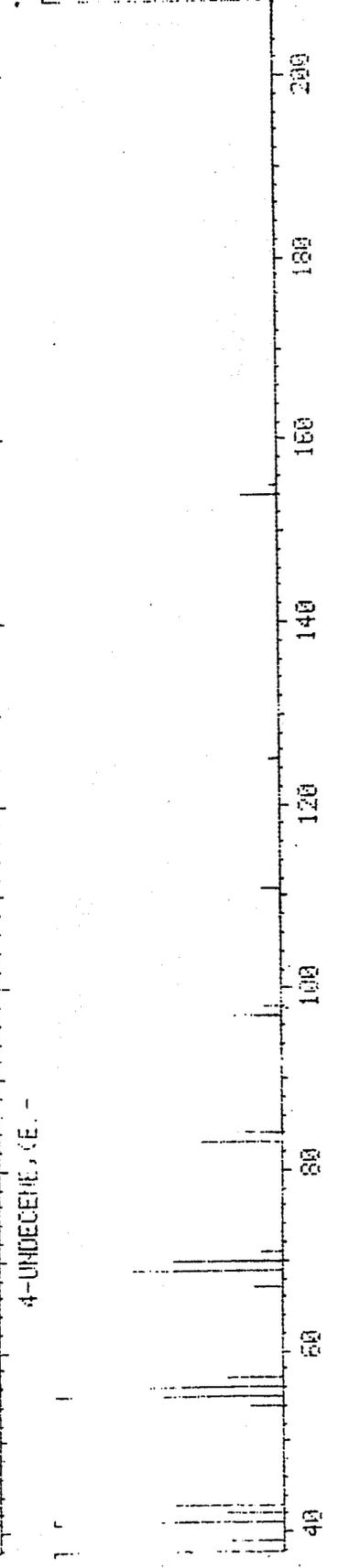
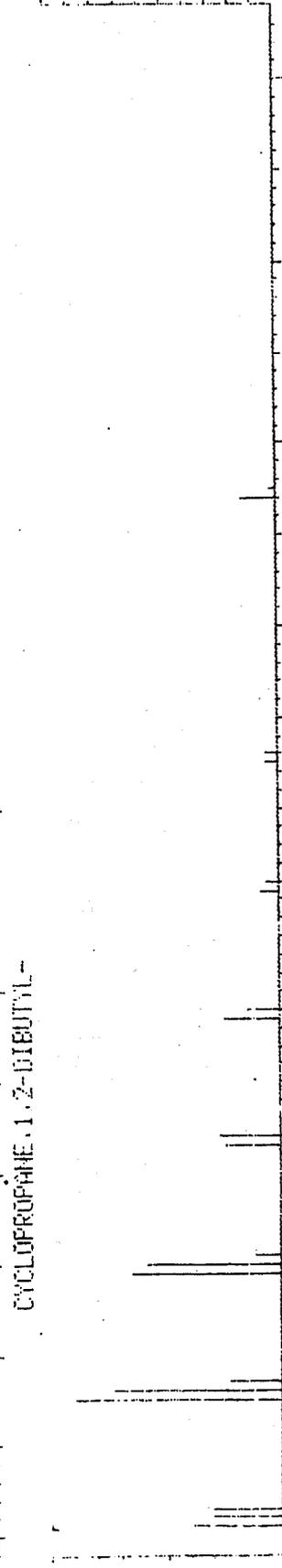
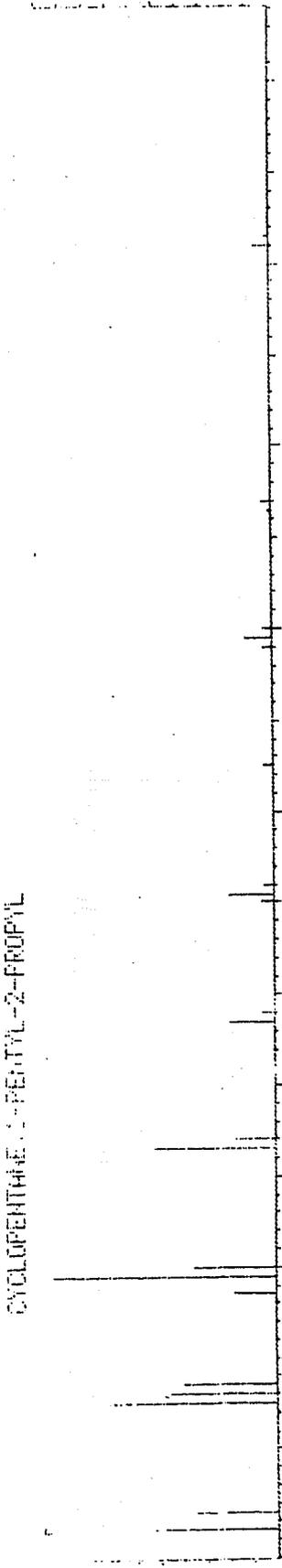
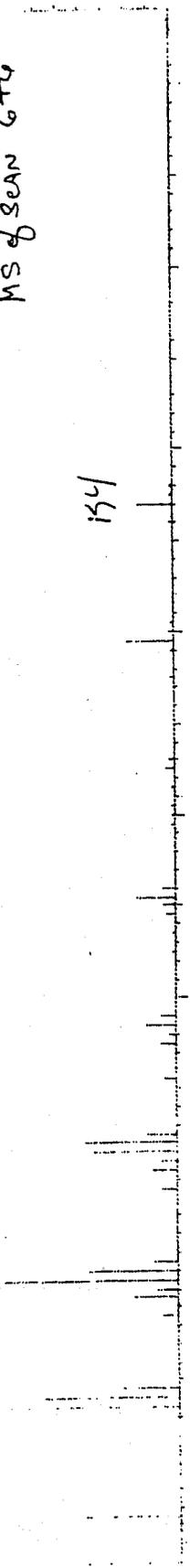
INSTRUMENT: AGN126 # 645

Figure 8
MS of SEAN 6TG

69

134

55



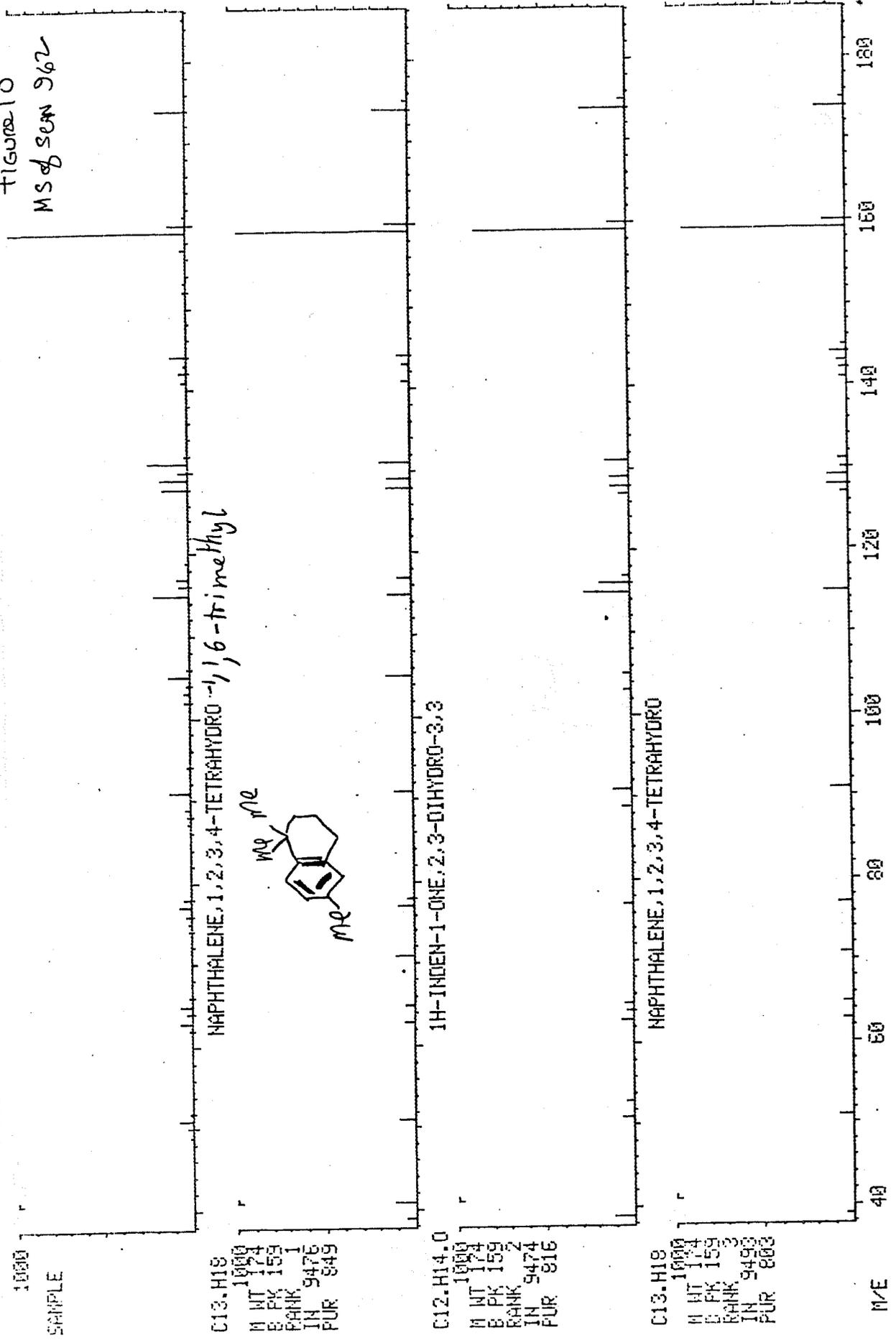
m/e

BASE M/E: 159
RIC: 393215.

DATA: BENZENE # 962

LIBRARY SEARCH
07/26/83 22:05:00 + 16:02
SAMPLE: 8305414
962 - # 963 X2.00

Figure 10
MS of SEM 962



LIBRARY SEARCH
07/26/83 22:05:00 + 16:36
SAMPLE: 8305414
996 - # 994 X1.00

DATA: AEN126 # 996
BASE.M/E: 188
RIC: 413183.

*unidentified
N containing cyclic
compound.*

189
189 ← m+

QUINAZOLINE, 4-(1-METHYLETHYL)-

Figure 11
MS of scan 996

PYRROLO[2,3-B]INDOLE, 1,2,3,3A,

NAPHTHALENE, 1,5-DIMETHOXY-

1000
SAMPLE

C11.H12.O.N2
M WT 188
B PK 188
RANK 1
IN 11319
PUR 619

C12.H16.N2
M WT 188
B PK 188
RANK 2
IN 11351
PUR 607

C12.H12.O2
M WT 188
B PK 188
RANK 3
IN 11342
PUR 524

M/E

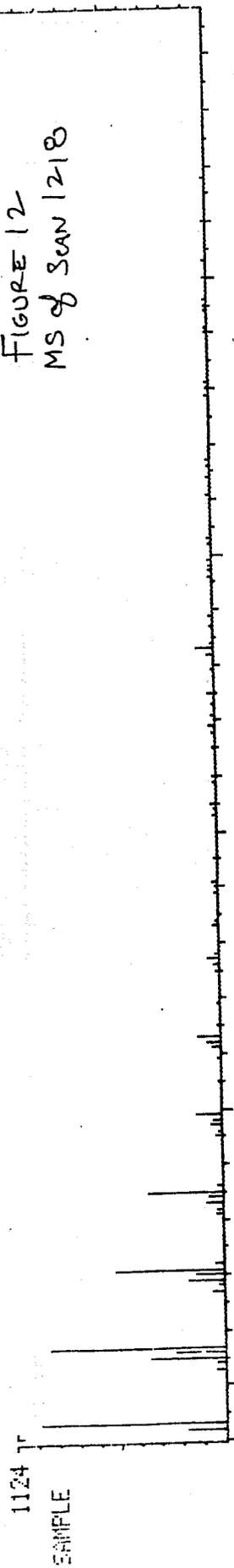
60 80 100 120 140 160 180 200

BASE M/E: 43
RIC: 1841150.

DATA: ABN126 #1218

LIBRARY SEARCH
07/25/83 22:05:00 + 20:18
SAMPLE: 8305414

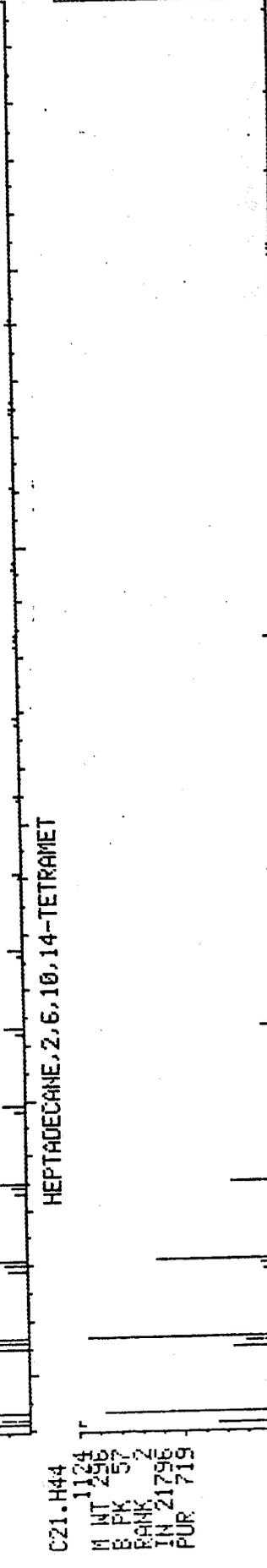
FIGURE 12
MS of SCAN 1218



HEPTADECANE

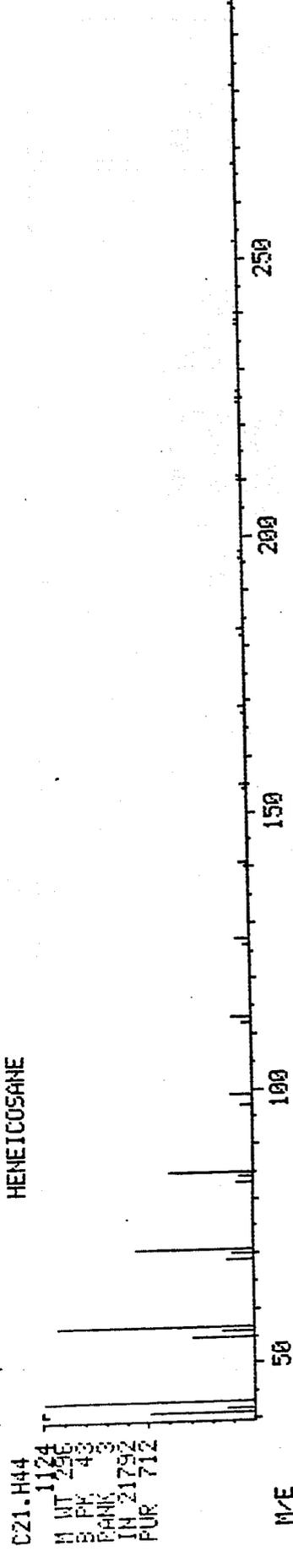
99

C17.H36
M WT 1124
B PK 57
RANK 1
IN 17150
PUR 729



HEPTADECANE, 2,6,10,14-TETRAMET

C21.H44
M WT 1124
B PK 57
RANK 2
IN 21796
PUR 719



HENEICOSANE

C21.H44
M WT 1124
B PK 43
RANK 3
IN 21792
PUR 712

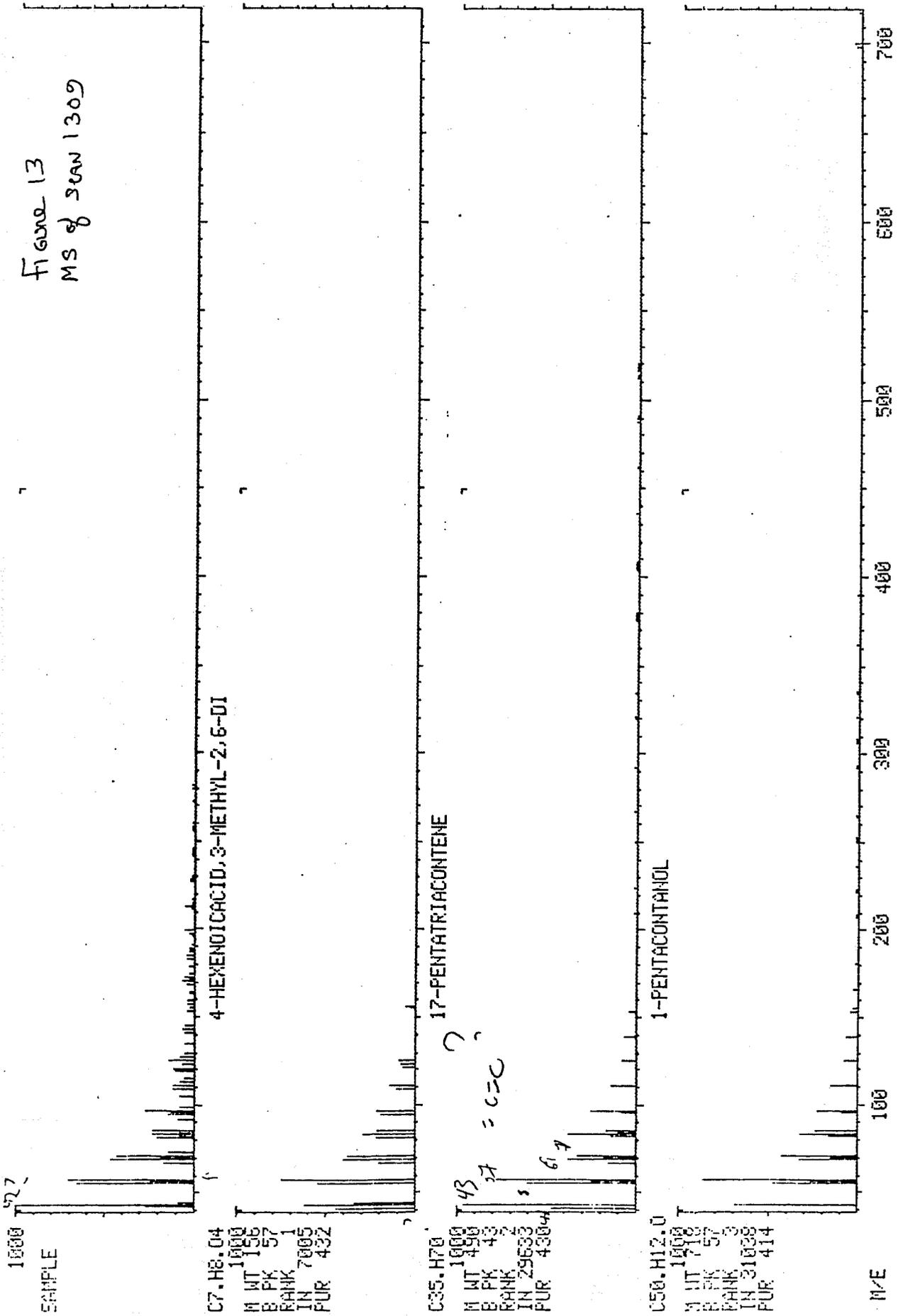
M/E

LIBRARY SEARCH
07/26/83 22:05:00 + 21:49
SAMPLE: 8385414

DATA: AEN126 #1309

BASE M/E: 43
R1C: 509439.

Figure 13
MS of scan 1309

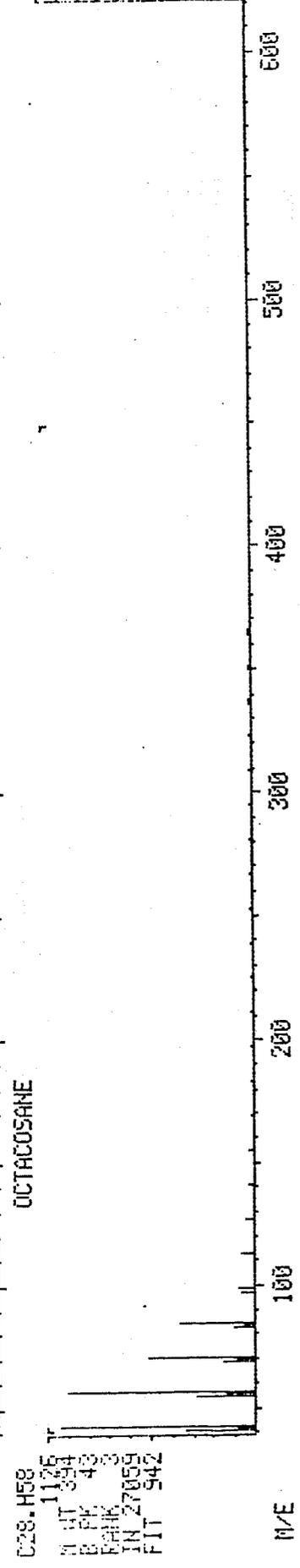
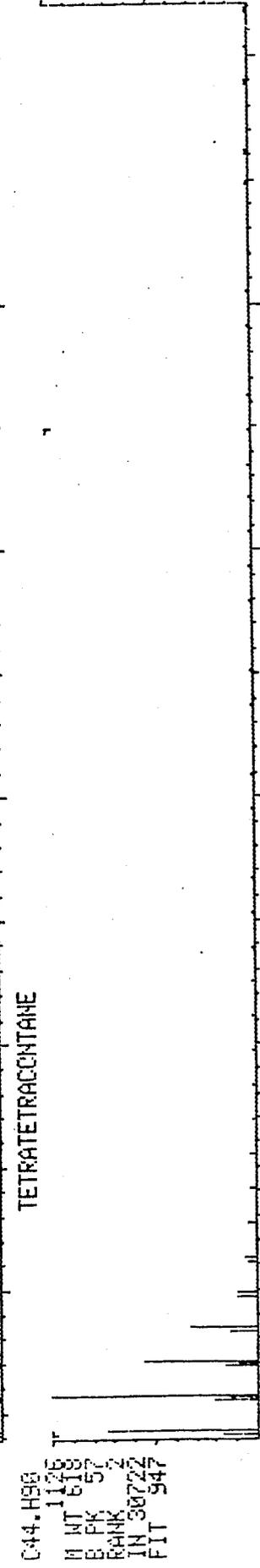
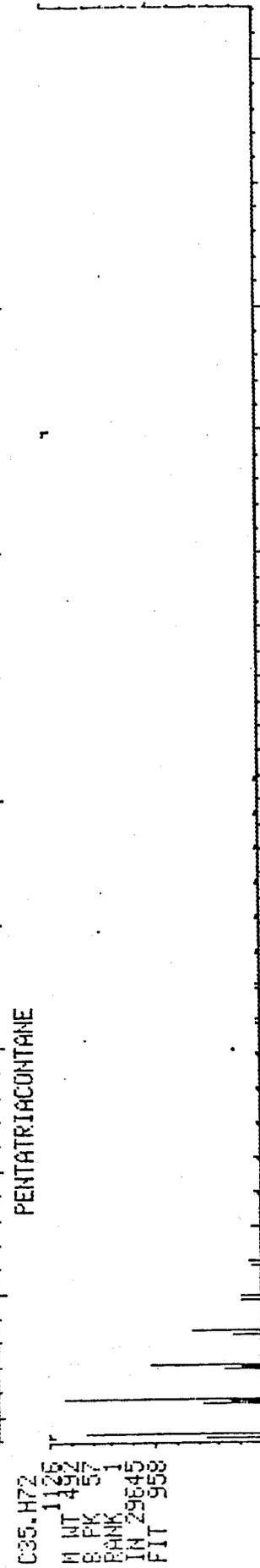
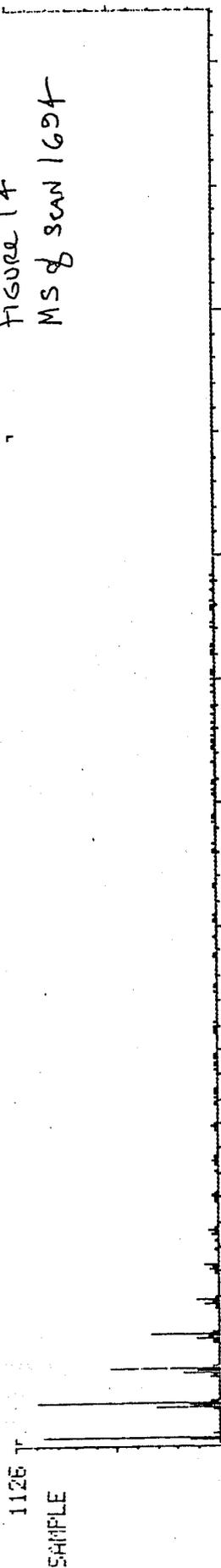


BASE N/E: 57
RIC: 604159.

DATA: ABN125 #1694

LIBRARY SEARCH
07/26/83 22:05:00 + 28:14
SAMPLE: 8305414
#1694 - #1697 X1.00

Figure 14
MS of scan 1694



Appendix C

EXPERIMENTAL RUN DATA SHEETS

Run #: 2
 Flow Run Time: 3 Hours
 Date: 04/20/83

Shale Particle Size: 500 um

Condenser Weight Initial: 1124.6 gms

Sample Extracted Weight: 9.0 gms

Water Extracted Weight: 9.0 gms

Oil Extracted Weight: _____

Shale Weight: 1599.5 gms Final: 1133.6 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1769	2000	1350	2100	1350
Chamber Temperature (°F)	140	155	159	153	162	147
Condenser Pressure (psi)	400	426	600	440	600	400
Condenser Temperature (°F)	40	36	33	42	43	25
CO2 Flow Rate (lpm)	_____	7.2	15	8.7	15	0

Comments:

Run #: 3

Flow Run Time: 1 Hour

Date: 04/25/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1119.8 gms

Sample Extracted Weight: 3.0 gms

Water Extracted Weight: 1.8 gms

Oil Extract Weight: 1.2 gms

Shale Weight: 1794.5 gms

Final: 1122.8 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1635	1800	1300	1800	1300
Chamber Temperature (°F)	140	142	147	142	147	139
Condenser Pressure (psi)	400	406	400	400	420	400
Condenser Temperature (°F)	40	33	24	42	42	24
CO2 Flow Rate (lpm)	—	4.9	6.3	7.4	7.4	5.3

Comments:

Run #: 4

Flow Run Time: 2 3/4 Hours

Date: 05/02/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1120.4 gms

Sample Extracted Weight: 9.7 gms

Water Extracted Weight: 7.6 gms

Oil Extract Weight: 2.1 gms

Shale Weight: 1770.5 gms Final: 1130.1 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1801	1800	1600	1950	1600
Chamber Temperature (°F)	140	146	158	139	158	136
Condenser Pressure (psi)	400	406	400	390	410	390
Condenser Temperature (°F)	40	39	45	47	47	29
CO ₂ Flow Rate (lpm)	_____	6.4	7.7	5.3	9.7	4.7

Comments:

Run #: 5
 Flow Run Time: 8 Hours
 Date: 05/19/83

Shale Particle Size: 1500 μ m

Condenser Weight Initial: 1117.4 gms Final: 1132.7 gms

Sample Extracted Weight: 15.3 gms

Water Extracted Weight: 11.0 gms

Oil Extract Weight: 4.3 gms

Shale Weight: 1749.8 gms Final: 1744.5 gms Difference: 5.3 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1837	1800	1775	1950	1750
Chamber Temperature ($^{\circ}$ F)	140	139	136	133	146	133
Condenser Pressure (psi)	400	413	410	420	430	390
Condenser Temperature ($^{\circ}$ F)	40	32	22	26	41	21
CO ₂ Flow Rate (lpm)	_____	5.5	5.8	1.3	8.5	1.3

Comments:

From this experiment, it can be concluded that CO₂ is absorbed in the shale resulting in an increase in weight of shale.

Run #: 9

Flow Run Time: 3 Hours

Date: 05/19/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1120.2 gms

Final: 1127.4 gms

Sample Extracted Weight: 7.2 gms

Water Extracted Weight: 5.7 gms

Oil Extract Weight: 1.5 gms

Shale Weight: 1784.6 gms

Final: 1782.9 gms

Difference: 1.7 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1831	1900	1850	1950	1750
Chamber Temperature (°F)	140	139	146	140	146	130
Condenser Pressure (psi)	400	398	410	400	420	380
Condenser Temperature (°F)	40	43	28	46	55	28
CO2 Flow Rate (lpm)	—	6.7	9.1	6.9	9.1	4.7

Comments:

There is an apparant gain in weight of shale due to absorption of CO2 in the shale.

Run #: 10
Flow Run Time: 3 Hours
Date: 05/19/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1119.5 gms Final: 1125.6 gms

Sample Extracted Weight: 6.1 gms

Water Extracted Weight: 4.3 gms

Oil Extract Weight: 1.8 gms

Shale Weight: 1790.5 gms Final: 1791.5 gms Difference: 1.0 gms (Increase)

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1744	1800	1450	1850	1450
Chamber Temperature (°F)	140	140	142	131	149	131
Condenser Pressure (psi)	400	411	420	410	420	410
Condenser Temperature (°F)	40	41	32	48	48	32
CO2 Flow Rate (lpm)		5.0	5.3	4.5	7.1	3.5

Comments:

Washed out condenser, caps, and metal spirals with methylene chloride, then boiled it off. Remainder 2.06 grams of oily substance, metal chips, green in color. Be- comes solid at around 30°F.

Run #: 11
 Flow Run Time: 3 Hours
 Date: 05/19/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1384.9 gms Final: 1193.2 gms

Sample Extracted Weight: 8.3 gms
 (Glass Beads)

Water Extracted Weight: _____

Oil Extract Weight: _____

Shale Weight: 1742.7 gms Final: 1738.4 gms Difference: 4.3 gms (Increase)

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1804	1800	1600	2000	1600
Chamber Temperature (°F)	140	137	144	132	144	130
Condenser Pressure (psi)	400	425	390	430	500	380
Condenser Temperature (°F)	40	34	24	37	53	22
CO2 Flow Rate (lpm)	_____	6.6	4.5	6.3	15.3	2.3

Comments: There is an increase in weight change in condenser compared to change in weight of shale, signifying that CO2 is absorbed in shale.

Run #: 12
 Flow Run Time: 3 Hours
 Date: 05/19/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1137.0 gms Final: 1147.3 gms

Sample Extracted Weight: 10.3 gms

Water Extracted Weight: 7.8 gms

Oil Extract Weight: 2.5 gms

Shale Weight: 1759.3 gms Final: 1747.6 gms Difference: 11.7 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	2500	2454	2450	2400	2550	2350
Chamber Temperature (°F)	200	203	193	206	208	193
Condenser Pressure (psi)	400	412	400	430	430	400
Condenser Temperature (°F)	40	38	30	41	43	30
CO ₂ Flow Rate (lpm)	_____	3.4	4.8	2.8	4.8	2.4

Comments:

Run #: 13

Flow Run Time: 3 Hours

Date: 06/15/83

Shale Particle Size: 1500 μ m

Condenser Weight Initial: 1127.8 gms

Sample Extracted Weight: 10.8 gms

Water Extracted Weight: 7.7 gms

Oil Extract Weight: 3.1 gms

Shale Weight: 1784.6 gms

Final: 1138.6 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	3000	3000	2800	3000	3200	2800
Chamber Temperature (°F)	200	200	197	203	205	197
Condenser Pressure (psi)	400	388	400	400	400	260
Condenser Temperature (°F)	40	45	45	36	67	36
CO ₂ Flow Rate (lpm)		3.2	3.6	4.3	5.8	0

Comments:

Run #: 15
 Flow Run Time: 3 Hours
 Date: 10/04/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1134.8 gms Final: 1140.5 gms

Sample Bottle Wt. Initial: 19.5 gms Final: 24.1 gms Difference: 4.6 gms

Shale Weight: 1818.9 gms Final: 1798.8 gms Difference: 5.7 gms

Sample Extracted Weight: 5.7 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1400	1329	1400	1350	1500	1100
Chamber Temperature (oF)	180	170	141	184	185	138
Condenser Pressure (psi)	400	244	0	400	420	0
Condenser Temperature (oF)	40	42	20	64	64	20
CO2 Flow Rate (lpm)		5.9	10.2	6.0	10.2	3.4

Comments: The shale is heated to an outside temperature (To) of 409oF and inside temperature (Ti) of 306oF. Since the sample extracted from the condenser essentially contained aqueous phase, it is considered that the difference between the sample extracted weight and the difference in sample bottle weight yields the oil contained in the condenser. The weight of oil extracted is 1.1 gms

Run #: 16
 Flow Run Time: 3 Hours
 Date: 10/06/83

Shale Particle Size: 1000 um

Condenser Weight Initial: 1125.6 gms Final: 1143.9 gms

Sample Bottle Wt. Initial: 19.6 gms Final: 33.1 gms Difference: 13.5 gms

Shale Weight: 1708.5 gms Final: 1684.3 gms Difference: 24.2 gms

Sample Extracted Weight: 18.3 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	2400	2115	2700	2400	2700	1800
Chamber Temperature (°F)	220	224	234	234	238	212
Condenser Pressure (psi)	400	404	400	420	420	400
Condenser Temperature (°F)	40	49	41	63	76	38
CO2 Flow Rate (lpm)	_____	4.9	6.1	5.5	6.1	1.7

Comments:

The shale is heated up to an outside temperature (To) of 450°F and inside temperature (Ti) of 294°F. The oil extracted is 4.8 grams.

Run #: 17
 Flow Run Time: 2.5 Hours
 Date: 10/14/83

Shale Particle Size: 1000 um

Condenser Weight Initial: 1125.8 gms Final: 1144.7 gms

Sample Bottle Wt. Initial: 19.8 gms Final: 33.7 gms Difference: 13.9 gms

Shale Weight: 1761.8 gms Final: 1733.0 gms Difference: 28.8 gms

Sample Extracted Weight: 18.9 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	2300	2409	2700	2400	2700	2200
Chamber Temperature (°F)	250	267	249	282	282	249
Condenser Pressure (psi)	400	398	400	400	400	380
Condenser Temperature	40	47	33	61	70	33
CO ₂ Flow Rate (lpm)	—	4.8	8.1	4.9	8.1	2.3

Comments: The shale is heated up to an outside temperature (To) of 260°F and inside temperature (Ti) of 165°F. The oil extracted is 5.0 grams.

Run #: 18
 Flow Run Time: 3 Hours
 Date: 10/17/83

Shale Particle Size: 500 um

Condenser Weight Initial: 1126.1 gms Final: 1142.4 gms
 Sample Bottle Wt. Initial: 19.3 gms Final: 32.4 gms Difference: 13.1 gms
 Shale Weight: 1550.7 gms Final: 1531.0 gms Difference: 19.7 gms
 Sample Extracted Weight: 16.3 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	2300	2283	2300	2300	2400	2200
Chamber Temperature (OF)	250	251	244	258	258	242
Condenser Pressure (psi)	400	400	400	400	420	360
Condenser Temperature	40	49	19	60	63	19
CO ₂ Flow Rate (lpm)	_____	5.7	7.2	5.2	7.7	3.2

Comments: The shale is heated up to an outside temperature (To) of 255OF and inside temperature (Ti) of 155OF. The oil extracted is 3.2 grams.

Run #: 20
 Flow Run Time: 3 Hours
 Date: 10/14/83

Shale Particle Size: 1000 um

Condenser Weight Initial: 1142.4 gms Final: 1148.3 gms
 Sample Bottle Wt. Initial: 19.5 gms Final: 1148.3 gms Difference: 5.9 gms
 Shale Weight: 1705.9 gms Final: 1699.3 gms Difference: 6.6 gms
 Sample Extracted Weight: 5.9 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	1800	1812	1750	1850	1900	1700
Chamber Temperature (oF)	140	144	144	145	156	138
Condenser Pressure (psi)	400	399	400	400	400	390
Condenser Temperature	40	41	30	60	68	22
CO2 Flow Rate (lpm)	_____	4.6	4.1	3.5	9.1	1.8

Comments: The amount of oil extracted is 2.1 grams.

Run #: 21
 Flow Run Time: 3 Hours
 Date: 11/17/83

Shale Particle Size: 1500 um

Condenser Weight Initial: 1140.3 gms Final: 1153.0 gms

Sample Bottle Wt. Initial: 19.7 gms Final: 28.4 gms Difference: 8.7 gms

Shale Weight: 1797.7 gms Final: 1785.5 gms Difference: 12.2 gms

Sample Extracted Weight: 12.7 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	2000	2004	2000	2000	2100	1950
Chamber Temperature (°F)	200	202	202	207	208	198
Condenser Pressure (psi)	400	400	400	400	400	400
Condenser Temperature	40	59	47	58	78	41
CO ₂ Flow Rate (lpm)	_____	.6	6.6	5.5	6.6	4.3

Comments: The amount of oil extracted is 4.0 grams.

Ethylene Run

Run #: 22
Flow Run Time: 1 Hour
Date: 11/22/83

Shale Particle Size: 1500 u

Sample Extracted Weight: -0- gms

Final: 1147.6 gms

Condenser Weight Initial: 11617.6 gms

Shale Weight: 1807.7 gms

	Desired	Average	Beginning	Final	High	Low
Chamber Pressure (psi)	770	714	740	640	740	640
Chamber Temperature (°F)	70	75	76	73	76	73
Condenser Pressure (psi)	200	190	150	200	200	150
Condenser Temperature	40	40	37	42	42	37
Flow Rate	—	1.0	0.4	1.4	2.4	0.4

Comments: P_c - 736 psi; T_c = 49°F

The following table shows the results of the curve fitting calculations for the oil and water extracts as a function of density and temperature. The data points are plotted on a graph of $\log(\text{viscosity})$ versus $\frac{1}{\rho T}$, where ρ is the density and T is the temperature. The linear relationship between $\log(\text{viscosity})$ and $\frac{1}{\rho T}$ is used to determine the activation energy of the flow process.

Sample	Temperature (°C)	Density (g/cm ³)	Viscosity (cP)
Oil	25	0.85	100
	30	0.84	80
	35	0.83	60
Water	25	0.99	1000
	30	0.99	800
	35	0.99	600

Appendix D

**CURVE FITTING CALCULATIONS
FOR OIL AND WATER EXTRACTS
AS A FUNCTION OF DENSITY AND TEMPERATURE**

The following table shows the results of the curve fitting calculations for the oil and water extracts as a function of density and temperature. The data points are plotted on a graph of $\log(\text{viscosity})$ versus $\frac{1}{\rho T}$, where ρ is the density and T is the temperature. The linear relationship between $\log(\text{viscosity})$ and $\frac{1}{\rho T}$ is used to determine the activation energy of the flow process.

The following table shows the results of the curve fitting calculations for the oil and water extracts as a function of density and temperature. The data points are plotted on a graph of $\log(\text{viscosity})$ versus $\frac{1}{\rho T}$, where ρ is the density and T is the temperature. The linear relationship between $\log(\text{viscosity})$ and $\frac{1}{\rho T}$ is used to determine the activation energy of the flow process.

The relationship between extract fractions and the density and temperature of the carbon dioxide solvent was discussed in the text. Below are the curve fitting procedures used to drive a relationship between extract fraction Y; reduced density ρ_r ; and reduced temperature Tr.

The relationship of oil extracted with the reduced temperature and density is represented as follows:

$$Y = A \rho_r + B T_r^n$$

To find A, B, and n, we need three points which are tabulated below. These points correspond to Runs 12, 13, and 15 (See Table 11 in text).

Reduced Density ρ_r	Reduced Temperature Tr	(<u>Oil Extracted</u> / <u>Amount of Shale</u>) 10^4
0.77	1.21	14.2
1.2	1.20	17.4
0.43	1.15	6.0

$$14.2 = A(0.77) + B(1.21)^n \dots \dots \dots (1)$$

$$17.4 = A(1.2) + B(1.20)^n \dots \dots \dots (2)$$

$$6.0 = A(0.43) + B(1.15)^n \dots \dots \dots (3)$$

Assuming an average Tr of 1.205 in (1) and (2) and subtracting (1) from (2), then

$$3.2 = A(0.43)$$

$$A = 7.44$$

Substituting the value of A in (2) and (3) and considering a value of Tr = 1.1 for (3), then

$$8.47 = B(1.205)^n \dots \dots \dots (4)$$

$$2.80 = B(1.10)^n \dots \dots \dots (5)$$

Divide (4) by (5), then

$$3.03 = 1.10^n$$

$$n = 12$$

Substituting n in (4), then

$$B = 8.47 / (1.205)^{12} = 0.90$$

The resulting equation is then

$$Y = 7.44 e_r + 0.90 Tr^{12}$$

Where Y is the oil extracted per the amount of shale.

The same type of equation can be used to predict the water extract of the run as well.

$$Y = A e_r + B Tr^n$$

To determine A, B, and n, the three points are required and are tabulated below. These points correspond to Runs 9, 10, and 12 (See Table 11 in text).

Reduced Density e_r	Reduced Temperature Tr	($\frac{\text{Water Extracted}}{\text{Amount of Shale}}$) ^{10⁴}
0.94	1.09	31.9
0.86	1.10	24.0
0.77	1.21	44.3

$$31.9 = A(0.94) + B(1.1)^n \quad \dots \dots \dots (6)$$

$$24.0 = A(0.86) + B(1.1)^n \quad \dots \dots \dots (7)$$

$$44.3 = A(0.77) + B(1.2)^n \quad \dots \dots \dots (8)$$

Subtracting (6) from (7), then

$$-7.9 = -0.08A$$

$$A = 98.75$$

Substituting the value of A in (7) and (8), then

$$-60.93 = B(1.1)^n \quad \dots \dots \dots (9)$$

$$-31.74 = B(1.2)^n \quad \dots \dots \dots (10)$$

Dividing (9) by (10), then

$$n = -7.50$$

Substituting in (9), then

$$B = -124.53$$

The resulting equation is then

$$Y = 98.75 e_r - 124.53 Tr^{-7.5}$$

Where Y is the water extracted per amount of shale.