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AFRPL-TR-77-45



**MANUFACTURE OF
PCDE PREPOLYMER**

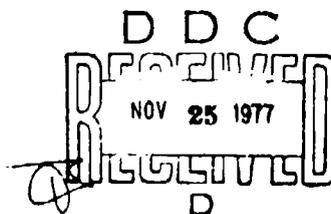
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84044

AUGUST 1977
Final Report for Period January 1973 - May 1977

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Prepared for:

AIR FORCE ROCKET PROPULSION LABORATORY
Director of Science and Technology
Air Force Systems Command
Edwards AFB, California 93523

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APPROVAL STATEMENT

This report was submitted by Hercules Incorporated, P.O. Box 98, Magna, Utah 84044, under contracts F04611-73-C-0051 and F04611-75-C-0024, with the Air Force Rocket Propulsion Laboratory, Edwards AFB, Ca 93523.

This report has been reviewed by the Information Office/DOZ and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations. This technical report has been reviewed and is approved for publication; it is unclassified and suitable for general public release.


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ORIGINAL CONTAINS COLOR PLATES: ALL DDC
REPRODUCTIONS WILL BE IN BLACK AND WHITE

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SECTION I

INTRODUCTION AND SUMMARY

Under Air Force Contract F33615-68-C-1568, Shell Development Company developed and evaluated a process for making PCDE, progressing through the intermediate steps of PECH, DEPECH, and PBEP. The latter two steps were operated successfully on a continuous basis at rates of 0.5 lb/hour. Preliminary cost estimates, including both capital and operating costs, were made for this process at rates of 200,000 and 3,000,000 lb/year.

Hercules Incorporated, under Shell Contract SDNO 84723, for Air Force Contract F33615-72-C-1446, successfully demonstrated the PBEP and PCDE processes at rates of 6 lb/hr. Under the Shell subcontract, other data pertinent to designing a large scale PCDE manufacturing plant were gathered.

The purpose of this document is to provide the final report of two PCDE production contracts, F04611-73-C-0051 and F04611-75-C-0024, for which a total of 1450 lb of PCDE were produced.

Another purpose of Contract F04611-73-C-0051 was to determine a method for increasing the molecular weight and functionality of PCDE. The approach taken was to improve these qualities in the PECH. The improvement would be carried forward to the final product. Shell Development, the manufacturer of PECH and DEPECH, was under subcontract to make the improvements and to supply samples of DEPECH made therefrom for evaluation.

Two methods of improving the PECH were studied. The first method was to subject "standard" PECH to treatment that would retain only the higher molecular weight fraction. The second method used was to vary the PECH process in order to increase the molecular weight and functionality. The latter approach, a low temperature process, was chosen as the best method for making improved product. The Shell Development report (Appendix A) gives details and reasons for this choice.

With the completion of the delivery of DEPECH for the final contract modification of Contract F04611-75-C-0024, Shell Development Company notified the Air Force that they would no longer be manufacturing DEPECH. Hercules was authorized under Amendment No. R00007 of Contract F04611-75-C-0024 to prepare 20 lb of DEPECH and convert this to PCDE for qualification as a source of DEPECH for future PCDE production efforts. The effort combining the manufacture of DEPECH at Allegany Ballistics Laboratory and the subsequent conversion of the DEPECH to PCDE is reported as Appendixes B and C to this final report.

As of August 1976, the two PCDE production contracts have been completed. A total of 1450 lb of PCDE have been shipped; 992 lb under F04611-73-C-0051 and 458 lb under F04611-75-C-0024. In addition to the specification material shipped, 63.3 lb of poor quality PCDE (Runs 14 and 20) were shipped to Naval Weapons Center, China Lake, California. Also, approximately 90 lb of material containing N-fluorazoxy contaminant were destroyed.

It is significant that the contracts covering a period of over 40 months of operation with hazardous materials, including fluorine and N_2F_4 , were completed safely with no major accident or injury to operating personnel. Incidents are reported herein in which the hazardous nature of fluorine is demonstrated including one in which an operator received second degree burns on one hand due to a fluorine fire.

During the course of the contract, hazards testing of PCDE was completed and shipping regulations established for 35 percent PCDE solution (Appendix D).

Production rates of 8 lb PBEP per hour and 6.6 lb PCDE per hour were successfully demonstrated. Procedures for plant operation and laboratory analyses are contained in the appendices.

SECTION II

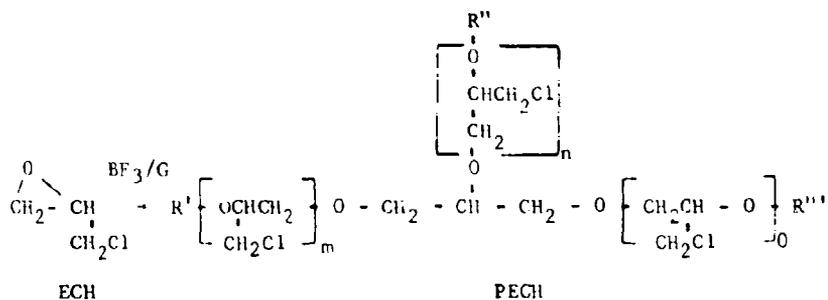
PCDE PROCESS AND PILOT PLANT DESCRIPTION

A. DEPECH

1. Chemistry

The DEPECH used for the production of PCDE was manufactured by Shell Development Company. To make DEPECH, epichlorohydrin (ECH) is polymerized in the first step to form polyepichlorohydrin, PECH, utilizing a boron trifluoride/glycerine complex as initiator as follows:

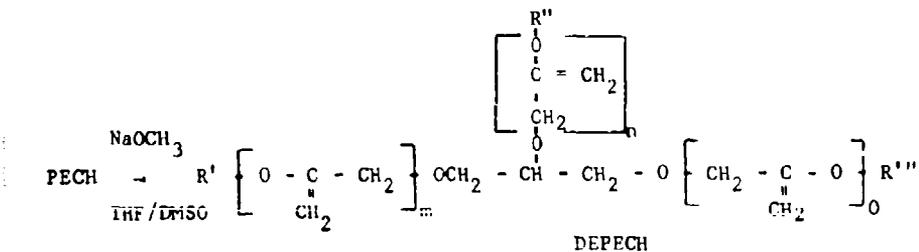
Step 1



On the average, 1.7 to 2.2 R groups are CH_2CHOH , 0.8 to 1.3 CH_2Cl groups are nonfunctionally terminated, and $m + n + 0 = 25$ to 30.

In step 2, PECH is dehydrochlorinated to form poly(2,3-epoxypropene), DEPECH, by treatment with sodium methoxide in 93/7 tetrahydrofuran/dimethylsulfoxide:

Step 2



The functionality remains essentially unchanged, and the terminal - CH₂ - CHOH groups of PECH are converted to - CH₂ - CHOH
CH₂Cl CH₂OCH₃
groups in this step.

2. Shell Development Study

One of the objectives of Contract F04611-73-C-0051 was to improve the molecular weight and functionality of the PCDE. A special high molecular weight, high functionality PCDE sample prepared by Shell Development in 1970 showed improvements in tensile strength and bonding properties in rocket motor propellant castings. The PCDE had been made from a high molecular weight PBEP recovered from hexane extraction of standard PBEP. As this method would prove prohibitively expensive, an attempt was made to improve the desired molecular weight and functionality in the PECH or DEPECH. The improvement in the desired properties would be carried through to the PCDE.

Shell Development investigated several processes for increasing the molecular weight and functionality of the DEPECH. Two approaches were chosen. The first was to subject PECH to treatment that would retain only the higher molecular weight fraction. The second was to alter the PECH reaction to produce a product of higher molecular weight.

The first method consisted of partitioning the standard PECH between two liquids to allow removal of the lower molecular weight fraction. Several solvents were investigated, with hexane and methanol chosen for study. The tests showed that hexane or methanol extraction was feasible, with certain advantages to either solvent.

Several methods of altering the PECH reaction were studied. Included in the study were: New initiators, altering reactant ratios and addition rates, purifying the ECH, and reducing the PECH reaction temperature. Only the latter, reducing the PECH reaction temperature from 40° to 10° C, increased the molecular weight and functionality of the PECH. The improvements in these properties were carried through to the DEPECH. Details of the Shell Development work are given in Appendix A.

Three special PCDE runs were made using the high molecular weight and functionality DEPECH prepared by Shell Development. The analytical results of the runs are shown in Table 1. A typical run with "regular" DEPECH is also shown.

Two pound samples of the PCDE were sent to AFRPL for evaluation in propellant. Based upon the overall cost of DEPECH production and upon the results of the propellant evaluation, the low temperature PECH process was chosen and the DEPECH was used for all Hercules runs, beginning with Run 31.

TABLE 1. HIGH MOLECULAR WEIGHT PCDF RUNS

DEPECH Lot No.	Preparation Method	DEPECH		Run No.	PCDF	
		Molecular Weight	Functionality		Molecular Weight	Functionality
153	Hexane Extracted	2000	2.5	13	3260	1.60
156	Methanol Extracted	2400	2.8	16	3280	1.96
111	Low Temperature PECH Process	2220	2.8	19	5740	1.90
151	"Regular" DEPECH	1850	2.0	12	2980	1.70

B. PBEP PROCESS

1. Chemistry

Poly 1,2-bis(difluoroamino)-2,3 epoxy propane (PBEP) is formed by the free radical addition of tetrafluorohydrazine (N_2F_4) to DEPECH in acetone solution. Figure 1 shows the reaction.

Shell Development showed that the reaction may be carried out in a temperature range from 60° to 130° C and in a pressure range of 300 to 400 psig. They recommended a nominal 50 percent excess of N_2F_4 in order to attain complete conversion of DEPECH to PBEP. Reactor residence time can vary from 15 minutes to many hours, depending on temperature and pressure.

2. Operating Conditions and Process Description

The PBEP is manufactured in the pilot plant which consists of three operating sections: (a) Fluorination, (b) N_2F_4 manufacture, and (c) Difluoroamination. The fluorination and N_2F_4 sections are described briefly in paragraph II.D below. The difluoroamination section is used for PBEP production. The process flow diagram for this operation is shown in Figure 2. Table 2 summarizes operating conditions for the PBEP runs covered by this report. The pilot plant is located in Building 2354 at Hercules Incorporated, Bacchus Works, Magna, Utah.

The continuous flow tubular reactor system in the pilot plant, originally designed for TVOPA manufacture, needed very few modifications for use in the PBEP reactor system. Reactor conditions could be set well within those recommended by Shell Development. The system is capable of operating at temperatures of over 130° C and pressures up to 1000 psig. PBEP residence times of over 40 minutes are possible.

Early in the program, reactor residence times were fairly long, ranging from about 20 to 30 minutes. With the long residence time, the reactor temperature was kept low at from 105° to 115° C. Following Run 29, the residence time was reduced to 15 minutes and the reactor temperature was standardized at 120° C. This allowed for higher production and did not adversely affect product quality. Reactor pressure was reduced from 500 psig to 400 psig after the first three runs; the latter being sufficient to maintain the proper N_2F_4 solubility. The N_2F_4 and acetone mixtures have been shown to be hazardous if the N_2F_4 is not kept in solution. Figure 3 shows the solubility of N_2F_4 in acetone as a function of temperature and pressure.

The following paragraphs describe how preparation is made and a PBEP/PCDE run made in the pilot plant. Before any runs are made with DEPECH that has not been previously tested or used, the solubility of the DEPECH is determined by establishing at what temperature a 10 percent (w) DEPECH mixture in acetone will go into solution in 30 minutes. The procedure is described in Appendix E.

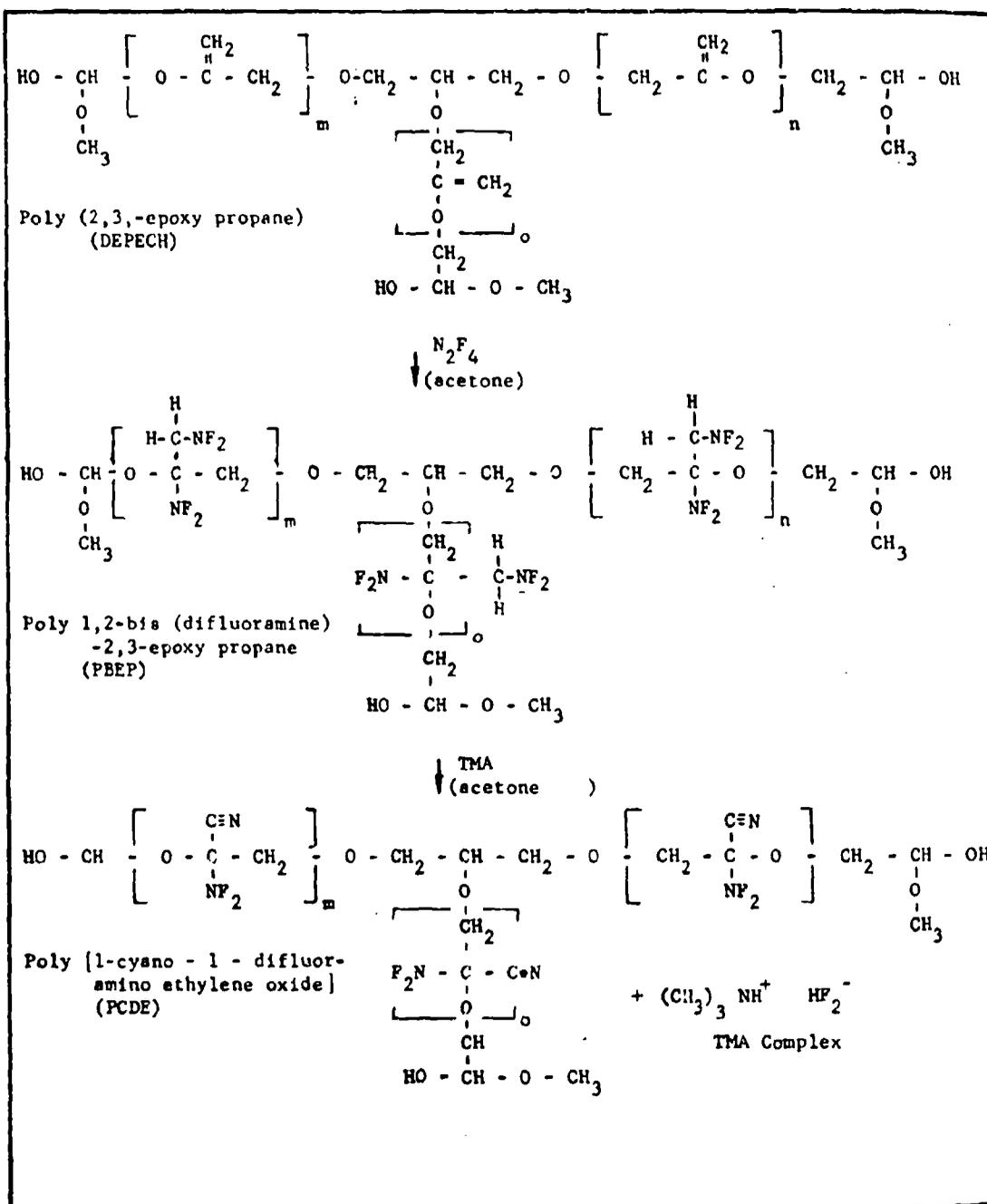


Figure 1. PCDE Chemistry

STRIP-IN

Figure 2. Process Flow Diagram (PBEP Synthesis)



TV-T-301
 2 GAL
 0 PSIG
 3155T

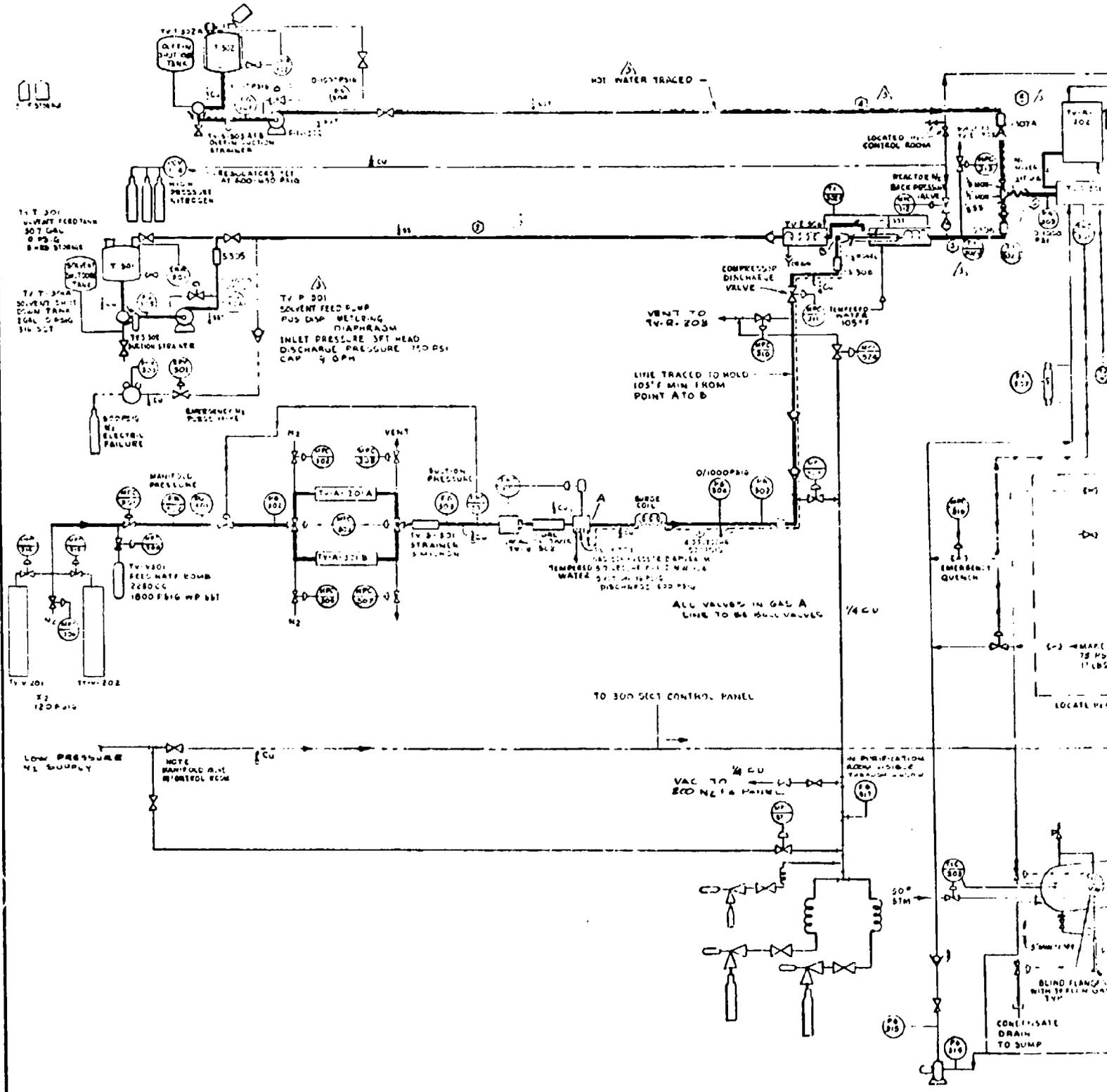
TV-T-302
 OLEFIN FEED TANK
 50 GAL
 74 PSIG WP (18 PSI MAX)
 1-8 STORAGE
 30 DIA
 30 HIGHT
 GLASS LINED

TV-P-301
 OLEFIN FEED PUMP
 1/2 HP
 1/2" DIA
 1/2" HEAD
 1/2" DISCHARGE PRESSURE

TV-C-304
 087-2154-53001-58U
 SOLVENT COOLER
 DUTY
 AREA 0.94 SQ FT
 COPR MTD
 NEW COEFF 870
 SHELL DESIGN
 DESIGN PRESSURE
 TUBES SHEET 1-8-10-11
 DES 50 500 PSIG 100' COIL

TV-E-301
 087-2154-53001-58U
 ABSORBER COOLER
 DUTY
 AREA 0.94 SQ FT
 COPR MTD
 NEW COEFF 870
 SHELL DESIGN
 DESIGN PRESSURE
 TUBES SHEET 1-8-10-11
 DES 50 500 PSIG 100' COIL

TV-R-301
 087-2154-53001-58U
 STAGE I REACTOR
 SHELL C S PIPE 12 IN M
 DESIGN 100 PSI
 TUBES: 316 SS
 O. 25 X 0.18
 155 FT LG



- TV-P-304
 HOT WATER CIRCULATOR
 88 PSI ΔP @ 0' FLOW
 28 PSI ΔP @ 10 GPM
- FILTERS**
- 8-302 CARTRIDGE 10μ POLYPROPYLENE
 - 8-303 CARTRIDGE 10μ POLYPROPYLENE
 - 8-304 STAINLESS CLOTH 5μ 10 10 IN
 - 8-305 SINTERED STAINLESS 2 50 IN
 - 8-306 STAINLESS CLOTH 10μ 60 50 IN
 - 8-307A SINTERED STAINLESS 2 50 IN
 - 8-307B SINTERED STAINLESS 2 50 IN

TV-R-301
081-2354-2201-5BU
STAGE 2 REACTOR
SHELL: C.S. PIPE 12 NOM
DESIGN 150 PSIG
TUBES: 316 SS
0.25 X 0.16
155 FT LG

TV-R-302
081-2354-2202-5BU
STAGE 3 REACTOR
SHELL: ALUMINUM
DESIGN 150 PSIG
TUBES: 316 SS CONTINUOUS
COIL
0.375 X 0.305
935 FT LG

TV-E-302
081-2354-23001-5BU
AFTERCOOLER
DUTY 3000 BTU/H
AREA 3.32 FT²
SHELL: CS
DESIGN 100 PSIG @ 21 F
TUBES: 316 SS
0.18 ID - 1447
DESIGN P. 400 PSIG @ 300 F

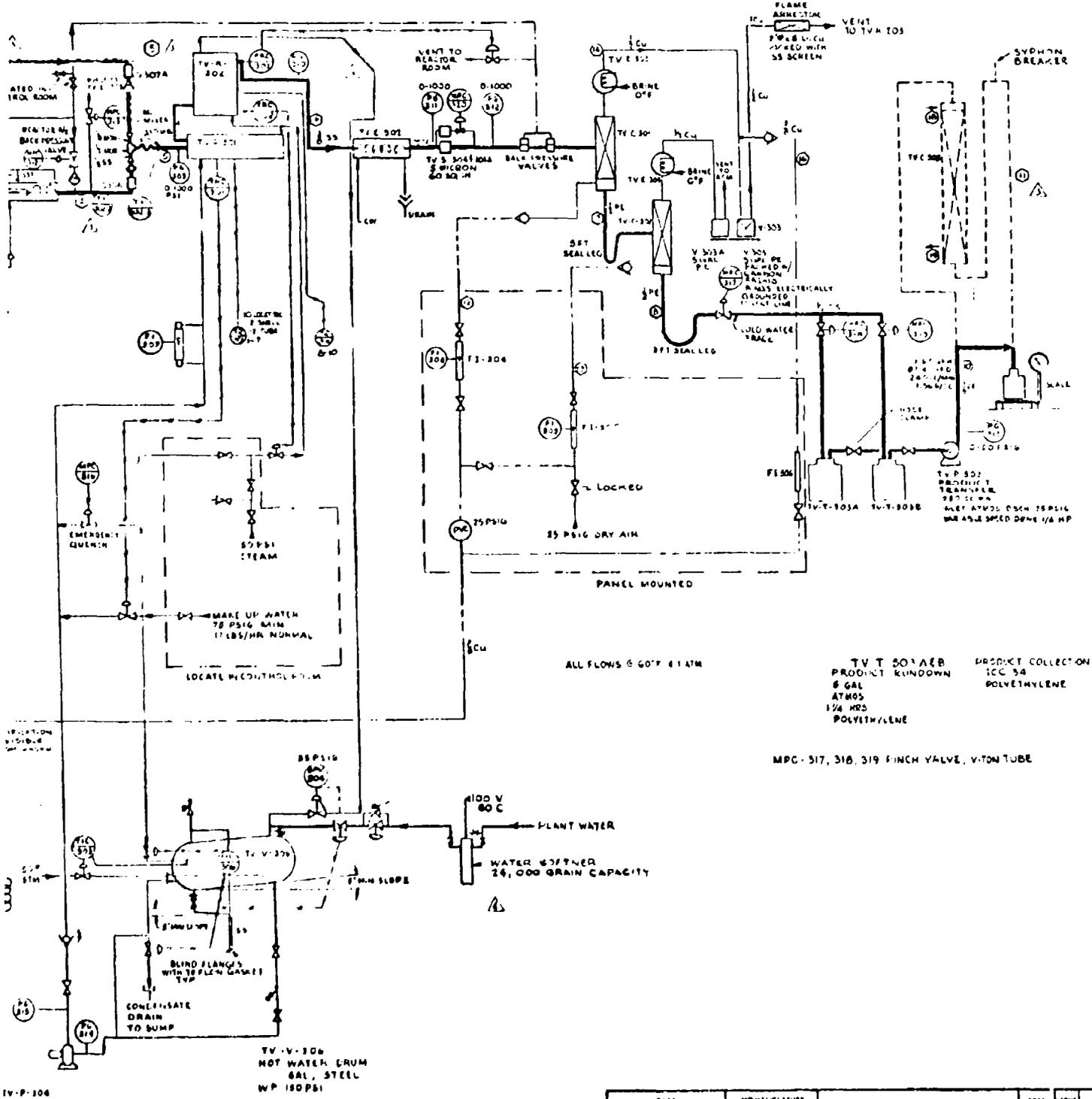
TV-C-301
081-2354-2205-5BU
STRIPPER
3 8-40 SIGSET
RASHING RINGS 216331

TV-C-302
081-2354-2206-5BU
STRIPPER
3 8-40 SIGSET
RASHING RINGS 216331

TV-E-303 & 304
081-2354-2301-5BU
ION EXCHANGE COLUMN
3 8-40 SIGSET
PACKING AMBERLMB35

TV-E-303 & 304
081-2354-2301-5BU
ION EXCHANGE COLUMN
PACKING AMBERLMB35
INSTALL WITH COLUMN

WARNING
ALL PARTS OF C-301, 102 & 303 & 304 & VENT LINES & VENTS MUST BE ELECTRICALLY BONDED TO GROUND AND GROUNDLED



TV-T-501A/B
PRODUCT RUNDOWN
8 GAL
ATMOS
1/4 HRS
POLYETHYLENE

PRODUCT COLLECTION
ICC 54
POLYETHYLENE

MPC-317, 318, 319 FINCH VALVE, V-TON TUBE

TV-P-306
NOT WATER CIRCULATOR
85 PSI ΔP @ 0' FLOW
28 PSI ΔP @ 10 GPM

TV-V-306
NOT WATER DRUM
8AL, STEEL
WP 180 PSI

QUANTITY SHOWN FOR EACH MATERIAL	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	MATERIAL	QTY REQ'D	QTY ON HAND	TO BE PURCHASED
LIST OF MATERIALS						
UNLESS OTHERWISE SPECIFIED DO NOT SCALE THIS DRAWING		APPROVALS				
DRAWN BY: _____ CHECKED BY: _____ DESIGNED BY: _____ PROJECT ENGINEER: _____ DATE: _____ APPROVED BY: _____ DATE: _____		CONTACT NO: _____ DRAWING NO: _____ SHEET NO: _____ OF _____		TV-500 PROCESS FLOW		
081-2354-11001-5BU-04						

TABLE 2. PBEP OPERATING CONDITIONS

PBEP Run No.	Date	Contract No.	DEPECH Lot No.	DEPECH Tank Temp. (°C)	DEPECH Con. (%)	PBEP Prod. Rate (lb/hr)	React. Res. Time (min)	Run Duration (hr/min)	PBEP Conc. (%)	N ₂ F ₄ Excess (%)	Acetone For N ₂ F ₄ (GPH)	DEPECH Feed Rate (GPH)	N ₂ F ₄ Rate (lb/hr)	F/S Reactor Temp. (°C)	S/S Reactor Temp. (°C)	Reactor Pressure (psig)
9	04/23/73	0051	150	55-65	16.0	4.0	29.7	9/20	11.0	25-44	3.40	1.50	3.25	115	115	500
11	05/16/73	0051	150	60-65	16.0	5.0	24.7	7/2	11.0	48.0	4.20	1.70	4.00	110	110	500
12	05/16/73	0051	151	60-65	16.0	5.0	26.1	9/59	11.0	57.0	4.00	1.57	3.38	110	110	500
13	05/25/73	0051	153	65	9.5	3.3	29.7	4/39	10.0	68.0	2.80	2.10	3.00	110	110	400
14	06/22/73	0051	151	65	16.0	5.0	23.7	5/41	11.0	41.0	4.10	2.05	4.10	110	110	400
15	06/28/73	0051	154	65	16.0	5.0	23.9	7/46	11.0	40.0	4.05	2.05	4.06	110	110	400
16	07/11/73	0051	156	65	16.0	5.0	22.2	7/0	11.0	48.0	4.40	2.05	4.30	110	110	400
17	07/19/73	0051	154	65	18.0	5.0	21.6	9/24	11.0	69.0	4.40	2.34	4.35	110	110	400
18	07/26/73	0051	155	65	18.0	6.0	19.4	6/43	11.0	49.0	5.30	2.20	5.20	110	110	400
19	07/31/73	0051	111	65	6.5	3.0	26.9	3/10	11.0	60.0	2.40	3.00	2.80	110	110	400
20	08/17/73	0051	155	70	20.0	6.0	21.8	6/7	11.0	24-35	Varied	Varied	Varied	105	105	400
21	09/06/73	0051	150, 151, 154	60-65	18.0	6.0	20.6	8/10	11.0	56.0	5.25	2.15	5.50	110	110	400
22	09/18/73	0051	92, 89	60-65	18.0	6.0	25.3	9/55	11.0	90.0	5.30	1.75	5.70	115	115	400
23	11/16/74	0051	157	62-65	9.5	4.0	28.0	0/31	11.0	100	--	2.84	--	110	110	400
24	01/31/74	0051	157	63-65	5.5	2.5	29.9	2/13	8.0	50.0	2.20	3.0	2.23	110	110	400
25	02/14/74	0051	160	53-70	5.5	2.5	19.6	2/5	8.0	46.0	1.94	2.92	2.25	110	110	400
26	02/21/74	0051	160	61-70	18.0	6.0	25.1	5/9	11.0	50.0	5.22	2.22	5.30	110	110	400
27	02/27/74	0051	160	58-70	9.5	4.0	15.4	2/27	10.0	43.0	3.05	2.74	3.33	110	110	400
28	03/12/74	0051	160	57-70	9.5	6.0	--	0/15	11.0	50.0	5.60	4.10	5.22	110	110	400
29	04/04/74	0051	160	62-70	9.5	6.0	15.4	5/47	11.0	35.1	5.52	3.95	4.53	120	120	400
30	04/23/74	0051	161, 162	52-75	10.0	6.0	15.8, 14.7	10/0, 3/15	10.0	58.1, 72.2	5.50, 7.1	3.70, 2.66	5.25, 4.1	120	120	400
31	05/03/74	0051	160	60-70	10.0	6.0	15.2	7/4	10.0	63.7	5.80	3.78	5.60	120	120	400
35	08/08/74	0051	161, 162	60-75	10.0	7.0	14.8	8/18	7.1	57.7	5.32	4.51	6.37	120	120	400
36	08/22/74	0051	161, 162	60-75	10.0	7.0	14.8	5/51	7.1	47.9	5.33	4.54	6.02	120	120	400
37	09/24/74	0051	161, 162	60-75	11.4	8.0	15.0	7/20	8.1	45.2	5.35	4.52	6.20	120	120	400
38	02/05/75	0051	161, 162	60-75	10.0	7.0	15.1	1/59	7.1	56.1	5.40	4.40	6.60	120	120	400
39	03/06/75	0051	161, 162	60-75	10.0	7.0	15.0	7/36	7.1	42.3	5.32	4.52	6.46	120	120	400
40	03/18/75	0051	162	70-75	10.0	7.0	15.1	3/47	7.1	50.0	5.30	4.53	6.50	120	120	400
41	04/25/75	0024	162	67-75	3.3	2.4	15.2	1/35	3.6	103	5.34	4.40	2.97	120	120	400
42	05/16/75	0024	165B	67-80	10.0	7.0	14.9	1/55	7.1	45.5	5.35	4.60	6.83	120	120	400

TABLE 2. PBEP OPERATING CONDITIONS (Cont)

PBEP Run No.	Date	Contract No.	DEPECH Lot No.	DEPECH Tank Temp. (°C)	DEPECH Con. (%)	PBEP Prod. Rate (lb/hr)	React. Res. Time (min)	Run Duration (hr/min)	PBEP Conc. (%)	N ₂ F ₄ Excess (%)	Acetone For N ₂ F ₄ (GPH)	DEPECH Feed Rate (GPH)	N ₂ F ₄ Rate (lb/hr)	F/S Reactor Temp. (°C)	S/S Reactor Temp. (°C)	Reactor Pressure (psig)
43	05/29/75	0024	165B	69-80	10.0	7.0	15.0	6/19	7.1	55.8	5.34	4.54	6.80	120	120	400
44	06/10/75	0024	165B	70-80	10.0	7.0	15.0	7/27	7.1	50.7	5.40	4.50	6.60	120	120	400
45	06/25/75	0024	165B	70-80	10.0	7.0	15.0	8/9	7.1	55.9	5.35	4.52	6.60	120	120	400
46	07/07/75	0024	165B	70-80	10.0	7.0	15.0	7/59	7.1	59.1	5.35	4.52	6.68	120	120	400
47	07/29/75	0024	161	70-80	10.0	7.0	15.0	7/58	7.1	57.1	5.36	4.52	6.80	120	120	400
48	08/12/75	0024	161	70-80	11.4	7.0	15.0	9/7	7.1	56.4	6.00	3.38	6.78	120	120	400
49	09/03/75	0024	161	70-80	10.0	7.0	15.0	7/50	7.1	47.5	5.37	4.53	6.50	120	120	400
50	09/09/75	0024	161, 163	71-80	10.0	7.0	15.0	7/40	7.1	48.1	5.37	4.53	6.67	120	120	400
51	09/25/75	0024	163	66-80	10.0	7.0	14.9	7/43	7.1	46.1	5.40	4.52	6.53	120	120	400
52	10/07/75	0024	163	65-80	10.0	7.0	15.0	7/50	7.1	66.1	5.36	4.52	7.31	120	120	400
53	11/05/75	0024	163	62-80	10.0	7.0	15.0	8/8	7.1	53.9	5.32	4.52	6.53	120	120	400
54	11/12/75	0024/0051	163, 165A	68-80	10.0	7.0	15.0	8/10	7.1	61.7	5.33	4.52	6.83	120	120	400
55	12/02/75	0024	165A	60-80	10.0	7.0	14.9	8/15	7.1	64.1	5.40	4.55	7.14	120	120	400
56	01/20/76	0051	165A	65-80	10.0	7.0	15.0	8/30	7.1	58.9	5.36	4.54	6.69	120	120	400
57	02/05/76	0051	165A	60-80	10.0	7.0	15.0	8/55	7.1	67.5	5.35	4.52	6.74	120	120	400
58	02/24/76	0051	164B	56-80	10.0	7.0	15.0	8/35	7.1	62.2	5.36	4.51	6.78	120	118	400
59	03/09/76	0051	164B	66-80	10.0	7.5	15.0	8/55	7.1	45.5	5.35	4.55	5.85	120	116	400
60	03/30/76	0051	164B	65-80	10.0	7.5	15.0	7/55	7.6	59.4	5.02	4.84	7.23	120	120	400
61	04/13/76	0051	164B, 165A	69-80	10.0	7.5	15.0	7/45	7.6	47.2	5.02	4.86	6.81	120	120	400
62	05/13/76	0024	30351-30353	68-75	10.0	7.5	15.0	8/13	7.6	56.6	5.02	4.84	6.94	120	120	400
63	05/25/76	0024	30252-30253	71-75	10.0	7.5	15.0	8/10	7.1	71.7	5.01	4.83	7.54	120	120	400
64	06/15/76	0024	30152-30154	73-75	10.0	7.5	15.0	8/5	7.6	49.9	5.02	4.82	6.67	120	120	400
65	06/29/76	0024	12516-36-2	74-75	10.0	7.5	15.0	8/0	7.6	44.1	5.01	4.85	6.46	120	120	400
66	07/13/76	0051	12516-36-2	74-75	10.0	7.5	15.0	7/55	7.6	48.6	5.02	4.88	6.14	120	120	400
67	08/03/76	0051	12516-36-2	71-75	10.0	7.5	15.0	4/55	7.6	54.3	5.03	4.85	7.04	120	120	400

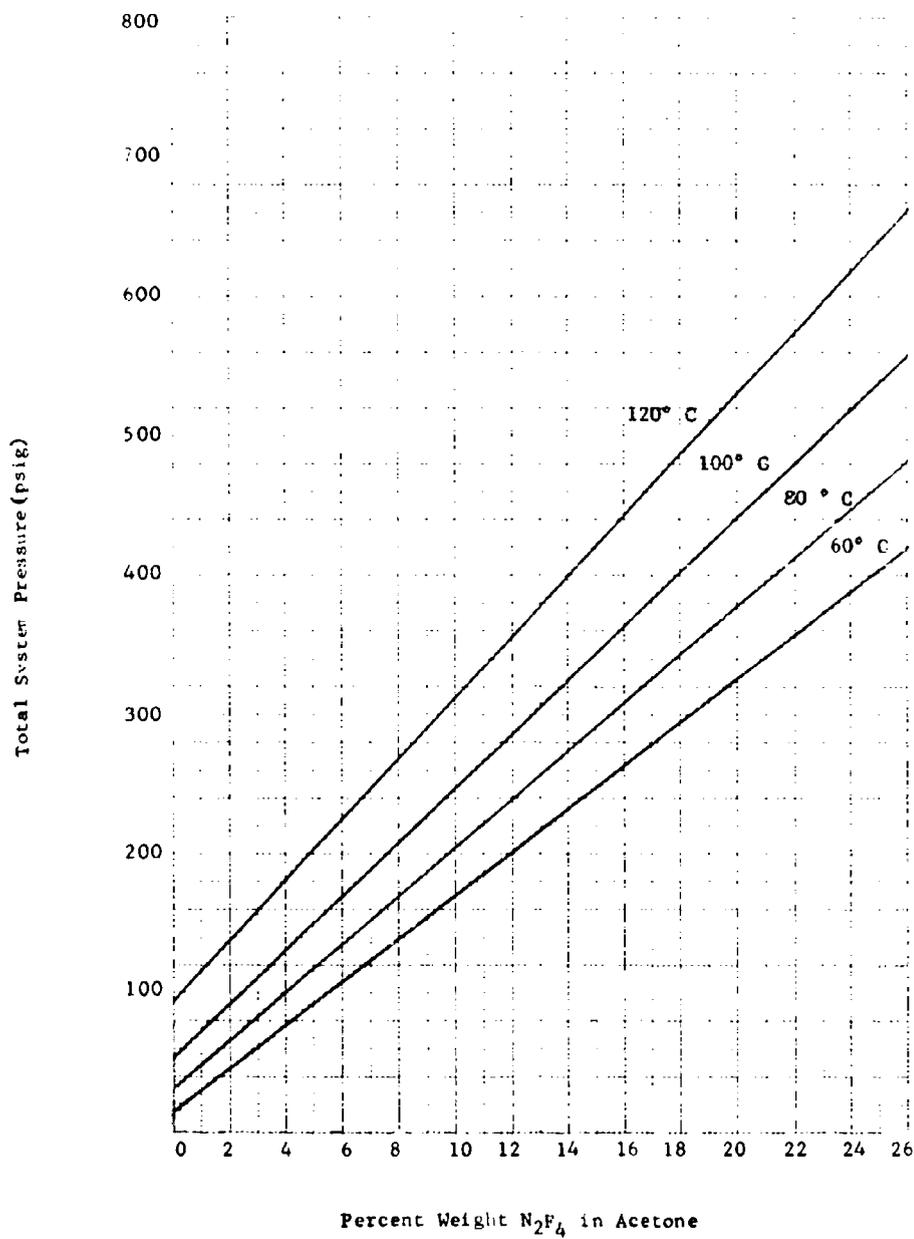


Figure 3. Solubility of N_2F_4 in Acetone

The PBEP process is a continuous operation and once established could operate indefinitely. The size of the run at the pilot plant is limited, however, both by the size of the DEPECH feed tank and the amount of N_2F_4 storage presently available. Batch sizes of from 40 to 50 pounds PCDF were accepted as being adequate.

In preparation for a run, acetone and DEPECH are mixed together in a jacketed vessel under a nitrogen blanket. The vessel is heated with steam to the dissolution temperature and held for 90 minutes with slow agitation. The vessel pressure is maintained at 15 to 20 psig for the dissolution period and during the run because the dissolution temperature is above the atmospheric boiling point of acetone.

During the DEPECH dissolution period, the PBEP reactor system is started. An N_2F_4 "burn" period of approximately 50 minutes is used in which the reactor system is operated without DEPECH feed but with other conditions, such as temperature and pressure, normal. The acetone stream of the N_2F_4 absorber is started and an N_2F_4 flow of approximately 2 lb per hour is fed to the absorber. The N_2F_4 -acetone stream then goes to the reactor system.

The N_2F_4 "burn" period has several purposes. First, it allows the system to be brought to operating condition slowly while the DEPECH is being dissolved. Second, any air in the system is purged during the "burn" period. Third, any adverse reaction between acetone and N_2F_4 will become evident during this period. Experience has shown that if air is in the system or if the N_2F_4 contains any oxygen, temperature excursions of from 50° to 75° C will occur in the reactor. A fourth reason for the burn period is to remove any trace product from a prior run that may have been left in the reactor system. If there are no temperature excursions and the equipment is functioning properly, the DEPECH is then committed and the run can start.

Ten minutes before starting the DEPECH flow, the N_2F_4 is brought to full rate and the DEPECH feed pump is started with acetone feed. After the 10 minute period at full rate, a switch from acetone to DEPECH is made and the run is underway.

The PBEP process consists of: (a) Absorbing N_2F_4 in acetone, (b) combining the N_2F_4 -acetone solution with the DEPECH-acetone solution in a tubular reactor under controlled conditions of temperature and pressure, and (c) stripping the excess N_2F_4 from the resulting PBEP product.

The N_2F_4 is fed from either of two storage banks by a compressor system through an HF trap and filter to an absorber to which acetone is also fed. The acetone is fed using a high pressure diaphragm metering pump. The absorber temperature is controlled with a tempered water system.

The stream from the absorber is mixed with the DEPECH feed stream, which is also pumped with a high pressure diaphragm metering pump. The combined streams pass through a short mix section and then into the first stage reactor consisting of 1/4-in. stainless steel tubing approximately 135 ft long. The tubing is jacketed, and tempered water is used for reaction temperature control.

The effluent from the first stage reactor then enters the second stage reactor consisting of a 3/8-in. stainless steel coil 900 ft long. The coil is contained in an insulated tank annulus, which is temperature controlled using tempered water.

The reactor effluent passes through a water-cooled heat exchanger for cooling and then through two "Grove" valves used for maintaining the reactor pressure. The product stream, now cooled to about 25 to 30° C and at atmospheric pressure, enters a two stage stripper system packed with 5/8-in. polypropylene Pall rings where the excess N_2F_4 is stripped using countercurrent nitrogen streams. The liquid streams are in series, and the gaseous stripping streams are in parallel through the stripping system. The N_2F_4 -nitrogen stream is vented to the atmosphere through a common vent. The PBEP acetone solution is collected in 5 gallon jugs.

Care is taken during startup and throughout the run to make certain flow rates, temperatures, and pressures are at flow sheet conditions. Hourly readings are taken of instruments. Tank dropout rates and N_2F_4 storage pressure drop checks are made every 1/2 hour as a check against the flow control instrumentation.

The first PBEP product is sampled, and an infrared scan is made to determine if the DEPECH is all converted and to check for impurities, such as N-fluorazoxy in the product. The PBEP conversion to PCDE is not started until the results of the sample are verified. If during the run there is an upset in any flow or any indication of a problem, the product is isolated and infrared scans are taken before the PBEP is converted to PCDE.

The PBEP is monitored to make certain that a small amount of unconverted or poor quality PBEP does not contaminate the product from the whole run. The PCDE product resulting from two jugs are collected in 55-gallon polyethylene drums. The product is sampled and an infrared scan made. If the scan shows complete conversion, the 55-gallon drums are transported to Building 2284 for further processing. As processing of the PCDE in the drums is done, the delay of sampling and analyzing does not delay the manufacturing process. If the infrared scans show incomplete conversion to PCDE, the product is reprocessed through the PCDE reactor. Only after the product from all drums are checked for conversion is blending of the product allowed.

C. PCDE PROCESS

1. Chemistry

Poly(1-cyano-1-difluoroamino-ethylene oxide) (PCDE) is produced from PBEP by dehydrofluoroamination of the primary difluoroamino groups in the PBEP molecule. The process was developed by Shell Development Company. Figure 1 shows the reaction in which trimethylamine (TMA) is used as the dehydrofluoroamination agent. The TMS was recommended by Shell Development after testing other mild bases, including ammonia. The reaction is exothermic and quite rapid and can be carried out as a batch or continuous reaction.

The process chosen for conversion of PBEP to PCDE at the pilot plant was a continuous tubular reactor with cooling water for heat removal. The TMA is added in an acetone solution (~ 12 percent TMA) at a 20 percent stoichiometric excess. A residence time of 2 minutes is adequate for conversion. The product stream is contacted with dilute (2 percent) sulfuric acid on leaving the reactor system to remove the excess TMA and thus prevent the possible degradation of the product by the mild base. If the product is not fully converted during the first pass, a second contact is possible to complete the reaction.

2. Operating Condition and Process Description

The PCDE reaction is performed in the pilot plant concurrently with PBEP production. Figure 4 shows the process flow diagram for the PCDE process. Table 3 lists the equipment description. The operating conditions are shown in Table 4.

In preparation for a run, a TMA acetone solution is made in a 55 gallon polyethylene tank. To make the solution, acetone is weighed into the tank and then TMA is condensed into the acetone. The TMA is added directly from cylinders through a 1/4-in. stainless steel coil immersed in an acetone-dry ice bath. Nominally a 12 percent acetone solution is made up. The solution is always analyzed for TMA concentration before use.

As mentioned in the previous paragraph, PBEP is collected in 5-gallon plastic jugs. When the results from the first PBEP sample is received and the product is of good quality, the PCDE reaction is started. The PBEP is pumped from the jugs with a peristaltic pump to the reactor. The TMA solution is also pumped into the reactor with a similar pump. The reactor consists of: (a) Two 1/4-in. stainless steel tubes 36-in. long, and (b) three 3/8-in. stainless steel coils having a total length of 145 feet. The 1/4-in. tube is enclosed in a 1/2-in. copper tube with cold water flowing in the annulus. The 3/8-in. coils are contained in a 55-gallon drum cold water bath.

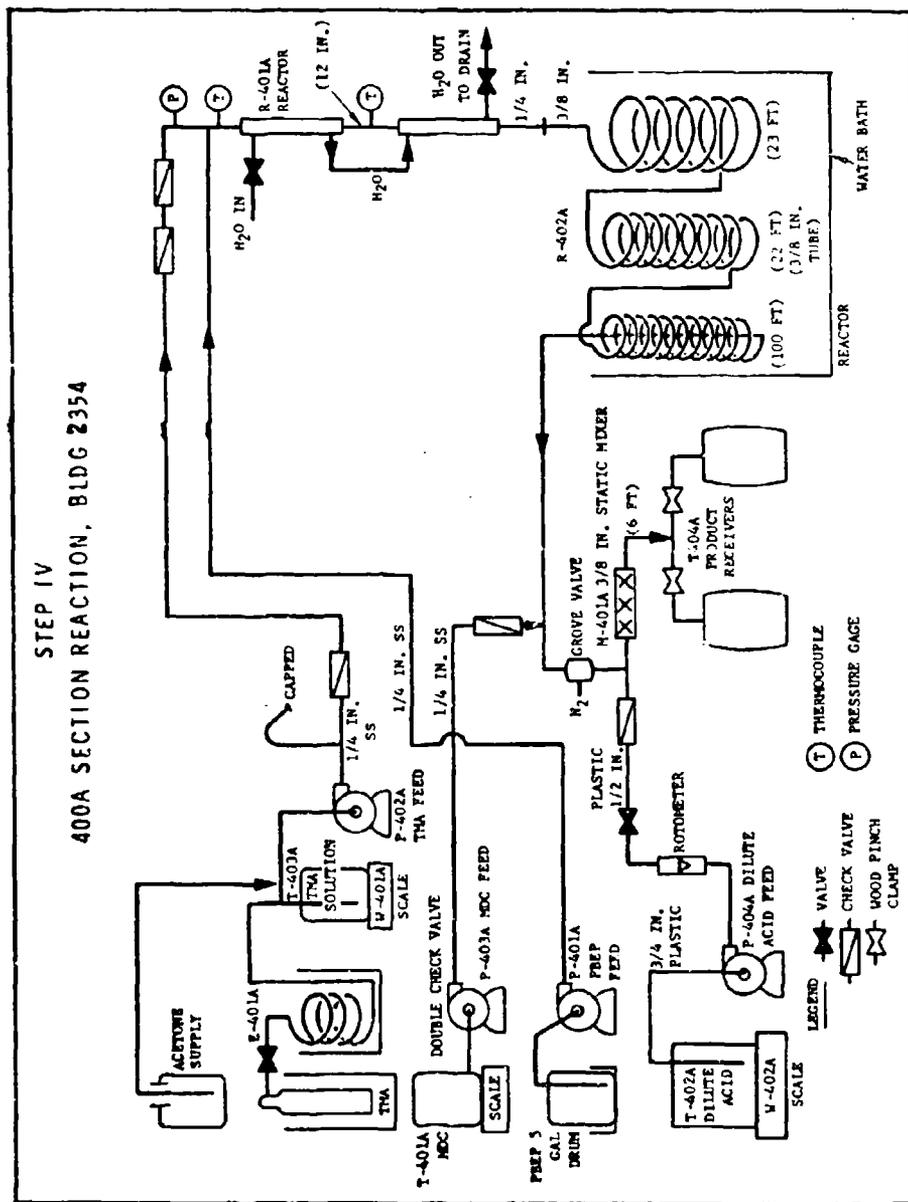


Figure 4. Process Flow Diagram (PCDE Synthesis, Bldg 2354)

TABLE 3. EQUIPMENT LIST PCDE PROCESS (BUILDING 2354)

Equipment No.	Designation	Description
P-401A	PBEP feed pump	Peristaltic, Masterflex, Nardel tube
P-402A	TMA feed pump	Peristaltic, Masterflex, Nardel tube
P-403A	MDC feed pump	Diaphragm, Whitey, stainless
P-404A	Dilute acid pump	Centrifugal, Eastern, MD50-polypropylene
T-401A	MDC	10 gal, steel
T-402A	Dilute acid	55 gal, polyethylene
T-403A	TMA solution	55 gal, polyethylene
T-404	Product receiver	55 gal, polyethylene
R-401A	Reactor	2 sections double pipe, 1/4 inch stainless steel inside 3/4 inch copper, each 3 ft. long
R-402A	Reactor	3 sections 3/8 inch stainless tube, respectively, 23 ft., 22 ft., and 100 ft., inside 55 gal water-filled tank
M-401A	Mixer	Static, Kenics, 3/8 inch ID x 11 inch long
E-401A	TMA condenser	1/4 inch stainless x 10 ft. long, coiled
W-401A	Scale	Over/under, sensitivity 0.01 lb.
W-402A	Scale	Platform, sensitivity 0.2 lb.

TABLE 4. PCDE MANUFACTURING - PCDE REACTION STEP

PCDE Run No.	Date	Residence Time (min)	TMA Concentration (%)	PBEP Concentration (%)	Temperature (°C)	TMA Rate (lb/min)	PBEP Feed (gal/hr)	MDC Rate (lb/min)	Acid Concentration (%)	Acid Rate (lb/min)	Prod. Rate (lb/hr)
9	04/23/73	5.2	10.0	9.7	38	.250	5.0	.37	1.25	2.8	3.2
11	05/16/73	3.8	11.4	11.7	30	.292	6.25	.37	1.6	2.1	4.0
12	05/18/73	3.8	11.4	11.7	30	.292	6.25	.38	1.6	2.1	4.0
13	05/25/73	4.7	14.9	10.0	43	.15	3.1	.29	1.6	1.5	1.6
14	06/22/73	4.0	13.8	11.7	53	.25	6.0	.25	1.6	2.1	4.0
15	06/28/73	3.8	10.7	11.7	57	.38	6.25	.39	1.6	2.2	4.0
16	07/11/73	3.8	18.5	11.7	40	.17	6.25	.39	1.6	2.5	4.0
17	07/19/73	3.8	15.2	11.7	54	.21	6.25	.39	1.6	2.2	4.0
18	07/26/73	3.4	13.4	13.0	50	.31	7.0	.28	2.0	2.4	4.7
19	07/31/73	4.4	10.9	8.4	40	.201	5.4	.21	2.0	1.3	2.4
20	08/17/73	3.4	16.0	11.0	45	.25	7.0	.30	2.0	2.2	4.7
21	09/06/73	3.4	12.4	11.0	35	.30	7.0	.33	2.0	2.2	4.7
22	09/18/73	3.4	17.4	11.0	40	.22	7.0	.40	2.0	2.2	4.7
23	01/16/74	--	--	--	--	--	--	--	--	--	--
24	01/31/74	4.8	19.2	7.7	35	.11	5.0	.20	2.0	1.1	2.0
25	02/14/74	4.8	18.9	7.7	35	.11	5.0	.20	2.0	1.1	2.0
26	02/21/74	3.4	13.4	11.0	59	.21	7.0	.33	2.0	2.2	4.7
27	02/27/74	4.0	13.4	10.0	45	.20	6.0	.30	2.0	2.2	3.2
28	03/12/74	--	--	--	--	--	--	--	--	--	--
29	04/04/74	2.7	13.3	9.5	30	.26	9.7	.37	2.0	2.2	4.7
30	04/23/74	2.7	17.8	10.0	32	.222	9.7	.32	2.0	2.2	4.7
31	05/03/74	2.1	16.1	10.0	35	.29	11.3	.32	2.0	2.2	5.5
35	08/08/74	2.6	12.4	10.9	34	.414	11.0	.40	2.0	3.0	6.2
36	08/22/74	2.6	13.4	10.9	35	.38	11.0	.40	2.0	3.0	6.2
37	09/24/74	2.6	12.1	11.0	35	.425	11.0	.40	2.0	3.0	6.2
38	02/05/75	2.4	8.6	10.0	27	.60	11.0	.40	2.0	3.0	6.2
39	03/06/75	2.4	12.6	10.0	29	.41	11.0	.40	2.0	3.0	6.2
40	03/18/75	--	--	--	--	--	--	--	--	--	--
41	04/25/75	2.4	12.1	3.6	20	.30	11.0	.30	2.0	3.0	2.0
42	05/16/75	2.4	12.2	10.0	32	.46	11.0	.40	2.0	3.0	6.2
43	05/29/75	2.4	12.4	10.0	34	.44	11.0	.40	2.0	3.0	6.2
44	06/10/75	2.4	19.6	10.0	38	.30	11.0	.50	2.0	3.0	6.2

TABLE 4. PCDE MANUFACTURING - PCDE REACTION STEP (Cont)

PCDE Run No.	Date	Residence Time (min)	TMA Concentration (%)	FBEP Concentration (%)	Temperature (°C)	TMA Rate (lb/min)	FBEP Feed (gal/hr)	MDC Rate (lb/min)	Acid Concentration (%)	Acid Rate (lb/min)	Prod. Rate (lb/hr)
45	06/25/75	2.4	20.0	10.0	37	.28	11.0	.50	2.0	3.0	6.2
46	07/07/75	2.4	11.3	10.0	39	.45	11.0	.50	2.0	3.0	6.2
47	07/29/75	2.4	13.0	10.0	40	.39	11.0	.60	2.0	3.0	6.2
48	08/12/75	2.4	13.8	10.0	40	.36	11.0	.60	2.0	3.0	6.2
49	09/03/75	2.4	11.9	10.0	41	.42	11.0	.50	2.0	3.0	6.2
50	09/09/75	2.4	11.7	10.0	41	.43	11.0	.50	2.0	3.0	6.2
51	09/25/75	2.4	12.5	10.0	40	.40	11.0	.50	2.0	3.0	6.2
52	10/07/75	2.4	12.5	10.0	33	.40	11.0	.50	2.0	3.0	6.2
53	11/05/75	2.4	10.8	10.0	33	.46	11.0	.50	2.0	3.0	6.2
54	11/12/75	2.4	12.9	10.0	32	.39	11.0	.50	2.0	3.0	6.2
55	12/02/75	2.4	12.4	10.0	34	.40	11.0	.50	2.0	3.0	6.2
56	01/20/76	2.4	13.8	10.0	25	.36	11.0	.50	2.0	3.0	6.2
57	02/05/76	2.4	14.1	10.0	25	.36	11.0	.50	2.0	3.0	6.2
58	02/24/76	2.4	11.8	10.0	24	.42	11.0	.50	2.0	3.0	6.2
59	03/09/76	2.4	11.3	10.0	30	.42	11.0	.50	2.0	3.0	6.2
60	03/30/76	2.4	11.2	10.7	32	.46	11.0	.50	2.0	3.0	6.6
61	04/13/76	2.4	12.2	10.7	33	.44	11.0	.50	2.0	3.0	6.6
62	05/13/76	2.4	12.6	10.7	32	.42	11.0	.50	2.0	3.0	6.6
63	05/25/76	2.4	12.8	10.7	33	.42	11.0	.50	2.0	3.0	6.6
64	06/15/76	2.4	11.8	10.7	35	.45	11.0	.50	2.0	3.0	6.6
65	06/29/76	2.4	12.8	10.7	38	.38	11.0	.50	2.0	3.0	6.6
66	07/13/76	2.4	11.9	10.7	40	.45	11.0	.50	2.0	3.0	6.6
67	08/03/76	2.4	12.0	10.7	42	.45	11.0	.50	2.0	3.0	6.6

TABLE 4. PCDE MANUFACTURING - PCDE REACTION STEP (Cont)

Feed Rate (gal/hr)	Water Column: 1 (lb/min)	Water Column 2 (lb/min)	Water Temperature (°F)	Dry Rate (gal/hr)	Sieves Used	Thermal Stability		PCDE Run No.
						cc/gm 140°C	(100 hr) 110°C	
6.7	3.5	2.2	Ambient	3.5	3A	236	8.8	9
3.8	2.1	2.5	60	2.7	3A	158	6.6	11
4.2	3.0	2.5	60	4.4	3A	142	8.4	12
2.4	2.4	2.4	66	4.2	3A	150	7.3	13
3.0	3.0	2.0	--	--	--	> 1000	--	14
5.0	3.0	2.1	44-50	2.5	13X	208	10.5	15
6.0	3.0	2.9	40	3.0	3A/13X	190,195	6.9,12.5	16
3.0	3.0	2.9	36-40	3.2	3A/13X	120,146	7.8, 7.2	17
3.0	3.0	2.9	45-50	3.0	3A/13X	142	9.0	18
3.0	3.0	2.9	45-50	3.0	3A/13X	110	4.8	19
4.0	2.5	2.5	49-53	1.5	3A/13X	> 1000	--	20
4.0/2.25	2.5	2.5	57	6.25	3A/13X	222	10.0	21
--	--	--	--	--	--	> 1000	--	22
--	--	--	--	--	--	> 1000	--	23
--	--	--	--	--	--	> 1000	--	24
6.0/1.7	2.5	2.8	60-64	5.0	3A/13X	140	--	25
--	--	--	--	--	--	960	--	26
--	--	--	--	--	--	> 1000	--	27
--	--	--	--	--	--	--	--	28
7.5/3.0	2.3/2.3	2.8/2.8	42-52	5.0	3A/13X	170	--	29
7.5/3.3	2.3/2.3	2.8/2.8	50-68	5.0	3A/13X	220	--	30
6.0/5.2	2.3/2.3	2.8/2.8	60	4.7	3A/13X			31
7.0/4.0	3.17/3.17	2.5/2.5	55-60	5.8	3A/13X			35
7.0/4.0	3.17/3.17	2.5/2.5	57-65	5.8	3A/13X			36
7.3/3.7	3.17/3.17	2.5/2.5	62	5.6	3A/13X	107	8.7	37
5.0	3.54	3.4	42	5.6	3A/13X	249	11.7	38
6.7	2.8	2.8	54-57	5.6	3A/13X	133	--	39
--	--	--	--	--	--	--	--	40
7.4	3.5	2.5	56	5.3	3A/13X	182	11.4	41
7.4	3.5	2.5	56	5.3	3A/13X	200	7.5	42
7.4	3.5	2.8	57	5.3	3A/13X	111	8.0	43
7.9	3.5	2.3	56	5.3	3A/13X	89	6.4	44

TABLE 4. PCDE MANUFACTURING - PCDE REACTION STEP (Cont)

Feed Rate (gal/hr)	Water Column 1 (lb/min)	Water Column 2 (lb/min)	Water Temperature (°F)	Dry Rate (gal/hr)	Sieves Used	Thermal Stability cc/gm (100 hr)		PCDE Run No.
						140°C	110°C	
8.1	3.5	2.3	57	6.6	3Å/13X	204	8.8	45
7.9	3.5	2.3	66	5.6	3Å/13X	120	7.4	46
7.9	3.5	2.3	60	6.0	3Å/13X	107	8.2	47
7.9	3.5	2.3	60	6.0	3Å/13X	190	10.1	48
7.9	3.5	2.2	60	6.5	3Å/13X	128	8.8	49
7.9	3.34	2.5	60	5.6	3Å/13X	133	9.2	50
7.5	3.34	2.5	60	5.4	3Å/13X	151	10.8	51
7.5	3.34	2.5	59	5.8	3Å/13X	115	6.7	52
7.5	3.34	2.5	60	6.6	3Å/13X	131	8.6	53
7.5	3.34	2.5	60	6.6	3Å/13X	211	8.4	54
7.5	3.34	2.5	60	6.6	3Å/13X	153	9.0	55
7.5	3.34	2.5	58	5.9	3Å/13X	138	7.5	56
7.5	3.34	2.20	55	5.9	3Å/13X	147	7.4	57
7.5	3.34/3.34	3.34/3.34	56	5.9	3Å/13X	160	8.2	58
7.5	3.34/3.34	3.34/3.34	56	5.8	3Å/13X	200	7.7	59
7.5	3.34/3.34	3.34/3.34	57	5.8	3Å/13X	186	8.5	60
7.5	3.34/3.34	3.34/3.34	57	5.8	3Å/13X	133	7.5	61
7.5	3.34/3.34	3.34/3.34	57	5.8	3Å/13X	71	6.3	62
7.5/7.5	3.34/3.34	3.34/3.34	58	5.8	3Å/13X	102	7.0	63
7.5/7.5	3.34/3.34	3.34/3.34	57	5.8	3Å/13X	80	7.0	64
7.5/7.5	3.34/3.34	3.34/3.34	56	5.8	3Å/13X	160	6.6	65
7.5/7.5	3.34/3.34	3.34/3.34	58	5.8	3Å/13X	71	5.0	66
7.5/7.5	3.34/3.34	3.34/3.34	57-60	5.8	3Å/13X	178	6.6	67



Following the reactor, methylene chloride (MDC), is pumped into the reactor stream. The product stream, consisting of PCDE and excess TMA in acetone and MDC, then flows through a pressure regulating "Grove" valve which maintains 5 to 10 psig backpressure on the reactor system.

A dilute (2 percent) sulfuric acid stream is then pumped into the process stream. The stream passes through a Kenics static mixer and discharges into a 55-gallon polyethylene drum where the aqueous phase and the product-bearing organic phase separate. The sulfuric acid stream is added for two purposes. First, the acid neutralizes the excess TMA, which would cause degradation of the PCDE under prolonged contact. Second, the stream acts as a first contact stage for removal of acetone from the product.

The methylene chloride added after the reaction step is the carrier solvent used for shipment of the final product. An attempt was made early in the project to add the TMA in a methylene chloride solution and eliminate the use of acetone, which later has to be removed. The TMA and MDC formed a solid complex, which caused plugging in the reactor system. Therefore, this method of TMA addition was abandoned.

The 55-gallon polyethylene drums, each containing PCDE product converted from two 5-gallon PBEP product containers, are transported to Building 2284 for acetone removal, drying, and packaging. Infrared scans of the product from each drum are checked. If any PBEP has not been completely converted to PCDE, that drum is reprocessed with TMA solution through the reactor system at the pilot plant.

Figure 5 and Table 5 describe the equipment at Building 2285 used for acetone removal, drying, and packaging.

The heavy organic phase in the drums containing the PCDE and about 30 percent acetone is pumped to the top of a countercurrent extraction column. Two 6-in. Pyrex columns 6-feet long are used in series. Cold water enters the bottom of these columns and strips the acetone from the product stream. The columns are packed with 5/8-in. polypropylene Pall rings. A second pass through the columns is normally required to remove the acetone to levels below 1 percent. The second pass through the columns is generally made at least 1 day following the first wash to allow the PCDE to settle. Intimate contact of the PCDE with water in the wash column causes inclusion of small water droplets in the PCDE. Experience has shown that, if this water separates before a second wash is made, the second wash is made easier with less emulsion formation in the column.

TABLE 5. EQUIPMENT LIST PCDE PROCESS BUILDING 2284

Equipment No.	Designation	Description
P-402B	PBEP transfer	Peristaltic, TAT HiCAP, Nordel tube
P-401B	PBEP feed	Peristaltic, Masterflex, Nordel tube
P-403B	MDC feed	Diaphragm, Whitey
P-404B	Dilute acid feed	Peristaltic, Masterflex, Tygon tube
P-405B	Column feed	Peristaltic, Masterflex, Nordel tube
P-407B	Waste water transfer	Peristaltic, TAT, HiCAP Nordel tube
P-406B-1	Extractor interstage	Diaphragm, double head Maden Metriflow
P-406B-2	Extractor heavy phase transfer	Teflon diaphragm
T-401	MDC feed	Steel, 10 gal
T-402	Dilute acid feed	Stainless steel, 55 gal
T-403	Product hold	Polypropylene, 20 gal
T-404	Column feed	Polypropylene, 30 gal
T-405	Waste water hold	Polypropylene, 55 gal
T-406	Waste treatment	Polyethylene, 350 gal
T-407	Product receiver	Polyethylene, 5 gal or steel, 5 gal
V-401	PBEP feed desiccator	Stainless, explosive standards, 55 gal
C-401	Extractor	6 in. dia x 6 ft long, Pyrex glass with polypropylene Raschig rings 1/2 in.
C-402	Extractor	4 in. dia x 6 ft long, Pyrex glass with polypropylene Pall rings 5/8 in.
C-403	Drying column	4 in. dia x 6 ft long, 304 stainless with 13X mole sieve 1/16 in.
C-404	Drying column	4 in. dia x 6 ft long, 304 stainless with 3A mole sieves 1/16 in.
R-401	Reactor	3/8 x 15 in. stainless
R-402	Reactor	3/8 x 100 in. stainless

During the wash steps, considerable emulsion is formed in the columns. The emulsion can cause flooding. The problem usually is greater in the second wash when most of the acetone has been removed. A wash water temperature of 50° to 60° F is best. Higher temperature gives more emulsion, and lower temperature proved no more effective and was not economical to maintain.

The PCDE from the column, following the second wash, is collected in a 30-gallon polyethylene tank and allowed to settle for 24 to 48 hours. Included water separates and rises to the surface. The product is then pumped in series through two 3-in. diameter x 72-in. long columns containing molecular sieves. The first column contains 13X sieves for acetone and water removal and the second contains 3A sieves for water removal. Usually the product is held for blending with a second run and then packaged for shipment in 5-gallon phenolic lined steel drums.

Blending and packaging of PCDE for shipment is done at Building 2284. The dried PCDE is collected in a 30- or 55-gallon polyethylene drum. The PCDE is sampled and analyzed for PCDE, water, and acetone concentration, and the thermal stability is tested at 110° C and 140° C. If the analysis is within specification, the material is blended with a second run.

If the composite blend is below 30 percent PCDE, the material is sparged with pure nitrogen to remove excess methylene chloride. A sample of the blend is taken and complete analysis of the product is reported on a data sheet shown in Appendix D.

Packaging is accomplished by pumping from the PCDE drum to phenolic-lined 5-gallon metal cans using peristaltic pumps. The cans are tared and exactly 50 lb of solution are pumped into each can. The last can, of course, containing somewhat less than 50 lb. To each can, 300 cc of 3A molecular sieves are added to keep the solution dry during shipment and storage.

Aqueous waste from the 55-gallon product drums and from the top of the extraction columns is collected in a 350-gallon polyethylene tank. The waste is neutralized with lime and sodium hydroxide to a pH of at least 10.5. The high pH destroys traces of PCDE contained in the waste water. The water is held at the high pH for at least 30 minutes, then adjusted to a pH of 5.5 to 7.0 using H₂SO₄ before draining to a waste evaporation pond near Building 2284.

D. DFU/N₂F₄

1. Process

The N₂F₄ gas used in the PCDE process is manufactured in the pilot plant. The process was installed as part of a manufacturing study for making TVOPA, and a detailed description of the process has been published. A brief description is given here because of the impact of maintenance, scheduling, and quality problems on the PCDE process.

The first step in the manufacture of N₂F₄ is the fluorination of urea to form difluorourea (DFU). This process is carried out in the pilot plant in a stainless steel batch fluorination reactor. The reaction is maintained at approximately 0° C using a refrigerated coolant (ethylene glycol). The coolant in the reactor flows through both coils and jacket. The batch size of DFU is determined by the beginning pressure and temperature of the 12 fluorine cylinders containing approximately 72 lb of fluorine. The amount of urea used depends upon the calculated fluorine content of the cylinders. The same amount of water is always used for dissolution of the urea, thus giving the same volume of solution in the batch fluorination reactor. This is important to maintain good circulation in the reactor during fluorination.

Fluorine and nitrogen are bubbled into the bottom of the reactor. The nitrogen acts as both a diluent and as a gas lift to provide mixing in the reactor. The process is continued until the pressure in the fluorine cylinders has dropped to 5 to 10 psig.

The above method of determining fluorine usage by calculation has proven to be better than fluorinating until breakthrough of fluorine occurs. Overfluorination apparently causes destruction of DFU already formed.

The flow of fluorine is controlled to keep the operating temperature of the reaction at $-1 \pm 1^{\circ}$ C. Normally, 4 to 5 hours is required to complete a batch of DFU. Once the DFU is formed, it is transferred to storage tanks where the temperature is maintained between -5° C and -10° C until used. The DFU should be converted as soon as possible for it degenerates on storing, even at the low temperatures. Freezing the DFU at -12° C would preserve it, but the long time required and the care needed in thawing make freezing impractical.

Handling of fluorine is a difficult problem because of its highly toxic and reactive nature. Great care must always be taken to maintain utmost cleanliness of any equipment used in handling fluorine. Because of its corrosive nature, frequent changes in process lines and equipment are necessary. The fluorination reactor is especially susceptible to corrosion because of the aqueous media in the reactor and the fact that for every mole of DFU formed two moles of HF are also formed. Equipment and process lines are frequently leak checked and inspected.

The DFU is converted to N_2F_4 in a two-step process. The continuous unit produces approximately 6 lb of N_2F_4 per hour. The DFU is first converted to HNF_2 by reaction in a Teflon reactor with concentrated sulfuric acid. The operating temperature is approximately $95^\circ C$. The HNF_2 and CO_2 formed in the reactor separate from the aqueous acid phase and pass to two packed columns where the HNF_2 is oxidized to N_2F_4 .

The gases then pass through a countercurrent sodium hydroxide column where the CO_2 is scrubbed out. The N_2F_4 gases pass through a Drierite packed column for drying and then through an HF trap before being compressed into one of two N_2F_4 storage banks.

Most of the equipment in the N_2F_4 manufacturing section is constructed of PVC or Teflon because of their corrosion resistance to the process streams. Because of the toxic nature of N_2F_4 and its flammability, the system is frequently leak checked.

A discussion of some of the specific problems occurring in the DFU- N_2F_4 systems are discussed in Section IV.

SECTION III

PRODUCTION SUMMARY

A total of 1450 lb of acceptable PCDE was produced under the two contracts; 992 lb under F04611-73-C-0051 and 458 lb under F04611-75-C-0024. In addition, 63.3 lb of off-grade material was shipped to Naval Weapons Center, China Lake, Ca., for experimental work. Several runs were made containing N-fluorazoxy and were destroyed. A total of approximately 90 lb of off specification material was disposed of for this reason.

The operation of the PCDE process is continuous; however, some physical restrictions currently in existence in the pilot plant limit the amount of PCDE produced in a run. The plant has been demonstrated capable of operating at 8 lb PBEP per hour (~ 6.2 lb PCDE per hour). The conversion of PBEP to PCDE has been demonstrated at the rate of 8 lb per hour. The PBEP reactor system as presently constituted may be capable of an additional 20 percent; however, this as yet has not been demonstrated.

The size of the DEPECH feed tank presently limits the size of a run. The DEPECH must be predissolved and kept under pressure and at a temperature of 60° to 70° C during the run. A total of about 60 minutes is required to bring the DEPECH into solution. The run then consists of the amount of DEPECH brought to solution in the tank. The maximum amount of DEPECH charge to the tank is 26 pounds, equivalent to ~45 pounds of PCDE.

A second limitation is the N_2F_4 operating storage capacity. Each of the two banks of 15 N_2F_4 cylinders hold enough N_2F_4 for one run (~ 45 lb PCDE). Operation of the N_2F_4 manufacturing system on a day shift schedule usually produces a little more than enough N_2F_4 in a week to make one run. The N_2F_4 production rate while on stream just about matches the amount needed to make 7 lb of PCDE per hour.

The tank size and operating rates of the washing and drying section of the PCDE process are currently sized for handling 50 lb runs.

Table 6 lists the product analyses for the material shipped under the contracts. Complete analyses were made only for the runs blended for shipment. The quality of individual runs was considered acceptable for blending when: (1) The infrared scan showed complete conversion of DEPECH through the PCDE, (2) there was no evidence of N-fluorazoxy, and (3) the thermal stability results were within the proper limits.

The results shown in Table 6 indicate that much variation in thermal stability and molecular weight occurred between runs that had the same operating conditions and same feed stock. It is recognized that small variations in temperature and pressure occur during a run and that conditions are never exactly identical. Small amounts of material of poor thermal stability produced for any reason could adversely affect the entire composited run.

TABLE 6. PRODUCT ANALYSIS

Lot No.	PCDE Runs	Concentration (%)	Molecular Weight By VPO	Nitrogen (%)	Fluorine (%)	Acetone (%)	Hydroxyl Equivalent per 100 gms		Hydroxyl Functionality		Thermal Stability cc/gm (100 hr)	
							Chemical Reactivity	Gelation	Chemical Reactivity	Gelation	110°C	140°C
9	9	12.5	2630	20.0	26.8	3.3	1436	1.83		8.8	236	
11	11	17.2	2940	21.1	27.5	1.8	1630	1.80		8.5	158	
12	12	8.4-10.2	2980	20.6	26.4	3.5	1762	1.70		8.4	142	
13	13	14.4	3260	20.8	26.4	1.7	1934	1.69		7.3	150	
15	15	18.3	2610	20.7	26.9	1.9	1750	1.49		10.5	208	
16A	16	9.9	3280	20.9	26.1	1.06	1760	1.96		6.9	190	
16B	16	12.0	3070	21.6	26.3	< 0.1	1841	1.66		12.5	195	
17A	17	12.0	3070	21.6	26.3	< 0.1	1831	1.65		7.8	120	
17B	17	18.9	3080	20.3	28.1	1.87	1678	1.83		7.2	146	
18	18	17.7	3080	23.8	26.7	0.8	1572	1.96		9.0	142	
19	19	11.0	3340	23.0	27.4	< 0.1	1752	1.90		4.8	110	
21	21	13.1	2650	21.5	26.8	1.03	1710	1.55		10.0	222	
31	25, 29, 30, 31	20.7	3040	21.6	27.2	< 0.1	1567	1.94		7.5	124	
36	35, 36	15.2	2970	21.5	27.2	0.1	1575	1.89		8.4	150	
37	37	23.2	3100	22.2	27.3	0.1	1557	1.99		8.7	107	
B-47	38, 39, 42, 43, 44	20.6	3045	21.0	27.0	0.53	1705	1.74	2060	8.8		
Blend 46	45, 46	23.1	3089	23.1	27.0	0.17	1830	1.69	2160	7.8		
Blend 48	47, 48	21.8	2439	23.3	27.4	0.13	1750	1.39	1793	9.1	159	
Blend 50	49, 50	24.9	2600	22.6	27.4	< 0.1	1690	1.54	1912	9.6	157	
Blend 54	51, 53, 54	20.6	2931	17.2	27.6	< 0.1	1760	1.67	2171	8.5	144	
Blend 55	55	19.7	2780	17.4	27.8	< 0.1	1730	1.61	2014	9.0	153	
Blend 57	56, 57	32.8	2700	18.6	27.7	0.7	1770	1.53	2061	7.9	177	
Blend 59	58, 59	28.7	3414	18.3	27.8	0.36	1690	2.02	2421	8.3	160	
Blend 61	60, 61	28.0	3194	20.0	28.5	< 0.1	1790	1.78	2515	7.6	110	
Blend 63	62, 63	29.0	3617	18.5	28.8	< 0.1	1790	2.02	3040	6.8	93	
Blend 65	64, 65	34.7	3021	18.8	27.3	0.218	1780	1.70	2306	6.8	173	
Blend 66	66	33.9	3441	18.8	28.9	0.127	1820	1.89	2709	5.0	71	
Blend 67	67	25.9	3644	18.7	27.7	< 0.1	1850	1.97	2869	6.6	178	
Blend 68	(a)	12.0	3260	18.6	26.4	0.349	1820	1.79	2650	6.9	107	
52	52	18.5	3348	18.6	26.0	< 0.1	1870	1.79	2657	6.7	115	
41	41	20.5	2950	18.7	26.9	1.56	1720	1.72	2252	17.4	182	

(a) Recovered product from emulsion from all runs following Run 45.

The DEPECH feed itself seemed to be the cause of some of the variation in product. Some lots of DEPECH produced PCDE that was more difficult to wash in the acetone removal step. Certain DEPECH lots required more heat to get into solution in acetone. The color and consistency of DEPECH lots varied considerably even when the chemical analyses were similar.

The molecular weights of the PCDE product was generally lower than would be expected based on the molecular weight of the DEPECH. The problem is probably due to cleavage of the molecule under the PBEP and PCDE reactor conditions.

The high temperature and pressure and presence of water and HF in the reactor could cause cleavage. Evidence of cleavage is indicated by the increase in the carbonyl band of the infrared scan of the PBEP and a further increase in the same band of the PCDE. Early tests were run in the laboratory holding DEPECH/acetone solutions at 60° F for several hours, and infrared scan showed no evidence of cleavage under the conditions in the feed tank.

Beginning with product blend 54, problems with the nitrogen analysis occurred. The fluorine and nitrogen in the product have a theoretical 1:1 mole ratio in PCDE and, while the fluorine results stayed fairly constant, the nitrogen value dropped. Both a new analytical machine and new operator were used beginning at that time and, although not resolved before the end of operation, the problem is believed to be analytical rather than a real change in the product.

Recommendations and suggestions given in Section VII may help to resolve some of the problems of process control and product quality in future runs.

Figures 6, 7, and 8 show typical scans of DEPECH, PBEP, and PCDE, respectively. Figure 9 shows PCDE product containing N-fluorazoxy.

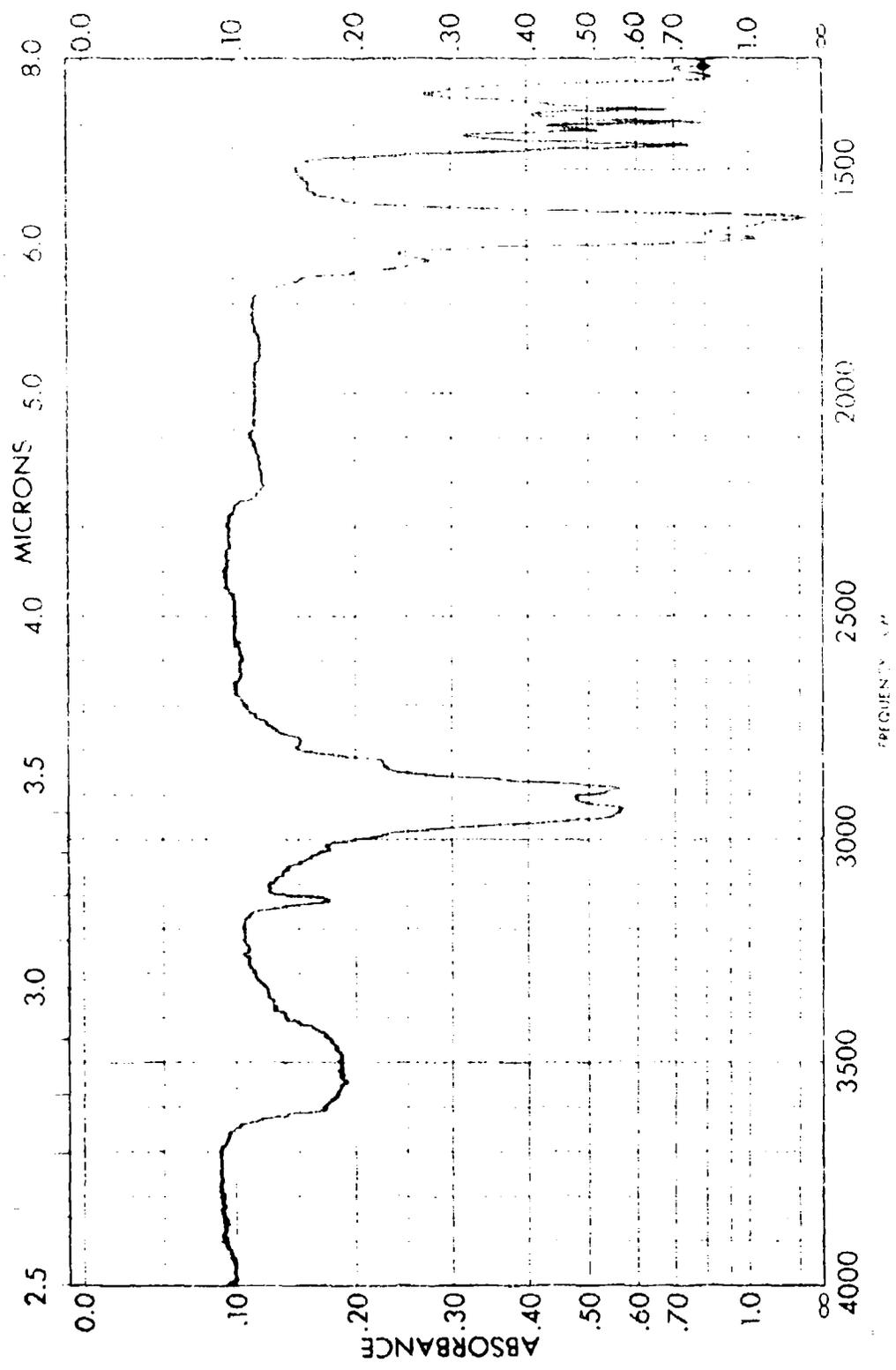


Figure 6. Infrared Scan of DEPECH (Lot 161/162)

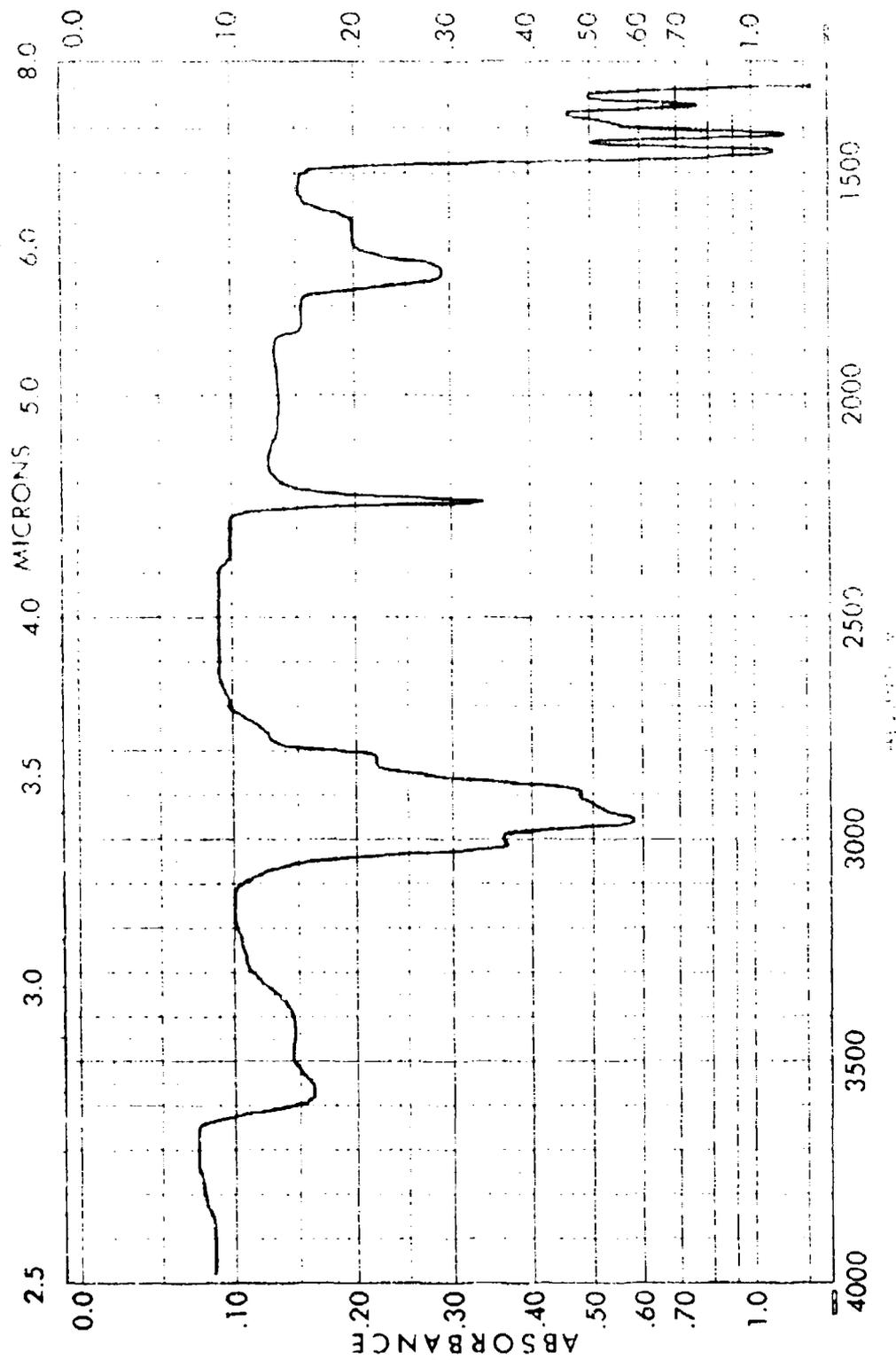


Figure 7. Infrared Scan of PREP (Run 64)

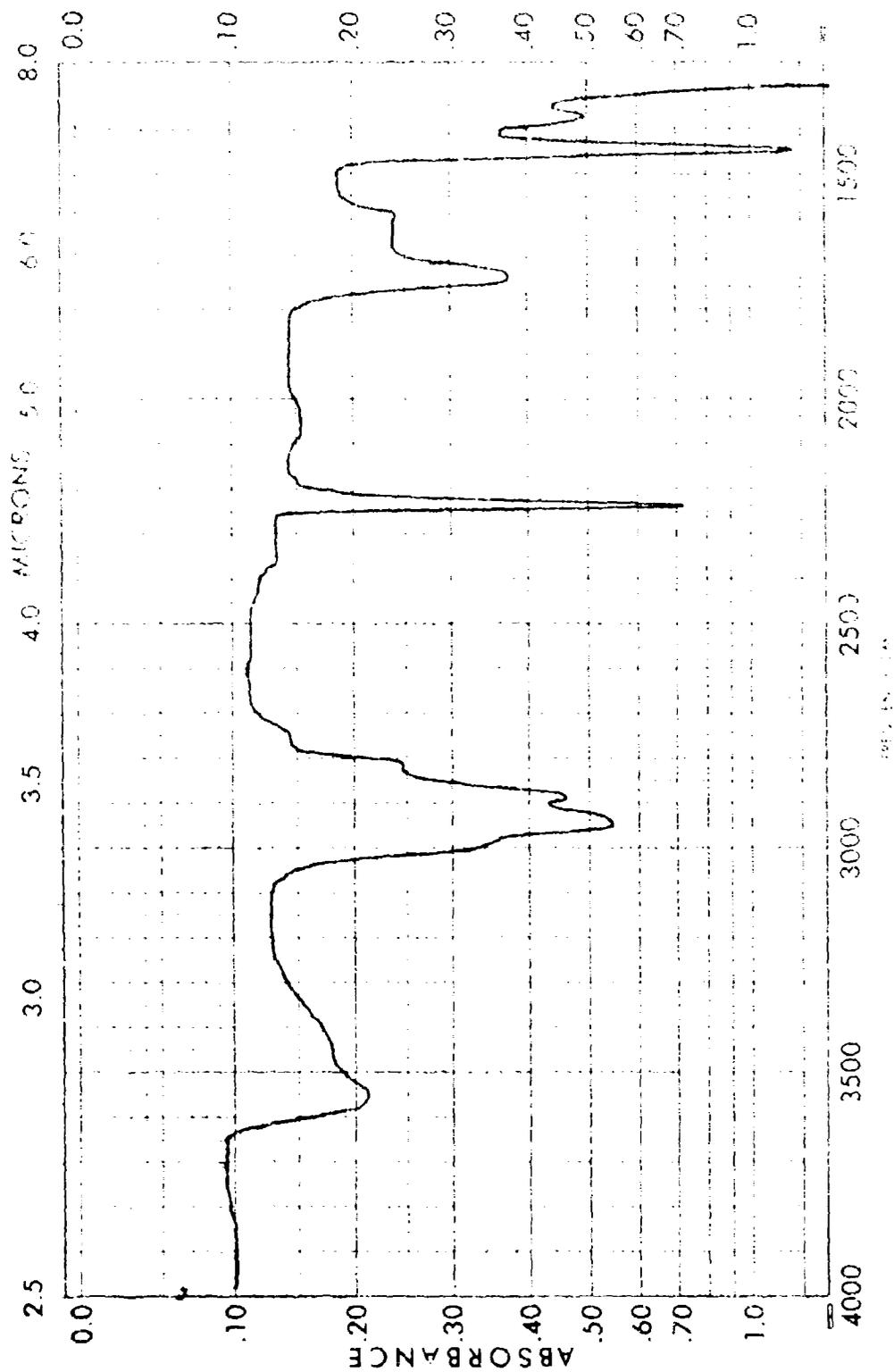


Figure 8. Infrared Scan of PCDE (Run 14)

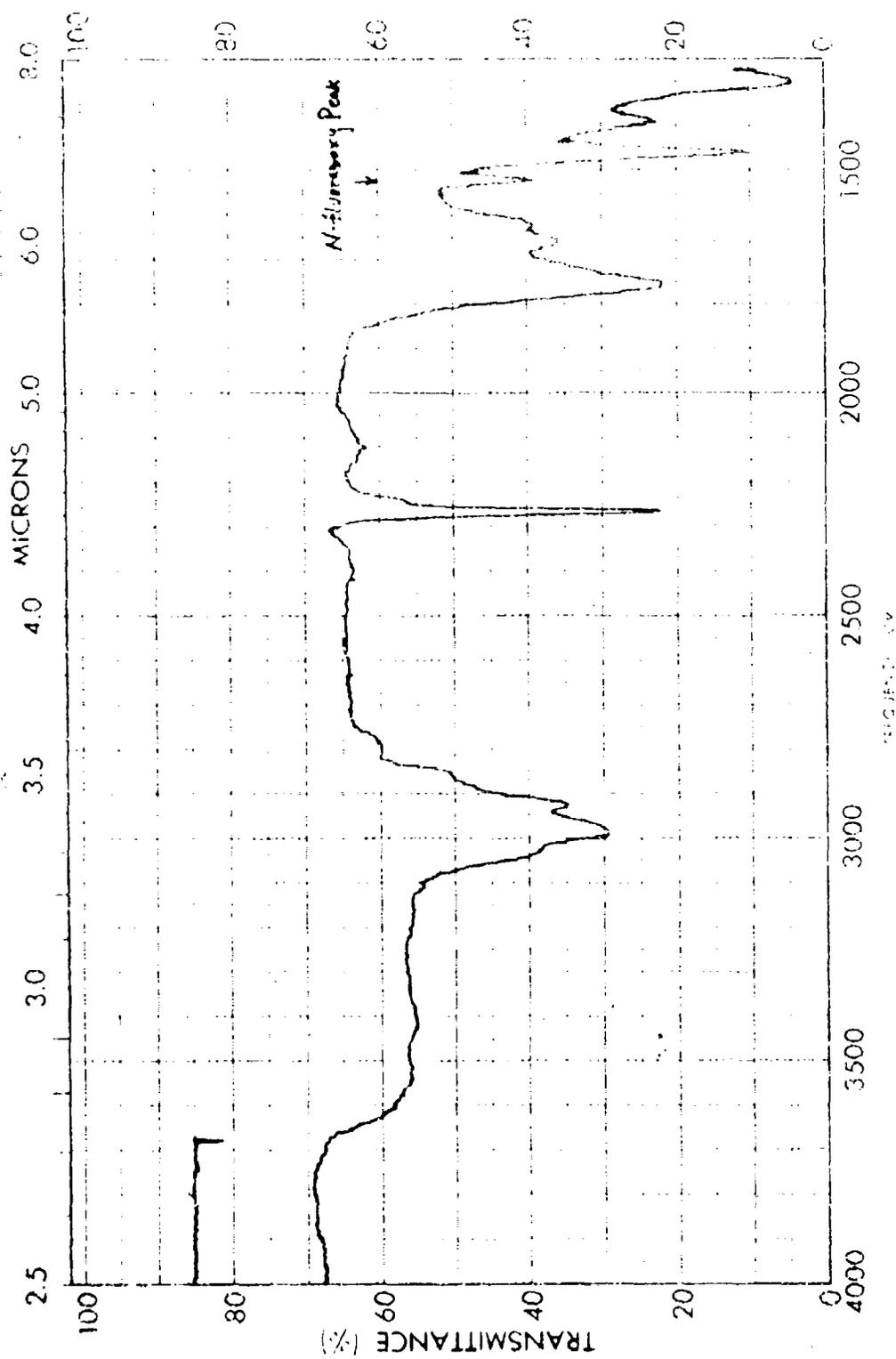


Figure 9. Infrared Scan of PCDE Containing N-fluorazoxy

SECTION IV

PROBLEM AREAS

A. INTRODUCTION AND SUMMARY

Problems which have occurred during the course of the PCDE program can be divided into two main categories: (1) Process or chemistry related problems and (2) maintenance or equipment problems. Some of these problems have been serious enough to delay production, and some have caused loss of product because of failure to meet product specification.

The problems are identified and a description of the solution to the problems is discussed in the next two paragraphs.

B. PROCESS PROBLEMS

1. Removal of Water from Acetone

a. Acetone Dried with Molecular Sieves

The presence of water from the acetone solvent in the DEPECH makeup tank heated up to 80° C and in the PBEP reactor at operating conditions may cause destruction of the DEPECH or PBEP molecules by hydrolysis cleavage. Degradation of the molecules could lead to lower molecular weight product and would be evidenced by increased carbonyl end groups formed at the cleavage points. The carbonyl peak is easily identified in the infrared scan of the product ($\sim 1720 \text{ cm}^{-1}$).

The water content of the acetone usually varies from 0.1 to 0.5 percent (w). The acetone used in the first PCDE production run was dried by passing it through a molecular sieve column. There is evidence of diacetone alcohol formation when acetone is treated with molecular sieves. Under the condition of temperature and pressure of the first stage PBEP reactor, the diacetone alcohol was converted to mesityl oxide, which then reacted with N_2F_4 forming a low molecular weight difluoroaminated product with a molecular weight of about 200. This more volatile product caused gassing during the thermal stability testing of the PCDE product. GPC analyses of the product confirmed the presence of a low molecular weight product (~ 200) in the PCDE product. This product disappeared on subsequent runs in which untreated acetone was used.

b. Acetone Dried with Calcium Sulfate

A second test was made with dry acetone for Run 67. The acetone was dried over nonindicating Drierite (CaSO_4). For the test, the reaction conditions and flow rates were the same as for Run 66. The DEPECH used was from the same lot as Run 66. The only change for the run was to use dried acetone for the DEPECH makeup and for the solvent stream in the PBEP reactor.

Sufficient acetone was dried for use in DEPECH makeup and for use in the PBEP reactor. As-received acetone was used to prepare TMA solution for the PCDE reaction. Samples of the acetone taken before and after drying show essentially no formation of diacetone alcohol. A sample of acetone left in contact with the CaSO_4 for a short test using N_2F_4 and acetone in the reactor at operating temperature and pressure gave no adverse effects and no dimer was formed. Table 7 lists the analysis of the acetone. Based on a value of 0.019 (the worst case), the acetone used would contain 0.012 lb water per gallon of acetone used in the test.

The results of the tests show no major improvement in product quality using the dried acetone. Listed below are some comparisons between the two runs:

	<u>Run 66</u>	<u>Run 67</u> <u>(Dried Acetone)</u>
Thermal Stability, cc/gm (100 hr)		
110° C	5.0	6.6
140° C	71	178
Molecular Weight	3441	3644
Carbonyl Peak IR Scan Ratio C = O/C-H		
PBEP	0.49	0.43
PCDE	0.70	0.75

The thermal stability is better for Run 66, although both are excellent. The molecular weight of Run 67 is among the highest produced but is not significantly better than Run 66. The infrared scans of the PBEP are better for Run 66 than for 67. The increase in carbonyl from the PCDE reaction is normal and the problem might be the TMA.

Based on the results of one test, there was no major improvement in product quality in using dried acetone.

2. Loss of Runs 14 and 20

Runs 14 and 20 produced PCDE that failed to meet specifications. The PCDE molecules contained double-bond sites that were not reacted in the PBEP reactor. The amount of material unconverted was small compared to the total double bonds reacted. However, it was large enough to cause high gassing rates during the thermal stability tests. The double bonds were identified by infrared scans.

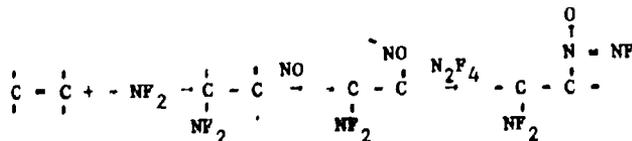
TABLE 7. DRY ACETONE TEST RUN ACETONE ANALYSIS

	H ₂ O (%)	Diacetone Alcohol (%)
Undried Acetone		
Barrel 1	0.095	Trace
Barrel 2	0.091	Trace
Dried		
Barrel 1	0.019	0.010
Barrel 2	0.017	0.021
Dried and in Contact With CaSO ₄ 10 Days	0.008	0.007
Reactor Effluent N ₂ F ₄ Contact Test	0.014	0.021
Dried Line Sample Day of Run 67*	0.008	0.010
* Acetone used for test run.		

Several factors led to the poor conversion of these runs. A power interruption and pump failure (as described in paragraph C) caused delay in processing. A leak in the DEPECH feed tank vent system caused a loss of acetone and an undetected concentration increase of the DEPECH feed. When the process was restarted, the ratio of N₂F₄ to DEPECH was inadequate to cause complete conversion of all the double bonds on the DEPECH. Installation of a new tank with a rupture disc assembly and fixing the pumping problems (described in the maintenance problem paragraph) have eliminated further problems of producing unconverted PBEP. All PBEP is checked for conversion at the beginning of the run.

3. N-Fluorazoxy in Product

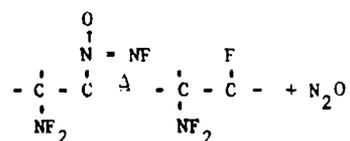
Beginning with Run 22, several runs were made in which the product contained an extraneous peak in the infrared scan that has been attributed to N-fluorazoxy. The peak of the infrared scan occurs at 1520 cm⁻¹. The mechanism for the reaction forming this material is believed to be as follows:



Nitrogen oxide (NO) is known to form by the rapid hydrolysis of N_2F_4 if oxygen is present.⁽¹⁾ The NO required for the above mechanism could be formed in the N_2F_4 process, in the PBEP reactor, or wherever the three composites of N_2F_4 , oxygen, and water are present together.

Any product with the N-fluorazoxy present gases too much to meet thermal stability requirements.

Pyrolysis of this material will give primarily N_2O as follows:



Gases from the heated sample of material containing the 1520 cm^{-1} peak showed the normal product of HCN, CO_2 , and HNF_2 , as well as large amounts of N_2O , thus indicating that N-fluorazoxy is probably the cause of the extraneous peak and low thermal stability of the product.

Corrective action included: (1) Prevention of air leaks into the reactor train during shutdown periods, (2) increased nitrogen sparging of the solvent and DEPECH feed tanks, and (3) maintaining a positive suction pressure on the DEPECH feed pump (by holding greater than 15 psig on the DEPECH feed tank). Runs following the above corrective action resulted in PCDE with no N-fluorazoxy present.

There was a recurrence of N-fluorazoxy in the PCDE at a later date (Run 40). The problem was traced to the presence of oxygen in the N_2F_4 . Investigation showed that the oxygen had probably been introduced into the production of N_2F_4 through the reagents used in the N_2F_4 manufacture. Additional nitrogen purging of the reagents was started and the problem was eliminated. Each batch of reagent was tested before use to make certain no oxygen was present. The test was performed by pumping the reagents through the reaction system as if making a run and using helium to simulate gas product. A sample of the helium was then taken after it had passed countercurrent through the reagent streams thus stripping any entrained gases. When the test showed no oxygen present, the reagents were approved for use. No problems with oxygen in the N_2F_4 have occurred since these procedures have been in use.

⁽¹⁾ Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems, NASA SP-3037, NASA/Lewis, 1967.

4. Fluorine Supply

A key component for making N_2F_4 and then PCDE is fluorine. Allied Chemical Company, the major supplier of gaseous fluorine to Hercules, closed their gaseous fluorine facility in Louisiana late in 1973. After that time, fluorine was supplied by them on a resale basis from Air Products Company. Problems of availability, packaging, and quality caused various delays in production.

To guarantee a fluorine source for this project, Hercules installed a liquid fluorine receiving facility with gasification capability. Two portable pallets of 12 cylinders for gaseous fluorine transfer were also constructed. The facility was placed in service in March 1975. Liquid fluorine supply for the facility from Allied Chemical Company is readily available.

The 12 cylinders on the transfer pallets hold the amount of fluorine needed to make a DFU run in the batch reactor in the pilot plant. Since the facility was placed in operation, the supply of gaseous fluorine has not been a problem and no delays have occurred from this source.

5. Acetone Removal

Acetone removal from the PCDE is accomplished by countercurrent extraction with water in a packed column. The wash columns are 6 in. in diameter by 6 ft long Pyrex glass and are packed with 5/8-in. polypropylene pall rings. The PCDE interface is maintained at the bottom of the column just below the water inlet nozzle.

The washing step has proven to be somewhat troublesome. Emulsions of PCDE in methylene chloride form with water in the columns and continue to build until flooding occurs and PCDE leaves the top of the column with the waste water. Methylene chloride will break the emulsion if pumped into the column through the feed line. The methylene chloride used dilutes the PCDE.

The glass columns have proven invaluable in operation of the wash column. Observation has been necessary to anticipate the formation of the emulsion and to pump in some methylene chloride to clear the columns.

Temperature of the wash water affects the emulsion formation. If the temperature of the water gets above 60° F, emulsion formation increases. Experience has shown that a temperature of between 50° and 60° F is best, giving a minimum of emulsion formation.

Most of the emulsion formed never breaks up, even upon settling for weeks. It remains as a distinct layer on top of the PCDE following the wash step. Much of the PCDE in the emulsion layer can be recovered

by vigorous agitation with methylene chloride and allowing the mixture to settle. Two phases appear immediately and upon settling for a few hours there is again a light emulsion layer over the methylene chloride phase containing some PCDE. A second treatment of the emulsion layer recovers little PCDE.

The PCDE recovered from the emulsion has properties similar to the product of the run that did not emulsify. About 16 lb of PCDE from the emulsions have been recovered and composited as "Blend 68." The analysis of the PCDE is shown in Table 6.

Diluting the PCDE to low PCDE concentration (below 5 percent) does eliminate the problem. This method is not used because the PCDE catch tanks are not large enough to contain a wash, and the PCDE would have to be concentrated for shipment.

6. Laboratory

The determination as to what is "good" and what is "bad" PCDE was not as clear-cut as would be desired at the beginning of the project. Infrared scans of the product are not necessarily conclusive. Molecular weight determination seems to give results that are good only to within ± 10 percent, thus giving results that are not well enough defined. Thermal stability results seem to be the best determination of PCDE usability.

Two thermal stability tests are used. One, a short term test, is run at 140° C for a period of 5 hours. The test is made by placing 0.25 gram on the plunger of a glass syringe (Tomac Syringe, Catalog No. 15634-310) and immersing the syringe in an oil bath controlled at 140° F. The amount of gassing is measured directly by reading the gas accumulated in the syringe. Care is taken to make sure the syringe does not stick. The second test is run similarly except at 110° C for a period of from 100 to 200 hours. Although there is some correlation between the two tests, the short term test results cannot be used to accurately predict the results of the 110° C test.

The thermal stability tests can be adversely affected if all of the solvent is not stripped from the PCDE. Stripping the acetone and methylene chloride requires good technique and training. The stripping procedure is listed in Appendix E along with the other laboratory procedure. Some practice is required to strip the sample to the proper condition. Some time was required at the beginning of the project before the stripping technique was mastered.

Another area of concern was not having immediate on line process control analyses. Much information can be gained from infrared scans of both PBEP and PCDE. Analysis of the scans can indicate if all DEPECH has been converted, if all PBEP has been converted, and the purity by indicating the presence of any N-fluorazoxy or excess carbonyl. About

50 minutes were required to send a sample to the laboratory for analysis. The problem was minimized by isolating the PCDE in small containers until infrared scans were available.

Most other analyses such as hydroxyl functionality, molecular weight (VPO), and gelation tests required too much time to be of use in process control.

C. MAINTENANCE AND EQUIPMENT PROBLEMS

1. Fluorine Handling

a. Fluorine Manifold

The fluorine manifold system was originally designed and built to connect 12 individual cylinders to the manifold. Twelve connections were required each time a run was made. Considerable time was required to make the hookup as each connection had to be carefully cleaned and the system pressure checked and passivated. Frequently, one of the connections was found to leak during the pressure check and the connection had to be replaced. Following the hookup, each cylinder had to be opened individually by manual, remote operation, again requiring considerable time. This system was necessary because the gaseous fluorine arrived on plant in individual fluorine cylinders.

The pilot plant fluorine manifold and the fluorine cylinder system was redesigned when the liquid fluorine facility was installed at Hercules. The gaseous fluorine transfer pallet containing 12 cylinders has only one connection to the pilot plant manifold. The cylinders remain open at all times and are isolated by double, remotely operated block valves on each pair of six cylinders common to the one connectine line. Having only one connection and remotely operating block valves has greatly simplified and speeded up this part of the operation.

Periodically, the 3/8-in. Swagelok connector, which attaches the pallet to the system, has required replacement. This has been required because of passivation and oxidation products buildup on the sealing surfaces.

During the initial operation of the above units, two small fluorine fires occurred when the connecting line failed and burned. The problem was traced to water contamination of the line. The cap on the connecting line had been left loose, and moist air leaked in the connection during the several days of nonuse, depositing water in the line. Normal purging of the line during connection failed to remove the water in the line and, when fluorine entered the system during the passivation step, reaction occurred and the line failed. The operator in both cases closed the remote block valves and the loss of fluorine and damage to the system was minimal. Once cause of the fires was recognized, the problem was eliminated by keeping the cap tight on the connecting line and on the fluorine pallet. No further incidents occurred.

One other fluorine fire occurred, unrelated to the connecting line, when a bellows failed on a hand operated fluorine valve while it was being operated. The operator received second degree burns on his hand when the fire came through the handle hole in the protective panel. The valve and about 18 in. of copper line were the only equipment pieces destroyed in the fire, although several pounds of fluorine were released. An automatic water deluge system activated and possibly helped to keep the damage to a minimum. No other injury beyond the thermal burn to the operator's hand was sustained.

It is significant to note that during the time when gaseous cylinders of fluorine were received on plant for hookup to the manifold system, a careful inspection and cleaning around the valve caps was necessary. Several times the cylinder valves were found to be dirty and actually covered with grease. Small amounts of fluorine under the valve cap could ignite the grease when the cap was loosened.

b. The DFU Reactor

Although the fluorine area reaction produces 2 moles of HF per mole of DFU, the stainless steel reactor has held up very well. Two areas have caused some maintenance problems. First, the original stainless steel tubing halo used to distribute the incoming gaseous fluorine and provide an air lift was of welded construction. Apparently the welding caused stress corrosion to occur. The halo failed and caused very poor gas distribution and air lift. The replacement halo and tubing were fabricated from one piece. No downtime has been recorded since its installation. Second, the bottom discharge valve is a stainless steel ball valve with Teflon packing. The ball experiences a high degree of corrosion and must be replaced periodically.

2. Pumps

a. N_2F_4 Synthesis

The original reagent pumps in the N_2F_4 production system required replacement. The pumps were incapable of maintaining constant flow with varying pressure in the reaction system. Sometimes they would stop suddenly and completely, thus interrupting the conversion of HNF_2 to N_2F_4 . The flow interruption would also cause further pressure fluctuations causing flooding of the columns. The pumps were replaced with plastic magnetic drive pumps that were not subject to significant flow variation with changes in backpressure. Since the pump replacement was made, no upsets have been experienced.

b. PBEP Manufacture

The diaphragm-operated positive displacement pumps for pumping acetone and acetone/DEPECH solutions into the reactor systems have characteristically given maintenance problems. The problems were caused by failure of the check valves to seat and by diaphragm failure.

During the first few PCDE runs, pumping problems due to sticking check valves were frequent. The problem was eventually traced to solids in the streams from impurities in the acetone (i.e., metal flakes from the acetone drum or tank) and precipitated DEPECH from the feed tank. A filter was placed in the acetone suction line, and the acetone/DEPECH line was traced with tempered water and insulated in order to keep the DEPECH in solution. Most of the check valve problems were eliminated by these solutions.

Diaphragm failure has also been eliminated by replacement of the polyethylene diaphragms with a neoprene diaphragm with a thin Teflon sheet bonded to the process side. The diaphragm is flexible and does not stress crack as did the polyethylene, and the Teflon is inert to chemical attack. The diaphragm is checked every three or four runs and is replaced only when signs of fatigue in either the neoprene or Teflon are noted.

3. Compressors

Compressor failure during a run, either N_2F_4 gas generation or PBEP manufacture, was a critical problem at the beginning of the project. Failures usually occurred with the compressor check valve or the diaphragms. Passivation film buildup on the check valves causes this failure. Replacement of the check valves after seven or eight runs has eliminated this problem. The check valves are very expensive, but can be cleaned and rebuilt in the Shop so that they work satisfactorily.

Compressor diaphragms are checked and replaced periodically. An early problem was eliminated when vertical standpipes for thermocouples were removed from the compressor head and an elbow was installed on the compressor outlet tubing. Passivation film was building up in these tubes and falling back on the diaphragm causing failure of the diaphragm.

SECTION V

SAFETY

A. GENERAL

Hercules maintains a continuing safety program at each facility to ensure a safe operation. This program has resulted in standards of safety that are highly effective.

Prior to working in hazardous areas, all workers are trained in specific operating procedures and are instructed in effective and detailed safety requirements. The workers are constantly made aware through lectures, visual aids, and written material of the need for mandatory compliance with stringent safety rules. All personnel working in sensitive areas are required to attend and take part in regular safety meetings.

Every operation at each plant is performed in accordance with a written standard operation procedure (SOP). The operating procedures comply with detailed safety standards which are approved by Hercules Systems Group management and maintained on a division-wide basis. These standards have as a specific objective the assurance that maximum safety will be applied in every plant operation dealing with sensitive materials. All plant operating procedures are reviewed and approved by the Manager of Safety at the various plants before being adopted.

A preliminary hazard analysis was conducted before construction of the Bacchus Pilot Plant. Subsequently, some refinements were made in the hazard data. Plant operations were designed insofar as possible to provide for "fail-safe" sequences. Where unknowns, such as explosive hazard or toxic gas release were possible, design of barricades and operating procedures mandated protection of personnel from serious injury.

Pilot plant operating personnel received formal classroom training and additional on-the-job training in the plant before being allowed to operate in any area in the pilot plant. The formal classroom training included films and lectures on fluorine handling, safety in explosive manufacturing, safe handling of acids, caustic and other corrosives, and first aid, including a special class in fluorine first aid.

On-the-job training by supervision included use of operating procedures for each section of the pilot plant, building safety procedures and regulations, care and use of respiratory equipment, handling and using solvents, and fluorochemical spill cleanup. If an operator is away from the plant for over 30 days, on-the-job retraining is mandatory.

In addition to the pilot plant personnel, fluorine training and hazards familiarization is given to all maintenance workers who visit the pilot plant on regular preventative maintenance duties or to repair

failed pilot plant equipment. Before work is done on any equipment or process line, it is thoroughly flushed and a work permit is signed by the pilot plant supervisor, safety engineer, and by the maintenance foreman. The work permit states that the equipment is adequately decontaminated and is in safe condition for repair to begin.

Another important safety consideration given to pilot plant personnel and others working routinely with fluorine and N_2F_4 gases are routine physical examinations. These people receive routinely a physical examination every 3 months. Procedures also require a doctor's examination if anyone is exposed to pilot plant process gases whether or not they suffer any adverse symptoms.

The overall result of the design and training procedures is that the pilot plant has operated without a lost time accident since initial startup in early 1972.

The philosophy of treating the various types of hazards and specific materials involved as identified in the hazards analysis is given in the following paragraphs.

B. TOXICITY PROBLEMS

1. Fluorine

Fluorine is considered toxic under prolonged exposure when it can readily be detected by smell (0.1 ppm smell threshold). Emergency tolerance limits of up to 15 ppm for 10 minutes are acceptable, and volunteers have been exposed to about 20 ppm for short duration without prolonged effect. However, in no circumstance should operation continue for over 15 minutes when the odor of fluorine is detectable by smell.^(1,2)

A water deluge system is provided in the event of a large fluorine spill. Test spills at AFRPL of over 1000 lb liquid F_2 showed this method to produce F_2 concentrations well below 100 ppm within 200 ft of the spill.

2. N_2F_4

The lethal concentration of N_2F_4 for rats is

$$LC_{50} = \frac{134,000}{(\text{exposure time, min})^{1.44}}$$

(2) Schmidt, H. W., Personal Communication of J. D. Marks, 1972.

During initial startup of the pilot plant N_2F_4 process, leaks were evident, and all operators were subjected to small doses of N_2F_4 without apparent ill effect. No one has been found whose olfactory sense loses all ability to detect the odor of N_2F_4 , but most people become used to low levels of odor. Therefore, operators should leave the control room or operating area on a periodic basis, preferably to outside air. On return to a contaminated area, any odor of N_2F_4 is immediately apparent.

One operator who mentioned that his sense of smell had been impaired from prior work was reassigned away from the N_2F_4 area as a precaution. However, even he could detect the odor of N_2F_4 in some concentrations. For safety, all operators working in any area in the plant should possess adequate olfactory senses.

Table 8 lists the vapor toxicity of several gases as a reference.

3. Trimethylamine (TMA)

Trimethylamine is a moderate ⁽³⁾ irritant and can cause serious damage to the eyes or respiratory system from extreme exposure. TMA should be stored and used in well ventilated areas. The odor is extremely noticeable and small leaks are quickly noticed. Concentrated TMA has the odor of ammonia while dilute TMA has an odor similar to decaying fish.

Exposure to the skin requires washing with water. In cases of extreme respiratory exposure, fresh air or oxygen therapy is required.

4. Solvents

The principal solvents used, acetone and methylene chloride, are typical chemical solvents and are handled with normal care in well-ventilated areas. They are not considered highly toxic; acetone having a threshold limit value (TLV*) of 1000 ppm and methylene chloride a value of 500 ppm, which compares favorably with kerosene at 500 ppm. In the event of a building fire, where methylene chloride could be heated to a temperature that could cause it to break down, toxic products could result.

5. DEPECH, PBEP, and PCDE

These materials possess a degree of oral toxicity but this is not considered a serious problem since ingestion is required. Cleanliness of operation is maintained as the major control.

⁽³⁾ Sax, N. I., Dangerous Properties of Industrial Materials, Reinhold, 1957.

* TLV values from American Conference of Governmental Industrial Hygienists, May 1968.

TABLE 8. GAS AND VAPOR TOXICITY

Gas	B.Pt °C	Tank		ACGIH Threshold Limit Value	Irritation (Eyes, Throat Coughing)	Dangerous but Nonlethal	Fatal	LC 50 Brief	LC 50 Extended	Remarks
		Acute	Chronic							
COCl ₂	+8.3	3	U	0.1 ppm air (vol) 0.4 mg/m ³ air	3 to 5 ppm in air	25 ppm for 30-60 min	50 ppm short exposure			Chlorine analog of COF ₂ . Hydrolysis to CO or CO ₂ , HCl when moist. Symptoms delayed, then pulmonary edema. ICC: Poison A, Sax, 3rd Ed., p. 1019
HCl (anhydrous)	-84.8	3	U	5 ppm air 7 mg/m ³ air	35 ppm air	1000 to 2000 ppm, brief				ICC corrosive 1 gal white coast guard. Green gas, Sax 3rd Ed., p. 821
HF (anhydrous)	+19.4	3	2	3 ppm in air 2 mg/m ³ air		50-250 ppm, brief				Ulcers of resp tract Sax, 3rd Ed., p. 1019 ICC corrosive liquid white label
COF ₂	-83	3	U							Powerful irritant. See HF, F ₂ . Hydrolyses Sax, p. 536
F ₂	-187	3	3/U	0.1 ppm air 0.2 mg/m ³						Powerful irritant. ICC flam gas. Red label. Sax, p. 779
N ₂ F ₄	-73				1% almost immediately	1% for 20 minutes	1% for 25 min	1000 ppm 30 min (R&H)	50 ppm 4 hours (R&H)	Methemoglobin formed but not sole toxic mechanism. Wang et al., AD681 161
CF ₄	-127.7	2	U	1000 ppm air for Freons 11, 12, DuPont Bull B2 p. 5						Less toxic than CCl ₄ , toxic Sax 535
CCl ₄	+76.8	3	1/3	10 ppm air 65 mg/m ³		1000-1500 several hr				Chlorine analog of CF ₄ . Injurious. Narcotic, liver, kidneys, lungs, Sax., p. 535. Toxicity not analogous to CF ₄
NO ₂	+21			5 ppm air 9 mg/m ³						ICC poison A highly toxic Sax., p. 968
NO	-151.8	3	U/2	25 ppm/30 mg/m ³	60-150 ppm	100-150 ppm	200-700 ppm brief			Resp., then nitrite blood poison
NF ₃	-129				Occurs at lethal levels 10 min before death	(@ 0.25% dogs reduce the methemoglobin faster than formed (2))	1% for 60-70 min 0.4% for (2) 225 min		3600 ppm 4 hr (R&H)	Forms methemoglobin, asphyxiates. Possible kidney involvement. (2) Wang et al., AD681161
HNF ₂								500 ppm (1/2 hr) 300 (1 hr)		R&H ROM. Few data
(CN) ₂	-21			5 mg/m ³						ICC poison A "Like HCN" (Sax)

6. Protective Equipment

Protective gear required by personnel involved in the synthesis of PCDE and intermediate compounds includes:

a. Protective Clothing

- (1) Flame retardant treated coveralls
- (2) Nonsparking, nonconductive, safety shoes that comply with ANSI specification Z41.4 - 1944
- (3) Solvent resistant neoprene gloves, five fingered with cuffs long enough to extend over the wrist
- (4) Neoprene jacket and pants

b. Eye Protection

- (1) Safety type spectacles meeting ANSI standard Z87.1 - 1968
- (2) Face shields

c. Hard Hats

Constructed of nonconductive, wear resistant material to comply with ANSI Specification Z89.1 - 1969

d. Respirator Equipment

- (1) Airline respirator - continuous flow of respirable air from an outside source
- (2) Self-contained respirator, such as Scot Air Pak

In addition, safety showers and eye wash fountains have been installed as needed near areas of fluorine use. Technicians work in pairs and within sight or sound of each other.

C. FLAMMABILITY

Fluorine, being a more active oxidizer than oxygen, presents special problems whenever it is handled. Thorough design reviews and operating procedures were provided to assure absolute cleanliness and to prevent inadvertent leakage or to control leakage that may occur. Free fluorine from the process (passivation, startup, process excess) is vented to a charcoal incinerator. Major leaks can be controlled by water deluge. AFRPL, NASA, and fluorine vendors were consulted in establishing the fluorine system and procedures. The liquid fluorine facility is located in a remote section of the plant.

In general, N_2F_4 has been considered the same as fluorine for design and handling purposes, except that many plastics incompatible with fluorine can be used with N_2F_4 . A more detailed description of N_2F_4 is given in Section VI.

Acetone and TMA are flammable fluids which require suitable storage and handling.

D. EXPLOSIVE PROPERTIES

Five of the materials processed have been reported to explode under some circumstances. They are: (a) difluoroures (DFU), (b) HNF_2 , (c) tetrafluorohydrazine (N_2F_4), (d) PBEP, and (e) PCDE. The hazards accompanying these materials depend on the state and purity. During normal operation these materials are handled in states and concentrations corresponding to minimum hazard.

1. DFU

Solid purified DFU is sensitive to impact. However, DFU does not occur as a crystalline solid in the process. Normally it is produced, stored, and handled in water solution. The solution also contains by-product hydrogen fluoride (HF).

Accidental solution spillage will not cause accumulation of the solid, because DFU is perishable. For instance, DFU solutions normally are processed and stored at $0^\circ C$ or below to retard decomposition. At higher temperatures, dissolved DFU decomposes (hydrolyzes) to an equimolar mixture of HNF_2 and carbon dioxide (CO_2), accompanied by ammonium fluoride. Thus, while a DFU solution spill is being concentrated by evaporation, it is being weakened by decomposition and diluted by accumulation of ammonium fluoride.

Care must be taken before neutralization of DFU spills to first dilute the spill with copious quantities of water. When undiluted spills have been neutralized with lime, considerable audible sputtering has occurred.

2. N_2F_4

Potentially hazardous reactions of N_2F_4 gas are decomposition and combustion.

a. Decomposition

Pure N_2F_4 gas can decompose to form NF_3 and N_2 . The heat of reaction at $25^\circ C$ is calculated as -38.5 ± 5 kcal/gm mole N_2F_4 . The reaction causes an increase in pressure due to the 5/3 increase of gas moles and to the temperature rise. Calculation shows that a storage vessel of pure N_2F_4 gas at 120 psi and $25^\circ C$, decomposing completely and adiabatically, will rise to 2100 psi at $2580^\circ C$.

Closed bomb tests by Rohm and Haas showed that N_2F_4 at partial pressures above certain values and initiated by an exploding bridgewire would rapidly decompose. On the basis of adiabatic calculations and their tests, Rohm and Haas established an upper pressure limit of 120 psig for storage of N_2F_4 gas when using 2200 psi rated cylinders. This practice has been followed by Hercules.

The N_2F_4 is produced at low pressure (below 15 psi), but is stored at pressures up to 120 psi to minimize storage space. The storage banks (two each) consist of 15 gas cylinders connected by a manifold. The cylinder valves are open and are never operated. Routing N_2F_4 to or from the storage banks is accomplished using remotely operated valves in the manifold system.

Extreme attention to cleanliness is considered of paramount importance in handling N_2F_4 . It has been treated on the same basis as fluorine in terms of line cleaning, passivation, and leak testing.

All equipment exposed to N_2F_4 at partial pressures over 40 psi, even though in solution, should be initially passivated by increasing total pressure to 50 psi. The initial exposures should be in the presence of nitrogen.

Care must be taken in design or in making any modifications to the plant to assure that: (1) All equipment is grounded to prevent static electricity buildup and (2) no hydrogen can be generated (i.e., reaction of metals with acid).

b. Combustion

The N_2F_4 can oxidize fuel-type contaminants such as hydrogen or hydrocarbon oils. Products are N_2 , HF, and (when carbon is present) CF_4 and C_2F_6 . When the fuel concentration is large, detonation can occur. When the contamination is small, reaction with the contaminant can initiate N_2F_4 decomposition, discussed above.

The pilot plant was designed to avoid fuel-type contamination. Vessels and pipes handling N_2F_4 with acid media are constructed of plastic. Metal corrosion may liberate hydrogen. Teflon, PVC, polyethylene, polypropylene, and acrylic resins (Plexiglas) have all been used successfully in the pilot plant.

3. PBEP

Neat PBEP is an explosive material. Bureau of Explosives special permit, originally issued in 1966 to Shell Development Company, and updated in 1969, permitted shipment in 35 percent solution as Class B explosive. By keeping the material in solution during processing, hazards are minimized.

In the synthesis of PBEP, zones containing concentrations of reactants and/or product and acetone solvent can lie within a potentially detonable region. The reaction concentrations were chosen so that under normal circumstances the reaction path lies outside the detonable region. Since, under abnormal circumstances an explosion can occur, both the reaction step and the separation of excess reactant were conducted remotely in a suitably barricaded area. Once reaction was started, personnel were precluded from the reaction area until the reactor had been cleared of explosives by solvent flushing.

In the solution and dissolution of N_2F_4 from acetone, a detonable two-phase region exists or can occur. Therefore, a dissolver and separator were designed to be as small as possible so that any damage would be minimized. Small diameters and packing were used to limit the development of any detonation waves. No problems have been encountered.

The PBEP reactor was designed as a series of flow tubes of small cross-sectional area to provide maximum heat transfer surface per unit volume of reaction solution. To assure complete removal of explosive material in the event of a problem, the tubes are oriented to be gravity draining. An emergency water deluge system was designed into the reactor system for rapid cooling of the reaction.

4. PCDE

Much of the same properties attributable to PBEP apply to PCDE. The process requires the solvent interchange from acetone to methylene chloride, which improves handling safety since a flammable solvent is eliminated. Here too, the explosive material is handled in dilute solution. After final removal of acetone from the methylene chloride extract, the solution is concentrated to near 35 percent w PCDE for shipment as a Class B explosive in 5-gallon DOT 17E containers overpacked in DOT 15A wooden boxes (BA 1721).⁽⁴⁾

5. Fittings

Construction requires selection of fittings which are safe to disassemble when potentially contaminated with explosive product. Tests were performed with Swagelok* double ferrule compression fittings, stainless steel tubing, and contaminated contact areas.

⁽⁴⁾ Per letter, R. M. Fraziano, Director, Association of American Railroads, Operations and Maintenance Department, Bureau of Explosives, Jan 9, 1974, to J. F. Cross, Manager, Safety, Hercules Incorporated, Magna, Utah.

* Swagelok is the registered trademark of Crawford Fitting Co., Cleveland, Ohio.

The tests performed indicated that the disassembly can be done without incident that would cause damage to the reactor or lines. Tests were performed on 1/4-in. Swagelok tube fittings with the threads contaminated with neat TVOPA. TVOPA, a liquid explosive, was the initial product produced in the pilot plant. Since it is more sensitive to friction than either PBEP or PCDE and can propagate in thin films, successful results with TVOPA may be translated to PBEP/PCDE use. The fittings were torqued to the recommended levels, then a breakaway was done to simulate a rapid release. In none of 15 trials were any reactions noted. Contaminated fittings were then torqued beyond recommended levels to approximately 40 ft-lb and rapid breakaway velocities simulated. No reaction occurred in 20 trials under these conditions.

Examination of the contaminated thread section of the fitting showed very little depositing on the threads before or after test, apparently due to the poor wetting of the TVOPA/stainless steel.

Additional tests were performed by coating the inside of the fitting, torquing the fitting to various levels, removing the nut section, then manually breaking the connection. Breaking the connection involved attempts to bind the inner surfaces and obtain as high a velocity release as possible by manual method. Loads of 10 to more than 60 lb were obtained. Velocity was not measured in these tests.

In no instance was any reaction obtained. Inspection of the surfaces at various times during testing showed TVOPA present on the inner fitting surfaces. The bearing surface of the fitting was checked and showed burnish marks at the fitting end of the tubing indicating good metal-to-metal contact during the test trials.

When required in practice, the actual fitting disassembly was done behind shielding after the tubing was flushed with solvent. No initiation hazard in the disassembly was ever experienced.

SECTION VI

PROPOSED SPECIFICATIONS

Raw materials used in the manufacture of PCDE are N_2F_4 , DEPECH, and trimethylamine. The process materials are acetone, methylene chloride, and molecular sieves. An intermediate material is PBEP. The proposed specifications for these materials as well as the final product, PCDE, are discussed in this section.

A. N_2F_4

Occurrence of N-fluorazoxy in the product created considerable difficulty. The cause was finally assigned to the occasional occurrence of trace oxygen in the N_2F_4 . Consequently, analysis requirements were introduced for the presence of oxygen in the N_2F_4 .^(a) Detection level using the pilot plant chromatograph is approximately 0.01 percent V (100 ppm). N_2F_4 containing any detectable oxygen is not used for production.

Table 9 lists the analyses of N_2F_4 used in the production of PCDE Runs 42 through 67 and compares these with the 110° C thermal stability results for the PCDE runs. The table summary gives the actual maximum and minimum values observed and compares them with the calculated statistical three sigma limits. The following recommended specification limits are proposed for any future program:

Proposed Specification Limits - N_2F_4

<u>Component</u>	<u>Percent, Volume</u>
N_2F_4	94 min
O_2	0*
CO	0.10 max
NO	0.60 max
CO_2	0.10 max
N_2O	0.50 max
N_2F_2	1.00 max
NF_3	0.20 max
N_2	5.00 max

^(a) Process changes eliminated any occurrence of trace oxygen. Please refer to Section II, para D of this report.

* Detection level 100 ppm or better.

TABLE 9. ANALYSIS OF N₂F₄ USES SINCE RUN 42

Run	No.	FCDE 110°C I.S.	O ₂	CO	NO	CO ₂	N ₂ O	N ₂ F ₂	NF ₃	N ₂	Impurities Other Than Nitrogen	N ₂ F ₄ by Difference
42A	1	9.8	0	.04	.02	.04	.26	.37	.01	1.98	0.74	97.28
42B	2	7.5	0	.04	.10	.039	.093	.19	.173	2.93	0.63	96.44
43	3	8.0	0	.04	.106	.06	.152	.342	.133	4.88	0.81	94.31
44a	4	6.4	0	.017	.037	.017	.251	.469	.028	1.45	0.82	97.73
45	5	8.8	0	.029	.035	.048	.243	.213	.017	1.24	0.59	98.18
46	6	7.4	0	.042	.024	.09	.29	.60	.003	1.59	1.05	97.36
47	7	8.2	0	.07	.05	.02	.34	.66	.03	2.3	1.17	96.53
48	8	10.1	0	.06	.07	.02	.36	.73	.05	1.99	1.29	96.72
49	9	8.8	0	.06	.11	.01	.35	.77	.05	2.69	1.35	95.96
50	10	9.2	0	.03	.60	.01	.34	.69	.09	2.23	1.76	96.01
51	11		0	.06	.26	.02	.28	.50	.10	2.26	1.22	96.52
52	12	6.7	0	.07	.44	.02	.32	.41	.08	2.00	1.34	96.66
53	13	8.6	0	.06	.12	.01	.40	.59	.05	2.58	1.23	96.19
54	14	8.4	0	.02	.16	.01	.31	.60	.05	2.22	1.15	96.63
55	15	9.0	0	0	.14	.01	.32	.55	.04	2.07	1.06	96.87
56	16	7.5	0	.03	.06	.01	.26	.47	.03	1.82	0.86	97.32
57	17	7.4	0	.03	.09	.01	.25	.51	.02	2.18	0.91	96.91
58	18	8.2	0	.02	.08	.01	.28	.51	.03	1.80	0.93	97.27
59	19	7.7	0	.03	.08	.01	.27	.51	.02	2.01	0.92	97.07
60	20	8.5	0	.04	.13	.01	.27	.48	.04	2.28	0.97	96.75
61	21	7.5	0	.02	.12	.01	.24	.38	.05	2.00	0.82	97.18
62	22	6.3	0	.02	.07	.01	.24	.49	.05	1.86	0.88	97.26
63	23	7.0	0	.04	.18	.01	.27	.49	.07	1.69	1.06	97.25
64	24	7.0	0	.03	.11	.02	.29	.57	.06	1.91	1.08	97.01
65	25	6.6	0	.05	.12	.01	.27	.57	.06	1.57	1.08	97.35
66	26	5.0	0	.04	.12	.01	.27	.50	.05	1.47	0.99	97.54
67	27	6.6	0	.05	.11	.01	.29	.53	.04	1.99	1.03	96.98

a. Liquid fluorine used for N₂F₄ manufacturing starting @ Run 44.

TABLE 9. ANALYSIS OF N₂F₄ USES SINCE RUN 42 (Cont)

	PCDE 110°C T.S.	O ₂	CO	NO	CO ₂	N ₂ O	N ₂ F ₂	NF ₃	N ₂	Σ Impurities Other Than Nitrogen	N ₂ F ₄ by Difference
Recommended Spec for N ₂ F ₄ Used in Producing PCDE:											
Maximum	12.0	0	.10	.60	.10	.50	1.0	.20	5.0	--	--
Minimum	--	-	--	--	--	--	--	--	--	--	94.0
Summary:											
\bar{X}	7.89	0	.0304	.1312	.0198	.2781	.5072	.0527	2.11	1.03	96.86
S	1.29	0	.0.74	.1350	.0180	.0608	.1349	.0373	0.672	0.25	0.72
$\bar{X} + 3S$	11.76	0	.0407	.5063	.0739	.4606	.9118	.1645	4.13	1.77	99.03
$\bar{X} - 3S$	4.02	0	< 0	< 0	< 0	.0957	.1025	< 0	0.10	0.29	94.70
Actual Maximum	10.8	0	.07	.6	.09	.40	.77	.17	4.88	1.76	94.31
Actual Minimum	5.0	0	0	.02	.01	.09	.19	.01	1.24	0.59	98.18

B. DEPECH

The relationship between a DEPECH lot and the PCDE produced therefrom has not been found to be straightforward. DEPECH is a high molecular weight polymer with the random properties attributed to mixtures of such molecules. Table 10 lists some analyses of DEPECH used for the control.

Molecular weight has been determined by vapor pressure osmometry (VPO) for both DEPECH and PCDE. The results plotted by PCDE run number and DEPECH lot are shown in Figure 10. Considerable variation occurred in the PCDE values observed despite relatively constant values reported for the DEPECH.

Thermal stability of PCDE produced is compared with the respective DEPECH used lots in Figure 11 and Table 11. Averages and standard deviations are given in the latter. No clear direction is indicated; however, a generalized improvement is expected as PCDE processing experience was gained.

The low temperature (higher molecular weight) DEPECH has exhibited a need for a generally higher dissolution temperature than material made by the original process. DEPECH solubility data are summarized in Table 12, but there are insufficient data to draw a firm conclusion. If too high a dissolution temperature is required, it is believed the molecule will begin to disintegrate.

Table 13 is a tentative specification for "low temperature" DEPECH for use in manufacture of PCDE. Two analysis levels are indicated, (a) purchase, and (b) preuse by the consuming facility.

The most critical determinations are:

- (1) Molecular weight
- (2) Hydroxyl functionality
- (3) Solubility in acetone
- (4) Carbonyl by IR
- (5) Odor - no acetic acid odor

The last three must be checked by the using facility within a short time (approximately 30 days) before use. Item 5 can and should be applied by the operators immediately at use.

TABLE 10. DEPECH LOT CHARACTERISTICS AND RELATED DATA

Lot No. DEPECH	Reported Mole Wt.	Cl-Z Corrected for Na Content	OH E/100 gm	OH Functionality	C-C' Mols/100 g	Analysis			Date Shipped	Quantity Shipped	Reference
						Na Weight %	Cl Weight %	CI			
11410-84	1760		0.13	2.3	1.44		0.4			2/14/73 from Elliott Ryder.	
11410-89	1840		0.14	2.6	1.41		1.3			Shell Letter June 15, 1973 UC, 73, 101209	
11410-89F	1790		0.17	3.0	1.37		1.2			Shell Letter June 15, 1973	
11410-92	1830		0.15	2.8	1.44		0.1			UC, 73, 100925	
270-90	1950	.139		2.4		0.02	0.07	05/11/73	2.8	Shell Letter June 15, 1973 UC, 73, 101209	
270-111	2220	.173		2.8		0.05	0.25	06/14/73	3.6 ^a	Shell Letter June 15, 1973	
271-150	1800	.091		2.1		07-16 .11	018-.40 .26	03/22/73 ¹	45 ¹	UC, 73, 100925	
271-151	1850	.092		2.0		.05	.13	04/16/73	45	UC, 73, 100955 UC, 73, 100925	
271-152	1900	.353		2.1		.05	.43	04/16/73	7.5	UC, 73, 100955 UC, 73, 100925	
271-153	2000	.638		2.5	1.465 ^c	0.04	0.70	05/11/73	7.5	UC, 73, 101209	
271-154	1900	Insufficient		2.2		0.07	0.10	05/11/73	45	Shell Letter June 15, 1973 UC, 73, 101209	
271-155	1700	Insufficient		2.3		0.06	0.09	06/14/73	45	Shell Letter June 15, 1973	
271-156	2400	.290		2.8		0.20	0.60	06/14/73	21	Shell Letter June 15, 1973	
271-157	1800	.007		2.2 ^b		0.06	0.1 ^c		10.5	Paul Van Shaw 8/24/73	
271-158	1800	Insufficient		2.2		.36	.34	10/02/73	20	Shell Letter Oct 4, 1973	
271-159	--	--	--	--	--	--	--	--	--	--	
271-160	2200+100	.149	0.13	2.8 ^b		.02	.18	12/18/73	87	UC, 74, 100260	
271-161	2200	.059				.12	.24	01/25/74	215	UC, 74, 100260	
271-162	2200	.059				.11	.23	01/25/74			
271-163 ^c	2160			2.8		.23	.25			UC, 74, 100260	
271-164B	2100+	Insufficient	0.13	2.7		<0.25	<0.25	11/13/74	100	Shell Letter Nov. 13, 1974	
271-165A	>2100	Insufficient	0.13	2.7		<0.25	<0.25	11/27/74	100	Shell Letter Nov. 27, 1974	
271-165B	2100-2200	Insufficient	--	2.7 ^b		<0.25	<0.25	12/12/74	100	UC, 74, 102432	

1. April 2, 1973, Freitas to Farber, Shipment of 45 lbs was on 22 Feb. 1973.

a. Shell letter 15 June 1973, Freitas to Phillips, calls out 3.7 pound shipment.

b. Low temperature DEPECH.

c. Phone call from Paul Van Shaw 19 August 1975, to J. D. Marks.

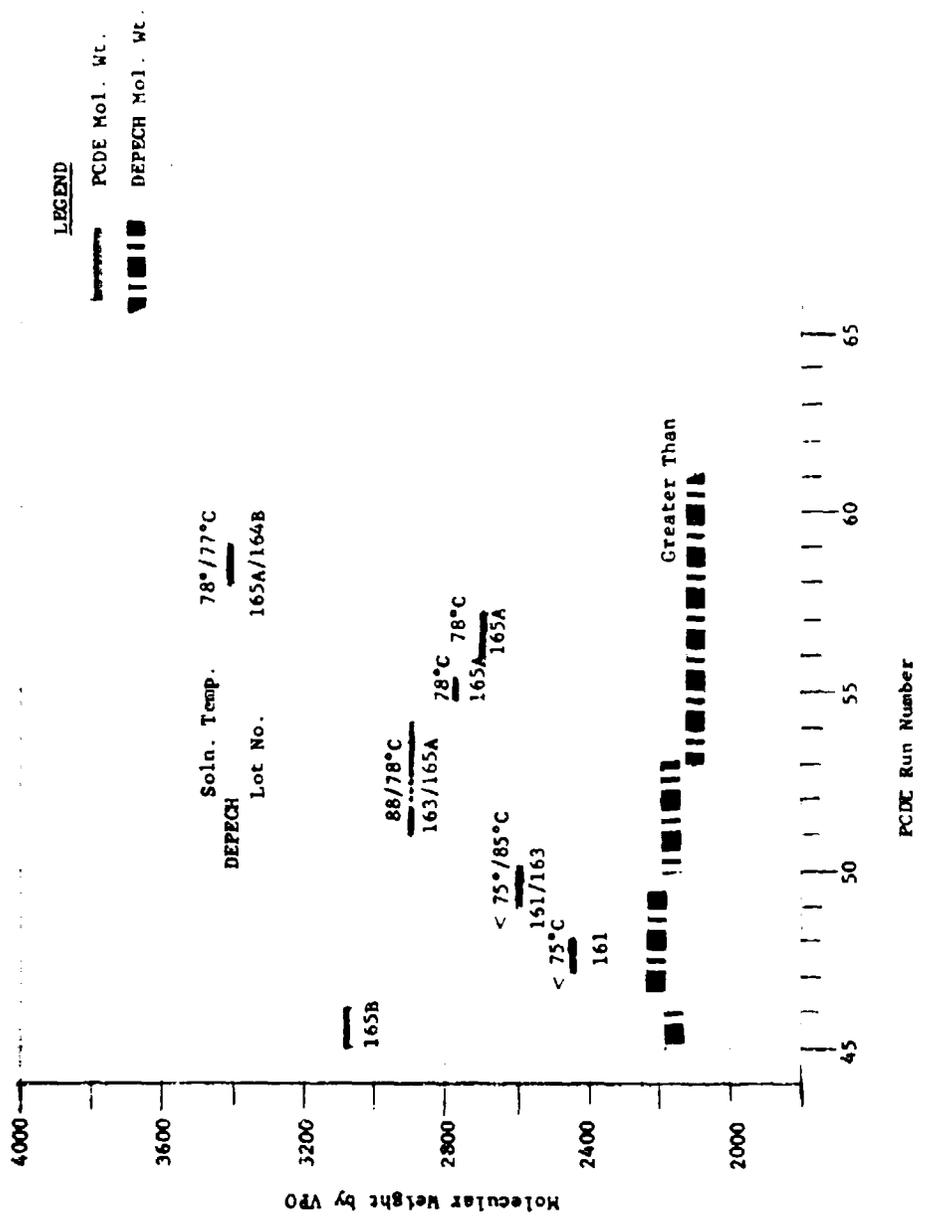


Figure 10. PCDE and DEPECH Molecular Weights VS PCDE Run Number

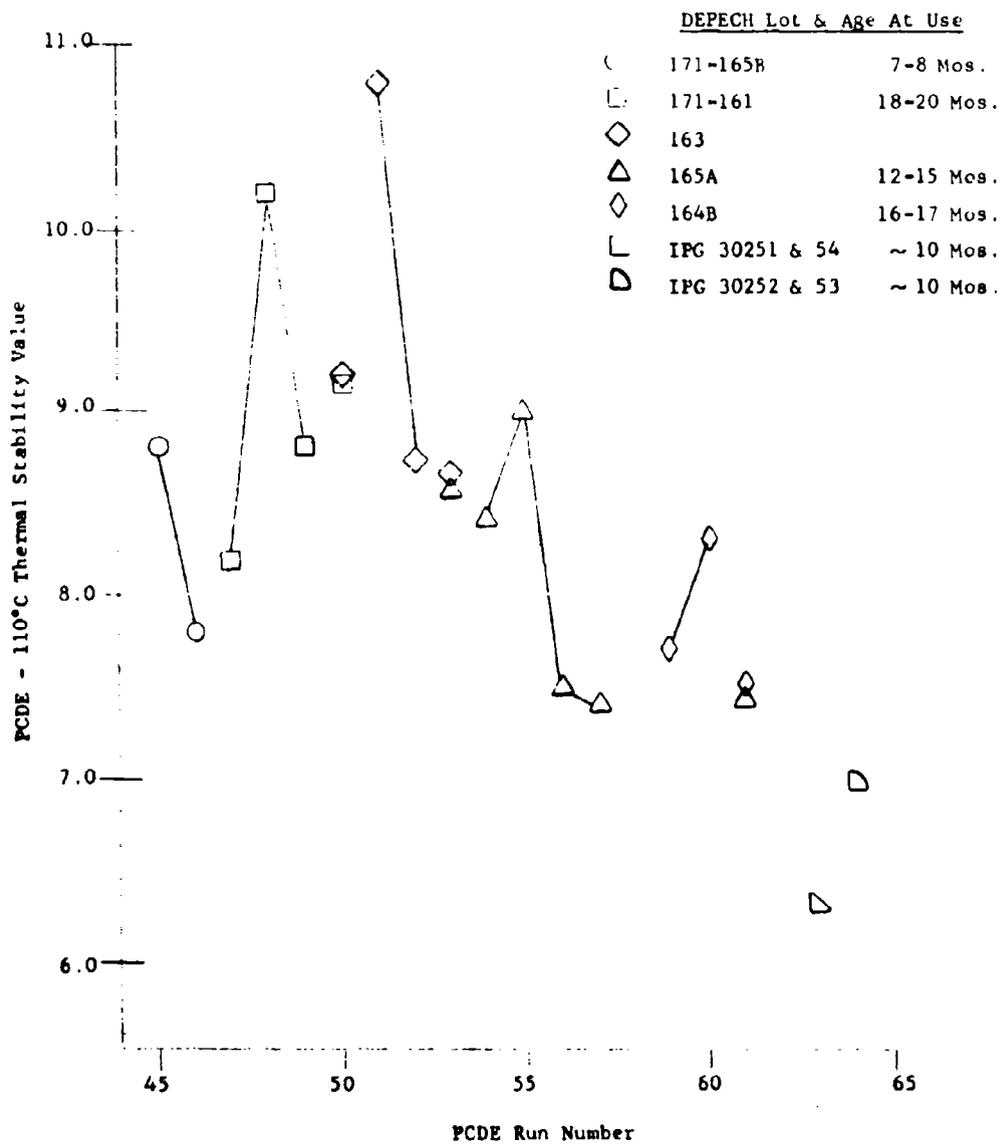


Figure 11. PCDE Thermal Stability VS Run Number and by DEPECH Lot Number

TABLE 11. DEPECH ANALYSIS VS PCDE THERMAL STABILITY

DEPECH Lot No.	PCDE		DEPECH Analysis						
	Run/Blend Number	Thermal Stability		MW VPO	Temperature For 10% Weight Solution in DMK (°C)	Functionality	Na % Weight	Cl % Weight	Cl/Na
		140°C	110°C						
271-160	25	140	Blend 7.5	2200±100	< 75	2.8	.02	.18	9.0
	29								
	30								
271-161, 162	31	124		2200	< 75	Not Reported	.11	.23	2.08
	38								
271-165B	39	298	11.7	2150±50	< 75	2.7	< .25	< .25	~1.0
	42A		12.3						
	42B		11.1						
	43		7.5						
	44		8.0						
	47A		--						
	47B		8.8						
	45		--						
	46		--						
	46B		7.8						
	165								
	271-161		47						
48		7.8							
48B		7.8							
49		8.8							
50		9.2							
271-161/163	50B	--	9.6	2160	80	2.8	.23	.25	1.1
	51		10.8						
271-163	52	191	8.7	> 2100	78	2.7	< .25	< .25	
	53		8.6						
271-163/165A	54B	144	8.5						
	54		8.4						
271-165A	55B	211	9.0	200	77	2.7	< .25	< .25	
	56		7.5						
	57		7.4						
	57B		7.9						
	58		8.2						
	58B		8.3						
	59		7.7						
	60		8.5						
	61B		7.6						
	61		7.5						
271-164B	59	200	7.7	> 2100	77	2.7	< .25	< .25	
	60		8.5						
271-164B/165A	61B	111	7.6						
	61		7.5						

TABLE II. DEPECH ANALYSIS VS PCDE THERMAL STABILITY (Cont)

DEPECH Lot No.	PCDE		DEPECH Analysis							
	Run/Blend Number	Thermal Stability		MW	VPO	Temperature For 10% Weight Solution in DMK (°C)	Functionality	Na % Weight	Cl % Weight	Cl/Na
		140°C	110°C							
IPC 30251 } 30254 }	62	71	6.3			< 75				
IPC 30252 } 30253 }	63	102	7.0			< 75				
IPC 3015, 2, 3, 4	64					< 75				
12516-36-2	65					< 70				
SUMMARY:										
n				7			5	4	4	
\bar{X}				2158.57			2.74	.12	0.23	
S				44.88			0.05	.09	0.03	
$\bar{X} \pm 3S$				2293-2023			2.90-2.58	.38-0	.32-.13	

TABLE 12. DEPECH SOLUBILITY

DEPECH Lot No.	Temperature At Which 10% W Soluble In 90% W Acetone (°C)
160	< 75 ^a
161	< 75 ^a
161/162	< 75 ^a
163	80
164B	77
165A	78
165B	
1 GP (All)	< 75 ^a
12516-30-2	< 70 ^a
<p>a. Temperature of test bath was at temperature stated. Dissolution may have occurred at a lower temperature.</p>	

TABLE 13. TENTATIVE SPECIFICATION FOR DEPECH

Item	Determination	Method	Requirement	Specification	Reference Lot
1	Molecular Weight	VPO	Purchase	> 2000	171-160, -161, -162, -163, -164B, -165A, -165B
2.1	OH, Eq./100 g		Purchase	Report	Same as above.
2.2	Hydroxyl Functionality	Calculate from Items 1 & 2	Purchase	> 2.6	Same as above.
3	Solubility in Acetone, 10% Soln.	Temperature at which completely soluble in 30 min.	a) Purchase b) Preuse ^a	Desirable Below 75°C	Same as above.
4.1	Na, % Weight			< 0.30	Same as above.
4.2	Cl, % Weight			< 0.35	Same as above.
5	Clefin, Mols/100 g		Purchase	Report	271-153
6	Carbonyl	IR	a) Purchase b) Preuse ^a	Less Absorption Than Methylene Peak	Telecon, Shaw & Ryder, 10 Mar. 1975.
7	Molecular Weight No. Avg. Weight Avg. Ratio No. Avg./Wt. Avg.	GPC	Purchase	Report	--
				Report	--
				Report	--
8	Odor	Smell	a) Purchase b) Preuse ^{a, b}	No Acetic Acid Odor	Telecon, Shaw & Ryder, 10 Mar. 1975.
9	Water	GPC	Purchase	< 0.25%	Run 69

NOTES: a. "Preuse" means by consuming facility and within 30 days of actual use.
b. At use.

C. OTHER RAW AND PROCESS MATERIALS

Acetone, methylene chloride, trimethylamine, and molecular sieves were obtained and used as standard commercial products. Government specifications are available and were used in the purchase of the first two listed.

1. Acetone, Technical

Acetone was procured in 55-gallon drums to Federal specification O-A-51F on a certificate of analysis. One problem which occurred early in the program was the presence of excess water. The water came from the local vendor who was filling wet drums from his large storage tank.

It is imperative that the using facility test all acetone used to assure compliance with the maximum water limitation of paragraph 3.7 "Impurities" of specification O-A-51F.

Another impurity that can exist in acetone is the dimer, diacetone alcohol. The material reacts to form a contaminant in the PCDE/PBEP product.

a. Recommendation

Purchase acetone to Federal specification O-A-51F on certificate of analysis. The specifications are quite detailed and a few of the more important specifications are given in Table 14. Also shown is the recommended specification for diacetone alcohol content. The using facility must recheck all new containers or tank shipments for excess water and diacetone alcohol within 30 days before use.

2. Methylene Chloride

Methylene chloride (dichloromethane) was purchased in 55-gallon drums and used without problem in the manufacture of PCDE. Procurement has been to MIL-D-6998C, Grade A. (Grade A specifies maximum acidity as 0.005 percent compared with Grade B at 0.010 percent).

a. Recommendation

Purchase methylene chloride to specification MIL-D-6998C, Grade A. Some of the important specifications are given in Table 15.

TABLE 14. SOME ACETONE SPECIFICATIONS FROM O-A-51F

Characteristic	Specifications
Specific Gravity (20°/20°C)	0.791-0.793
Distillation Range	Entirely within 1°C range, including the temperature 56.1°C.
Color	No darker than No. 5 on platinum-cobalt scale.
Odor	Characteristic nonresidual odor.
Permanganate Reduction	Retain color at least 30 minutes at 25°C in dark.
Water Miscibility	Miscible with distilled water in all proportions.
Impurities:	<u>Max. Limit</u>
Nonvolatile Matter, gm/100 milliliter	0.005
Water, %, w	0.50
Acidity (as CH ₃ COOH), %, w	0.002
Alkalinity (as NH ₃), %, w	0.001
Aldehydes (as HCHO), %, w	0.002
Diacetone Alcohol, %, w	0.1
* Not Federal specification.	

TABLE 15. METHYLENE CHLORIDE SPECIFICATION FROM MIL-D-6998C

Characteristics	Minimum	Maximum
Color (Platinum-Cobalt)		No. 20
Specific Gravity, 25°/25°C	1.317	1.322
Distillation Range		
Initial Boiling Point, °C	39.0	
Dry Point, °C		41.0
Nonvolatile Matter, %w		0.002
Acidity (as HCl)		0.01
Water Content, %w		0.02
Free Halogens		To Pass Test
Residual Odor		None

3. Trimethylamine (TMA)

TMA was purchased in 125-lb net cylinders at 99 percent weight minimum purity. The commercial product has the following specification requirements:

<u>Component</u>	<u>Weight (%)</u>
Trimethylamine	99.0 min
Monomethylamine	0.1 max
Dimethylamine	0.4 max
Ammonia	0.0 max
Water	0.5 max
Formaldehyde	0.0 max

a. Recommendation

Purchase commercial trimethylamine to above analytical specification. Require a Certificate of Compliance.

4. Molecular Sieves

Two grades of molecular sieves were used in the process, each with a different function. They were purchased as a commercial product, bead shape, 8 to 12 mesh size, standard type, as follows:

<u>Molecular Sieve</u>	<u>Effective Pore Opening (Å)</u>	<u>Grade^(a)</u>
13X	9-10	544
3A	3	564

a. Recommendation

Purchase commercial grade molecular sieves to above description, packaging for convenience. Care must be taken to reseal opened containers immediately after withdrawal to seal out moisture.

D. PCDE SPECIFICATION

The ultimate decision on the acceptability of PCDE is made depending upon the results of its use in a given propellant formulation. The formulation data have not been made available and/or are still in evaluation. Therefore, only the results of direct analytical measurements of the PCDE shipped can be examined. Data obtained before the N-fluorazoxy problem was resolved and data related to the lower molecular weight DEPECH feed stock are omitted as nonrepresentative of future production.

Thermal stability (T.S.) results from PCDE Runs 38 through 67 and for the shipment of PCDE are repeated in Table 16. The ranges for 110° C thermal stability were 11.7 to 5.0 for the individual runs and 9.6 to 5.0 for the blends. Application of the statistical three sigma value to the average makes the anticipated ranges 12.3 to 3.7 and 11.6 to 4.0, respectively. No clear relationship was found between the values of

^(a) Grades are those of Davison Chemical Division, W. R. Grace & Co., and define the specific material used in the program for producing acceptable PCDE. No endorsement is given, express or implied. There is no present reason to believe that similar materials of other vendors would not perform equally. Linde 13X cylindrically shaped sieves were used very early in the program.

TABLE 16. PCDE THERMAL STABILITY RESULTS

Run Number	Production Runs		Blend No.	Shipments	
	T.S. @ 110°C	T.S. @ 140°C		T.S. @ 110°C	T.S. @ 140°C
38	11.7	249			
39	--	133			
42	7.5	200			
43	8.0	111			
44	6.4	89	B47	8.8	186
45	8.8	204			
46	7.4	120	46	7.8	165
47	8.2	107			
48	10.1	190	48	9.1	159
49	8.8	128			
50	9.2	133	50	9.6	157
51	10.8	151			
53	8.6	151	54	8.5	144
54	8.4	211			
55	9.0	153	55	9.0	153
56	7.5	138			
57	7.4	147	57	7.9	177
58	8.2	160			
59	7.7	200	59	8.3	160
60	8.5	186			
61	7.5	133	61	7.6	110
62	6.3	71			
63	7.0	102	63	6.8	93
64	7.0	80			
65	6.6	160	65	6.8	173
66	5.0	71	66	5.0	71
67	6.6	178	67	6.6	178
<u>Samples</u>	26	27		13	13
\bar{X}	8.01	146.5		7.83	148.1
S	1.45	45.7		1.27	35.2
$\bar{X} \pm 3S$	12.3	283.5		11.6	253.8
$\bar{X} - 3S$	3.7	9.6		4.0	42.5

individual runs and that of the blends into which they are mixed. For example, Blend 50, made from Runs 49 and 50, has a higher T.S. at 9.6 than either of the individual runs at 8.8 and 9.2, respectively; while Blend 54, made from Runs 51, 53, and 54, has a T.S. of 8.5 which is near the smallest value of the three lots blended; 10.8, 8.6, and 8.4, respectively.

From inspection of these data and considering the number of samples available, statisticians recommend that the specification values for the 110° C T.S. be set at 12 cc/gm-100 hr, with realization that provision be made for about 5 percent line loss. If formulation requirements dictate a lower value, a higher line loss provision must be made until additional experience is gained.

Table 17 is a tabulation of recommended tests for PCDE production and sale. Supporting data are summarized in Table 18. Most of the items listed are self-explanatory; however, some comments are in order.

Infrared is used as a process control to assure that complete conversion from PBEP to PCDE has occurred and to assure that no "N-fluorazoxy" is present.

The T.S. at 140° C, while not a contractual requirement for PCDE acceptance, is useful as a measure of the T.S. of the PCDE. Generally speaking, a "good" 140° C T.S. indicates that a "good" 110° C T.S. will follow. The 140° C T.S. test takes only 5 hours vs 8 days for a 110° C T.S. This short time required will allow plant personnel to make decisions regarding the next production runs without having to wait several days for 110° C T.S.

Although a molecular weight of greater than 3000 is desired, values determined for the blends have ranged from 2400 to 3644. Therefore, the 3000 value should not be made a firm specification requirement at this time.

Beginning with Run 54, the molecular weight determinations were possible by gel permeation chromatography. Table 19 lists the results of this analysis compared to the VPO numbers. The results are inconclusive as the GPC numbers actually have a greater variance than do the VPO numbers. Further study could be made using the GPC, as this method is a much faster analysis than VPO and, if proven reliable, could be an aid in process control.

Both elemental fluorine and elemental nitrogen in the PCDE have been determined. Since their ratio in the molecule is fixed by molecular structure, and since serious alteration of molecular structure would be apparent by the occurrence of an unusual infrared scan, only fluorine analysis should be made in the final product.

The process control analysis requirements for the intermediate PBEP are given in Table 20.

TABLE 17. PCDE PRODUCTION TESTS

Item	Determination	Method	Requirements	Specification	Notes
1.0	Completeness of Conversion				
1.1	PBEP Content	IR	Process	< 2.7% (Limit of Detectability)	See Memo, Hass to DuBois, 10 June 1975 (Appendix)
2.0	Thermal Stability				
2.1	N-Fluorazoxy	IR	Process	None Detectable	
2.2	Gassing @ 140°C	Shell T.S.	Process	Report Only	Actual Range 71-298
2.3	Gassing @ 110°C	Shell T.S.	Final Product	< 12 cc (100 hr)	Actual Range, Blends 7.4-9.6
3.0	Solids Content, % weight				Actual Range 19.7
4.0	Molecular Weight				
4.1	\bar{M}_N - Osmotic	VPO	a) Process b) Final Product	Report > 20; < 35	
4.2	\bar{M}_N - Gel Permeation \bar{M}_w \bar{M}_w/\bar{M}_N Complete Scan	GPC	Final Product a) Process b) Final Product	> 3000 Desired - None -	Actual Range 2439 to 3414 Recommended Test for process analysis most useful if also performed on DEPECH & PBEP
5.0	Hydroxyl Equivalent per 100 gms				
5.1		Chemical Reactivity	Use to Calculate Functionality	- None -	Actual Range 1690-1830
5.2		Effective Gelation	Use to Calculate Functionality		Actual Range 1793-2421

TABLE 17. PCDE PRODUCTION TESTS (Cont)

Item	Determination	Method	Requirements	Specification	Notes
6.1	VPO + Chemical Reactivity	Calculate From 4.1 & 5.1	Final Product	> 1.65 Desired	Actual Range 1.39-2.02
6.2	VPO + Effective Gelation	Calculate From 4.1 & 5.2	Final Product	Report Only	Actual Range 1.31-1.48
7.0	Residual Acetone, % Weight		a) Process b) Final Product	Report Only < 0.5 % Wt.	Actual Range 0-0.7
8.0	Moisture, ppm		Final Product	< 100	Actual < 50
9.0	Infrared Scan	IR	Furnish With Shipment		
10.0	Fluorine, % Weight			< 26.5	Actual 27.0 to 27.8
11.0	Nitrogen, % Weight			Recommend Discontinue	

TABLE 18. PCDE BLEND LOT ANALYSIS SUMMARY

Test Method Para. Ref. Table (D-2)	3.0 Solids (%)	4.1 Molecular Weight VPO	5.1 Hydroxyl Equivalent Chemical Reactivity		5.2 Gelation	6.1 Hydroxyl Reactivity		6.2 VPO & Gelation	7.0 Residual Acetone (%)	8.0 Moisture (ppm)	9.0 F ₂ (%w)	10.0 N ₂ (%w)
			Reactivity	Reactivity		Reactivity	Reactivity					
Blend of Runs												
B-47, -38, -39, -42A, -42B, -43, -44	20.6	3045	1750	2060	1.74	1.48	0.53	< 50	28.1 ^a 27.0	20.7 ^a 21.0		
B-46, -45, -46	23.1	3089	1830	2160	1.69	1.43	0.17	< 50	28.1 ^a 27.0	20.7 ^a 23.1		
B-48, -47, -48	21.8	2439	1750	1793	1.39	1.36	0.13	< 50	27.4	23.3		
B-50, -49, -50	24.9	2600	1690	1912	1.54	1.36	<0.1	< 50	27.4	22.6		
B-54, -51, -53, -54	20.6	2931	1760	2171	1.67	1.35	<0.1	< 50	27.6	17.2		
B-55, -55	19.7	2780	1730	2014	1.61	1.38	<0.1	< 50	27.8	17.4		
B-57, -56, -57	32.8	2700	1770	2061	1.53	1.31	0.7	< 50	27.7	18.6		
B-59, -58, -59	28.7	3414	1690	2421	2.02	1.41	0.36	< 50	27.8	18.3		
B-61, -60, -61	28.0	3194	1790	2515	1.78	1.27	<0.1	< 50	28.5	20.0		
B-63, -62, -63	29.0	3617	1790	3040	2.02	1.19	<0.1	< 50	28.8	18.5		
B-65, -64, -65	34.7	3021	1780	2306	1.70	1.31	0.218	< 50	27.3	18.8		
B-66, -66	33.9	3441	1820	2709	1.89	1.27	0.127	< 50	28.9	18.8		
B-67, -67	25.9	3644	1850	2869	1.97	1.27	<0.1	< 50	27.7	18.7		
n	13	13	13	13	13	13	13	13	13	*		
\bar{X}	26.44	3070	1769	2310	1.73	1.34	0.22	< 50	27.76	*		
S	5.22	383	49	381	0.20	0.08	0.19		0.62	*		
$\bar{X} + 3S$	42.11	4220	1916	3452	2.33	1.57	0.80		29.62	*		
$\bar{X} - 3S$	10.77	1921	1623	1168	1.14	1.10	<0		25.91	*		

NOTES: a. Superscript is theoretical value based on VPO molecular weight of PCDE.
* Not calculated, includes questionable analyses.

TABLE 19. PCDE MOLECULAR WEIGHT COMPARISON VPO VS GPC

Blend	VPO/MW	\bar{M}_N	\bar{M}_W	\bar{M}_W/\bar{M}_N
54	2931	2930	8,120	2.77
55	2780	2780	7,410	2.67
57	2700	2810	9,870	3.51
59	3414	2800	10,500	3.75
61	3194	2850	9,920	3.48
63	3617	3610	12,200	3.38
65	3021	3300	9,460	2.87
66	3441	3730	9,260	2.48
67	3644	3210	9,460	2.95
68	3260	3300	8,689	2.63
41	2950	2860	9,840	3.44
52	3348	3760	10,370	2.76
n	12	12	12	12
\bar{X}	3192	3162	9,592	3.06
s	315.2	377.1	12,198	.43
$\bar{X} + 3s$	4137	4293	13,251	4.34
$\bar{X} - 3s$	2246	2030	5,932	1.78

TABLE 20. PBEP PROCESS CONTROL ANALYSES

Item	Determination	Method	Requirement	Specification
1.0	Carbonyl	IR	Process Control	
2.0	Olefin	IR	Process Control	None Detectable
3.0	N-fluoroazoxy	IR	Process Control	None Detectable
4.0	Molecular Weight	GPC	Process Analysis	None
4.1	\bar{M}_N			Report
4.2	\bar{M}_W			Report
4.3	\bar{M}_W/\bar{M}_N			Report
4.4	Complete Scan			Report
5.0	Solids Content		Process Control	Report

SECTION VII

RECOMMENDATIONS

A. TRIMETHYLAMINE (TMA) SUBSTITUTE

Although TMA is a relatively weak base and the concentration used (~12 percent w) is fairly low, a noticeable increase occurs in the carbonyl bond of the infrared scan in converting from PEP to PCDE. The increase is attributed to cleavage of the PBEP molecule by TMA in the PCDE reaction. It would be desirable if a substitute base be found that would be less harsh and still get complete conversion to PCDE from PBEP.

TMA has another undesirable trait that would warrant a substitute. It has a very unpleasant odor that remains with the waste water from the process and creates a smell about the operating areas. The odor lingers and in summer months is extremely unpleasant.

If substitution of TMA is proven impractical, a method of treatment of the waste to remove the TMA or complex it to remove the odor would be desirable.

B. SOLVENT SUBSTITUTE

Another possible method of reducing the cleavage of the PBEP molecule in the reactor system would be to find a substitute solvent for acetone. At present, no solvents are recommended and the task may not be an easy one as some work has already been done in this area by others (Shell, Rocketdyne). The solvent must readily dissolve DEPECH, be relatively inexpensive, be nontoxic, and give an improved PBEP. Also, the solvent would have to be compatible with the PCDE reaction system and be easily removed in order to facilitate use as a propellant ingredient.

C. CHARACTERIZATION OF DEPECH

As noted elsewhere in this report, the PCDE quality seems to be dependent on the DEPECH feed. DEPECH from separate lots with apparently the same chemical analysis and no noticeable difference in infrared spectra give PCDE with noticeably different thermal stability and color characteristics. A better characterization of the DEPECH feed would be desirable.

D. DRY ACETONE

Two tests were conducted using acetone dried of water for the PBEP reaction in order to see if a reduction of carbonyl in the PCDE would result. The tests discussed in Section IV showed no improvement in product quality; however, further testing is needed before the desirability of dried acetone is determined.

E. N_2F_4 RECYCLE

A major expense of the PCDE process is the use of excess N_2F_4 in the PBEF reaction. A 40 to 50 percent excess N_2F_4 is required in the reactor. For the contracts reported, the excess N_2F_4 was vented to the atmosphere and lost. Two problems occur when large quantities of PCDE are being produced: the expense and the impact on the environment.

Hercules made some preliminary tests on an N_2F_4 recovery system under a separate contract and successfully operated with N_2F_4 recycle. Further testing to assess the impact of prolonged recycle would be necessary to ensure product quality.

APPENDIX A

MODIFICATION AND SUPPLY OF DEPECH
SHELL DEVELOPMENT COMPANY INTERIM REPORT

MODIFICATION AND SUPPLY OF DEPECH

Interim Progress Report

Subcontract 0136-03001

Prime Contract FO4611-73-Q-0014

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SHELL DEVELOPMENT COMPANY
A Division of Shell Oil Company
Houston, Texas

Period Covered: February - June, 1973

Date Issued: July, 1973

ABSTRACT

Modified PECH of improved molecular weight and functionality has been produced by using either hexane or methanol to extract a solution of standard PECH in methylene dichloride. In addition, improved PECH has been directly prepared by using a low temperature polymerization technique. It has been established that properties of both types of modified PECH carry through to the DEPECH derived from them. Accordingly, sufficient quantities of both types have been prepared to permit their conversion to PCDE by Hercules Incorporated. A rough cost estimate has been prepared for the PCDE process including PECH extraction as an additional step. In addition, 180 pounds of standard quality DEPECH was prepared in our pilot plant facilities for use by Hercules in meeting current Air Force requirements for PCDE supply.

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PECH Improvement by Alteration of Processing Conditions

Preparation of PECH with New Initiators

1,1,1-Trimethylolethane

1,1,1-Trimethylolpropane

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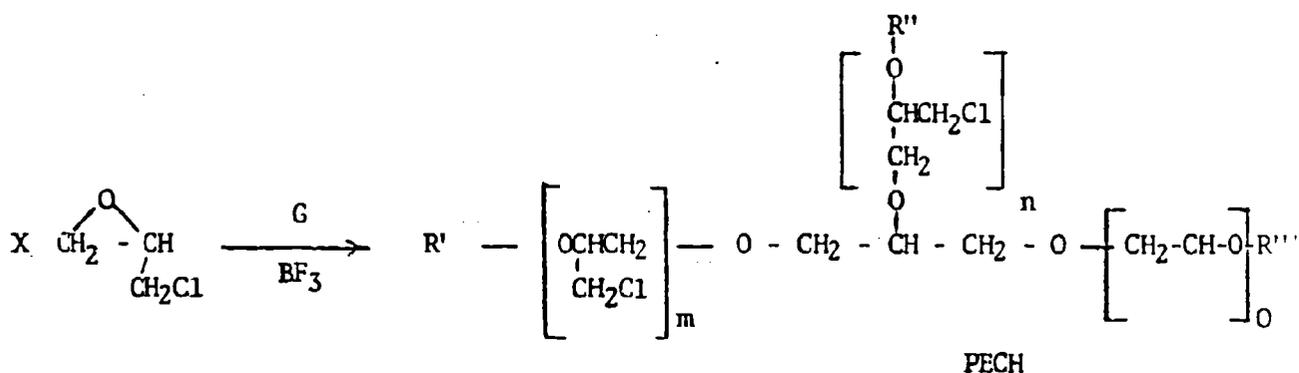
ABBREVIATIONS AND SYMBOLS

DEPECH	Poly (2,3-epoxypropene)
DMSO	Dimethyl sulfoxide
ECH	Epichlorohydrin
EPC	Equivalent Process Capital
G	Glycerol
MDC	Methylene dichloride
PECH	Polyepichlorohydrin
THF	Tetrahydrofuran

Introduction

PCDE is a thermally stable, energetic binder component for solid fuel rocket motors. It was first prepared by Shell Development Co. in 1969 from PBEP, a more energetic though less thermally stable material intended for the same end use. The work leading to the establishment of the manufacturing process for PCDE has been carried out under various contracts (1,2,3,4,5) sponsored by the Air Force.

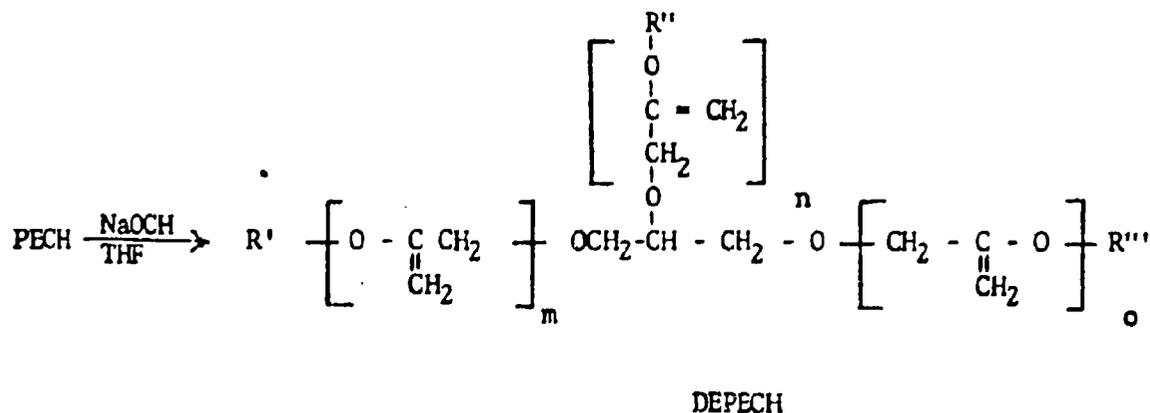
The synthetic route leading to standard PCDE is divided into four steps. In Step 1, epichlorohydrin (ECH) is polymerized to form polyepichlorohydrin (PECH) utilizing a boron trifluoride/glycerine (G) complex as initiator.



On the average 1.7 to 2.2 R groups are CH_2CHOH , 0.8 to 1.3 groups are non- CH_2Cl

functionally terminated, and $m+n+o = 25$ to 30.

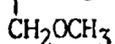
In Step 2, PECH is dehydrochlorinated to form poly (2,3-epoxypropene) (DEPECH) by treatment with sodium methoxide in a 93/7 tetrahydrofuran (THF)/dimethylsulfoxide (DMSO) reaction medium.



The functionality of the PECH remains essentially unchanged as it is converted to DEPECH. The terminal $-\text{CH}_2-\text{CHOH}$ groups of the PECH are converted to



$-\text{CH}_2-\text{CHOH}$ groups in this step.



In Step 3, PBEP is prepared from DEPECH. The hydroxyl functionality of this product is in the range of 1.6 to 2.0 and the molecular weight is 3000 to 4000.

In Step 4, PBEP is converted to PCDE. The hydroxyl functionality of the product is essentially unchanged from that of the starting material. The molecular weight falls in the range 2800 to 3000.

During the past eight years several hundred pounds of PBEP and nearly 150 pounds of PCDE have been prepared by Shell Development Co. for evaluation by various propellant processors designated by the Air Force. Standard PCDE has a typical molecular weight of 2900 and a functionality of 1.8. While we understand that cureability of this material has been acceptable and tensile properties of the cured specimens adequate for the intended application, an improvement in both these qualities was desired by the Air Force. A small sample (3.5 pounds) of PCDE prepared from a high molecular weight, hexane precipitated sample of PBEP was sent to Edwards Air Force Base July 10, 1970 for evaluation. This sample possessed a molecular weight of 3750 and a hydroxyl functionality of 2.0. We understand that samples of this material (LR-9851-169) demonstrated significantly improved tensile properties, and that rocket motors cast from it did not require the use of a bonding agent. From the improved properties reported for this PCDE sample there evolved the current project, one of the goals of which is development of means for preparation of higher molecular weight, higher functionality PCDE.

Hercules, Inc. has been awarded a contract by the Air Force, FO-4611-73-Q-0014, with two requirements: (1) To supply standard PCDE to the Air Force for further evaluation work; and (2) To develop means for preparation of higher molecular weight, higher functionality PCDE. Hercules has negotiated a subcontract with Shell Development Co. (0136-03001) with the two goals listed below.

- (1) Development of methods for producing a PCDE of improved molecular weight and functionality
- (2) Production of 180 pounds of standard DEPECH to be delivered to Hercules for conversion to PCDE.

The impracticality of preparing improved PCDE by the previously employed means of hexane precipitation of PBEP was recognized immediately, and this procedure was not seriously considered as a means of achieving the desired goals of the project. It was obviously much more practical to consider processes which would operate on one of the two PBEP precursors, DEPECH or PECH. Since DEPECH is highly unsaturated and would be expected to be the less stable of these two polymers, it was felt that the more fruitful approach would be one which was concerned with upgrading PECH.

Promising methods of upgrading PECH discovered during the laboratory investigation would be utilized for preparing larger samples (3-6 pound) which would then be dehydrochlorinated by Shell, converted to PCDE by Hercules, and evaluated by the Air Force.

Two methods of upgrading PECH were to be investigated during this program: (1) Subjection of standard PECH to a treatment which would retain only the higher molecular weight, higher functionality components, and (2) Alteration of the conditions of the PECH preparation step so as to produce directly a polymer improved in molecular weight and functionality.

The first method was to be limited to an investigation of various means by which standard PECH could be extracted or partitioned between two liquids such that the lower molecular weight components would be selectively removed, thereby producing a higher molecular weight, higher functionality product. It was hoped that this product would then retain its improved properties as it was carried through the next three steps of the PCDE process.

The second method for producing an improved PECH was to be concerned with two different process variants in the PECH preparation step. One variant involved the use of a polymerization initiator containing three primary hydroxyl groups, instead of the two primary and one secondary contained in the usual initiator, glycerine. The other variant involved increasing the ratio of ECH monomer to initiator during the polymerization step.

In accord with terms under subcontract 0136-0300, findings and conclusions from our pertinent product improvement and supply efforts are presented in the following report.

PECH Fractionation

Introduction

In some early work on the PBEP program (6), an exploratory methanol extraction of PECH was reported to have given a raffinate polymer with both higher molecular weight and functionality. DEPECH (7) and PBEP (8) have also been solvent extracted. Both appeared to give improved final products. As a result of these observations, initial study in present work was aimed at confirming the utility of solvent extraction of PECH by determining the extent to which molecular weight and functionality could be raised in this manner. It was hoped that if the quality of the PECH were markedly improved, a comparable improvement in the quality (and performance) of the derived PCDE would result.

Solvent Survey

A first approximation of the mutual solubility of two liquids can be made from a knowledge of their cohesive energy densities (Hildebrand's solubility parameter, δ) (9). Polymer theory and solubility parameters will indicate the role of the third component, namely the polymer. Normally, two immiscible or partially miscible solvents are chosen and the distribution of the third component between these solvents is studied. When the third component is a polymer, however, it is possible in many cases to use a pair of completely miscible solvents. The presence of the polymer more often than not produces a two-phase region in the ternary isothermal (10). The system of greatest utility for polymer fractionation usually consists of two mutually soluble liquids of which one is completely miscible with the polymer and the other is either a non-solvent or a poor solvent for the polymer. While these isothermal phase relationships are normally drawn as conventional 3-component diagrams, it must be kept in mind that the polymer almost always consists of a mixture of molecular species differing in molecular weight or functionality or both. Variations in the nature of the polymer (average molecular weight, etc.) lead to changes in the shape of the binodal region of the ternary isothermal. However, these changes are minimal when dealing with a single type polymer whose properties vary little from batch to batch. For simplicity, therefore, the present ternary diagrams treat PECH as if it was a single pure compound. In addition, the solvent of the ternary system, solvent/non-solvent/polymer, is conveniently methylene dichloride (MDC), the solvent used in the PECH preparation step. Thus, the problem reduces itself to identifying a non-solvent which will selectively separate PECH into fractions differing from each other in molecular weight and functionality.

As a first step, exploratory scouting extractions were run using 12 different non-solvent candidates. Included were compounds both higher and lower in solubility parameters (δ) than MDC and PECH, both of which have solubility parameters of 9.7.^a) Table 1 below summarizes the data.

a) $\delta_{25^\circ\text{C}}$ for PECH was calculated from theory

TABLE I. PHASE RELATIONSHIPS IN THE PECH/MDC/NON-SOLVENT SYSTEM
 BASIS: 25 ml solvent plus 25 ml PECH/MDC solution, 25°C

Solvent	$\delta_{25}^{\circ}\text{C}$	Feed, %w PECH in MDC	Volume of Lower Layer, ml					
			60	30	15	7	4	0
n-hexane	7.3		21	13	7	3	0.2	m ^(a)
cyclohexane	8.2		23	17	m	-	-	m
ethylbenzene	-		-	m	-	-	-	m
diethyl ether	7.4		-	m	-	-	-	m
p-dioxane	9.9		-	m	-	-	-	m
glycerine	16.5		25	-	-	-	-	25
ethanol (95%)	12.7 ⁺		21 ^(b)	10	m	-	-	m
acetone	10.0		-	m	-	-	-	m
isopropanol	11.5		21 ^(b)	12	m	-	-	m
methanol	14.5		25 ^(b)	m	-	-	-	m

a) homogeneous

b) addition of water ($\delta_{25}^{\circ}\text{C}=23.4$) increases size of lower layer

Successive extractions of 60% PECH and also 30% w PECH in MDC with n-hexane showed that the lower layers could become so rich in polymer that they became essentially intractable, viscous masses at room temperature. The n-hexane would so concentrate the polymer in the lower layer (ca. 80%w PECH) that the layers separated very slowly, if at all. These observations suggest that within the bounds of economics the most dilute (MDC rich) solutions possible should be used in the extractions if n-hexane is the non-solvent. In addition, it is known from polymer theory that the efficiency of molecular weight separations is greater the more dilute the system (11).

Out of the qualitative screening experiments described above, two solvents were chosen for further study: n-hexane ($\delta_{25}^{\circ}\text{C}=7.3$) and methyl alcohol ($\delta_{25}^{\circ}\text{C}=14.5$).

Ternary Diagrams

The ternary isothermals (23°C) for PECH-MDC-n-hexane and PECH-MDC-methanol have been determined. Figures 1 and 2 and Tables II and III give the data. The n-hexane system has a much larger binodal area than the methanol system. Extrapolation of the data for n-hexane suggests that PECH and n-hexane are, for all practical purposes, mutually insoluble.

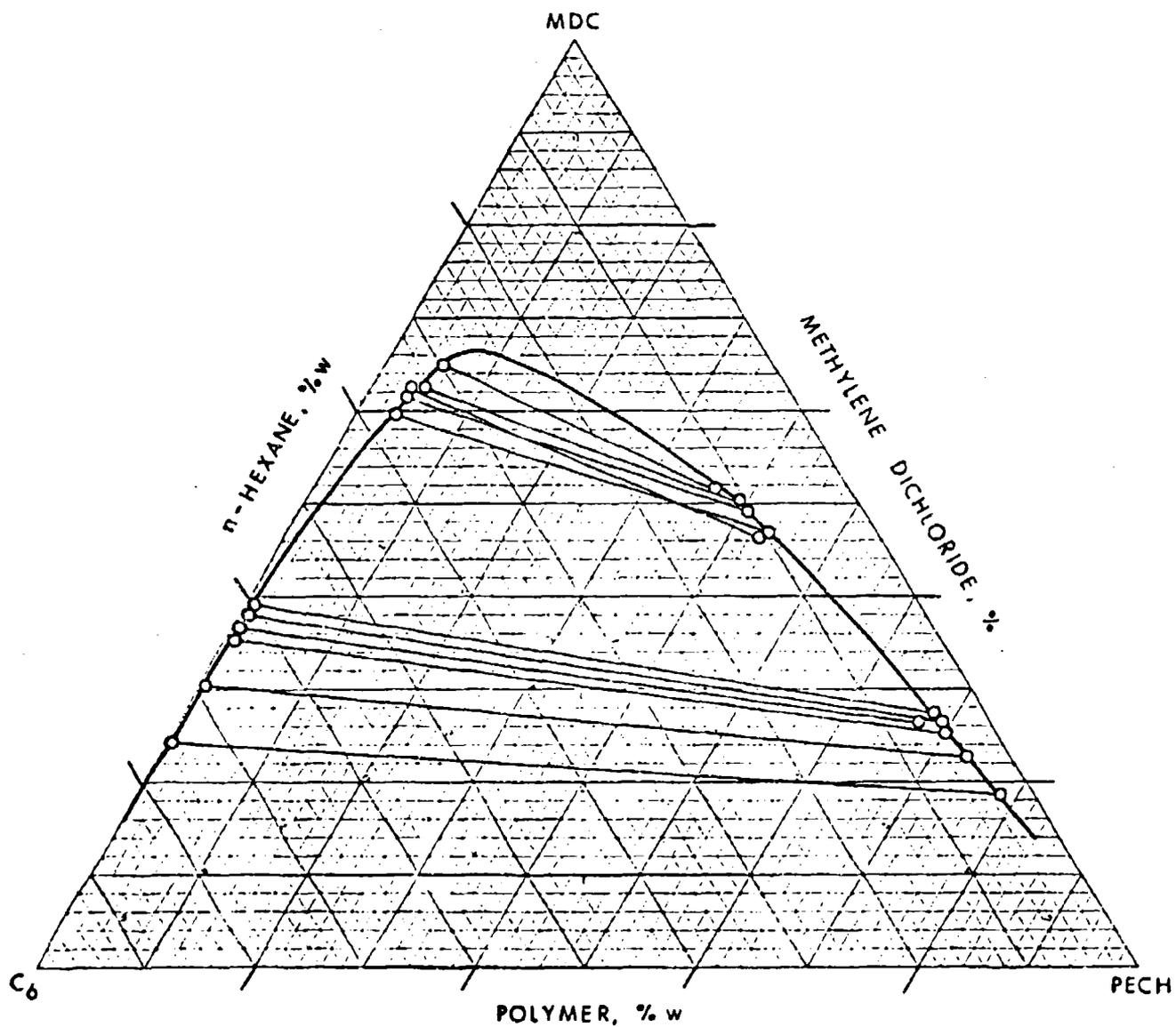


FIGURE 1 TERNARY DIAGRAM OF THE SYSTEM PECH-MDC-C₆ at 23°C

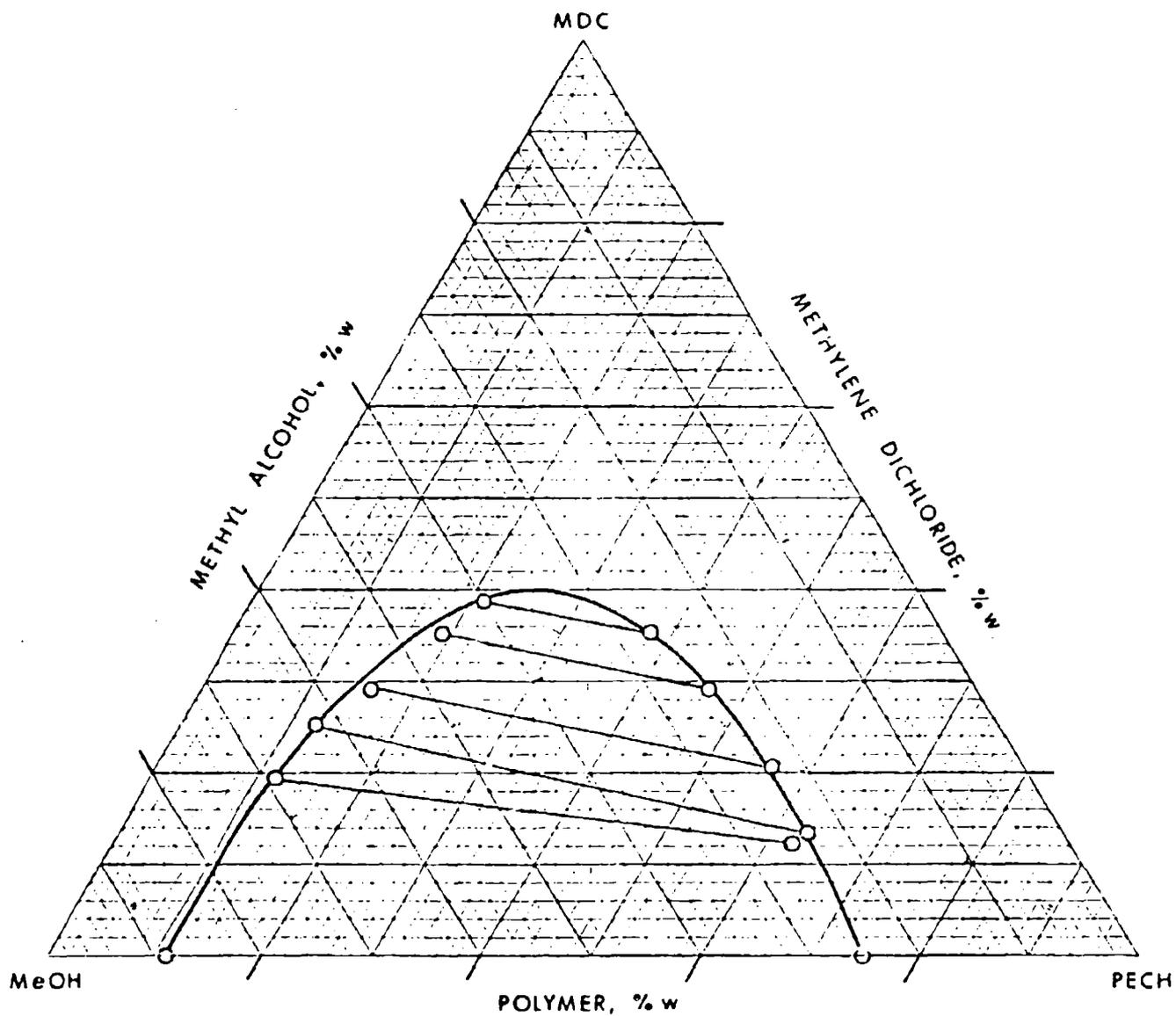


FIGURE 2 TERNARY DIAGRAM OF THE SYSTEM PECH-MDC-METHANOL AT 23°C

TABLE IX. SUMMARY OF DATA: FECH-MDC-METHANOL SYSTEM AT 23°C

Run No.	Charge, wt %			Total Composition, wt %			Analysis, wt %			Lower Layer		wt % Extracted						
	FECH	MDC	MeOH	FECH	MDC	MeOH	Upper Layer	Lower Layer	Mol OR H ₂ O	Functionality								
							FECH	MDC	MeOH	FECH	MDC	MeOH	wt %					
251-	-	-	-	61.8	38.2	-	-	-	-	-	-	-	-					
57(Feed (2PI))	-	-	-	61.8	38.2	-	-	-	-	2232	0.069	0.15	1.81 ^(b)					
64	100	50	155	23.7	32.6	43.7	18.2	32.5	49.3	46.2	29.0	24.8	3280	0.073	0.035	2.40	72.9	
66	100	-	100	35.2	21.9	42.9	15.2	23.2	55.6	56.3	20.9	22.3	-	-	-	-	19.3	
68	110	-	150	33.8	21.0	45.2	12.1	25.4	62.5	62.9	13.5	23.5	3180	0.074	0.048	2.35	24.0	
70	75	50	120	23.0	39.0	38.0	21.2	38.6	40.2	38.0	35.4	26.5	3720	0.068	0.081	2.53	86.7	
76	-	-	-	-	-	-	11.0	0.0	89.0	74.8	0.0	25.2	-	-	-	-	-	-
112	800	-	1091	34.2	21.1	44.7	11.6	19.7	68.7	62.5	12.3	25.2	2885 ^(a)	0.082	0.059	2.36	29.2	
													Upper Layer (1502	0.144	0.108	1.56		

a) DEFECH made from this material had a molecular weight of 2130 (see also Run 251-104, Table III).

b) Average of six determinations: 1.54, 1.54, 2.0, 1.9, 1.9, 2.0

TABLE III. SUMMARY OF DATA: DEPCB-MDC-HEXANE SYSTEM AT 23°C

Run No.	Charge, CC		Total Composition, %w		Analysis, %w				Lower Layer		Wt. Extracted	
	DEPCB	MDC	DEPCB	MDC	Upper Layer DEPCB	Upper Layer MDC	Lower Layer DEPCB	Lower Layer MDC	Mol Wt. OH eq/100g	H ₂ O Functionality		
251-	-	-	61.8	38.2	-	-	-	-	2232	0.069	0.15	1.81 ^(b)
57(Feed 12P1)	100	50	49.8	30.7	19.5	0.45	39.0	60.5	67.5	27.6	4.8	1.78
46	100	100	41.9	16.2	31.9	0.27	30.2	69.5	73.4	22.9	3.7	0.31
50	100	200	34.3	21.5	44.2	0.12	24.2	75.7	78.2	18.6	3.2	0.21
52	100	100	37.2	42.1	20.7	3.32	59.7	37.0	43.6	46.6	9.8	7.30
54	100	200	15.2	59.8	25.0	4.55	62.9	32.5	38.9	50.1	11.0	21.2
58	50	100	23.4	53.2	29.8	5.07	65.6	34.5	36.1	51.0	12.9	-
60	50	150	11.6	65.9	22.5	5.19	66.1	26.7	31.4	54.5	14.1	39.8
78	50	25	24.3	34.7	41.0	0.29	38.3	61.4	69.1	26.8	4.1	0.82 see-46
80	25	50	9.0	36.0	55.0	0.25	35.2	64.5	70.0	25.4	4.6	2.18 see-46
104	300	900	11.5	68.0	30.5	3.46	61.9	34.6	40.4	49.2	10.4	33.5
93(Feed 12P2)	-	-	61.0	39.0	-	-	-	-	-	-	-	-
88	100	50	46.7	31.3	20.0	0.55	35.0	64.4	67.0	27.7	5.3	0.34 see-46
90	100	200	17.0	56.4	26.6	3.18	61.0	35.8	43.1	46.3	10.6	15.3 see-54

a) DEPCB made from this material had a molecular weight of 2180 (see also Run 251-112, Table II).

b) Average of six determinations: 1.54, 1.54, 2.0, 1.9, 1.9, 2.0

Methanol and PECH, however, are mutually soluble to a limited extent. In addition, a few qualitative experiments involving changing the temperature of two phase compositions in both the hexane and methanol systems near their respective plait points suggested that the binodal region of the methanol system is more sensitive to temperature.

Reproducibility was tested for the n-hexane ternary in two ways. One was to test the variation of tie-lines using different feeds. The other was to vary the total composition along the same tie-line. Table IV below shows the reproducibility using two feeds.

TABLE IV. REPRODUCIBILITY OF EXPERIMENTS IN THE PECH-MDC-HEXANE SYSTEM

PECH Feed Batch No.	Composition, %w		Layer	Molecular Weight
	PECH	MDC		
I2P2 (a)	0.6	35	UL	-
"	67	28	LL	2400
"	3.2	61	UL	-
"	43	46	LL	2700
I2P1 (b)	0.5	39	UL	-
"	68	28	LL	2500
"	4.5	63	UL	-
"	39	50	LL	2700

a) MW = Ca. 2300

b) MW = Ca. 2200

The results are in fair agreement in terms of both liquid layer compositions and the improvement in molecular weight.

The conjugate solution compositions for a given tie-line are relatively constant even though the ratio of the two phases is varied. Table V below illustrates this point.

TABLE V. COMPOSITION OF CONJUGATE SOLUTIONS IN THE PECH-MDC-HEXANE SYSTEM

Weight Ratio, UL/LL	Composition, %w			
	Upper Layer		Lower Layer	
	PECH	MDC	PECH	MDC
0 (Feed)	-	-	62	38
0.4	0.5	39	68	28
1.9	0.3	38	69	27
6.1	0.3	35	70	25

As might be expected, the depth of extraction varied for the runs given in Table V, and the greater the depth of extraction the greater was the improvement in molecular weight of the polymer left in the lower layer. The deviation from a constant molecular weight reflects the "pseudoternary" nature of the system.

Table VI shows this deviation.

TABLE VI. MOLECULAR WEIGHT OF RAFFINATE VS DEPTH OF EXTRACTION IN PECH-MDC-HEXANE SYSTEM

<u>Weight Ratio UL/LL</u>	<u>Extraction Depth, %</u>	<u>PECH Product, Molecular Weight</u>
0 (Feed)	0	2200
0.4	0.28	2500
1.9	0.82	2700
6.1	2.8	2800

The depth of extraction using n-hexane can be varied not only by changing the total composition along a given tie-line (Table VI) but also by changing to another tie-line (at a constant phase ratio) located toward the plait point and thus in the direction of lower polymer concentrations. Similar variations in total composition were not studied in the methanol system, but the same trends probably exist.

Functionality and Molecular Weight

The objective of the extractions is not only to increase the molecular weight of the raffinate but also the functionality (the number of hydroxyl groups per molecule). Both n-hexane and methanol accomplish this.

The PECH used in the extractions should have, according to the stoichiometry of the reaction, a molecular weight of 4040 g/mol and a functionality of 3.0. Typically, however a feed will have before extraction a molecular weight of approximately 2200 to 2400 and a functionality of 1.7 to 2.2. The PECH on which most of the extraction studies were made had a molecular weight of 2230 and a functionality of 1.8. Table II and III summarize the extractions using methanol and hexane, and give the resulting molecular weight of the PECH product in the raffinate (lower) layer. Extraction with either solvent invariably improved molecular weight. It is also significant to note that very shallow extractions (i.e. <1%w) led to large increases in molecular weight, and that deeper extractions were less and less effective. Apparently, the feed PECH contains a small amount of relatively low molecular weight material. It is important to note, nevertheless, that molecular weight and functionality are generally improved by deeper cuts. Table VII and Figures 3 and 4 illustrate these observations.

TABLE VII. MOLECULAR WEIGHT OF PECH VS. DEPTH OF EXTRACTION

<u>Extraction Depth, %w</u>	<u>Solvent</u>	<u>Feed Mol. Wgt.</u>	<u>Product Mol. Wgt.</u>
0.28	hexane	2200	2500
15	hexane	2300	2700
40	hexane	2200	3100
87	methanol	2200	3700

Gel Permeation Chromatography

A limited number of gel permeation chromatograms (GPCs) were obtained in an effort to show the effect of solvent extraction on the molecular weight

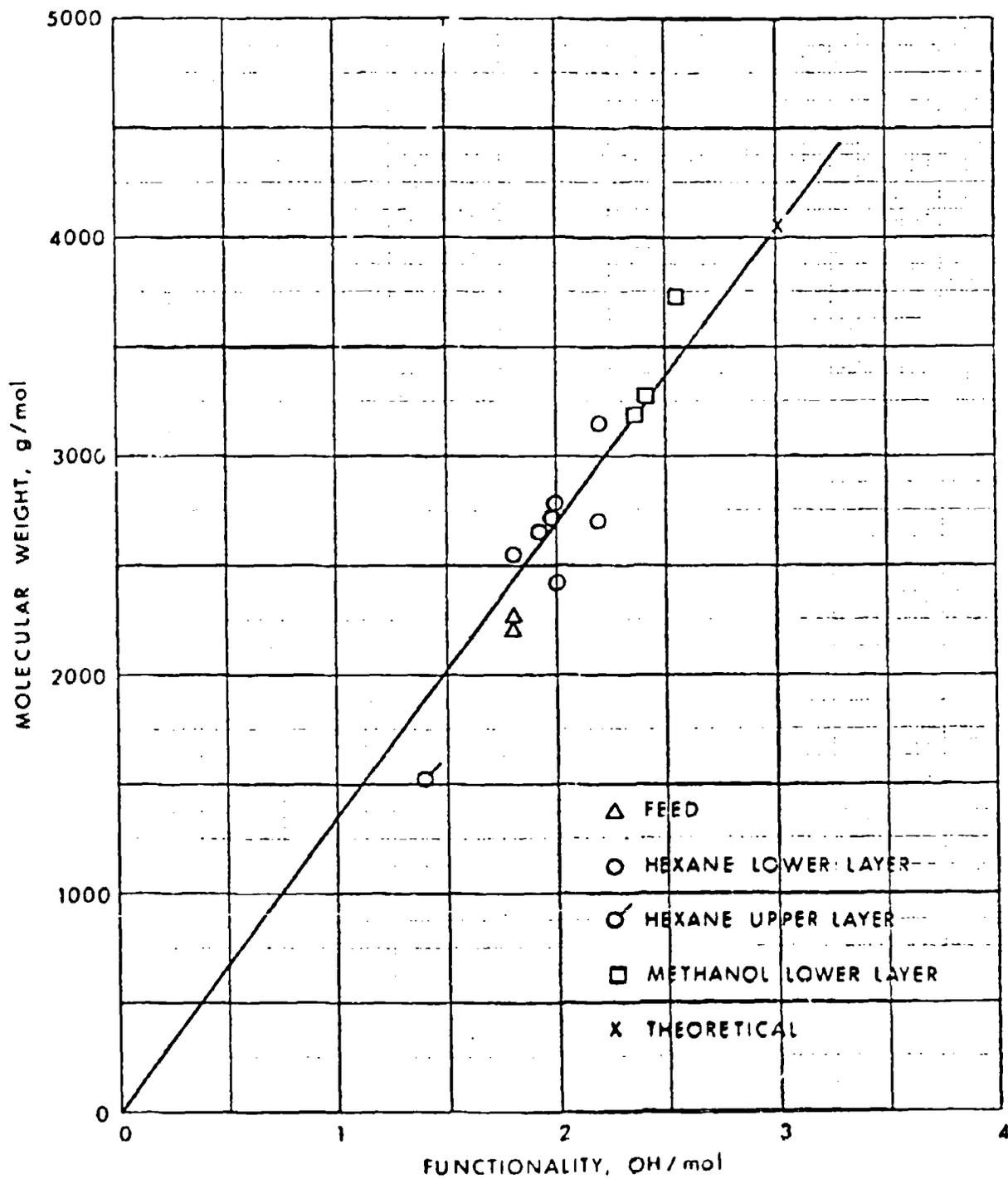


FIGURE 3 PECH SAMPLES: MOLECULAR WEIGHT VS. FUNCTIONALITY

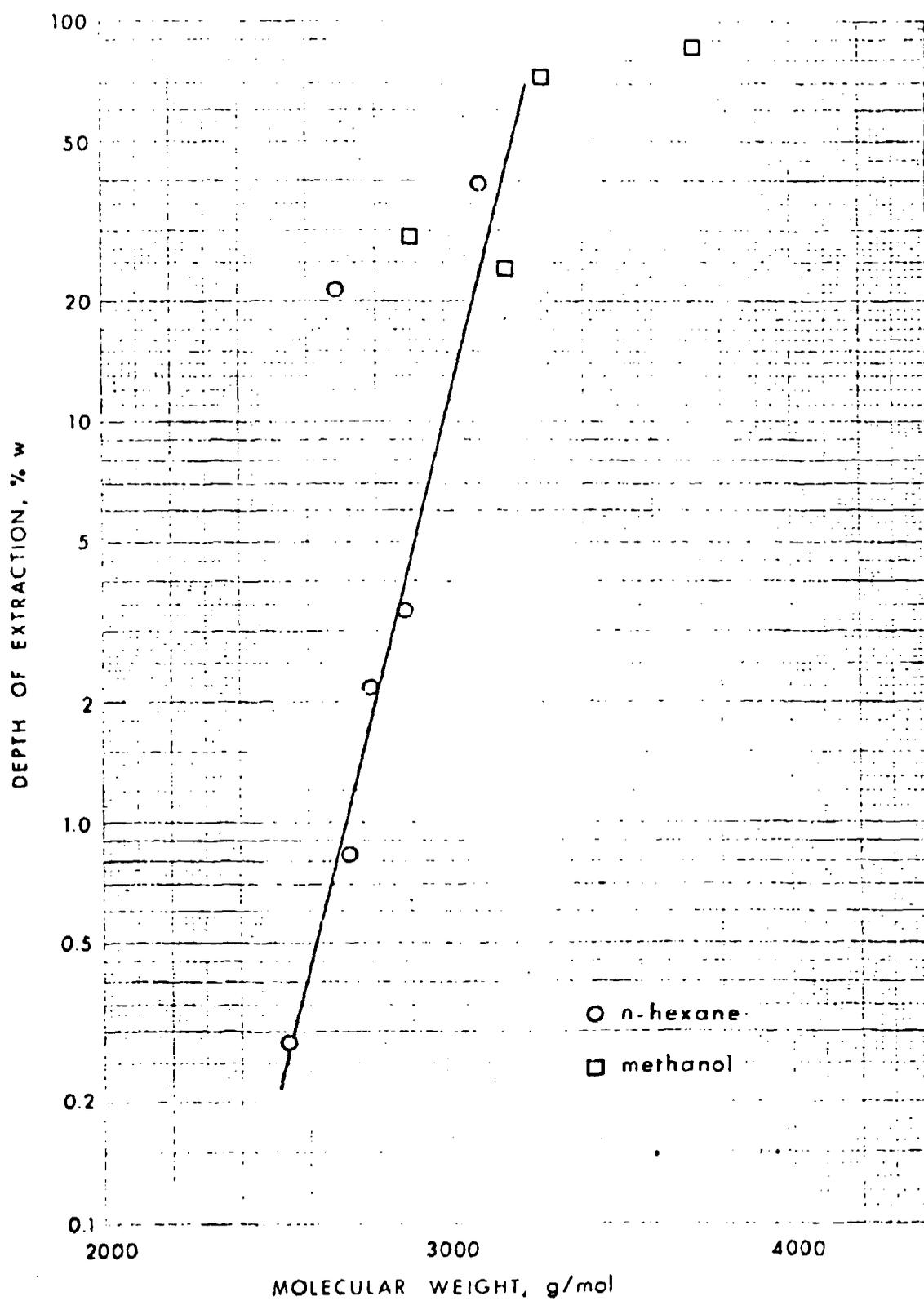


FIGURE 4 PECH RAFFINATE: MOLECULAR WEIGHT VS DEPTH OF EXTRACTION

distribution of PECH. Examination of the GPCs of the extracted, low molecular weight fractions is especially interesting. GPCs of the PECH from the upper layers of three hexane extractions are shown in Figure 5. Table VIII below summarizes pertinent data for these extractions, and Table III gives greater detail.

TABLE VIII. PROPERTIES OF SAMPLES EXAMINED BY GPC

<u>Run No.</u>	<u>Extraction Depth, %</u>	<u>Molecular Weight, g/mol</u>	
		<u>Upper Layer</u>	<u>Lower Layer</u>
251-50	0.21	-	-
251-80	2.18	-	2780
251-54	21.2	1520	2691

The important point established by these chromatograms is that raw PECH contains some quite low molecular weight material. At the low depths of extraction (0.21 and 2.18%w) a number of quite sharply defined peaks representing low molecular weight materials are evident. At the 21.2% extraction depth, it is evident that the extraction is not as selective: it cuts into the range of desirable molecular weights and thus tends to obscure the presence of the low molecular weight materials.

It should be noted that since the GPC analyzer was not calibrated using PECH, the molecular weight values assigned to the peaks in Figure 5 are merely relative and should not be construed as absolute values.

DEPECH from Extracted PECH

A batch of PECH solution was extracted to a depth of 33.5% (run 251-104) using hexane. The molecular weight increased from 2230 to 2880 g/mol and the functionality from 1.81 to 2.42. This PECH was converted in the laboratory to DEPECH, and the resulting product had a molecular weight of 2180. Had the PECH not been extracted a molecular weight of approximately 1800 would have been expected for the DEPECH. Similarly, a second batch of PECH was extracted with methanol to a depth of 29.2%w and then dehydrochlorinated. The resulting DEPECH had a molecular weight of 2130. It thus appears that extraction should be beneficial for improving the properties of the polymer at least through the DEPECH step.

Conclusions

The relative merits of hexane versus methanol as the extracting liquid have not been completely worked out in the limited time available. A few observations, however, can be made. The hexane system will be the easier to use if a very small depth of extraction is desired. This is due to the shape and position of the binodal region in the ternary isothermal. For the same reasons the methanol system will be the easier to use if it is desired to extract the PECH deeply. The methanol system also has another advantage. It appears that at all concentrations the viscosities of the methanol solutions are much lower than in the hexane system. Indeed, concentrated lower layers in the hexane system could be most difficult to separate. Especially with

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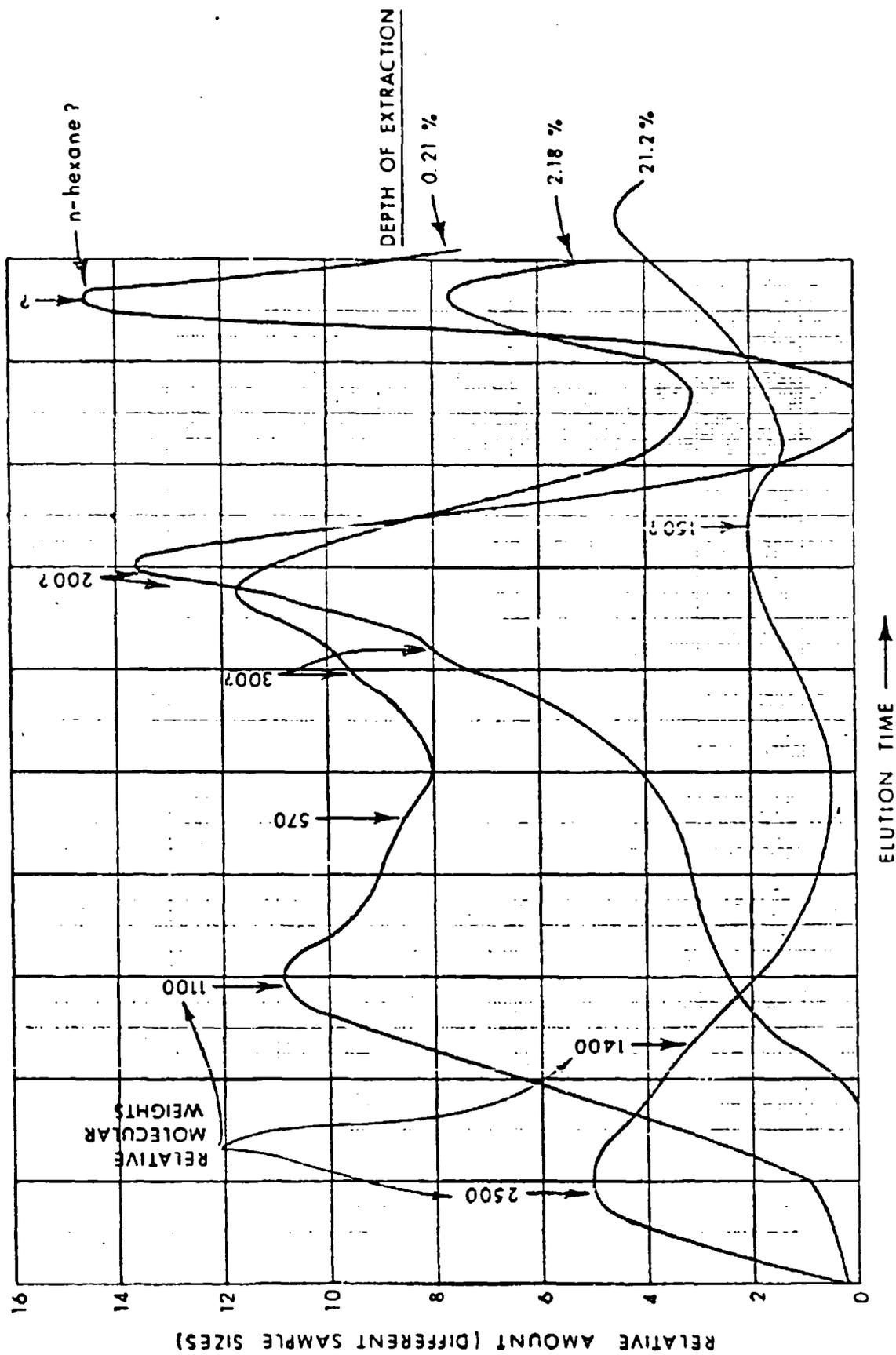


FIGURE 5 GEL PERMEATION CHROMATOGRAMS OF HEXANE EXTRACTS OF PECH

repetitive extractions (i.e. cross-current operation) using hexane the high viscosities of the concentrated lower layers gave rise to serious phase separation problems. On the other hand, a mixture of pure PECH and methanol showed no difficulty in phase separation. In addition, though not studied under the present subcontract, methanol offers the opportunity of adding water to the system in order to obtain a potentially wider range of mutual solubilities and possibly more selective separations.

Economics of PECH Extraction

In view of the interest in solvent extraction as a means to obtain PECH with potentially improved properties, a crude, range-finding economic evaluation of extraction to various depths has been carried out. Although the study was a superficial one, the results may be of value in future program planning and are therefore included here.

At low to moderate depths of extraction, the process can be carried out batchwise in an over-sized reactor. Only a solvent recovery still would need to be added to the normal process train. For deeper extraction, a separate contacting device would have to be provided. The economic factors determining the cost of PECH extraction are:

1. The value of the rejected PECH and its disposal cost.
2. Incremental utilities costs; mainly those connected with solvent recovery.
3. Incremental capital costs.
4. Incremental labor requirements.

For the purposes of this scope estimate, cost factor (1) was taken at 25 cents per pound of PECH rejected for a 1.6×10^6 lb/yr plant. Incremental utilities costs were based on $\$1/10^6$ BTU for heat and $\$2/10^6$ BTU of refrigeration requirement. Incremental capital costs for the various cases examined were developed using short-cut estimating procedures. Labor requirement differentials have been ignored.

The cases examined are compared on the basis of "equivalent process capital" (EPC, where $\Delta EPC = 3.5 [\Delta \text{Annual cost}] + 1.2 [\Delta \text{Capital}]$). The base case is a plant producing 1.6×10^6 lb/yr of standard Step 4 product. The factors 3.5 and 1.2 are appropriate for a commercial venture with ca 12% earning power and a projected 15 year life. These may not be appropriate assumptions for this case, but there is currently no basis for choosing another set.

Figure 6 shows, estimated ΔEPC as a function of depth of extraction for both single-stage and counter-current, multi-stage operation. These results are based on hexane extraction, but probably apply equally well to methanol extraction. From examination of the results, it is apparent that:

1. The addition of an extraction step adds, for a shallow extraction, about $\$100,000$ to the EPC. As the depth of extraction increases, the value of the rejected PECH soon becomes the over-riding factor as capital and operating cost factors increase slowly with depth of extraction.

2. Based on past estimates of the cost of step 4 product (ca \$7/lb), PECH extraction to moderate depths has little influence on the cost of the final product. It is shown as an example that a AEP of \$390,000 corresponds to a Δ Step 4 product cost increase of only 7 cents/lb (or ca 1%).

3. There is little difference, at least at low depths of extraction, between the costs for single- and multi-stage extraction.

PECH Improvement by Alteration of Processing Conditions

Preparation of PECH with new Initiators

In the preparation of PECH by the standard procedure glycerine is used as the initiator and boron trifluoride as the catalyst, and 42.5 moles of ECH are added per mole of initiator. If, as desired, the polyepichlorohydrin chain grew exclusively on the three hydroxyl groups of glycerine, the molecular weight of the final product would be slightly in excess of 4000. In fact, the molecular weight of the standard PECH product is 2200 to 2400; therefore, it is evident that side-reactions do occur to a significant extent, forming low molecular weight entities. The glycerine molecule possesses one secondary and two primary hydroxyl groups. It has been shown (12) that secondary alcohols react more slowly with propylene oxide under BF_3 catalysis than do primary alcohols. It has also been found by Shell Development workers that in the reaction of glycerine and epichlorohydrin under BF_3 catalysis the initial three ECH molecules which react leave the secondary hydroxyl of the glycerine almost untouched. In view of these observations, the present contract called for investigating possibilities of improving PECH quality by employing as initiator a triol containing three primary hydroxyl groups.

1,1,1-Trimethylolethane

The initial triol employed in this phase of the work was 1,1,1-trimethylolethane (TME), a commercially available material. A solution of prepolymer was prepared in the standard manner in which two moles of ECH were caused to react with each mole of TME in the presence of one mole of BF_3 for each 8.1 moles of TME. Details of a standard prepolymer preparation may be found at the end of this section.

To a portion of this prepolymer dissolved in MDC was added enough ECH such that the standard 42.5 moles of ECH per mole of initiator was maintained in the final reaction mixture. Further details for a standard PECH preparation may be found at the end of this section. This product possessed molecular weight of 2500 and a hydroxyl functionality of 2.0. The values are comparable to those found for standard PECH. Since the use of TME as initiator did not produce a PECH which was clearly superior to standard product, no further work was carried out with this material.

1,1,1-Trimethylolpropane

Another readily available triol containing three primary hydroxyl groups is 1,1,1-trimethylolpropane (TMP). A sample of this material was converted to prepolymer by the standard technique. It was noted that the

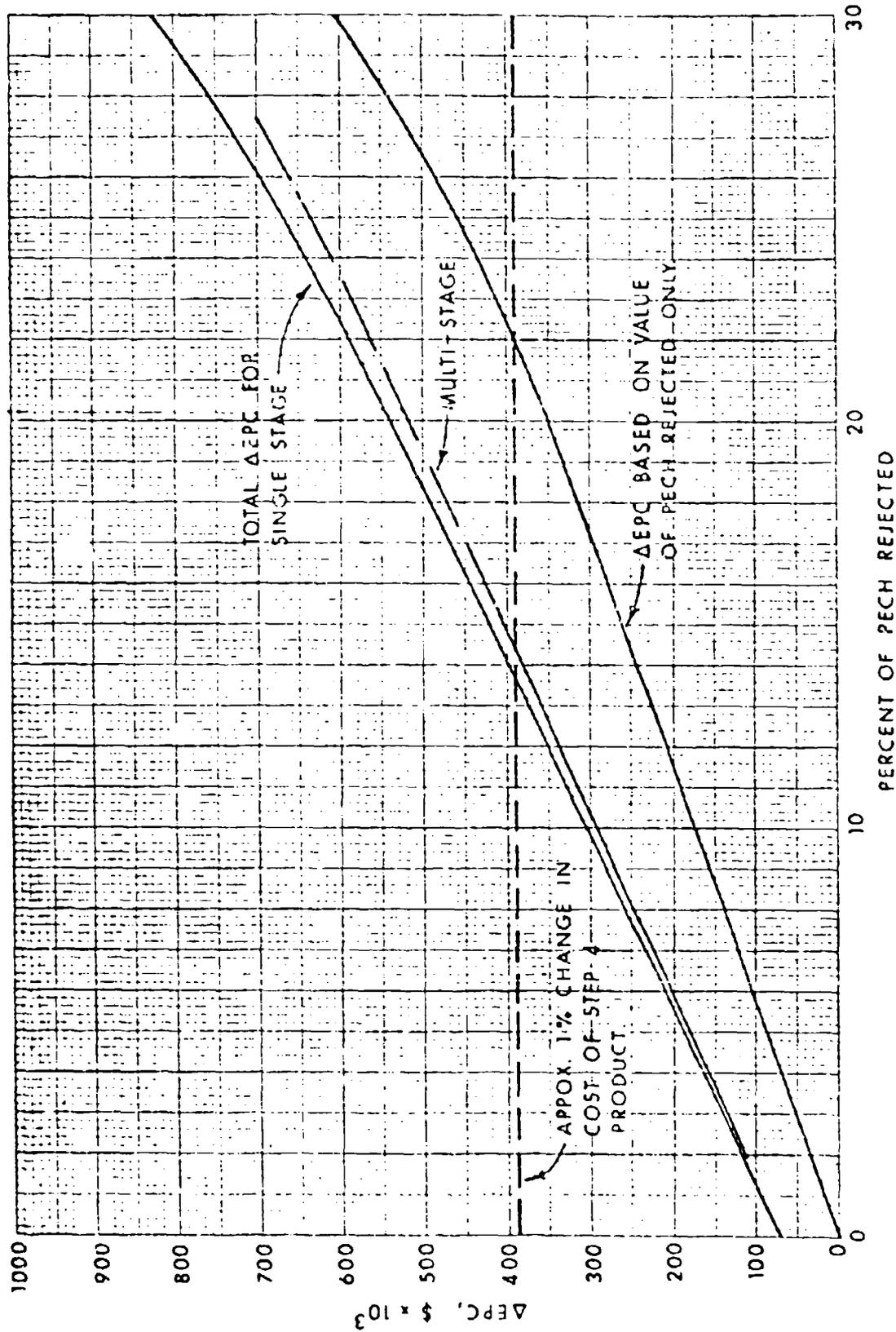


FIGURE 6 ECONOMICS OF PECH EXTRACTION

reaction mixture became homogeneous after the addition of 0.3 moles ECH per mole TMP whereas when prepolymer is prepared from glycerine, 1.6 moles of ECH must be added per mole of triol before homogeneity of the reaction mixture is observed. When TME was employed in the prepolymer preparation step, 1.6 moles ECH per mole TME was also required to achieve homogeneity. It is indeed surprising that the addition of the equivalent of only one methylene group to the TME molecule suffices to change its solubility so markedly in the prepolymer reaction medium.

A 6.4 pound batch of PECH was prepared in the laboratory under standard conditions utilizing the TMP derived prepolymer. The product possessed a molecular weight of 2500 and a hydroxyl functionality of 2.1.

Though the molecular weight and functionality of this product did not differ significantly from those of standard PECH, the decision was made to prepare DEPECH from it for further evaluation of its cureability after conversion to PCDE. This course of action was taken since it seemed possible the change in structure of the initiator could bring about a change in structure of the PECH and DEPECH which would lead to improved ultimate properties of the cured PCDE.

A small scale preliminary dehydrochlorination was carried out under standard conditions. A standard laboratory DEPECH preparation is described at the end of this section. Surprisingly, it was found that approximately six times as much chlorine (1.2% vs. 0.2%w) remained in the final product as is found in standard DEPECH. It is not clear why this new PECH should undergo the dehydrochlorination reaction at a decreased rate, but since the current contract would not be served by further pursuit of the explanation, work was directed toward altering the reaction conditions such that the usual high degree of dehydrochlorination could be achieved. It was found that increasing the dimethylsulfoxide and sodium methoxide levels by 25% and increasing the reaction period from four hours to six hours were sufficient to produce a DEPECH with the usual low chlorine content (0.26% in this case). Three larger batch dehydrochlorinations were then carried out in the laboratory under these more vigorous reaction conditions yielding 2.9 pounds of DEPECH with the following analysis.

Analysis of DEPECH Lot 270-90

Molecular Weight	1950
Hydroxyl Functionality	2.4
Unsaturation, eq./100g.	1.43
Chlorine, %w	0.17
Sodium, %w	0.02
Water, %w	0.40

This sample was sent to Hercules, Inc. on May 10, 1973 for conversion to PCDE and for ultimate evaluation at Edwards Air Force Base after curing in an energetic formulation.

Preparation of PECH with Increased ECH/G Ratio

It was planned in this portion of the product improvement program that PECH would be prepared with an increased ratio of ECH/G in an effort to produce a higher molecular weight polymer. Since success in maximizing

molecular weight by this approach requires concurrent minimizing of side reactions, a sample of highly purified ECH was prepared for this work. Commercial 99%w ECH was purified by distillation through a 28 inch by 1 inch column filled with Cannon packing. A ten percent light ends cut was removed at a 50/1 reflux ratio. Then, 79% of the initial charge was collected as product at 2/1 to 5/1 reflux ratios. The remaining 11% was discarded as a heavy ends cut. Analysis of the heart cut fraction by GC indicated that the impurity level had been reduced by approximately one order of magnitude.

At this point in the experimental program there became available a series of samples taken during a PECH preparation in the pilot plant. The molecular weights of these samples were measured and are plotted in Figure 7. The straight line represents the molecular weights which theoretically should be observed during the course of the polymerization as a function of the amount of ECH added. From the plotted data points it is evident that the addition of more ECH is unlikely to result in a significant increase in molecular weight.

Preparation of PECH with Purified ECH

It has always been observed that during the course of the polymerization the color of the reaction mixture progressively becomes darker red such that at the end of a standard PECH preparation the product appears to be almost black. This dark color is believed to be due to a complex involving BF_3 since the color is greatly decreased in intensity upon the addition of ammonia at the end of the preparation step. (Ammonia is added to deactivate the BF_3 catalyst by formation of $\text{BF}_3 \cdot \text{NH}_3$ which is later removed by filtration.) If commercial ECH contained an impurity which could complex with BF_3 to form this colored material, it can be postulated that the colored material catalyzes those side reactions responsible for the less than theoretical molecular weight of the product. Therefore, an experiment was carried out to determine if any benefits could be derived from using highly purified ECH in a standard PECH polymerization. However, the product from this experiment was comparable to standard PECH; it had a molecular weight of 2450 and a hydroxyl functionality of 2.0. The same dark red color developed during the polymerization and was mostly dispelled, as usual, upon the addition of ammonia. Since the molecular weight was identical to that of standard PECH shown in Figure 7, it was not deemed worthwhile to carry out the proposed experiment using higher ratios of ECH/G together with the highly purified ECH.

Preparation of PECH with Slower Monomer Addition Rate

Side reactions leading to low molecular weight products derived from ECH would very likely be promoted by high concentrations of free ECH during the polymerization. A PECH preparation was carried out in which this possibility was decreased by lengthening the monomer addition time to eight hours from the usual four hours. The net effect was a decrease by a factor of two in the average concentration of unreacted ECH (from 0.4% to 0.15%w) observed throughout the polymerization. Once again the product molecular weight, 2490, was comparable to that obtained under standard conditions. The usual dark color developed during the polymerization.

Preparation of PECH at Reduced Reaction Temperature

In many polymerization systems, chain transfer and other side reactions have a greater temperature coefficient than the primary reaction and in such

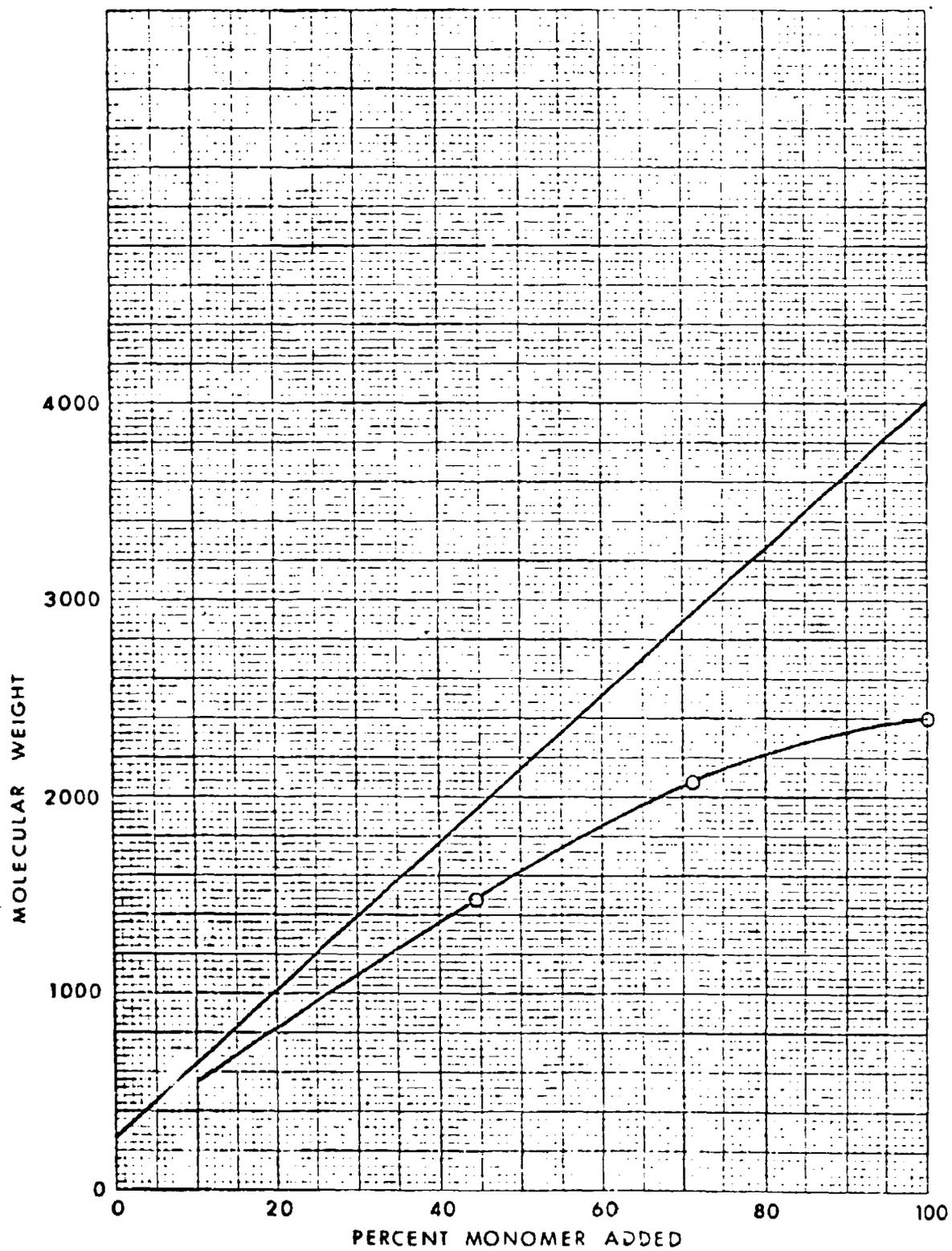


FIGURE 7 THEORETICAL AND OBSERVED MOLECULAR WEIGHT VS. PERCENT MONOMER ADDED FOR STANDARD TECH

cases selectivity to the desired polymer can be improved by reducing the temperatures. In early exploratory work (13) on ECH polymerization, no change in molecular weight or functionality had been reported to take place upon reducing the polymerization temperature from 41°C to 0°C. This result was viewed as surprising and worthy of further investigation. A small scale laboratory polymerization was carried out at 20°C with monomer addition over an eight hour period. The resulting product possessed a molecular weight of 2840, an increase of about 15% over that obtained under standard conditions. Another small scale experiment was then carried out at 10°C with monomer addition over eight hours to give a product of molecular weight 2790, i.e. unchanged from that obtained at 20°C.

Due to time limitations on the project no further work of an exploratory nature was carried out on the effect of temperature of polymerization. By mutual agreement between Hercules and Shell, it was decided to substitute a DEPECH sample made from this low temperature PECH for the one originally proposed to be made at higher ECH/G ratio. Accordingly, a larger laboratory batch was prepared under the 10°C, 8-hour reaction conditions; it yielded 6.3 pounds of PECH with a molecular weight of 2760.

In all the experimental batches described above, the prepolymer came from the same source, i.e., the prepolymer batch prepared using highly purified ECH. The remainder of the ECH used in each polymerization except for the batch using all highly purified ECH was commercial material. Though not proven, we feel that prepolymer quality did not appreciably influence the course of the polymerizations conducted at low temperature.

During preparation of the 6.3 pound batch, samples were taken when 25, 50, 75, and 100% of the ECH monomer had been added. The molecular weight of these samples is plotted in Figure 8 along with the data described earlier for a standard PECH preparation. As may be seen the points are best plotted on a straight line suggesting that, if desired, more monomer could be added to produce a still higher molecular weight product. On the current project, time did not permit further pursuit of this point. It is also of interest to note that in the 10°C preparation the reaction mixture at the end of the polymerization was a very light brown color; in contrast, a deep red-black color is always observed in runs made at 40°C. After addition of ammonia the light brown solution prepared at 10°C became almost water white. This observation, coupled with the 15% higher molecular weight, offers evidence of a significant difference in temperature coefficient between the polymerization reaction and the side reactions. That is, upon reducing the reaction temperature, the rates of undesired reactions evidently decline faster than does the rate of the desired reaction.

The 6.3-pound PECH sample was dehydrochlorinated under standard conditions in four laboratory batches. After compositing, we recovered 3.8 pounds of DEPECH with the following analyses.

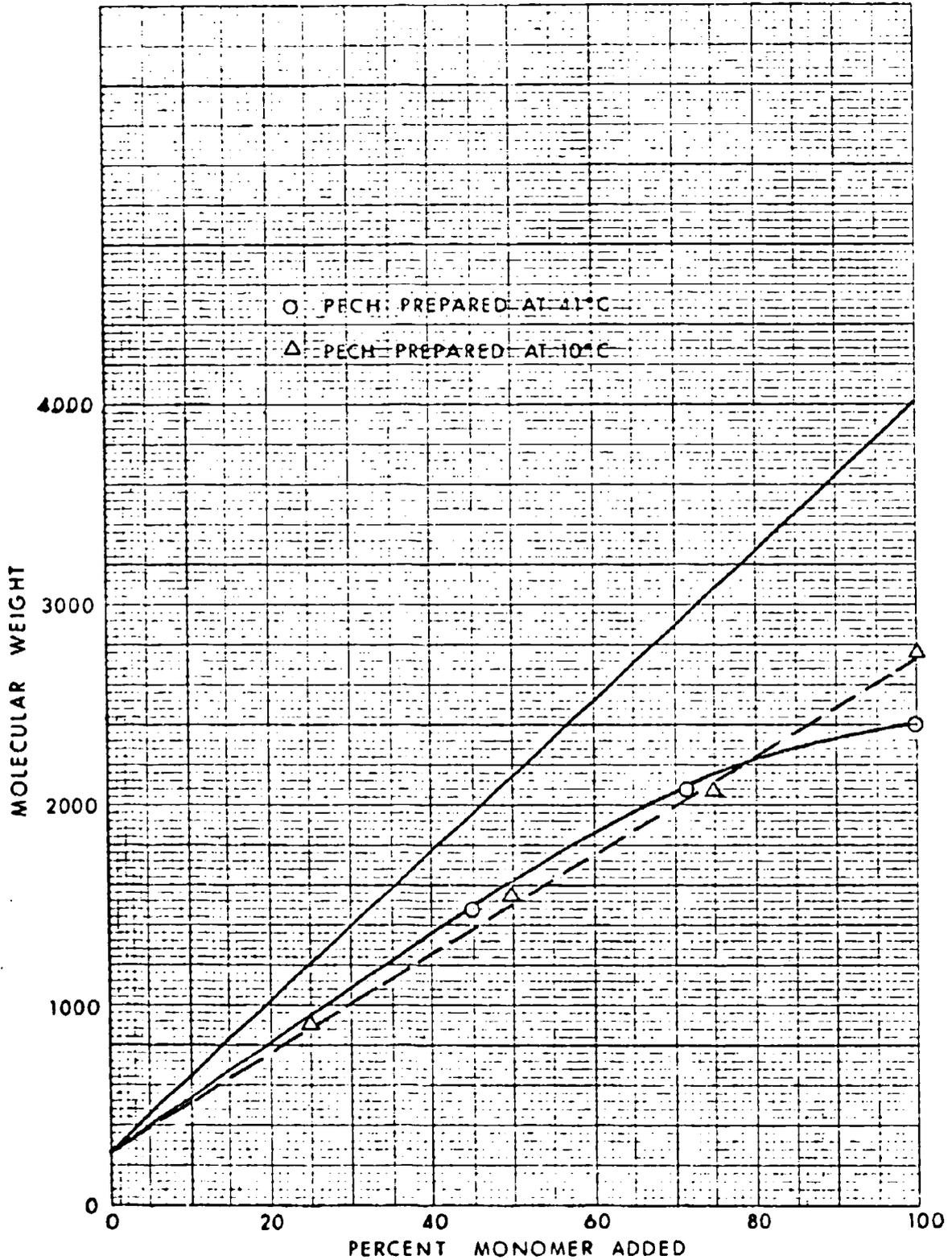


FIGURE 8 THEORETICAL AND OBSERVED MOLECULAR WEIGHT VS PERCENT MONOMER ADDED FOR PECH PREPARED AT 41°C AND 10°C

Analysis of DEPECH Lot 270-111

Molecular weight	2170
Hydroxyl functionality	2.7
Unsaturation, eq/100g.	1.48
Chlorine, %w	0.025
Sodium, %w	0.05
Water, %w	0.20

This lot was sent to Hercules on June 4, 1973 for conversion to Step 4 product and evaluation of its performance in the ultimate end use.

Standard Laboratory Preparations

The following are detailed descriptions of the laboratory methods employed in the preceding work.

Laboratory Preparation of Standard Prepolymer

Into a 1000 cc, three neck, round bottom flask equipped with a stirrer and condenser and capped with nitrogen was placed 150 g (1.63 mole) glycerine and 285 g MDC. A 1/8" metal diptube reaching the bottom of the flask was inserted through a neck of the flask such that atmospheric moisture was excluded. While the reaction mixture was vigorously stirred, 12 g of BF₃ (0.176 mole) was bubbled into the liquid through the diptube over the course of fifty minutes. Any heat evolution or escape of gas during the BF₃ addition was minimal. The gas addition tube was replaced with a similar line leading from the discharge of a small Lapp pump.

The reaction mixture was heated to a gentle reflux, the heat source was removed, and the addition of 300 g (3.24 mole) ECH was begun. The ECH was added at a uniform rate over a two hour period. Gentle reflux continued throughout the addition from the heat of reaction and stopped three minutes after the last ECH was added. The crystal clear, very light brown solution was stored in a glass container until needed.

Laboratory Preparation of Standard PECH

To a 1000 cc, three neck, round bottom flask equipped with a stirrer and reflux condenser and capped with nitrogen was added 250g MDC and 45g standard prepolymer solution containing the equivalent of 0.1 mole triol. With moderate stirring the mixture was heated to reflux, and then the source of heat was removed simultaneously with the start of addition of ECH. A pumping system similar to that described for the prepolymer was employed to add 374 g (4.05 mole) ECH at a uniform rate over four hours. Stirring was continued for thirty minutes longer to assure completion of reaction, and then ammonia gas was sparged into the liquid phase at a moderate rate for three minutes. During the ammonia addition the color of the reaction mixture changed from a very dark red to a light orange. A typical sample of this product showed the following analysis.

Typical Analysis of Standard PECH

Molecular Weight	2450
Hydroxyl, eq./100g	0.08
Hydroxyl functionality	2.0

Laboratory Preparation of Standard DEPECH

To a 1000 cc, three neck, round bottom flask equipped with stirrer, reflux condenser, and dropping funnel was added 93g sodium methoxide (95%w), 181 g THF, and 22g dimethylsulfoxide. The reaction mixture was then capped with nitrogen and heated to gentle reflux while stirring. Over thirty minutes 198g 50%w PECH in THF was added. Reflux was continued for four hours after the addition of the PECH was completed. The reaction mixture was cooled below 30°C and poured into 1600g deionized water initially at 20-25°C while stirring at a moderate rate. Stirring was continued ten minutes at which point the product was in the form of solid 500 μ spheres. The product was collected by suction filtration and washed in place by adding more water, slurrying on the filter, allowing to stand three minutes, and removing the wash water by applying suction to the filter. This washing was repeated four more times. The last wash was carried out with a 0.05%w solution of hydroquinone in water. The product (30% solids) was dried by heating 16 hours at 50°C and 1 Torr. Analysis of the product gave the following typical results.

Typical Analysis of Standard DEPECH

Molecular Weight	1900
Hydroxyl, eq./100g	0.12
Hydroxyl functionality	2.3
Unsaturation, eq./100g	1.45
Chlorine, %w	0.25
Sodium, %w	0.05
Water, %w	0.25

Pilot Plant Production of DEPECH

Description of Pilot Plant and Procedures

Figure 9, is a schematic diagram of the PECH/DEPECH pilot plant. The PECH reactor is a 50 gallon capacity inconel autoclave equipped with a modified turbine agitator, heating/cooling jacket, and internal heating/cooling coils. It is used both to prepare prepolymer (initiator) solution and to carry out the preparation of PECH.

In a typical prepolymer preparation, 135 lbs. of dry MDC solvent and 45 lbs. of glycerine are charged into the reactor and mixed. BF_3 gas, 3.7 lbs., is slowly metered in via the diptube.

The two-phase mixture is then heated to 40°C by circulation of tempered water. Finally, 90 lbs of dry ECH is metered in over a period of ca 4 hours. The resulting clear, homogeneous solution is discharged to a storage drum. One batch of prepolymer solution is sufficient to prepare about 12 fifty gallon batches of PECH, each of which will yield about 300 lbs of product.

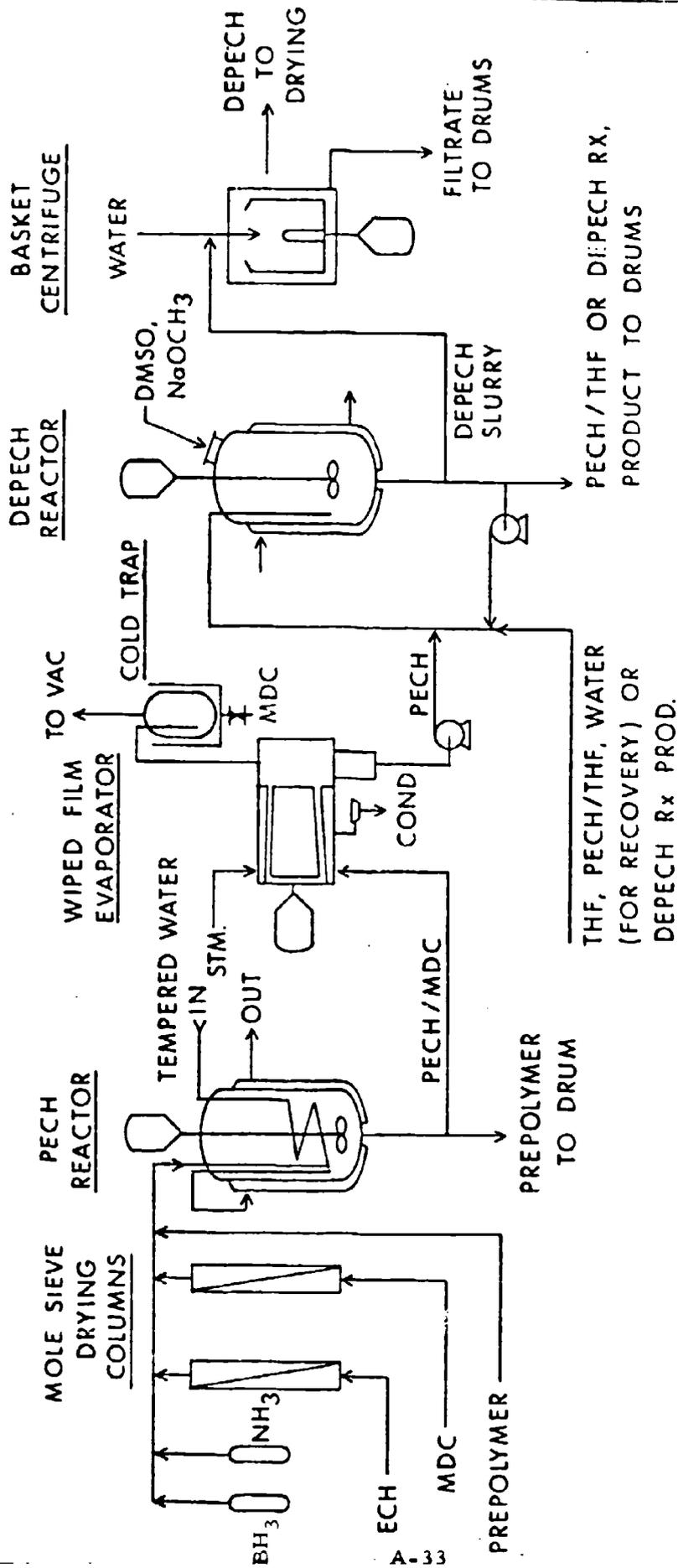


FIGURE 9 SCHEMATIC FLOW DIAGRAM OF DEPECH PILOT PLANT

In a typical PECH preparation, 42 lbs of prepolymer solution and 180 lbs of dry MDC are charged to the PECH reactor, mixed, and heated to 40°C using tempered water. Dry ECH, 286 lbs, is then metered in over a 4 hour period while the temperature is maintained at 40°C. After all the ECH has been added, the reaction is stirred at 40°C one half hour longer to assure maximum conversion of the ECH. Approximately 1 lb of NH₃ gas is then charged in to deactivate the BF₃ catalyst.

Typical PECH has a molecular weight (determined by vapor-pressure osmometry) of 2200 to 2400 and a hydroxyl functionality of ca 1.7 to 1.9. One batch is sufficient to make 3 fifty gallon batches of DEPECH each of which yields 50-60 lbs of product.

MDC solvent is removed from the PECH by stripping in a 0.8 ft² "Kontro" wiped-film-evaporator. The PECH is pressure-fed at ambient temperature via a 10 μ polypropylene cartridge filter. The evaporator is operated at a pressure of 100 Torr. with the temperature of the product PECH maintained at ca 110°C. The stripped PECH is continuously blended with THF previously charged into the DEPECH reactor. Upon completion of a stripper run, the PECH/THF mixture (ca. 65%w PECH) is discharged to a storage drum.

The DEPECH reactor is a 50 gallon stainless steel autoclave fitted with a marine propellor type agitator, a cooling/heating jacket, and a reflux condenser. In a typical DEPECH preparation, 213 lbs of THF, 17 lbs of DMSO, and 75 lbs of NaOCH₃ are charged to the reactor, mixed, and heated to 60-65°C. The 65%w solution of PECH in THF (132 lbs) is then metered in over a 2 hour period while the reaction temperature is maintained at 60 to 70°C. The mixture is held at 65°C for 4 hours after addition of all the PECH solution. The product mixture is then cooled and discharged to a storage drum.

The DEPECH reactor vessel is also used for DEPECH precipitation. Typically, the vessel is charged with 265 lbs of ambient-temperature deionized water (or recycled wash water) and the agitator is started. DEPECH reaction mixture (ca 100 lbs) is then pressured in via the diptube over a 15-30 minute period. The product slurry is agitated for a minimum of 15 minutes before filtering.

DEPECH recovery from the above slurry is carried out using a Komline-Sanderson basket centrifuge with a 10" diameter, perforated bowl. The bowl is lined with 1/16" mesh SS wire screen and is fitted with a medium-weight polypropylene canvas filter bag. The DEPECH slurry (ca 11% solids) is pressure fed at a rate of ca 3 gpm with the bowl turning at ca 1200 rpm. The DEPECH filter cake is then washed in place using 20-40 lbs water/lb DEPECH, and is finally washed with 4 lbs/lb of a 0.05%w solution of hydroquinone in water. Typically, the final wet cake contains 40 to 50%w solids.

The DEPECH is dried overnight under vacuum. Both a tray drier and a tumble drier have been used. In either case, the drying is conducted at ca 29" Hg vacuum and at a temperature of 50 to 60°C.

Standard DEPECH Production Summary

Standard DEPECH production under the subject contract covered the period February-June, 1973. Four 45 lb. lots of DEPECH were prepared and shipped to Hercules. Production of these 180 lbs of material required the preparation of one batch of prepolymer solution, two batches of PECH, and 5 batches of DEPECH. Recovery of DEPECH solids from these 5 batches required that 20 batch precipitations be carried out. Only one of these 20 batches failed to meet specifications. Table IX below summarizes the relevant analytical results for the four 45 lb composites of material shipped to Hercules.

TABLE IX. SHELL ANALYSES OF DEPECH SHIPMENTS TO HERCULES

<u>Lot. No.</u>	<u>Date of Shipment</u>	<u>Mol¹⁾ Wgt.</u>	<u>Hydroxyl²⁾ Functionality</u>	<u>Cl, %w</u>	<u>Na%w</u>
271-150	3-15-73	1800	2.1	0.28 ³⁾	0.11 ³⁾
271-151	4-15-73	1800	1.9	0.13	0.05
271-154	5-7-73	1900	2.2	0.10	0.07
271-154	6-4-73	1700	2.3	0.09	0.06

(1) by vapor pressure osmometer

(2) OH equivalents per gram x molecular weight

(3) Cl and Na values for composite 271-150 obtained by averaging values for individual batches.

Production of Modified DEPECH

The DEPECH pilot plant was also used to prepare three special batches of potentially improved DEPECH. These special batches, based on the results of the parallel laboratory DEPECH improvement program, comprised 1) a 7.5 lb batch derived from PECH from which ca 2% of low molecular weight moieties had been removed by hexane extraction; 2) a similar batch derived from PECH from which ca 6% of low molecular weight material had been extracted and 3) a 21 lb batch derived from PECH from which ca 40% of low molecular weight material had been removed by methanol extraction.

The preparation of the two batches based on hexane-extracted PECH employed an additional (30 gal) vessel not shown on the attached flow diagram. This smaller vessel was used to carry out the single stage batch extractions and to effect the dehydrochlorination reactions.

In the preparation of Lot 271-152, 25 lbs of 64%w standard PECH in MDC was mixed with 25 additional lbs of MDC and 14 lbs of hexane. The total system composition was 25%w PECH, 53%w MDC, and 22%w hexane. This mixture was agitated for 30 minutes in a 50 gal glass-lined autoclave at ca 19°C. After settling for 60 minutes, 29 lbs of upper (hexane) layer analyzing 3.4%w PECH and 35 lbs of lower layer analyzing 42.8%w PECH were recovered. By material balance, ca 6.2% of the original PECH was rejected. The residual PECH solution was solvent-stripped, converted to DEPECH, and recovered in the usual manner. Analytical results showed the following molecular weights and hydroxyl functionalities:

Analytical Data for Lot 271-152

<u>Sample</u>	<u>% of Orig.</u>	<u>Mol Wgt.</u>	<u>Hydroxyl Functionality</u>
Original PECH	100	2300	1.7
Rejected PECH	6.2	n.d.	n.d.
Residual PECH Product	93.8	2400	2.1
DEPECH 271-152	-	1900	2.0

Approximately 7.5 lbs of the latter material was shipped to Hercules on April 16, 1973.

In the preparation of Lot 271-153, 24 lbs of the original PECH solution were mixed in an analogous manner with 48.5 lbs of additional MDC and 96 lbs of hexane. The total system composition was 9%w PECH, 34%w MDC and 57%w hexane. After separation, 146 lbs of upper (hexane) layer and 22.5 lbs of lower layer were recovered. Analyses showed 0.2%w PECH in the upper layer and 68% in the lower layer. By calculation, about 2% of the original PECH was rejected. The lower layer was stripped of solvent and converted to DEPECH in the usual manner. Analytical results showed the following molecular weights and functionalities:

Analytical Data for Lot 271-153

<u>Sample</u>	<u>% of Orig.</u>	<u>Mol Wgt.</u>	<u>Hydroxyl Functionality</u>
Original PECH	100	2300	1.7
Rejected PECH	1.9	n.d.	n.d.
Residual PECH Product	98.1	2500	2.2
DEPECH 271-153	-	2000	2.5

Approximately 7.5 lbs of the latter material was shipped on May 7, 1973.

In the preparation of Lot 271-156, 136 lbs of a 61%w solution of standard PECH in MDC were mixed with 44 lbs of additional MDC and 173 lbs methanol. The total system composition was 23.5%w PECH, 27.5%w MDC, and 49%w methanol. This mixture was agitated for 15 minutes while cooling to 23°C and for 5 minutes at 23°C. After standing for 1 hour, 90 lbs of lower layer containing 49 lbs of PECH along with 263 lb of upper layer were recovered. The lower layer was stripped of solvent and converted to DEPECH in the usual manner. Analyses of samples taken during the preparation are shown below:

Analytical Data for Lot 271-156

<u>Sample</u>	<u>% of Orig.</u>	<u>Mol. Wgt.</u>	<u>Hydroxyl Functionality</u>
Original PECH	100	2300	n.d., 1.7 est.
Rejected PECH	40	1900	n.d.
Residual PECH Product	60	3000	n.d.
DEPECH 271-156	-	2400	2.8

Approximately 21 lbs of the latter material was shipped to Hercules on June 4, 1973.

Of these three lots of special material, only one, 271-156, appears on the basis of DEPECH analyses to be markedly different from standard quality DEPECH. It is also of interest to note that 271-153 has, apparently, both higher molecular weight and functionality than the similarly prepared 271-152 derived from more deeply extracted PECH. This result was unexpected and is not readily explainable on the basis of the limited data available. It is perhaps significant that the ratio of upper to lower layer in the PECH extraction was ca 0.8 for 271-152 compared to ca 6.5 for 271-153. Also, the PECH content of the total mixture was 25%w in 271-152 and 9%w in 271-153. As has been mentioned in the discussion of the exploratory extraction studies, there is theoretical basis to suggest that polymer extractions carried out in dilute solution should be more selective (in this case for the extraction of low M.W. species) than those carried out in more concentrated solutions. It is conceivable that such an effect is showing up in the comparison of results for these two preparations; in any future program involving PECH extraction, this possibility should be investigated.

SUMMARY

The work program covered by the present report had two primary technical objectives. The first was to investigate prescribed possible routes to improve the molecular weight and functionality of PECH. If the improvement carries through to the DEPECH stage, samples of improved quality DEPECH would be supplied to Hercules for their conversion to PCDE to determine if the improved quality persists in the end use performance. The second objective was to supply to Hercules Incorporated a prescribed quantity of standard quality DEPECH for their conversion to standard PCDE needed to fulfill current Air Force requirements for this material.

In one portion of the quality improvement study, exploratory extraction of a solution of PECH in methylene dichloride was carried out using hexane or methanol as a nonsolvent component. Substantially improved molecular weight and functionality were achieved. The degree of molecular weight improvement was generally found to be directly related to the depth of extraction. Methanol generally afforded deeper extraction than did hexane. Improved PECH could be dehydrochlorinated to produce DEPECH with the same degree of improvement in molecular weight and functionality.

In another laboratory study, synthesis was carried out with new initiators which differed from the standard initiator, glycerine, by possessing three primary hydroxyl groups. No improvement was found in molecular weight or functionality. However, a PECH made at low temperature (10°C instead of 41°C) did possess higher molecular weight and functionality, and this quality improvement carried through to the DEPECH derived from it. A 3.8 pound sample of DEPECH was made from low-temperature PECH and shipped to Hercules.

In the supply portion of the program, 180 pounds of standard quality DEPECH was prepared in our pilot plant facilities and shipped to Hercules. We also shipped to Hercules several medium-sized samples of improved DEPECH prepared in our pilot plant from hexane or methanol-extracted PECH.

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APPENDIX B

HERCULES DEPECH QUALIFICATION RUNS

CONTRACTS

F04611-73-C-0051 AND F04611-75-C-0024

A. INTRODUCTION AND SUMMARY

Upon delivery of the DEPECH for Contract F04611-75-C-0024, Shell Development notified the Air Force they would no longer be manufacturing DEPECH. Hercules was authorized under Amendment No. R00007 of Contract F04611-75-C-0024 to prepare 20 pounds of DEPECH and convert to PCDE in order to qualify as a source of DEPECH. The DEPECH was manufactured at Hercules Allegany Ballistics Laboratory (ABL), Cumberland, Maryland, and sent to Hercules Bacchus for conversion to PCDE. This report discusses the results of conversion of the ABL DEPECH to PCDE and has as an attachment the final report on DEPECH production by ABL.

Since the PCDE pilot plant had been out of service for several months, a two hour pilot run using Shell DEPECH was made prior to the ABL DEPECH conversion. The run was successful in that no operating problems occurred and the product was of good quality.

Conditions for the first ABL DEPECH run were the same as the pilot run. N_2F_4 from the storage banks was used. The product quality, however, was not good. There appeared to have been a degradation of product in the reactor system.

Laboratory comparison of the Shell and ABL DEPECH show they are of good quality as measured by infrared scan, gas permeation chromatography (GPC) and nuclear magnetic resonance (NMR). The difference between the ABL and Shell DEPECH appears to be the water content of the ABL DEPECH (4%).

The excess water and excess pH in the ABL DEPECH is believed to have caused the problem of poor product. Since almost half the DEPECH was water, the amount of N_2F_4 used was excessively high (235% excess). Water is also believed to cause adverse effects on the reaction. Combination of water and HF present in the reactors under high temperature and pressure caused hydrolysis of the DEPECH. The infrared scan of the PBEP shows a large carbonyl band indicating cleavage of the molecule.

A second run was made with the ABL DEPECH to determine if the water caused the poor product. Approximately four pounds of DEPECH from the same lot used for the first run was washed with two gallons of distilled water and dried in a vacuum oven to a dryness of <0.26 percent. Infrared scan, NMR and GPC showed no degradation of the DEPECH from washing and drying.

The DEPECH was used to make Run No. 70 on May 10. The run was successful in that the PBEP and PCDE were of good quality as measured by infrared scan.

B. DISCUSSION

1. Processing

Shell Development Company, the only producer of DEPECH, has informed the Air Force that they no longer wish to produce DEPECH. The

Air Force authorized Hercules by Amendment R00007 of Contract F04611-75-C-0024 to prepare 20 pounds of DEPECH and convert PCDE for evaluation.

Several small batches of DEPECH were produced by Hercules at the Allegany Ballistics Laboratory using the process provided by Shell. The DEPECH was then to be converted to PCDE by Hercules at the Bacchus Plant. The results of the runs were to be used to qualify Hercules as a source for DEPECH for the Air Force.

Prior to making a run using ABL DEPECH, a pilot run was made using Shell DEPECH. The purpose of the run was to make certain the PCDE pilot plant was operating properly as it had been out of service for several months. The Shell DEPECH run (No. 68) was made on April 4, 1977. Conditions for the run were to be as near the normal production run as practical. Operating temperatures, pressures, and reactor residence times were to be as normal. The concentration of DEPECH in the feed stream was cut in half to 5% w in order to conserve the limited supply of N_2F_4 gas. Table B-1 lists the reactor conditions as compared to those of a normal production run. Table B-2 lists the N_2F_4 analysis. The run was very uneventful with no operating problems. The product was of good quality as measured by infrared scan (Figures B-1 and B-2).

On April 6, the ABL DEPECH (No. 69) was made. Conditions for this run were the same as the Shell DEPECH run so that a valid comparison could be made. N_2F_4 from the same storage bank was used for both runs. The acetone used to make the DEPECH solution for both runs came from the same drum. Table B-1 shows the run condition for the first ABL DEPECH run. The figures in parenthesis are the actual conditions calculated after it was found the ABL DEPECH contained 45 percent water.

Run No. 69 operated fine mechanically. However, early in the run it became apparent that conditions were not normal. The product was dark and had a much stronger smell than usual. Also, the steam valve on the second stage reactor remained completely closed yet the temperature was maintained at close to 120° C indicating that there was an unusual exothermic reaction taking place. Normally, even with 10% w DEPECH feed, some steam is required to the reactor to maintain the reaction temperature. Infrared scan (Figure B-3) of the PBEP product showed that there were several extraneous peaks and that the carbonyl peak was excessively high.

All PBEP was converted to PCDE. The infrared scan of PCDE (Figure B-4) showed the same extraneous peaks as the PBEP. Very little nitrile peak is evident in the PCDE scan.

Laboratory analysis showed the ABL DEPECH to be the same as Shell DEPECH except for the large amount of water present and the higher pH. See following section. The remaining DEPECH (~4 pounds) from lot 983-12 used for Run No. 69 was washed with two gallons of distilled water, filtered and dried in a vacuum oven at 105° F. Ten days were required to get the water content to 0.26 percent.

On May 20 another PCDE run was made using two pounds of the dried DEPECH. The run conditions, similar to Runs 68 and 69, are shown in Table B-1. The run was normal with no excursions, exotherms or signs of plugging noted in Run No. 69. The product, PBEP and PCDE, was normal as measured by infrared scan (Figures B-5 and B-6). It therefore appears as if is the water content of the DEPECH that caused the problems of Run No. 69.

2. Laboratory Investigation

Analysis of the ABL DEPECH (983-6, -8) had shown the product to be of comparable quality as the Shell DEPECH as measured by infrared scan, GPC, Cl^- and Na^+ content and solubility in acetone. These are the standard acceptance tests that have been used for DEPECH since the start of these programs. Table B-3 is a summary of this early analysis. Figures B-7 and B-8 are the infrared scans of the early ABL DEPECH lots. When the product from converting ABL DEPECH to PBEP was not satisfactory, further analysis of the ABL DEPECH was performed. ABL lot number 983-12, the lot used in Run No. 69, was analyzed along with Shell DEPECH IP6P301S1 (Run No. 68). Both DEPECH samples were run on infrared scan, GPC and NMR. The results show that the DEPECH samples were essentially the same. Figure B-9 through B-14 show NMR, GPC, and infrared scan of the Shell DEPECH and ABL DEPECH 983-12 as received.

The ABL DEPECH appeared to be somewhat damp and moldable. Using gas chromatography, the water content of the ABL DEPECH was found to be 45% while the Shell DEPECH was 0.06%. No other significant levels of solvent could be found by GC. A check by gravimetric moisture analysis confirmed the moisture content. The high moisture content of the ABL DEPECH was surprising as the material appeared to be moldable but not wet.

A check of the pH of the two DEPECH samples was made by placing half gram samples in 50 cc of water. The pH of the slurries were 7.2 and 5.2 for the ABL and Shell material respectively. The higher pH of the ABL material may or may not be significant.

The remaining DEPECH from ABL Lot 983-12 was washed with two gallons of distilled water then dried in a vacuum oven. Analysis shows no degradation of the product as measured by NMR, GPC, and infrared scan (Figures B-15 and B-16).

C. FUNCTIONALITY DETERMINATION OF ABL DEPECH

The functionality of ABL-manufactured DEPECH was established. In addition, a lot of Shell DEPECH was also carried through the testing. The functionality of ABL lot 983-12 DEPECH was 2.47 while the value for Shell lot 16P301S1 DEPECH was 2.66.

To obtain these functionalities the hydroxyl content (in g/eq) and the number average molecular weight (M_n) of each DEPECH sample were measured. The functionality was then calculated by dividing the M_n figure by the

hydroxyl content. The data for each measurement and the functionalities are compiled in Table B-4. The hydroxyl content of ABL DEPECH was significantly higher than the Shell material; 922 g/eq versus 839 g/eq. The \bar{M}_n values were 2278 for ABL DEPECH while the Shell material was 2231. Shell originally obtained an \bar{M}_n near 2200 for this lot. Moisture values are also included in Table B-4. The ABL DEPECH contained 0.31 percent water and Shell DEPECH 0.19 percent as measured by gas chromatography. The water analyses were made both to correct calculations and to assure that the moisture levels were not so high as to effect the tests.

The methods used to obtain the data were for the most part the same as used by Shell. The analysis for hydroxyl content did differ. Shell employed a procedure based on reacting lithium aluminum hydride (LiAlH_4) with the active hydrogen of the hydroxyl group. This reaction results in quantitative evolution of hydrogen gas which is measured with a gas burst. Neither the reagent nor the gas burst set-up were available here.

Rather than the LiAlH_4 approach, Hercules attempted the toluenesulfonyl isocyanate (TSNCO) method which worked successfully with PCDE. Two variations of the TSNCO procedure were investigated; one employing an infrared (IR) determination of isocyanate consumed, the other a titrimetric measure of TSNCO reacted with hydroxyl. Both approaches gave very low hydroxyl content figures. This was probably due to hydrolytic breakup of the DEPECH catalyzed by small amounts of acid in the TSNCO reagent. Vinyl ethers such as DEPECH are very susceptible to this reaction whereas with PCDE hydrolysis is not such a problem.

A direct IR measurement was finally selected for determining the hydroxyl content. A dichloroethane (DCE) solution of DEPECH was prepared and scanned between 3500 and 3800 cm^{-1} . The absorbance at 3590 cm^{-1} was measured using 3800 cm^{-1} as the baseline. Known concentrations of diethylene glycol in DCE were used for calibration. Both samples and standards were dried over molecular sieve prior to analysis.

The \bar{M}_n of DEPECH was determined by vapor phase osmometry (VPO) in a manner similar to the Shell method. Samples were dissolved in DCE by warming and then measured shortly after cooling. The higher concentration samples were found to gel if allowed to sit too long. Although the gel could be broken by shaking, the results were erratic. The VPO was calibrated against a polystyrene standard of $\bar{M}_n = 2100$. Shell used a lower molecular weight compound for calibration but the close agreement between labs on the Shell DEPECH indicated that either standard was suitable.

The \bar{M}_n of polymers can be obtained much more rapidly by gel permeation chromatograph (GPC) than by VPO. However, VPO data is necessary to calibrate the GPC for DEPECH. In the case that DEPECH analyses might be required in the future, Hercules also ran GPC scans of both the ABL and Shell materials. The GPC column set used for these runs is now "partially" calibrated in that the VPO data provided us two absolute \bar{M}_n data points. Interestingly, the GPC column set previously had been calibrated against a series of known \bar{M}_n polystyrene standards. Based on the polystyrene calibration, the \bar{M}_n of both Shell and ABL DEPECH was 3735. Thus, while

polystyrene standards are suitable for calibration of the VPO for DEPECH analysis, they are not acceptable for GPC analysis of DEPECH.

D. CONCLUSION

DEPECH supplied by Hercules ABL is comparable to Shell DEPECH and can be used to make good PBEP/PCDE if it is properly dried. The question of higher pH should be investigated. It is not known if it is necessary to reduce the pH of the DEPECH to a low level.

The GPC chromatograms of all three samples (Figure B-11, B-12, and B-16) are essentially the same. A small amount of higher molecular weight material can be seen in the Shell sample at about 20-23 counts. The "dried" ABL sample shows a very slight indication of a little higher molecular weight specie too. However, the molecular weights of the bulk polymer are identical for each specimen. (The upper output line in each chromatogram should be ignored.)

TABLE B-1. OPERATING CONDITIONS

Run 68 Run 69 Run 70 Normal Run
Apr. 4, 1977 Apr. 6, 1977 May 20, 1977 Conditions

PBEP REACTOR CONDITIONS

Residence Time (min)	16.4	16.0	15.0	15.0
Temperature First Stage (°C)	120	120	120	120
Temperature Second Stage (°C)	120	119	117	120
Pressure (psig)	400	400	400	400
Production Rate (lb/hr)	3.5	3.5 (1.9)	2.9	7.0
DEPECH Lot No.	Shell 16 P301S1	ABL 983-12	ABL 983-12	-
DEPECH Concentration (% w)	5.0	5.0 (2.8)	5.0	10.0
DEPECH Feed Rate (gal/hr)	4.0	4.25	4.0	4.85
Solvent (Acetone) Feed Rate (gal/hr)	5.02	5.02	5.87	5.02
N ₂ F ₄ Excess (%)	121	94 (253)	50.5	30

PCDE REACTOR CONDITIONS

Residence Time (min)	2.0	2.0	2.0	2.0
TMA Concentration (% w)	10.6	10.6	6.5	10.6
Temperature (°C)	30	25	35	35-40
Production Rate (lb/hr)	3.0	3.0 (1.7)	2.5	6.0

EXTRACTION

Feed Rate (gal/hr)	7.5	-	-	7.5
Water, Both 6" Column (lb/min)	3.34	-	-	3.34
Water Temperature (°F)	50	-	-	50-55

TABLE B-2. N_2F_4 IMPURITIES

	<u>N₂</u>	<u>O₂</u>	<u>CO</u>	<u>NO</u>	<u>NF₃</u>	<u>N₂F₂</u>	<u>CO₂</u>	<u>N₂O</u>
Run 68 & 69	1.98	0	0.05	.11	0.04	0.53	0.01	0.29

Analysis taken August 1976

TABLE B-3. DEPECH ANALYSIS

<u>Test</u>	ABL DEPECH		SHELL DEPECH
	<u>983-6</u>	<u>983-8</u>	<u>Lot 11410-84</u>
Cl ⁻ , wt. %	0.24	0.29	0.40 (a)
Na ⁺ , wt. %	0.12	0.093	
Molecular Weight			1760 (a)
VPO			
GPC			
Aw	85.6	70.7	93.9
An	74.2	81.2	72.6
P	1.15	1.15	1.3
Solubility Temp.	< 70°	< 70°	< 70°
10% solution (Acetone)			
30 minutes			

(a) Reported by Shell

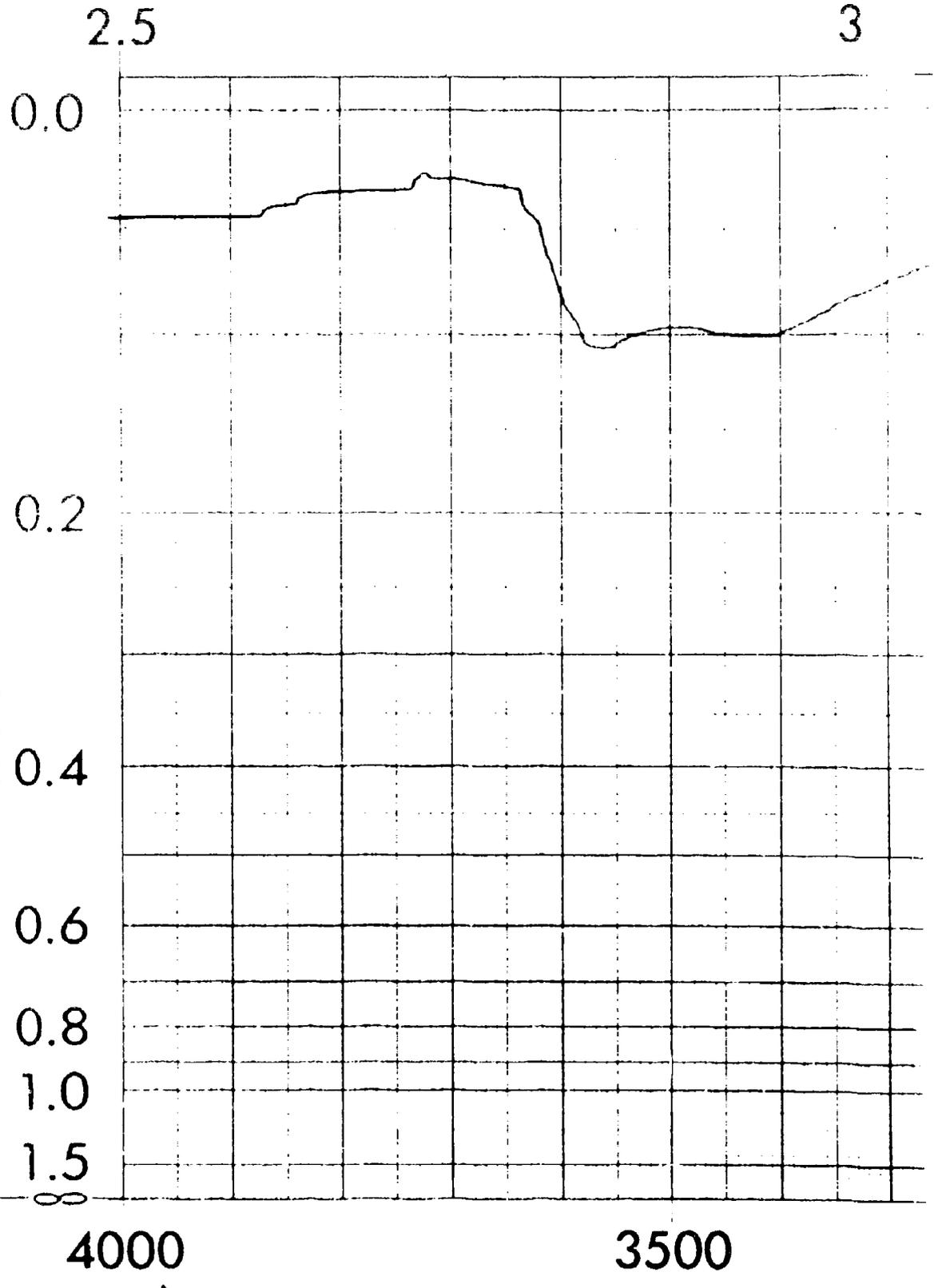
TABLE B-4. DEPECH ANALYSES

<u>Test</u>	<u>DEPECH Source</u>	
	<u>ABL (983-12)</u>	<u>Shell (16P30151)</u>
Hydroxyl Content, g/eq	922	839
Molecular Weight (\bar{M}_n)	2278	2231
Functionality	2.47	2.66
Water Content, %	0.31	0.19

Grab 68

SAMPLE

ABSORBANCE



2.5

3

0.0

0.2

0.4

0.6

0.8

1.0

1.5

4000

3500

1.6

0.8

1.0

1.5

2.0

WAVELENGTH (μ)
4

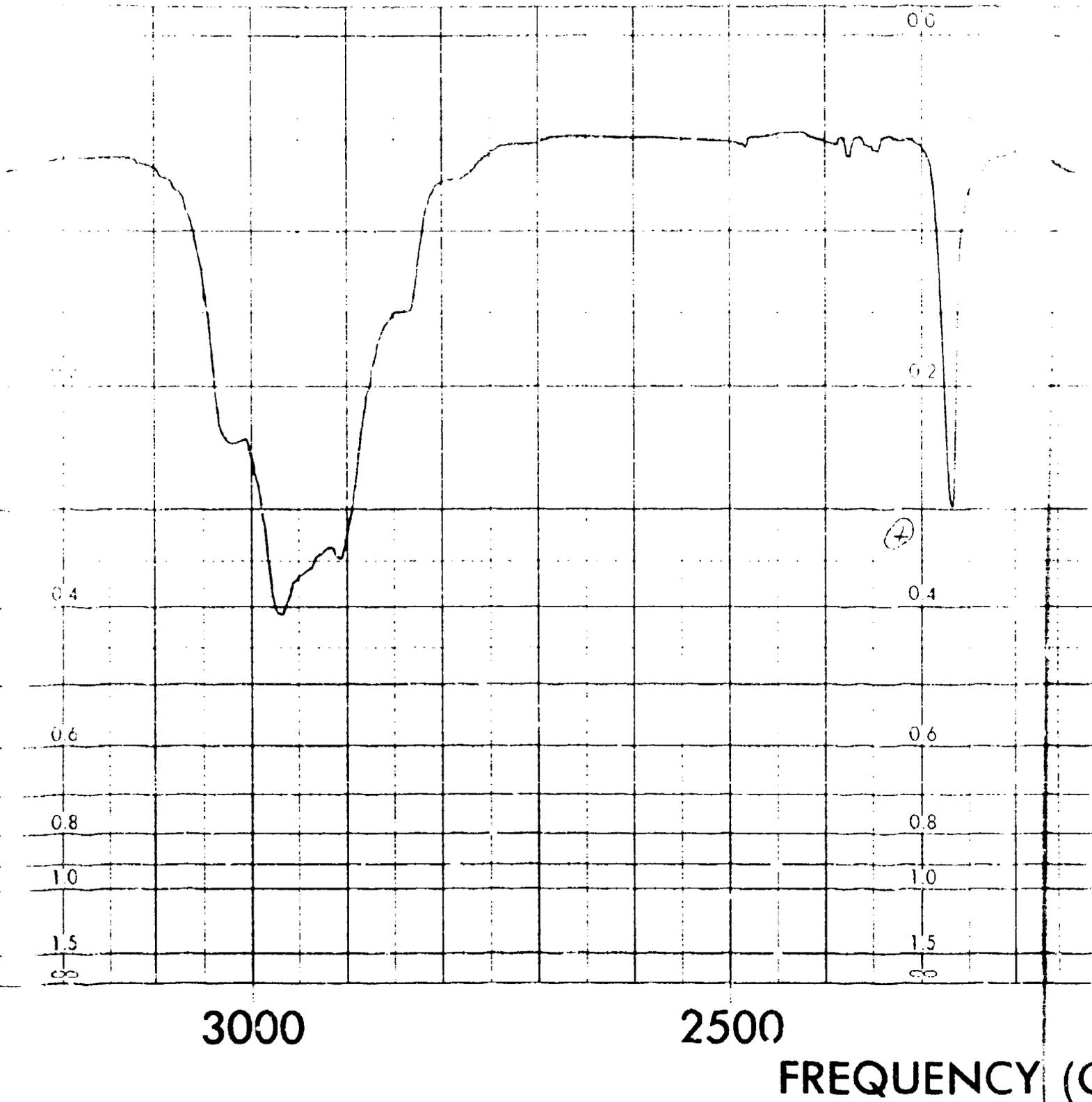


Figure B-1. PBEP Product Shell

2

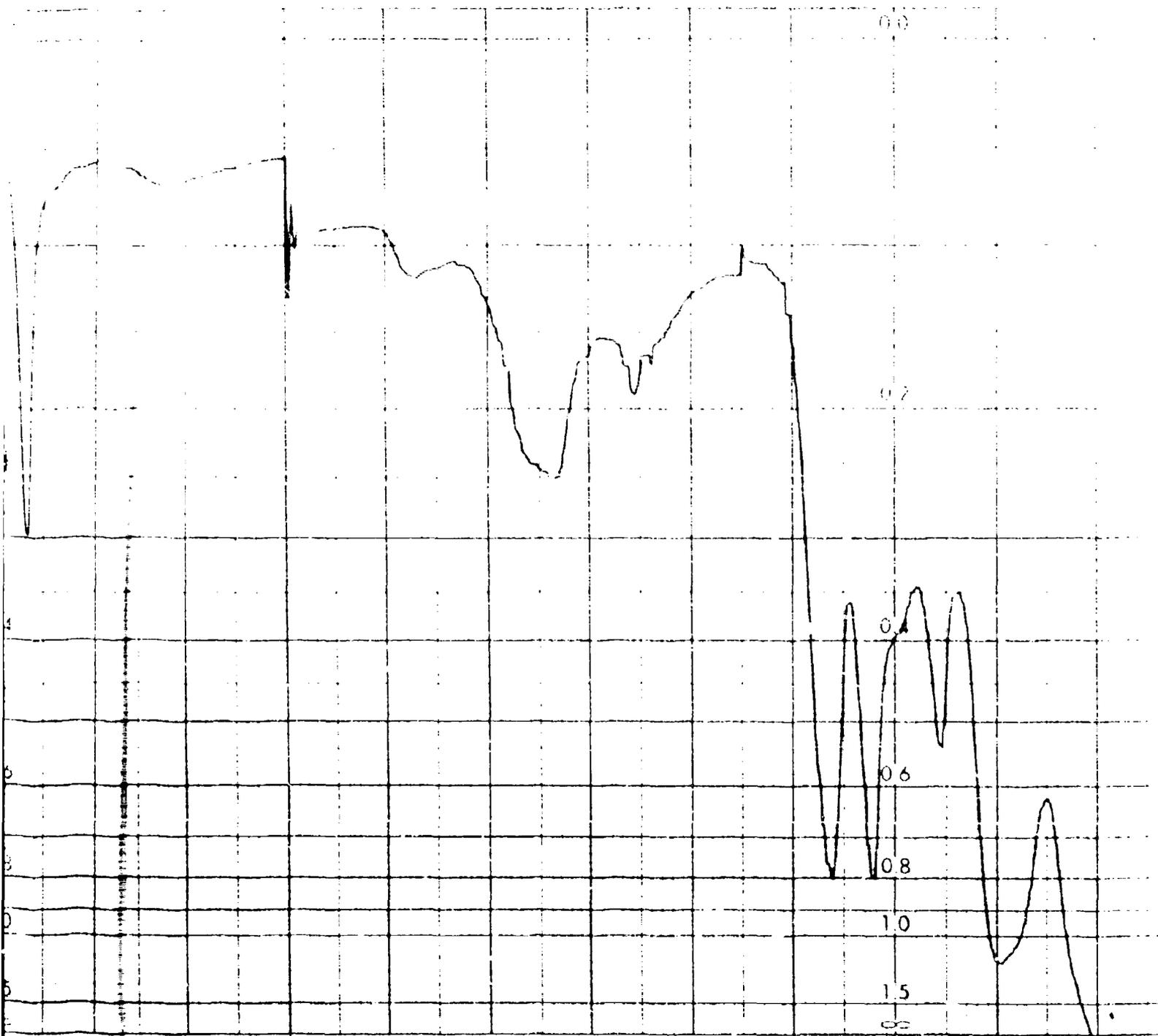
WAVELENGTH (MICRONS)

5

6

7

8



2000

1500

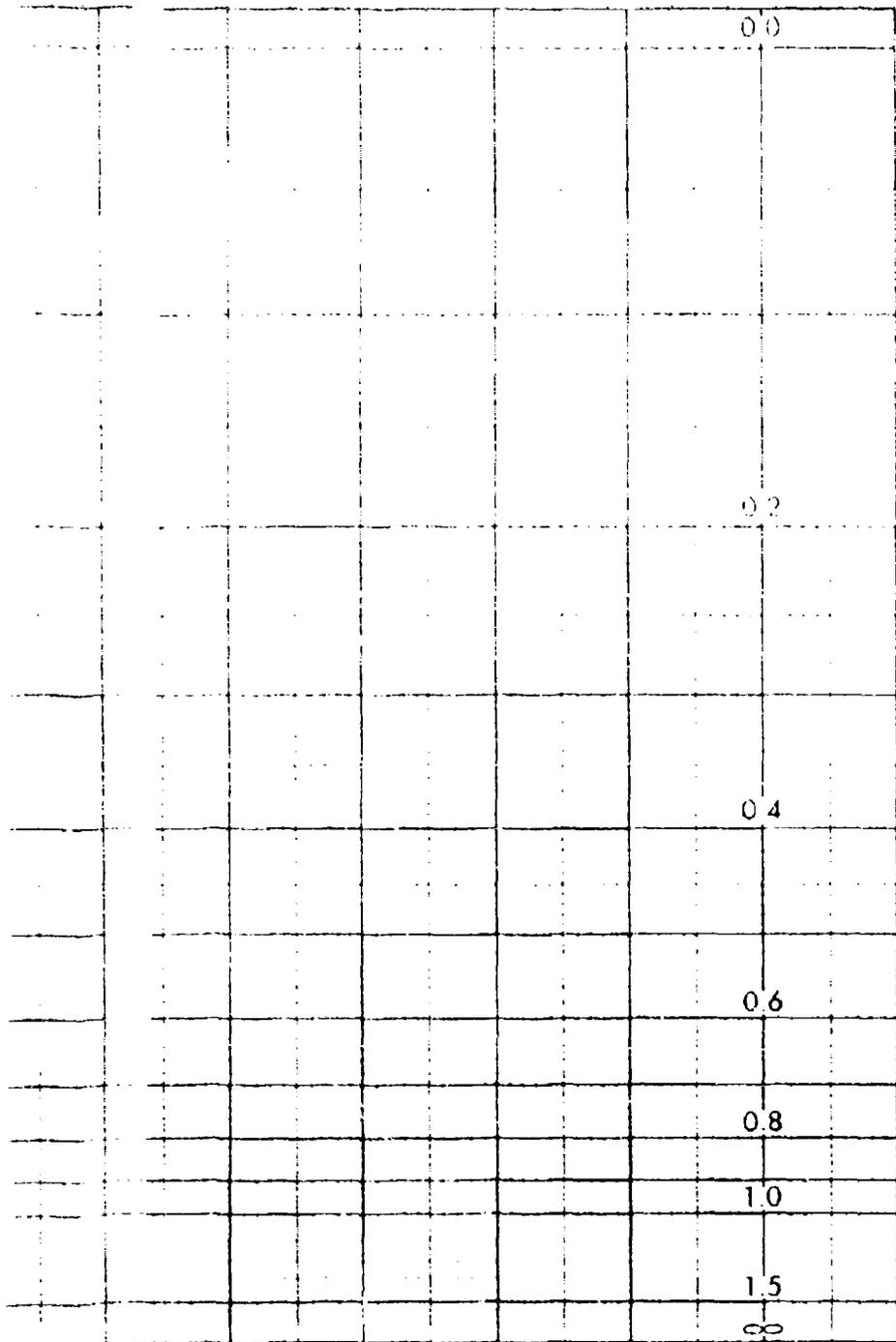
FREQUENCY (CM⁻¹)

Product Shell DEPECH Run No. 68

3

shell

9 10 12 15 20



SPECTRUM NO

SAMPLE **PTSEP - (SHELL DEPOSIT)**
Run 68

ORIGIN

PURITY

PHASE

THICKNESS

1

2

3

DATE **APRIL 4, 1977**

OPERATOR

REMARKS

INTERCHANGE

SLIT PROGRAM

GAIN

ATTENUATOR SPEED

SCAN TIME

SUPPRESSION

SCALE

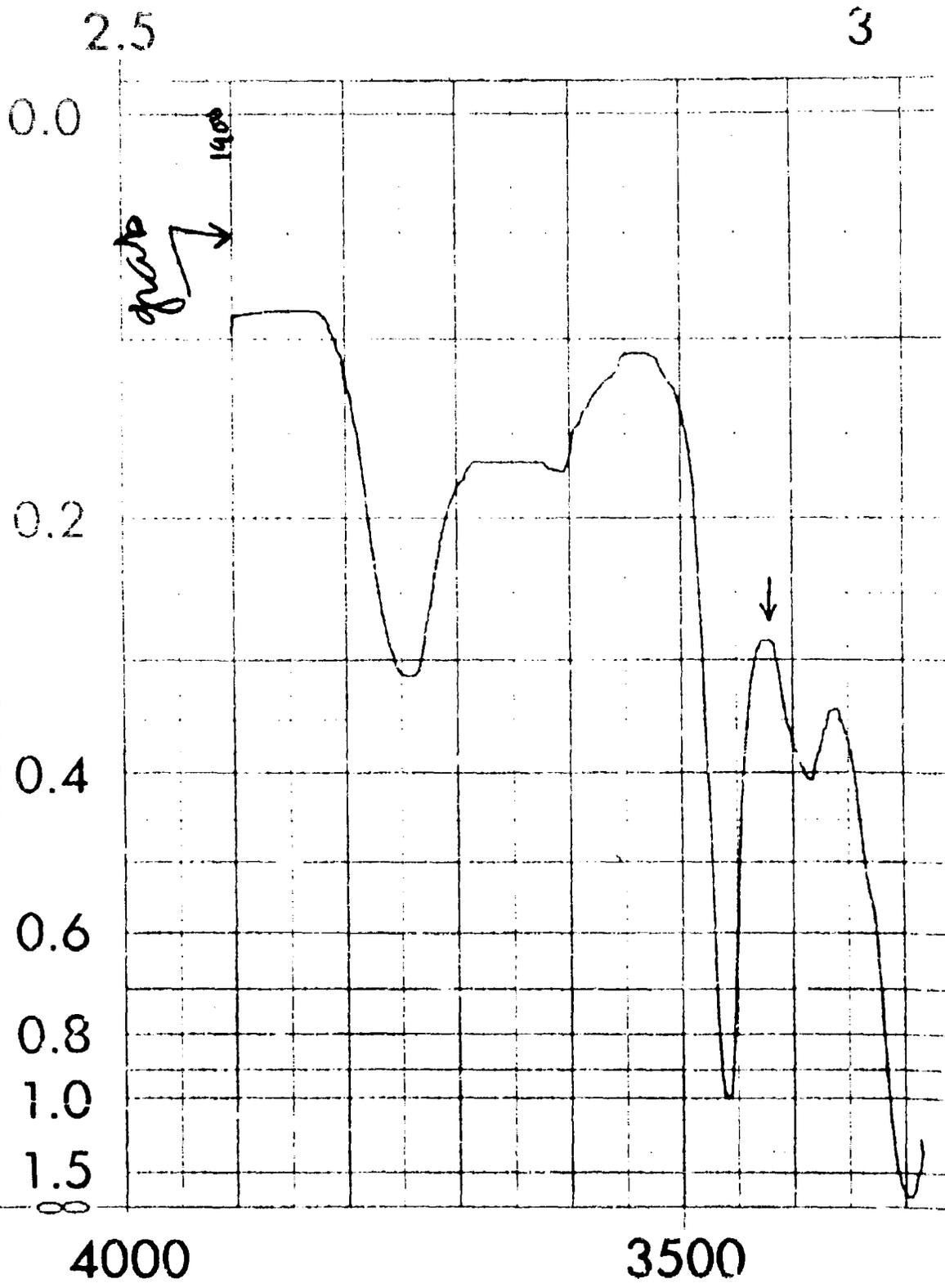
SOURCE CURRENT

RECORDING CHARTS
MADE IN U.S.A.
BUREAU OF INSTRUMENTS
NEW YORK
PR 1131
(221-1600)

B-11

SAMPLE Run #68
PCOE

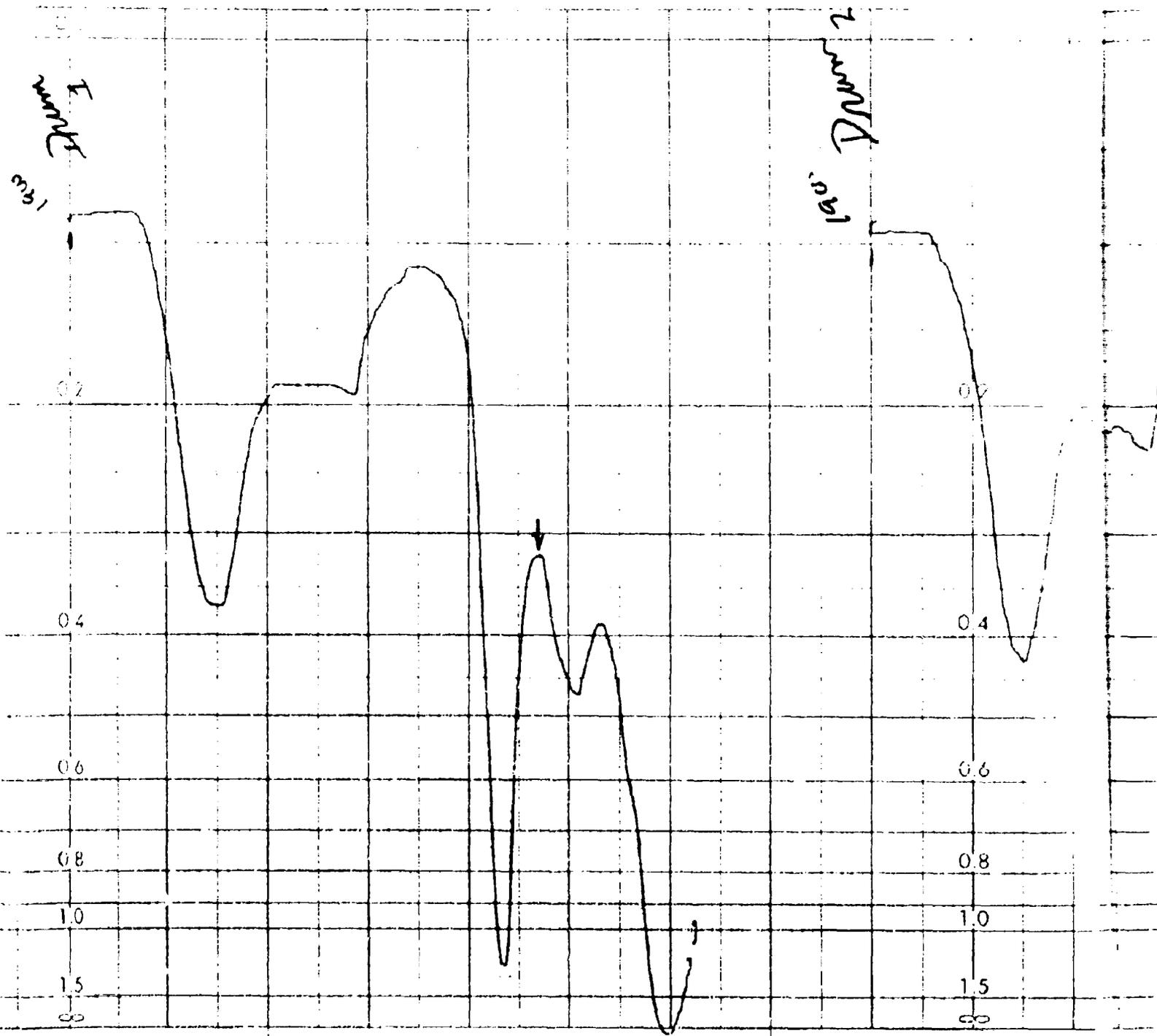
ABSORBANCE



I want
this

WAVELENGTH (M)

4



3000

2500

FREQUENCY (C)

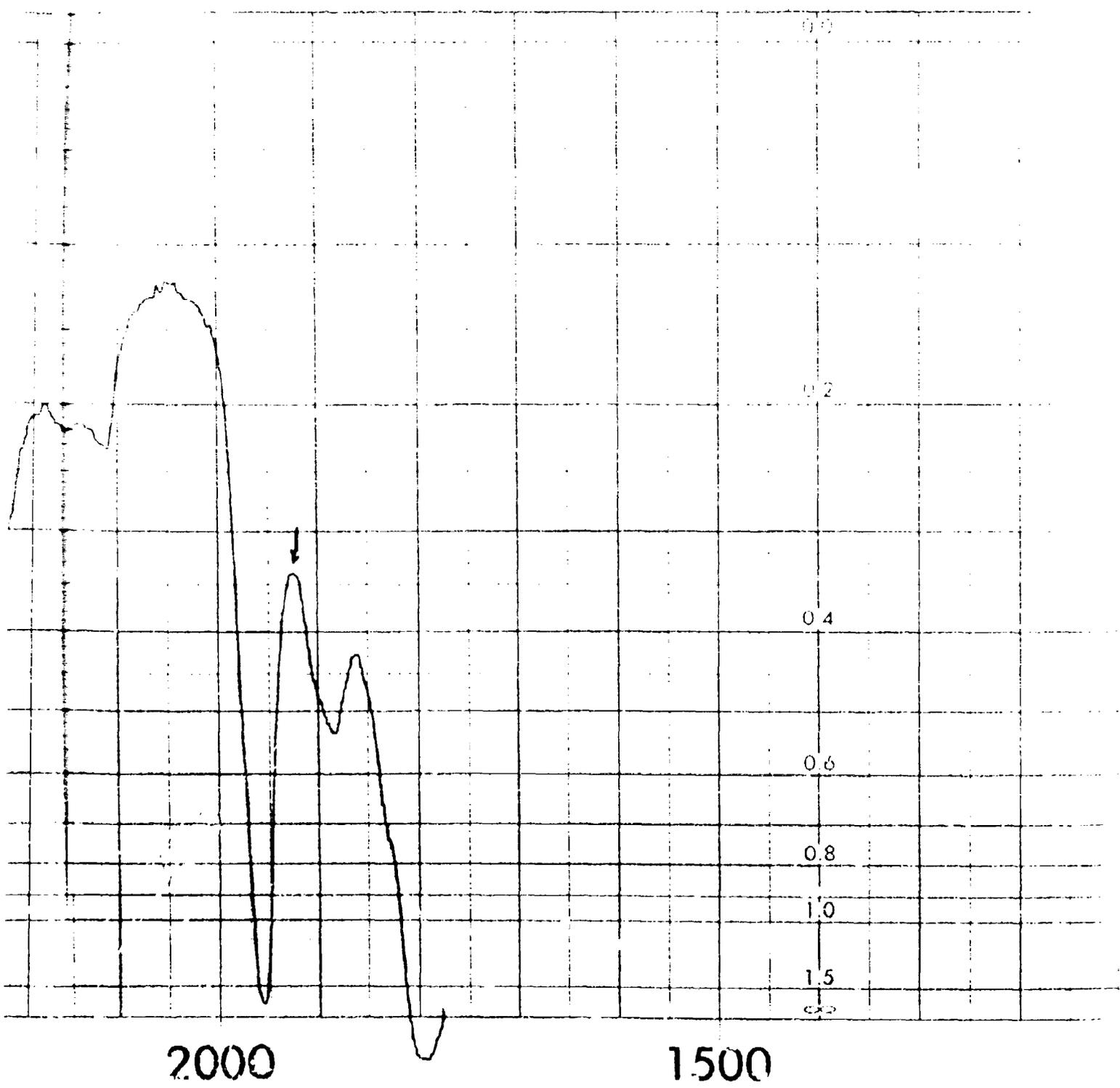
H (MICRONS)

5

6

7

8



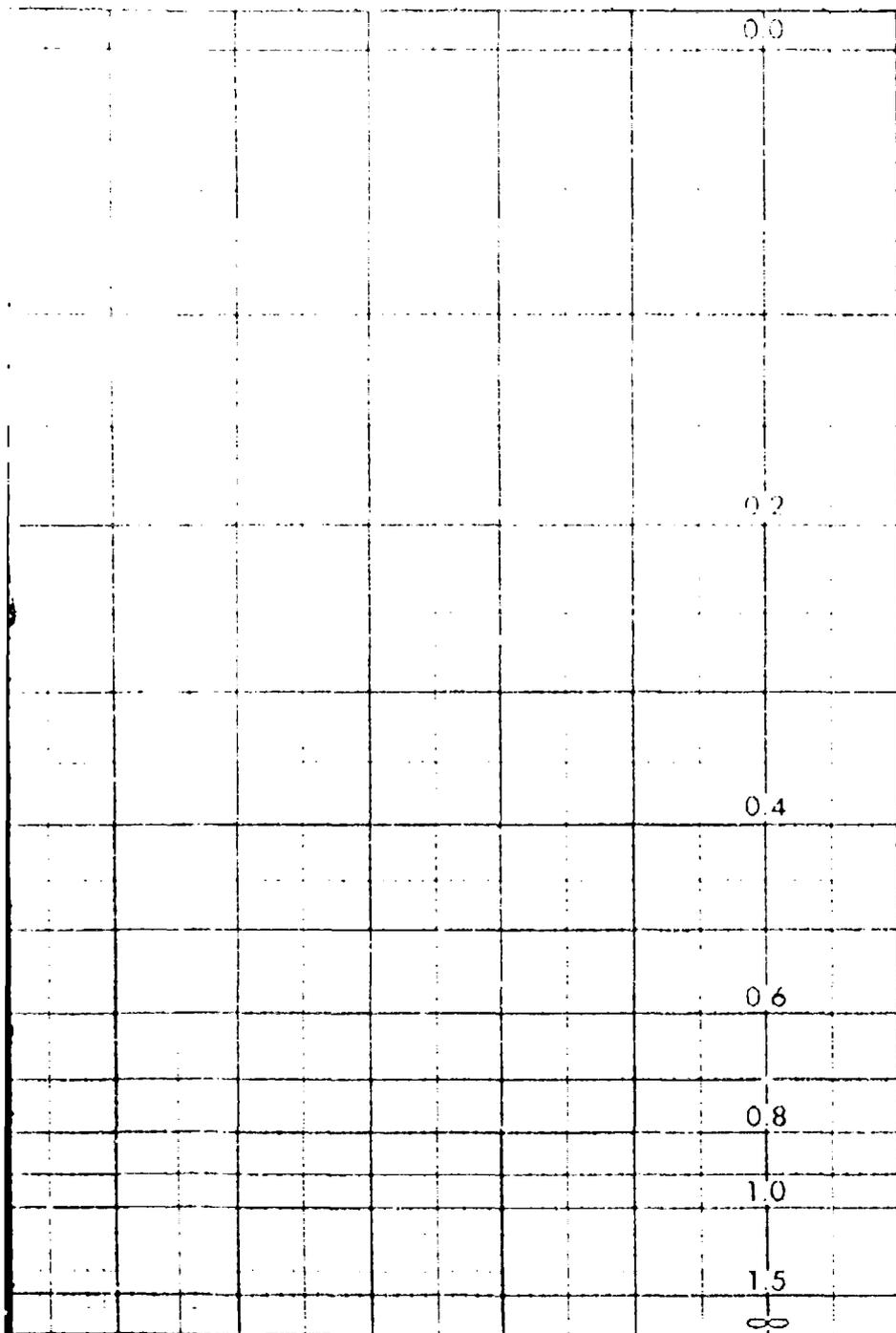
2000

1500

WAVENUMBER (CM⁻¹)

3

9 10 12 15 20



SPECTRUM NO.

SAMPLE **PCDE (SHELL DEFECT)**
Run 68

ORIGIN

PURITY

PHASE

THICKNESS

1.

2.

3.

DATE **APRIL 4, 1977**

OPERATOR

REMARKS **Three Samples**

Scans begin at 1900 cm⁻¹

INTERCHANGE

SLIT PROGRAM

GAIN

ATTENUATOR SPEED

SCAN TIME

SUPPRESSION

SCALE

SOURCE CURRENT

1000

500

RECORDING CHARTS
PR 1131
(221-1600)

B-12

4

SAMPLE 80-7

Run 69 404

Second Grid

PBEP

ABSORBANCE



4000

3500

0.4

0.6

0.8

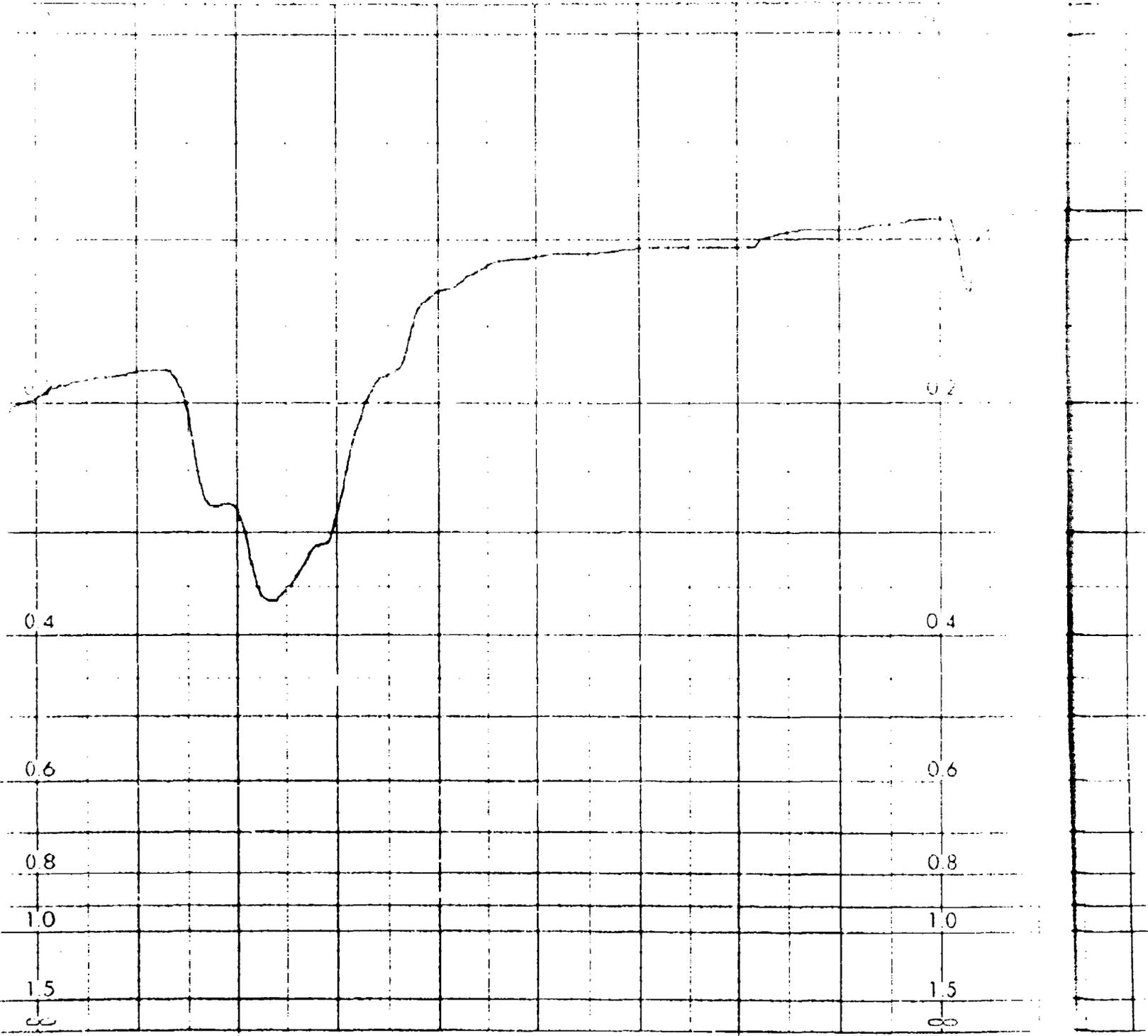
1.0

1.5

2.0

WAVELENGTH (M)

4



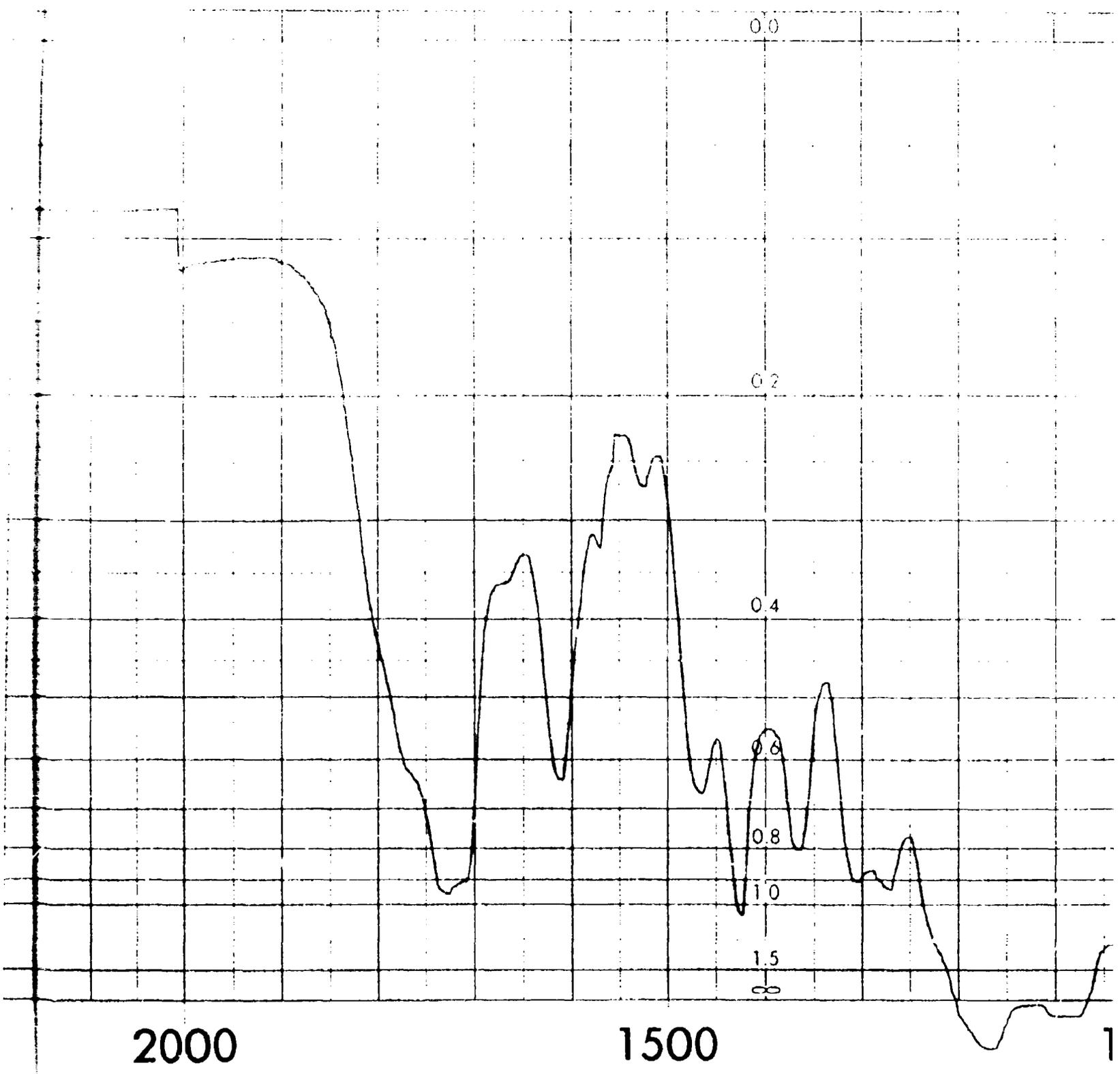
3000

2500

FREQUENCY (CM⁻¹)

T (in SONS)

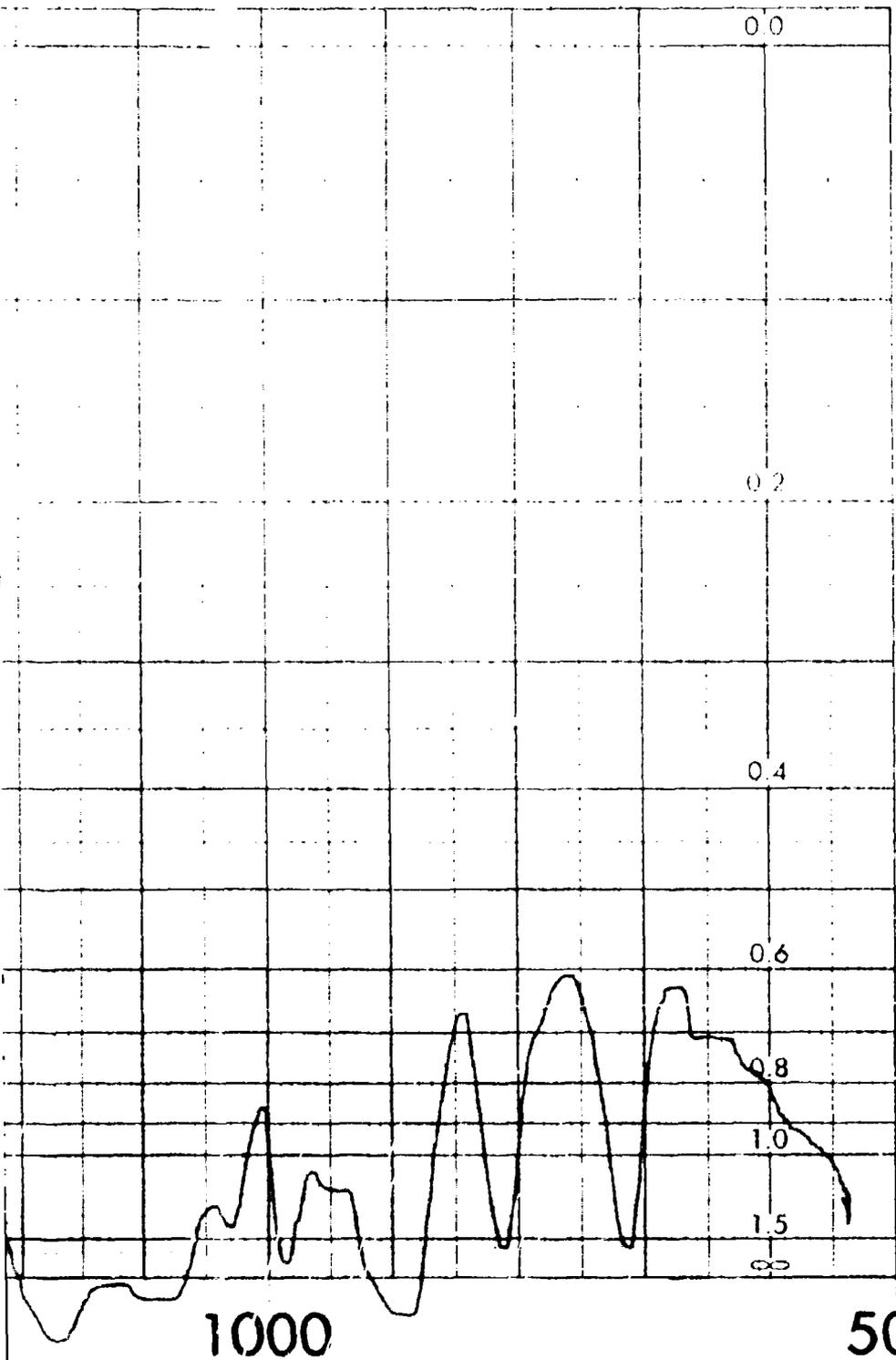
5 6 7 8 9



Y (CM⁻¹)

ABL DEPECH Run No. 69

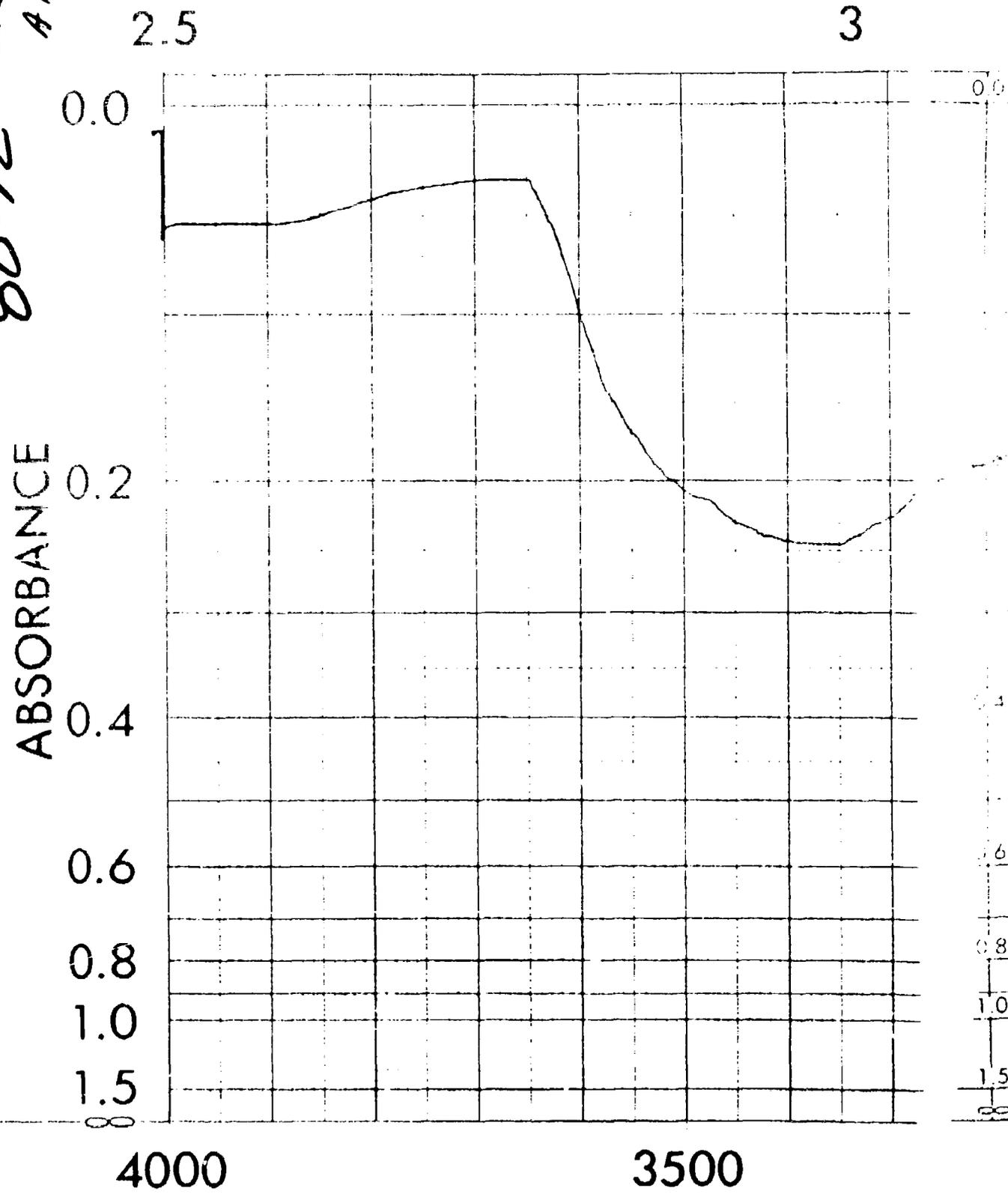
9 10 12 15 20



SPECTRUM NO
SAMPLE **PBEP (ABL DEPECH)**
Run #69
ORIGIN
PURITY
PHASE
THICKNESS
1
2
3
DATE **April 6, 1977**
OPERATOR
REMARKS
INTERCHANGE
SLIT PROGRAM
GAIN
ATTENUATOR SPEED
SCAN TIME
SUPPRESSION
SCALE
SOURCE CURRENT

RECORDING CHARTS
MILITARY ELECTRONICS CORPORATION
ROSELAND, NEW YORK
PR 1131
(221-1600)

SAMPLE PDE Grab
80-12 Run 69
ABL



WAVELENGTH (M)
4

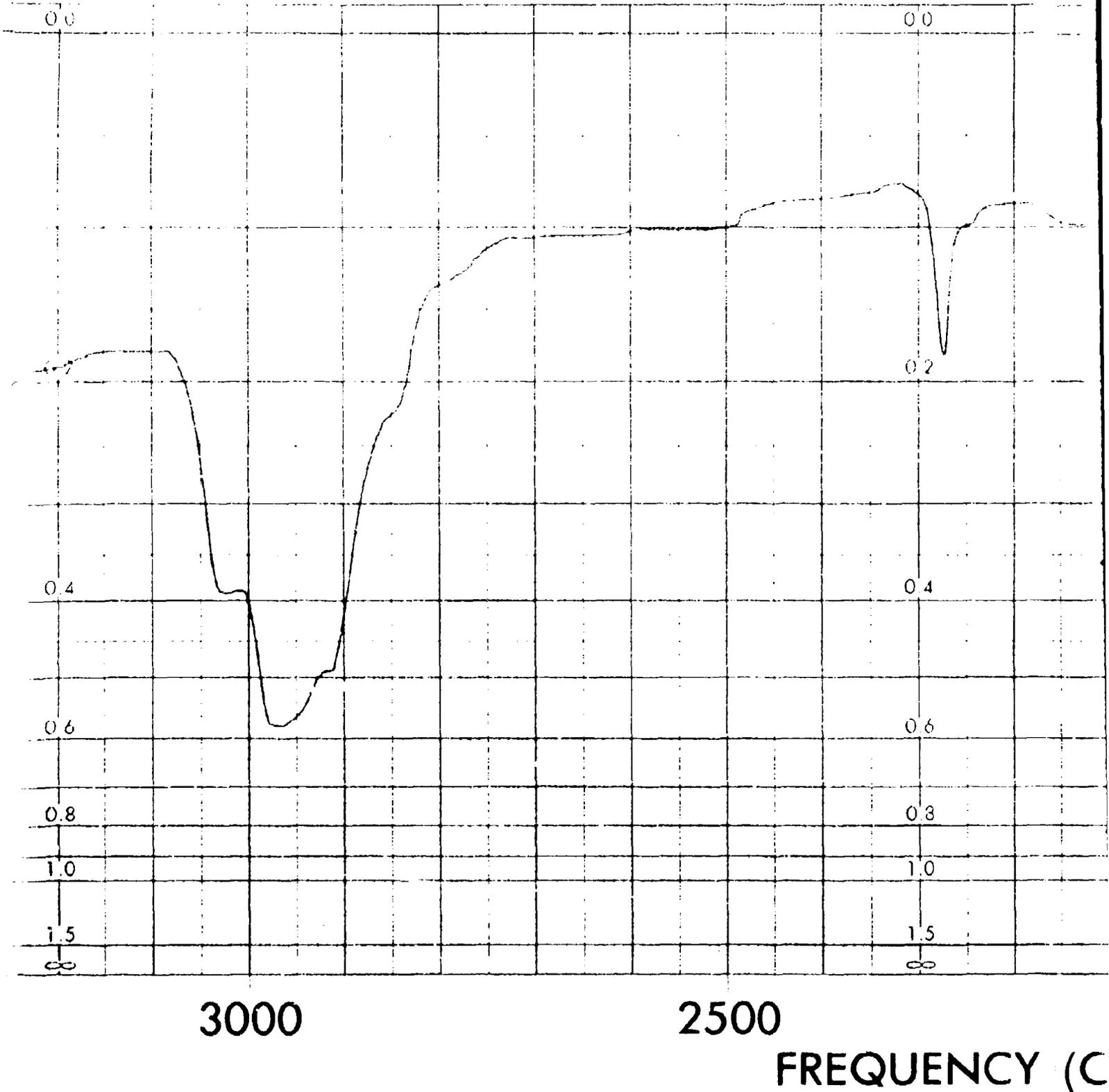


Figure B-4. PCDE Product ABL DE

2

λ (MICRONS)

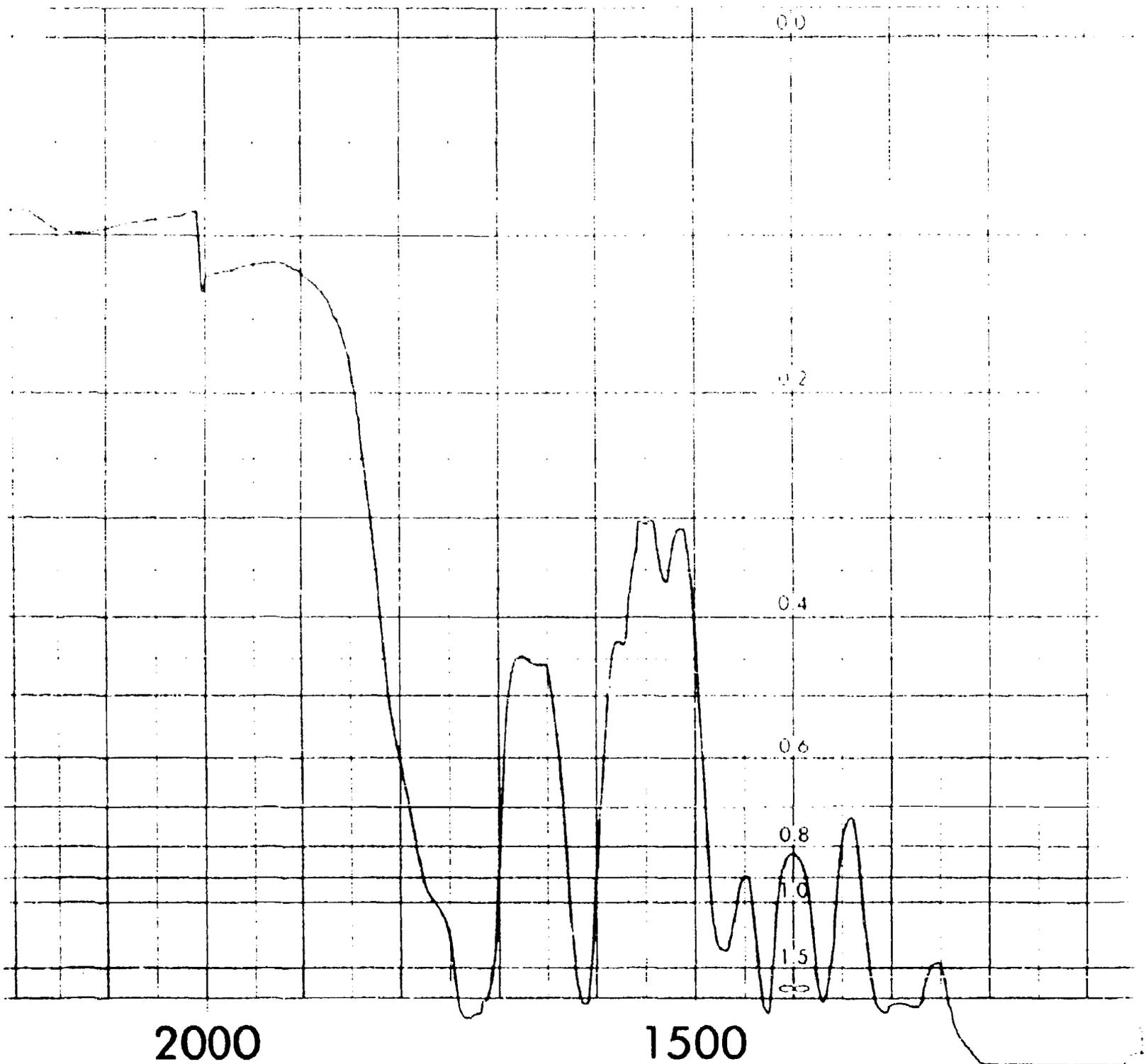
5

6

7

8

9



2000

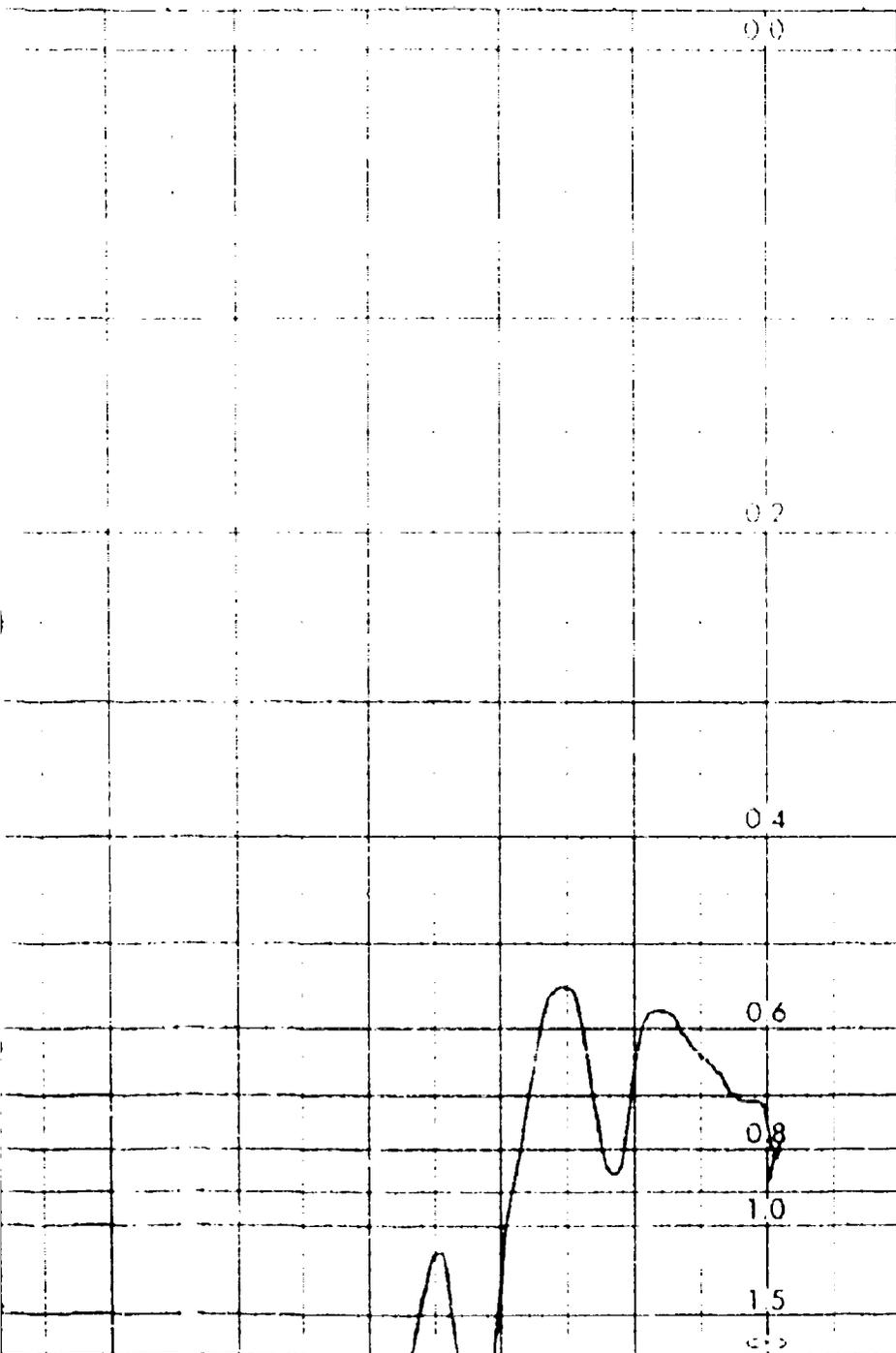
1500

ν (CM⁻¹)

ABL DEPECH Run No. 69

3

9 10 12 15 20



1000

500

SPECTRUM NO.
SAMPLE **PCDE (ABL DEPECH)**
Run #69

ORIGIN

PURITY

PHASE

THICKNESS

1

2

3

DATE **April 6, 1977**

OPERATOR

REMARKS

INTERCHANGE

SPLIT PROGRAM

GAIN

ATTENUATOR SPEED

SCAN TIME

SUPPRESSION

SCALE

SOURCE CURRENT

RECORDING CHARTS

PR 1131
(221-1600)

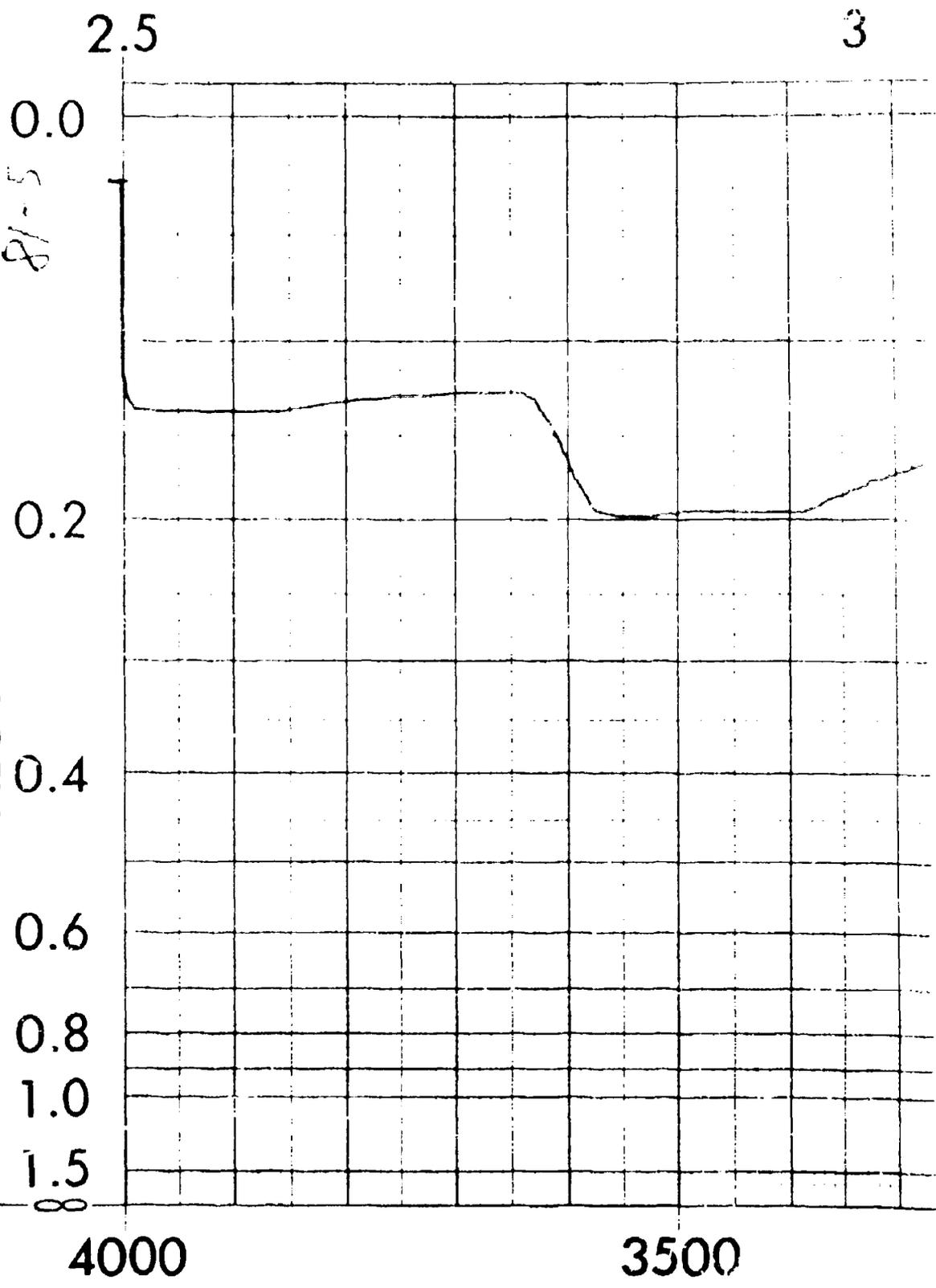
B-14

4

SAMPLE PBE P

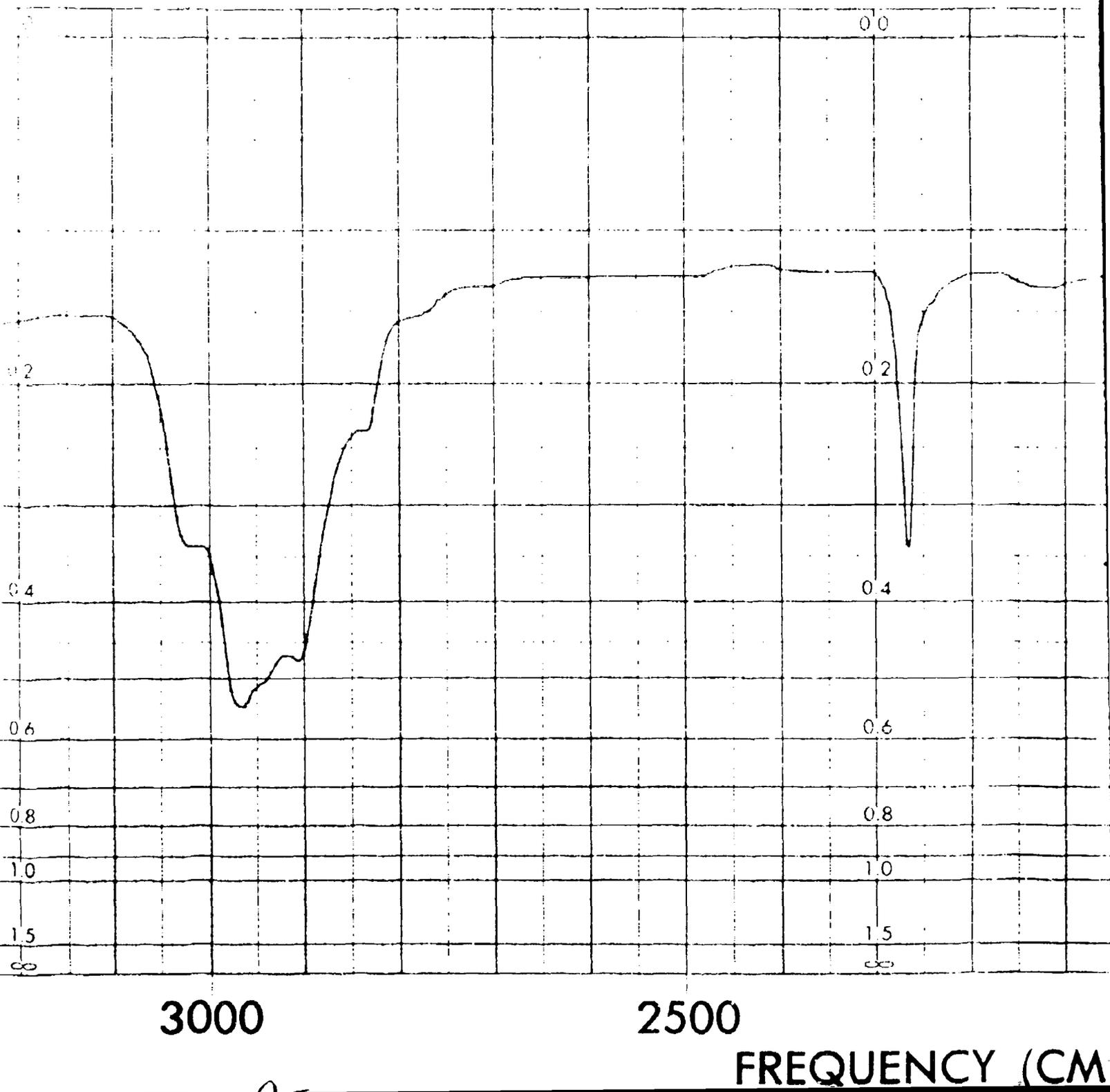
81-5

ABSORBANCE



WAVELENGTH (MIC)

4



(MICRONS)

5

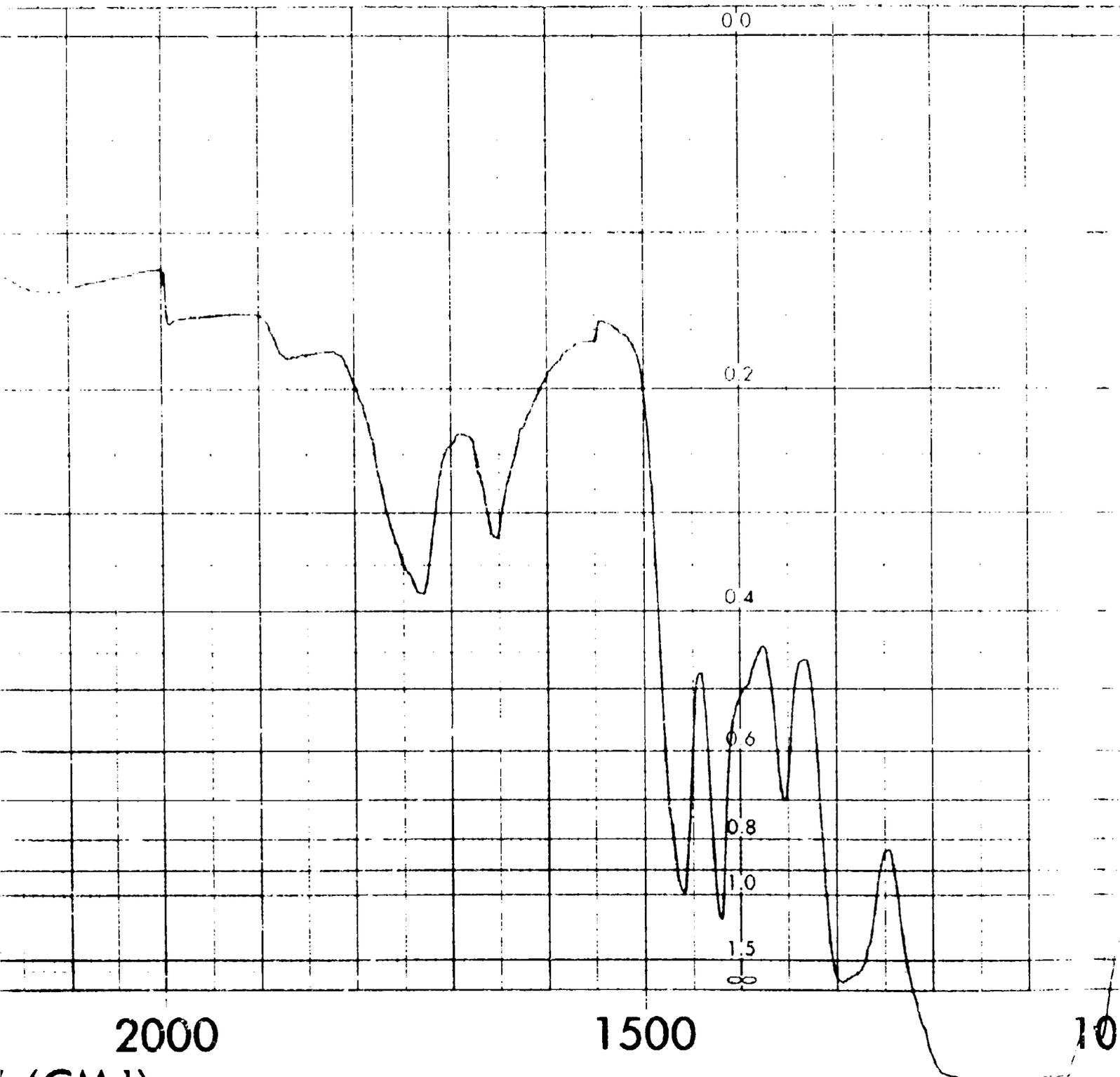
6

7

8

9

10



2000

1500

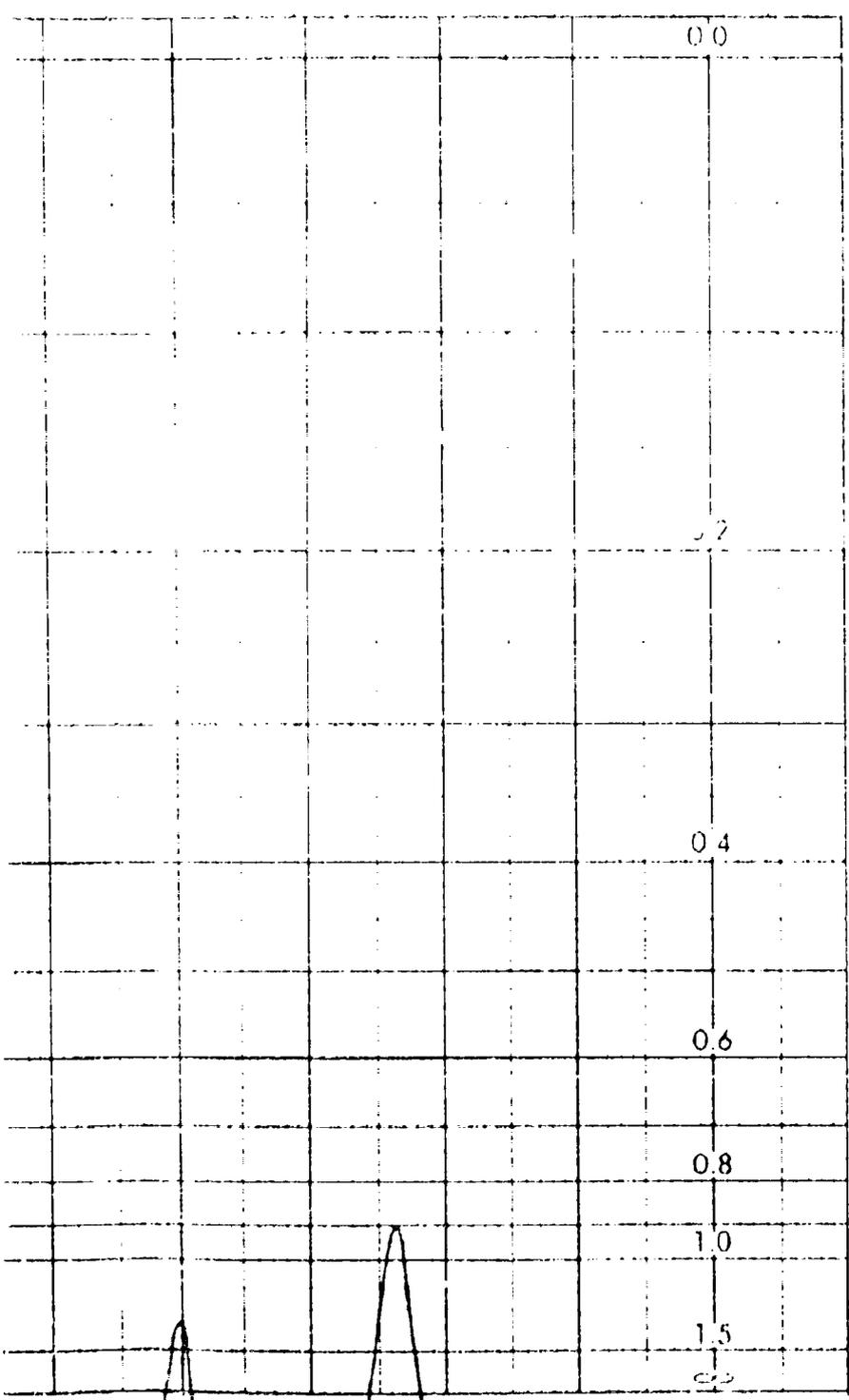
1000

(CM⁻¹)

ABL DEPECH Run No. 70

3

9 10 12 15 20



SPECTRUM NO.
 SAMPLE
 ORIGIN
 PURITY
 PHASE
 THICKNESS
 1
 2
 3
 DATE *MAY 20, 1977*
 OPERATOR *Run #70*
 REMARKS *(ABL 983-12 Dried) PSEP Composite*

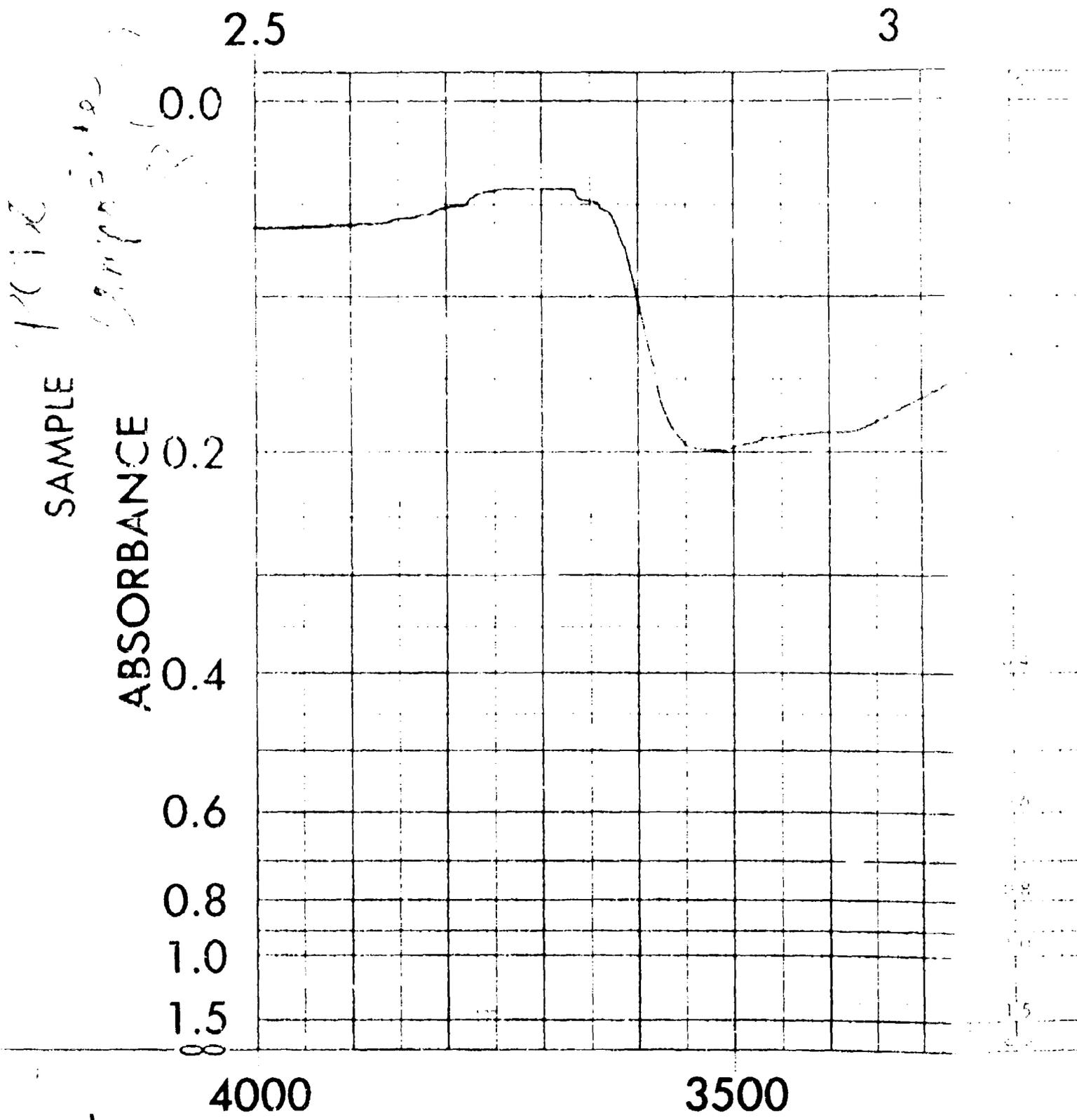
INTERCHANGE
 SEE PROGRAM
 GAIN
 ATTENUATOR SPEED
 SCAN TIME
 SUPPRESSION
 SCALE
 SOURCE CURRENT

RECORDING CHARTS

PR 1131
(221-1600)

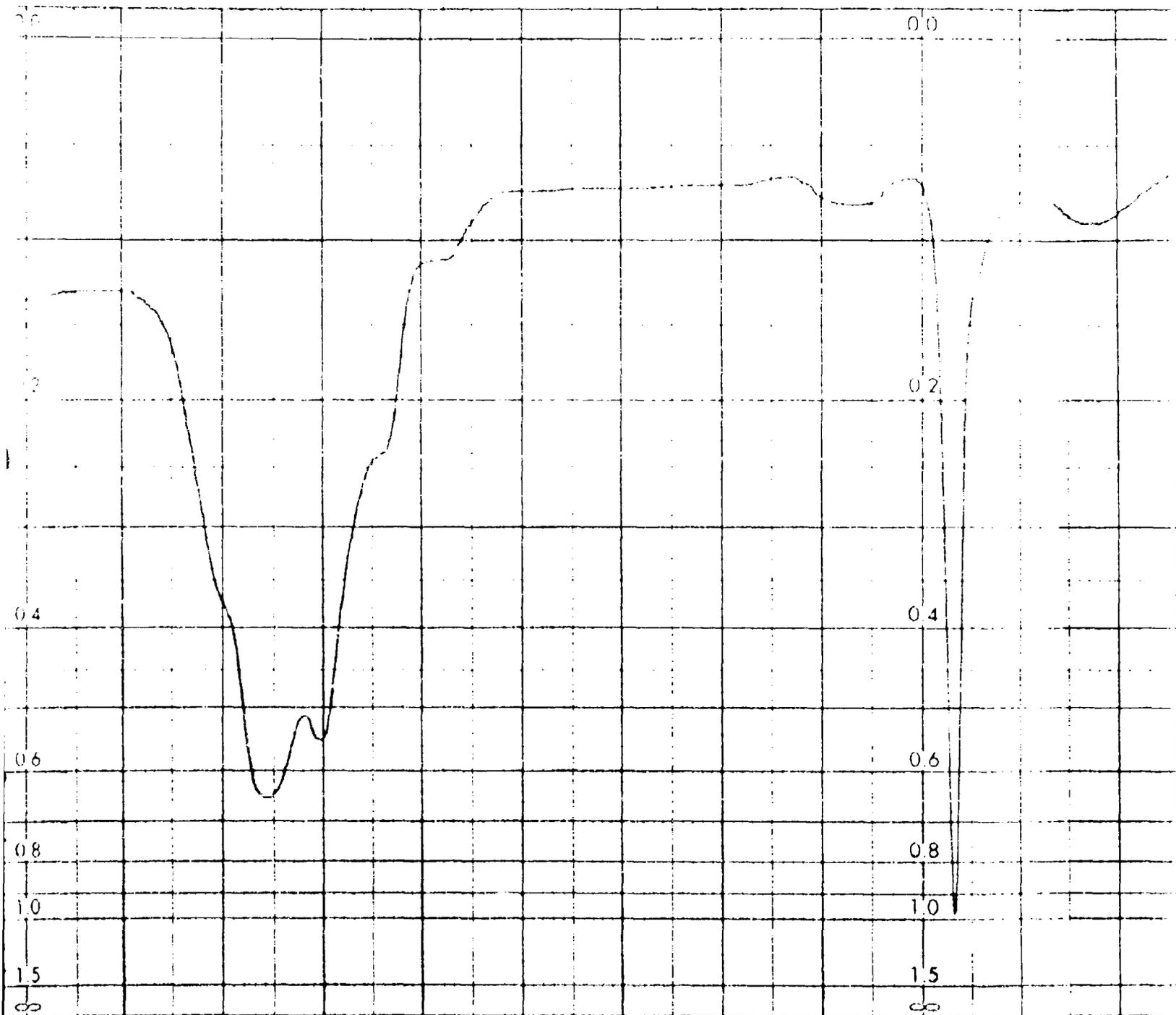
B-15

4



WAVELENGTH (MICRONS)

4



3000

2500

FREQUENCY (CM⁻¹)

Figure B-6. PCDE Product ABL DEPE

2

(MICRONS)

5

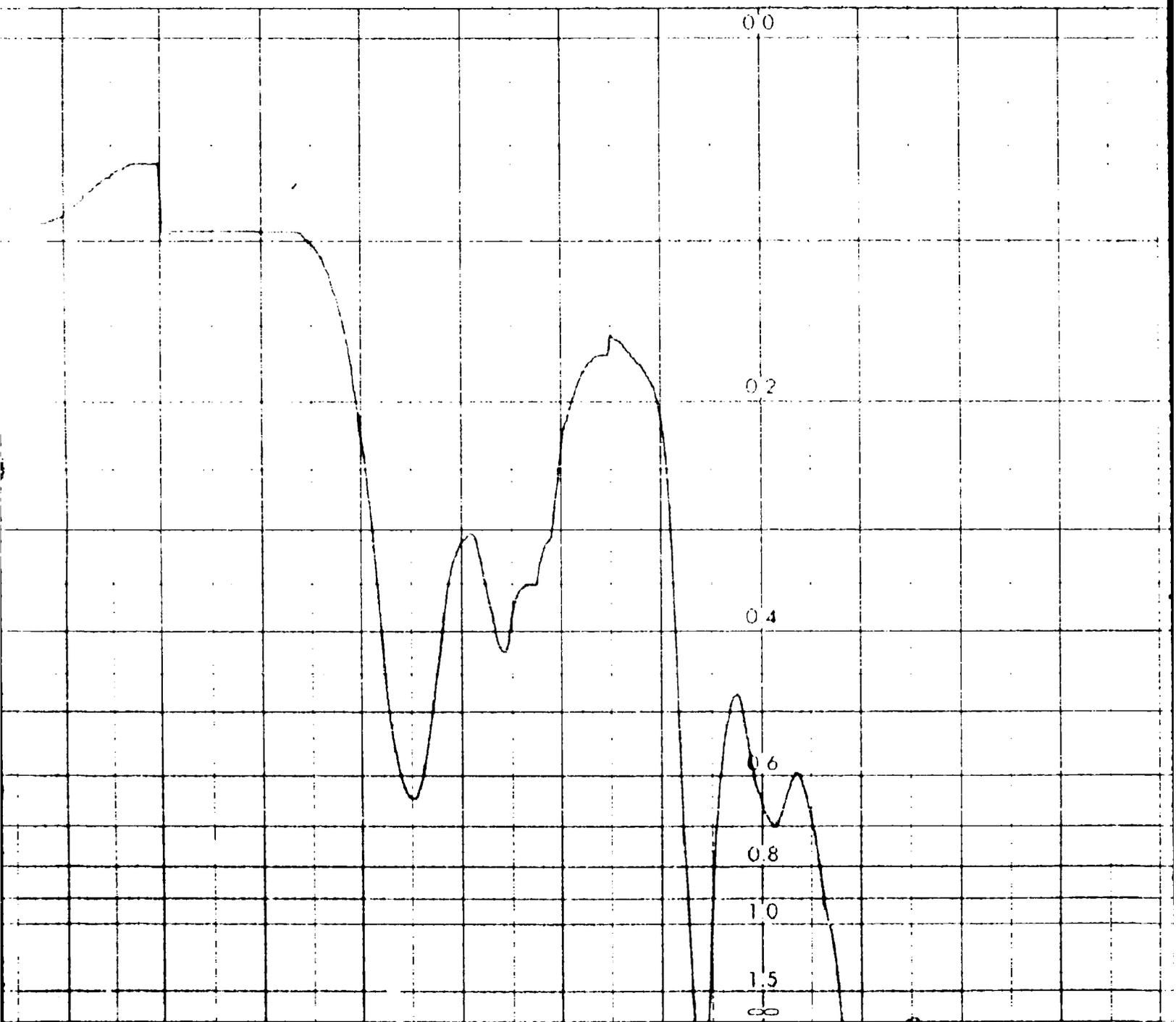
6

7

8

9

10



2000

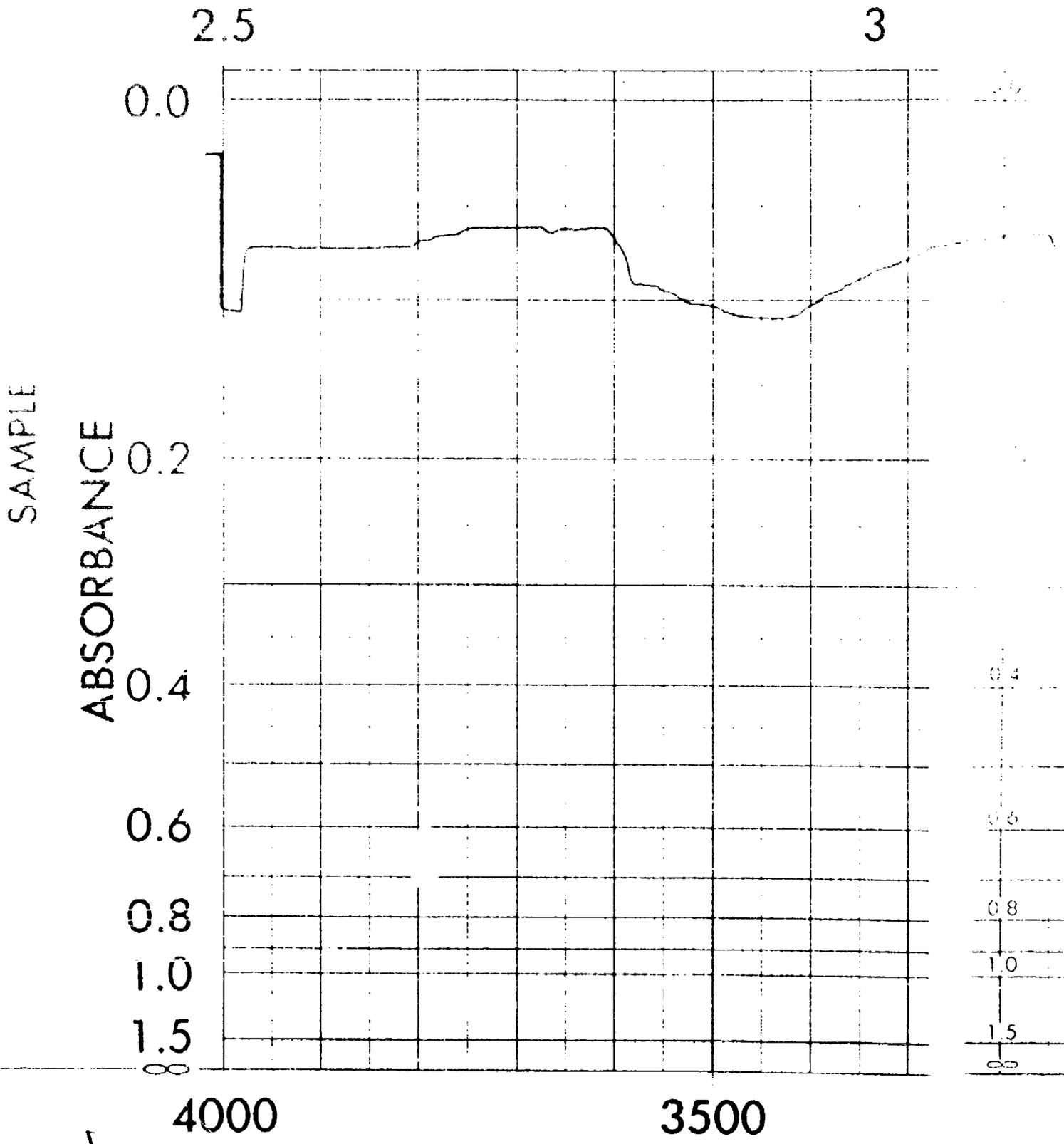
1500

1000

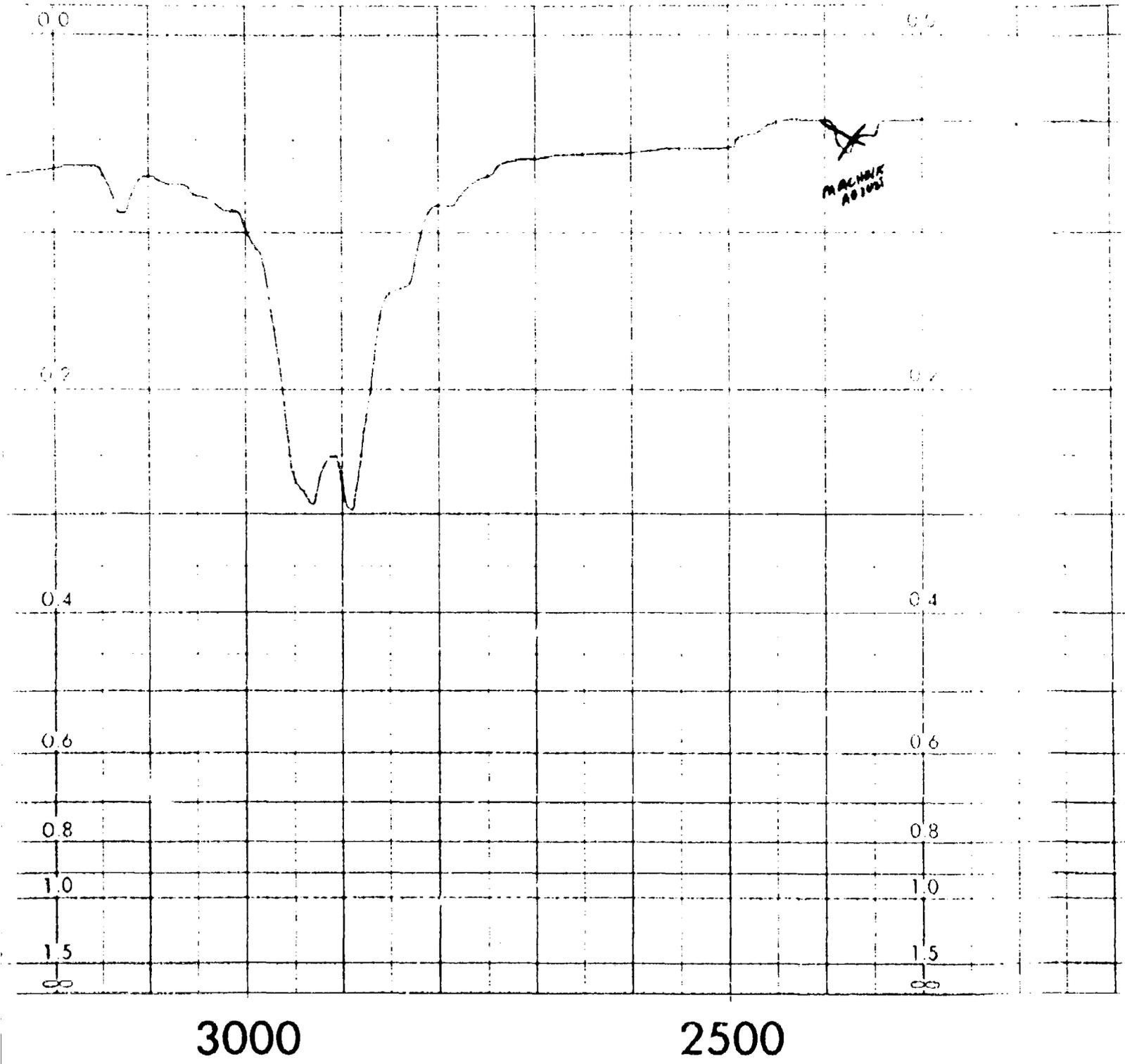
(CM⁻¹)

BL DEPECH Run No. 70

3



WAVELENGTH (MIC)
4



FREQUENCY (C/

Figure B-7. ABL DEPECH Lot

(MICRONS)

5

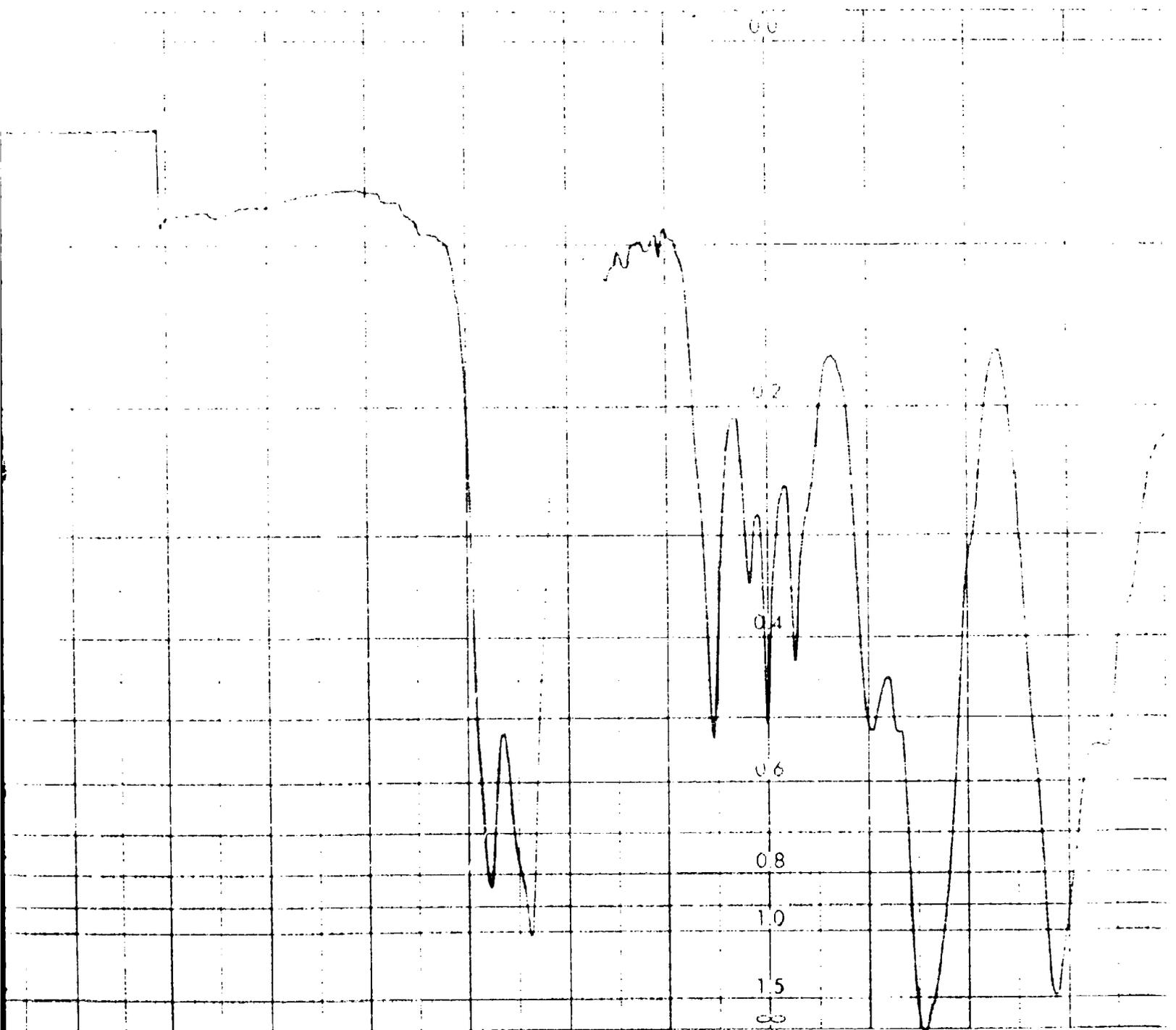
6

7

8

9

10



2000

1500

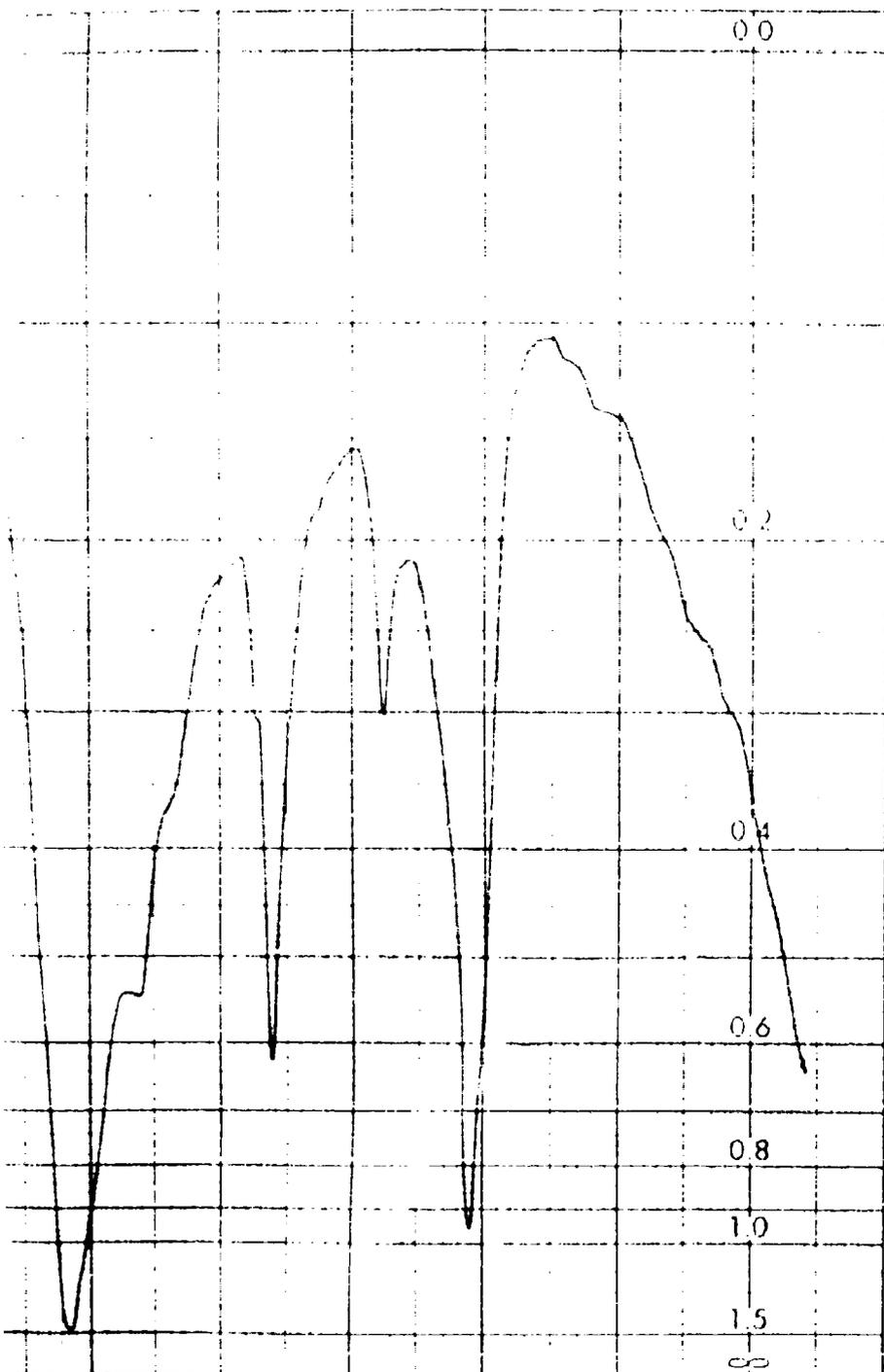
10

(CM⁻¹)

3

Lot 983-6

9 10 12 15 20



SPECTRUM NO

SAMPLE **ABL DEPECH**
LOT 983-6

ORIGIN

PURITY

PREP

THICKNESS

DATE **Nov 1976**

OPERATOR

REMARKS

INTERCHANGE

SPLIT PROGRAM

GAIN

ATTENUATOR SPEED

SCAN TIME

SUPPRESSION

SCALE

SOURCE CURRENT

RECORDING CHARTS

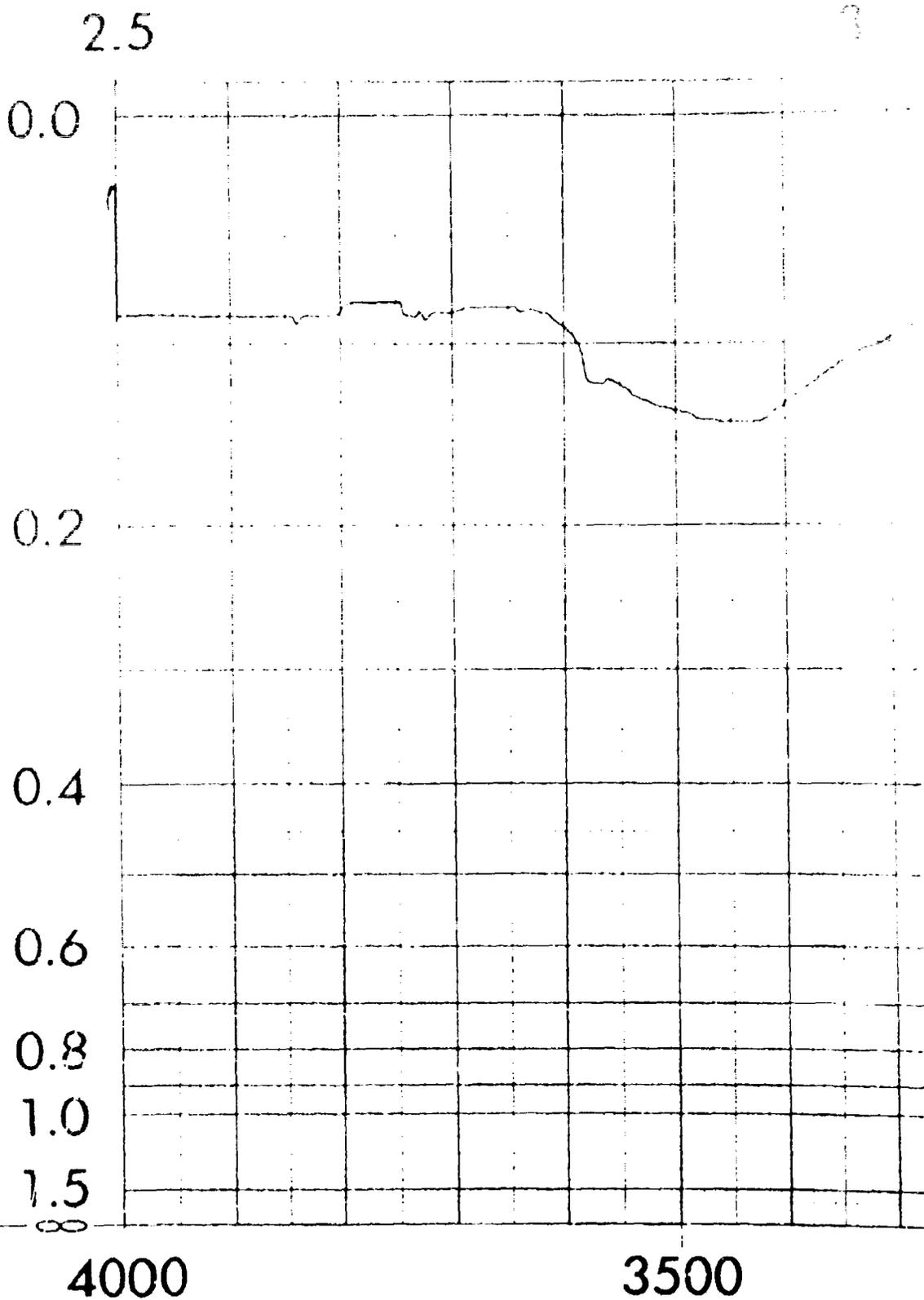
PR 1131
(221 1600)

B-17

4

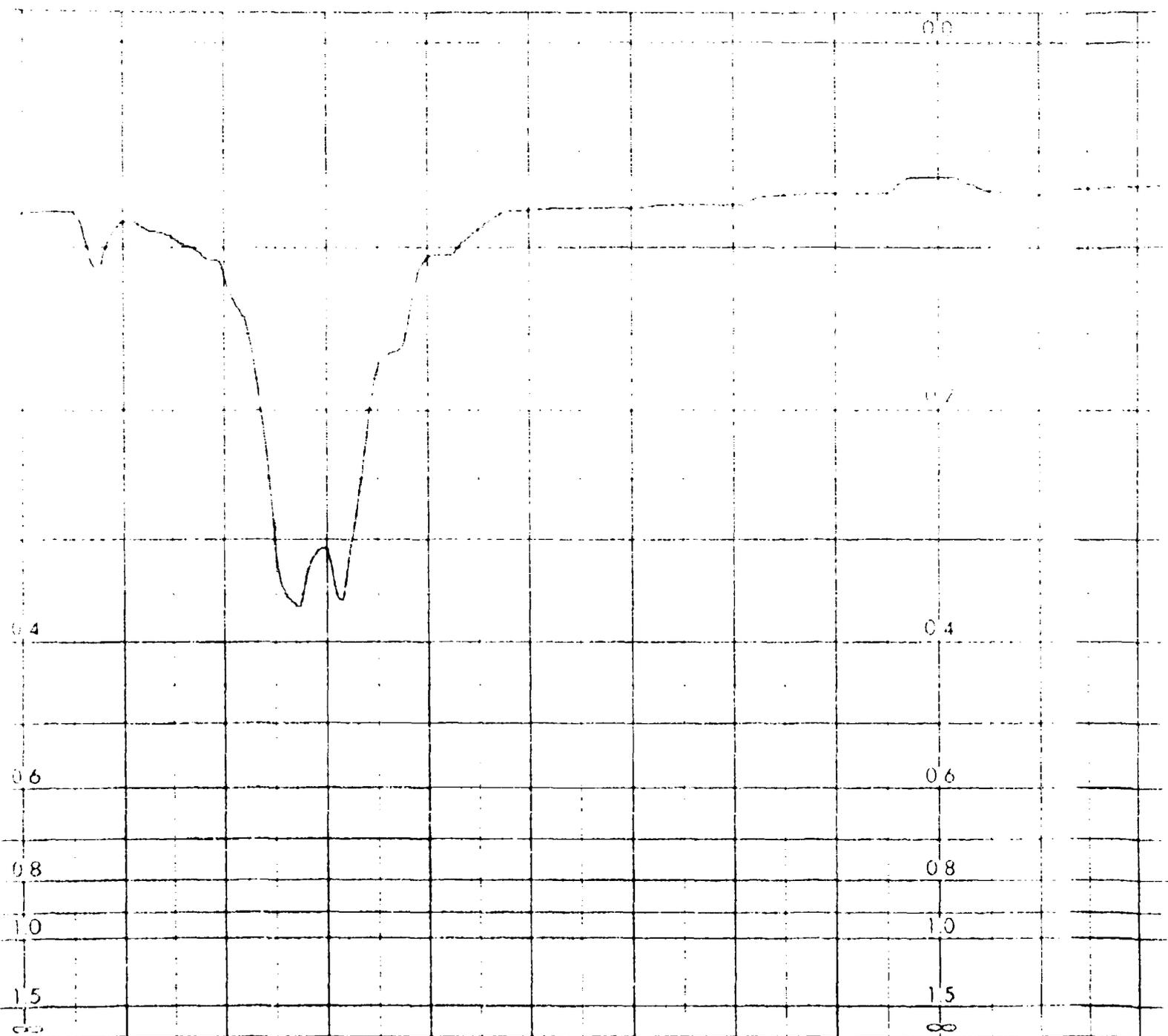
SAMPLE

ABSORBANCE



WAVELENGTH (MIC)

4



3000

2500

FREQUENCY (CM)

Figure B-8. ABL DEPECH Lo

(MICRONS)

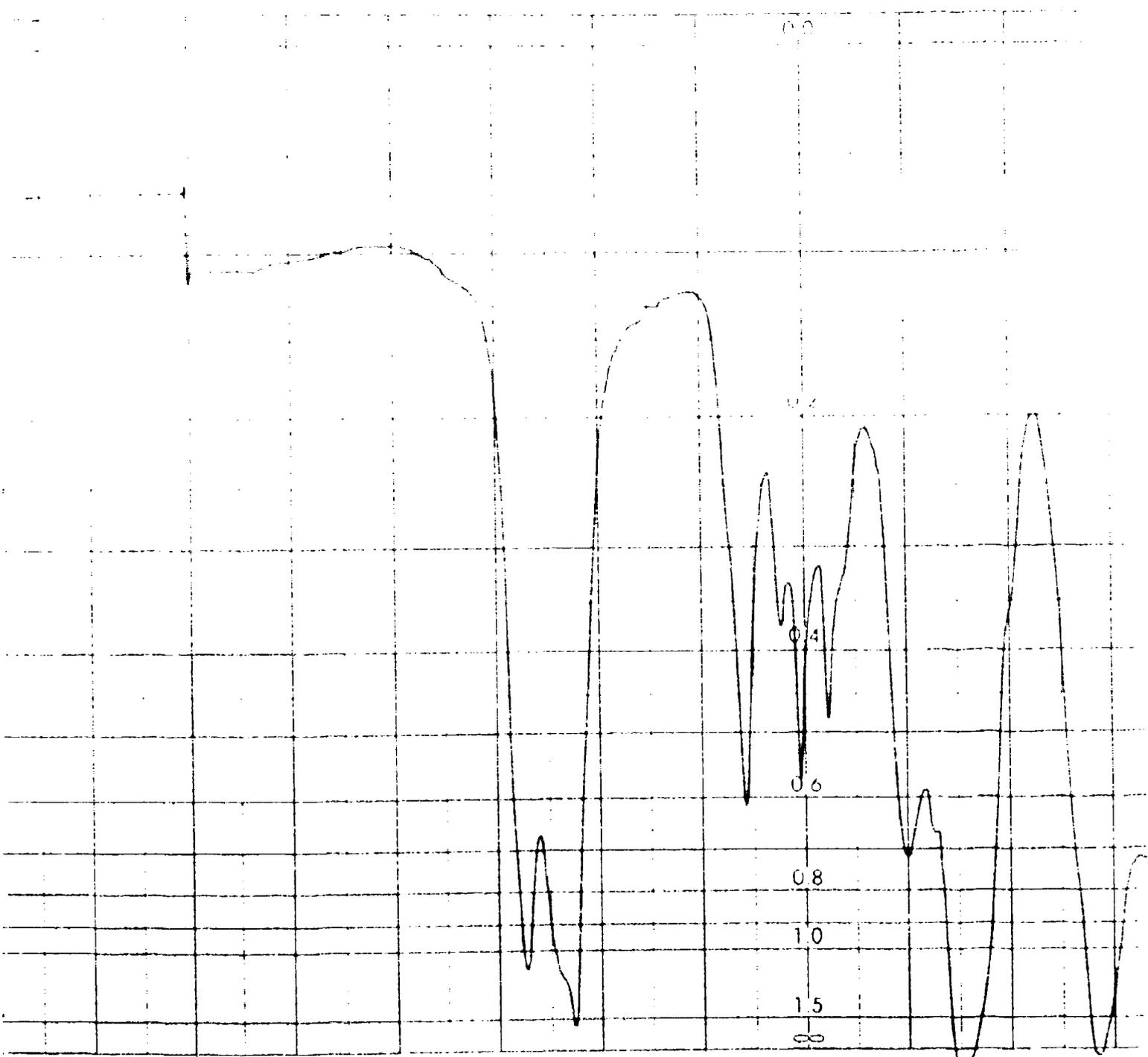
5

6

7

8

9



2000

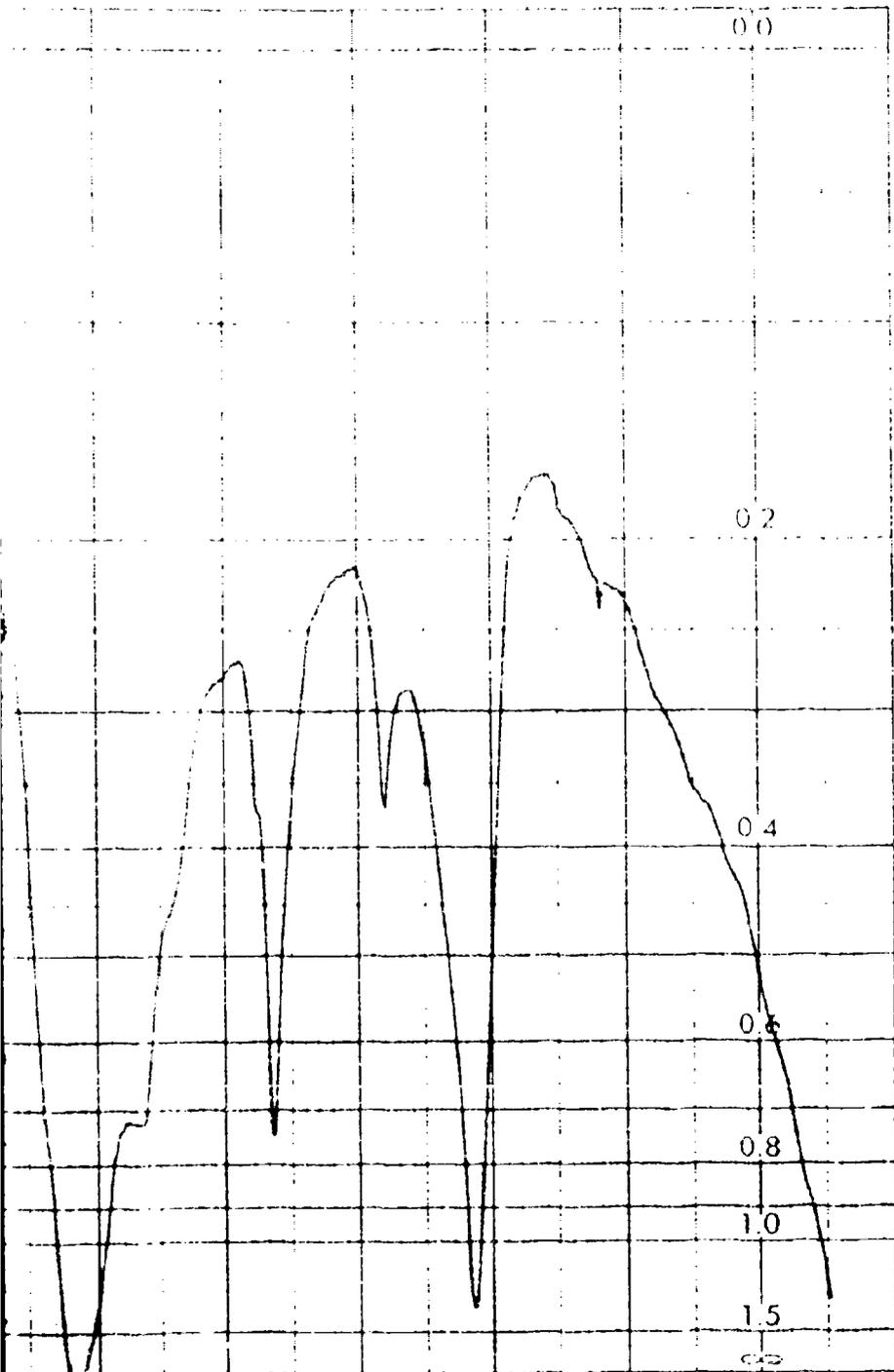
1500

Y (CM⁻¹)

PECH Lot 983-8

3

9 10 12 15 20



1000

500

4

SPECTRUM NO.

SAMPLE **ABL DEPECH**
Lot 983-8

ORIGIN

PURITY

PHASE

THICKNESS

1

2

3

DATE **Nov 1976**

OPERATOR

REMARKS

INTERCHANGE

SLIT PROGRAM

GAIN

ATTENUATOR SPLED

SCAN TIME

SUPPRESSION

SCALE

SOURCE CURRENT

RECORDING CHARTS

PERFORMED BY

PR 1131
(221 1600)

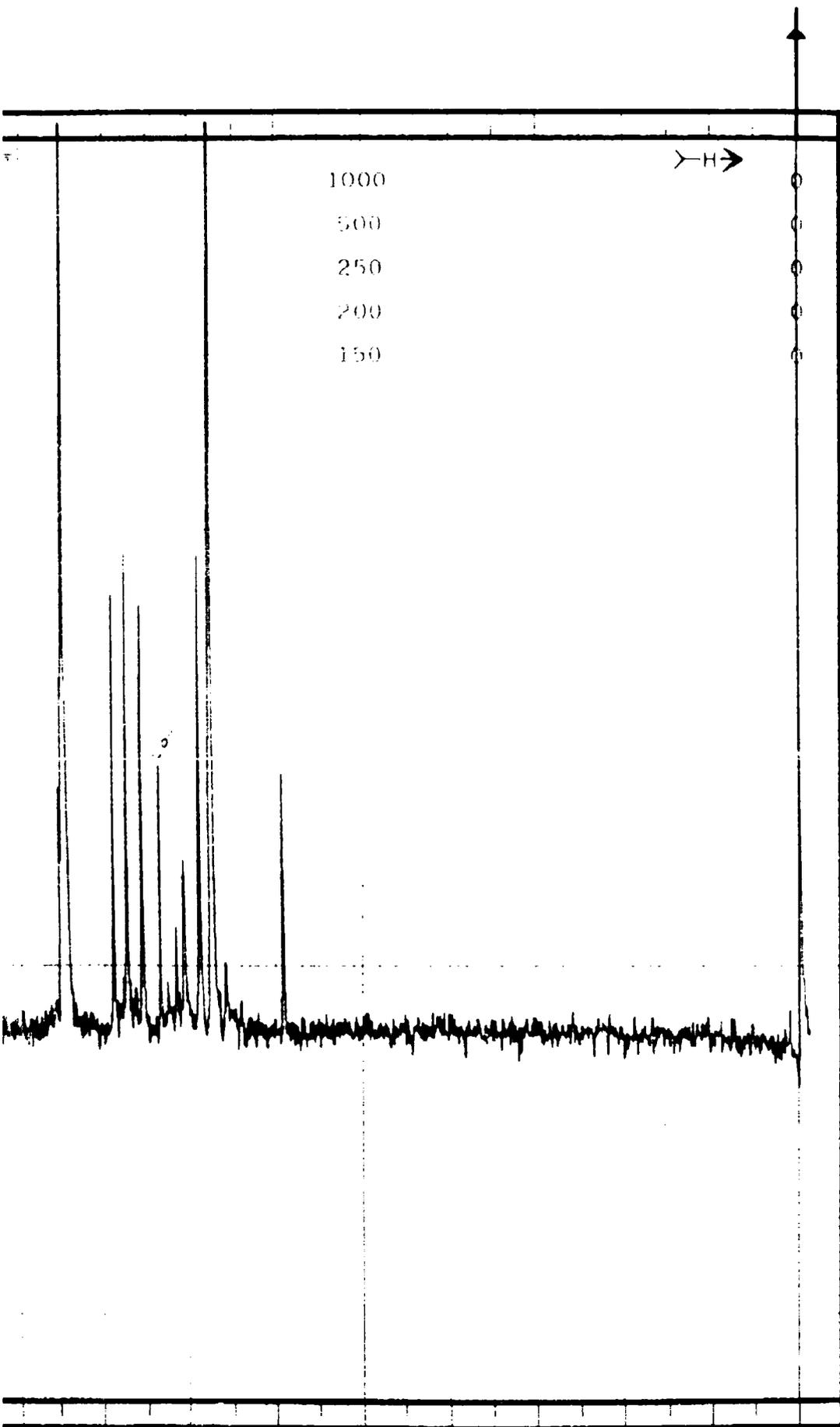
B-18

4000Hz 200 ppm
 2000 100
 1000 50
 800 40
 600 30

3000
 1500
 75
 60
 45

			2000
			1000
1	7	3185.6	159.28
2	9	3175.8	158.84
3	10	3175.0	158.75
4	6	3172.1	158.59
5	35	3144.6	157.47
6	130	3143.7	157.28
7	7	3091.7	154.55
8	5	1900.0	95.15
9	5	1907.5	95.97
10	28	1694.0	84.70
11	41	1690.1	84.10
12	148	1676.2	82.51
13	39	1681.0	84.04
14	7	1574.1	78.70
15	51	1574.0	78.69
16	7	1549.8	77.49
17	58	1541.3	77.09
18	5	1536.4	76.71
19	5	1524.5	76.22
20	49	1509.8	75.49
21	31	1470.6	73.53
22	6	1452.0	72.59
23	12	1429.6	71.28
24	20	1411.1	70.55
25	55	1374.1	68.70
26	200	1350.5	67.52
27	8	1318.5	65.92
28	30	1185.4	59.27
29	172	0.0	0.00
30	5-	7.0-	0.25

Figure B-9. NMR of Shell DEPEC



CFT-20 SPECTRUM NO. _____
 OPERATOR *Haas* DATE *4-11-72*

SAMPLE *Shell Depech*
IGP3 DIS1

LOCK SIGNAL *CDCl3*
 SPIN RATE _____ rps. TEMP _____ °C

ACQUISITION
 SPECTRAL WIDTH (SW) *4000* Hz
 NO. OF TRANSIENTS (NT) *8000*
 ACQUISITION TIME (AT) *1.02* sec
 PULSE WIDTH (PW) *8* sec
 PULSE DELAY (PD) *1* sec
 DATA POINTS (DP) *8192*

TRANSMITTER OFFSET (TO) *50*
 HIGH FIELD LOW FIELD _____
 RECEIVER GAIN (RG) *3*

DECOUPLER MODE (DM) *1*
 DECOUPLER OFFSET (DO) *52*
 NOISE BANDWIDTH (NB) *1* kHz

DISPLAY
 SENS. ENHANCEMENT (SE) *-8* sec
 WIDTH OF PLOT (WP) *4000* Hz
 END OF PLOT (EP) *-20* Hz
 WIDTH OF CHART (WC) *4000* Hz
 END OF CHART (EC) *0* Hz
 VERTICAL SCALE (VS) *200*
 REFERENCE LINE (RL) *DMS*

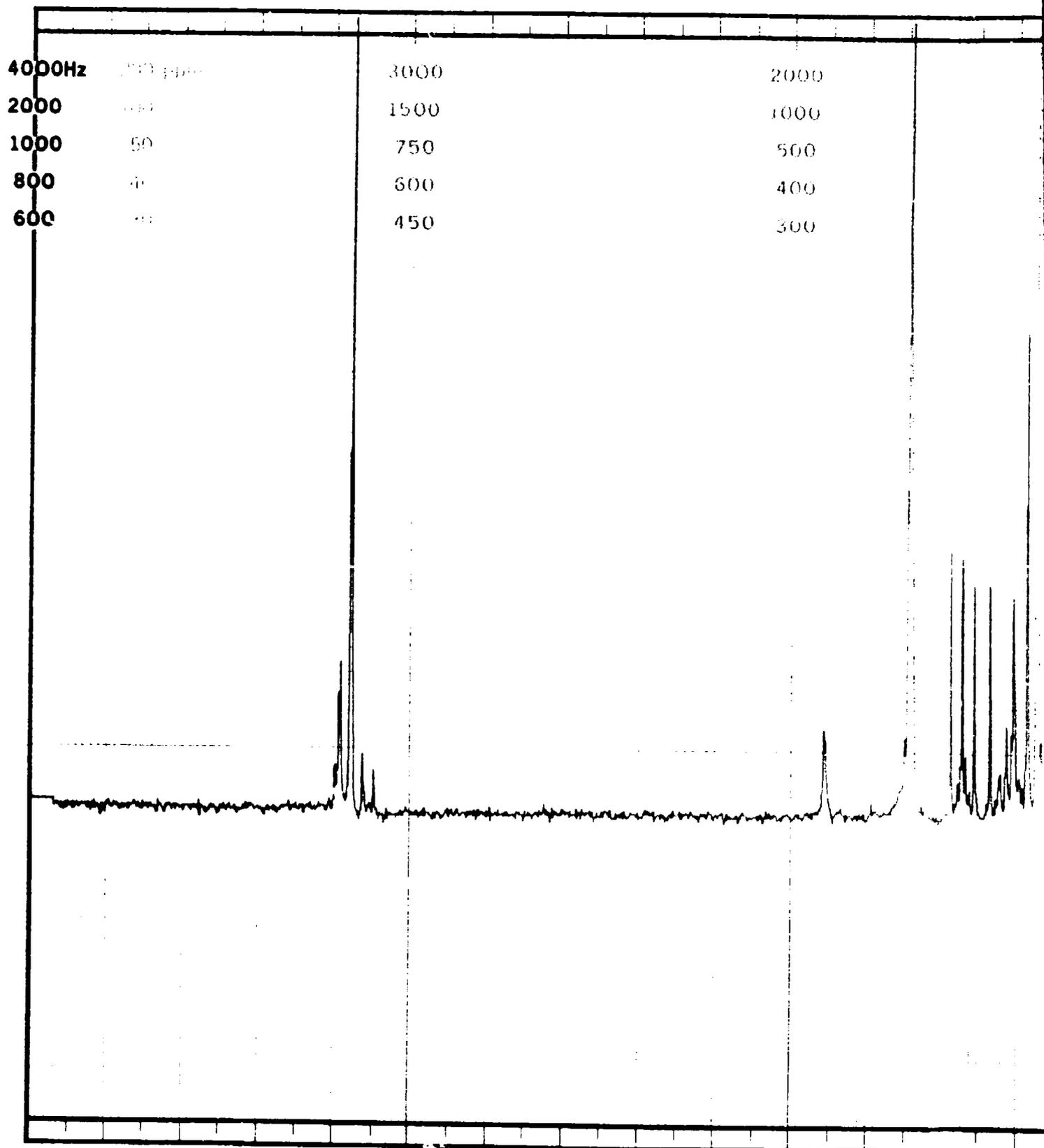
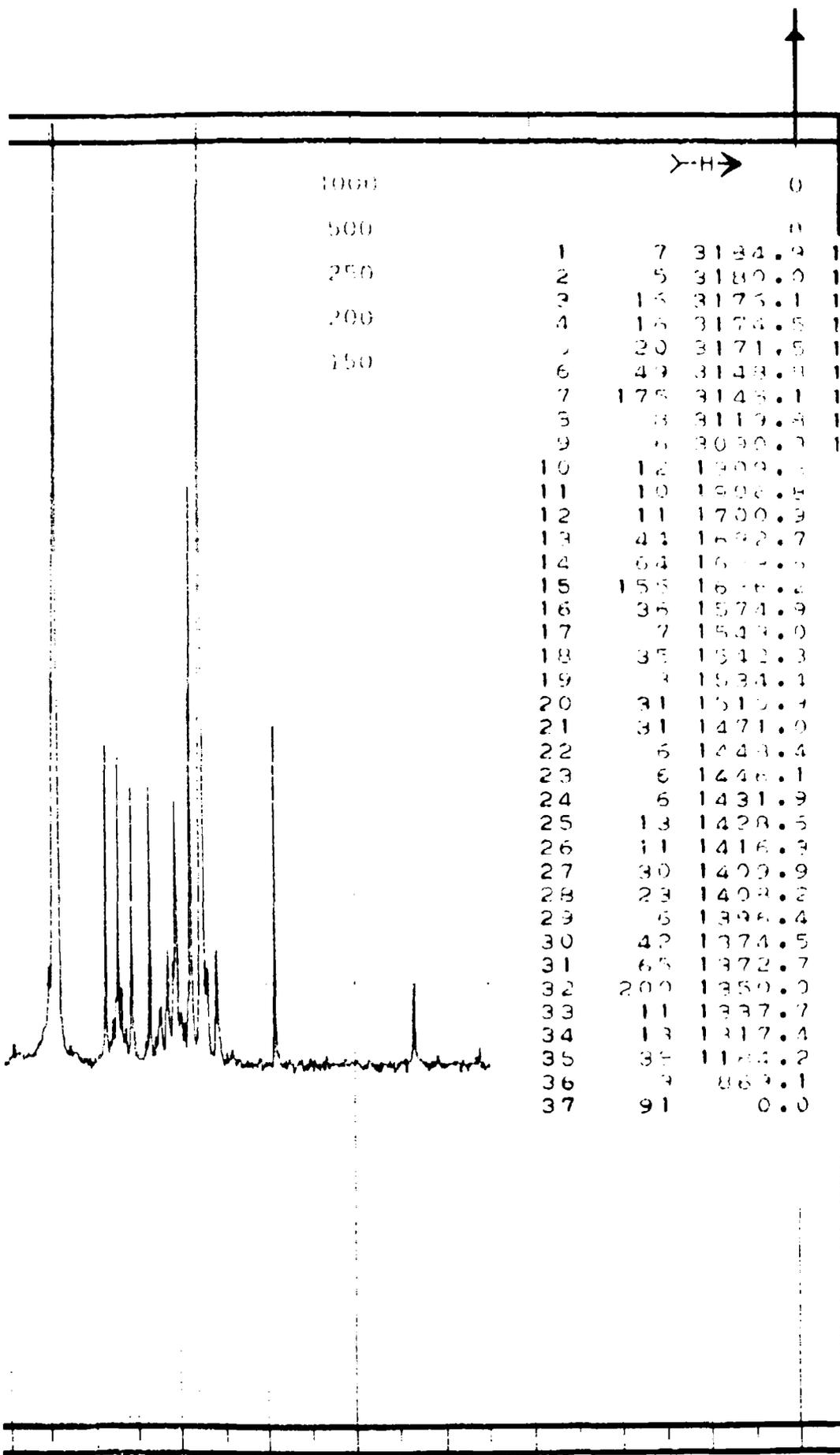


Figure B-10. NMR of ABL

CFT-20 SPECTRUM NO. _____
 OPERATOR HAAS DATE 4-2-77

SAMPLE ABL-DEPECH
983-12



1	7	3134.9	159.24
2	5	3180.0	159.00
3	13	3175.1	158.40
4	15	3173.5	158.32
5	20	3171.5	158.27
6	49	3148.9	157.17
7	178	3145.1	157.05
8	3	3119.8	155.09
9	6	3090.0	154.00
10	12	1900.0	95.00
11	10	1898.5	94.94
12	11	1700.9	85.04
13	41	1632.7	81.03
14	64	1610.0	81.00
15	155	1610.0	81.00
16	35	1574.9	78.74
17	7	1549.0	77.44
18	35	1512.3	77.14
19	3	1534.1	76.71
20	31	1510.4	75.54
21	31	1471.0	73.74
22	6	1448.4	72.41
23	6	1446.1	72.20
24	6	1431.9	71.59
25	13	1428.5	71.49
26	11	1416.9	70.81
27	30	1409.9	70.49
28	23	1408.2	70.41
29	5	1398.4	69.82
30	42	1374.5	68.72
31	65	1372.7	68.63
32	200	1350.0	67.00
33	11	1337.7	66.88
34	13	1317.4	65.87
35	35	1182.2	59.21
36	9	869.1	43.45
37	91	0.0	0.00

AL CDCl₃
 rps. TEMP °C

ION
 WIDTH (SW) 4000 Hz
 TRANSIENTS (NT) 20000
 RUN TIME (AT) 1.02 sec
 PULSE WIDTH (PW) 8 sec
 DELAY (PD) 1 sec
 TRANSFER (TS) (DP) 8192

PHASE OFFSET (TO) 50
) LOW FIELD
 GAIN (RG) 3

R MODE (DM) 1
) R OFFSET (DO) 52
 NOISE BANDWIDTH (NB) 1 kHz

DISPLAY
 SENS. ENHANCEMENT (SE) -8 sec
 WIDTH OF PLOT (WP) 4000 Hz
 END OF PLOT (EP) -20 Hz
 WIDTH OF CHART (WC) 4000 Hz
 END OF CHART (EC) 0 Hz
 VERTICAL SCALE (VS) 2.0
 REFERENCE LINE (RL) DM3

Figure B-11. CPL of Shell DEPECH

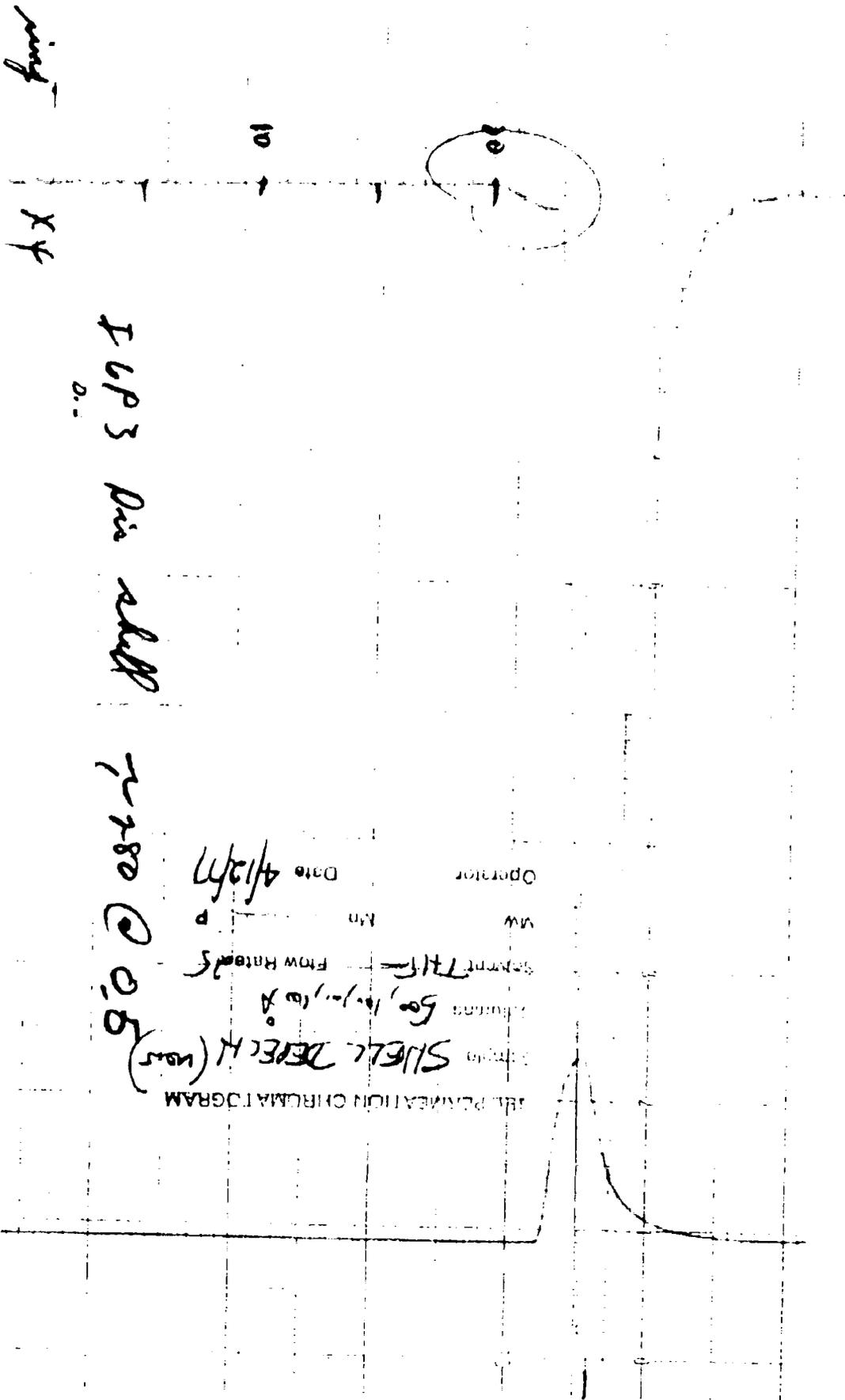
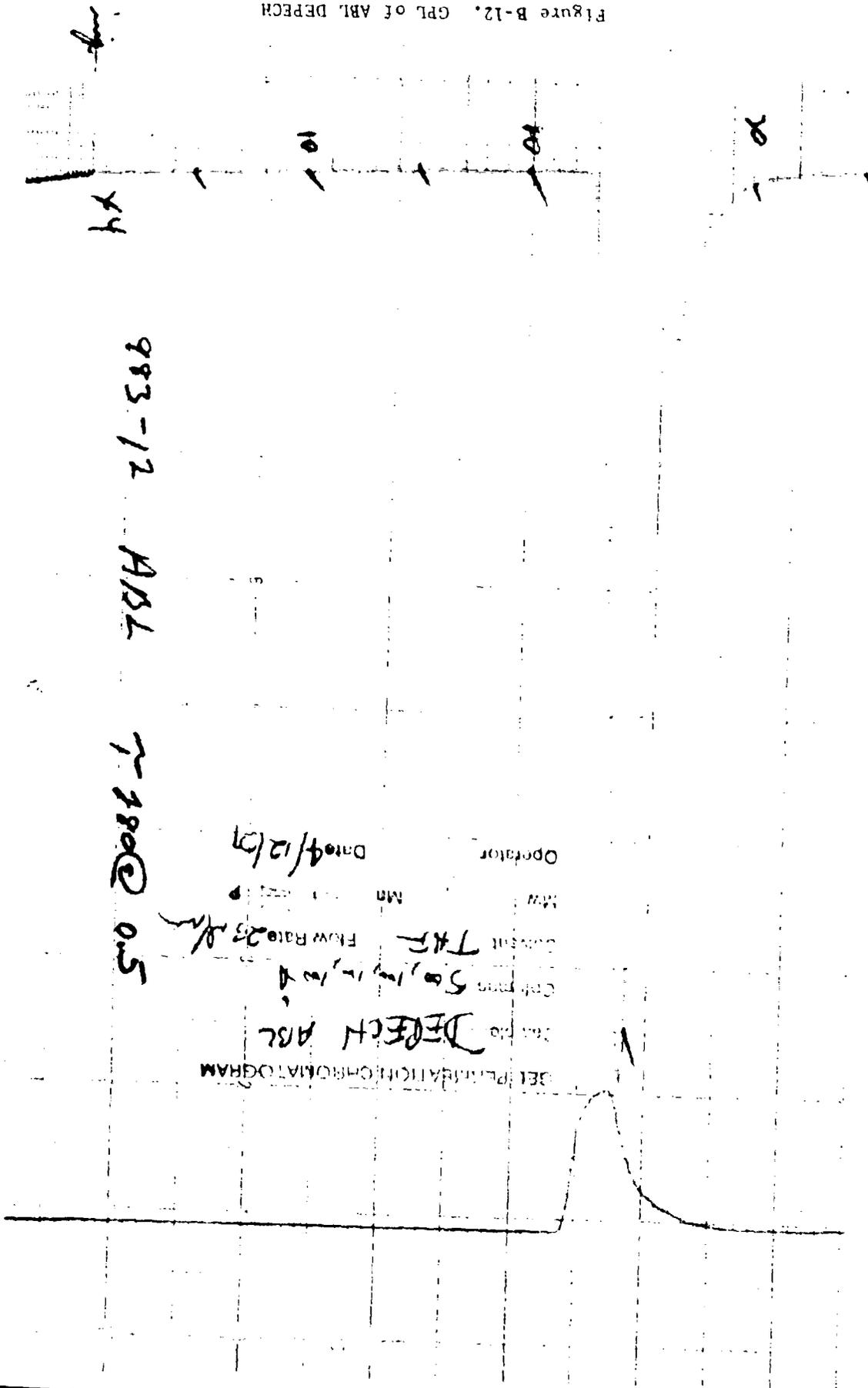


Figure B-12. GPL of ABL DEPECH



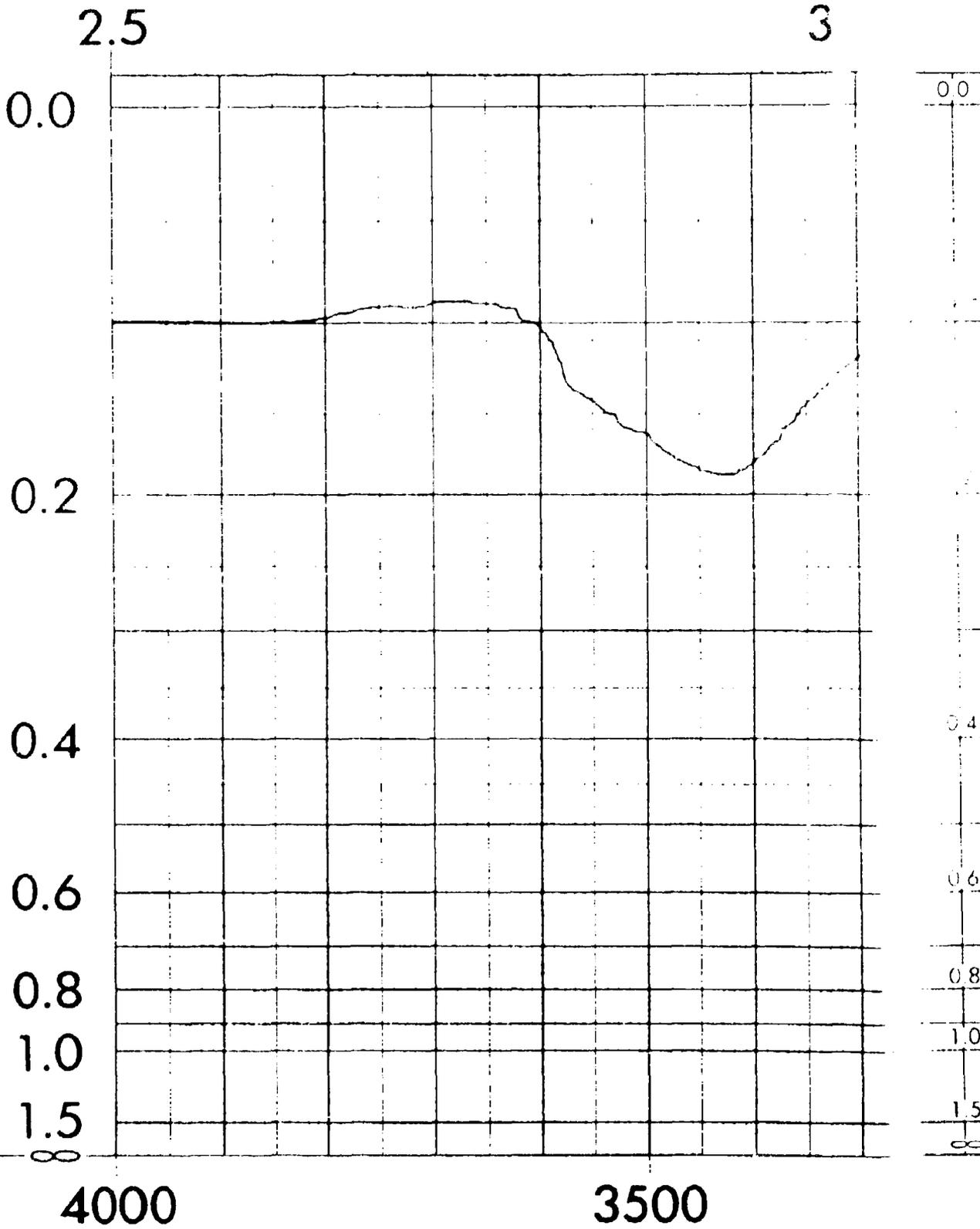
983-12 ABL
 7-1800 @ 0.5

GC PLUMATION CHROMATOGRAM
 Sample DEPECH ABL
 Column 50m x 0.25mm ID
 Carrier Gas TMS
 Flow Rate 23 ml/min
 MW
 Operator
 Date 4/12/07

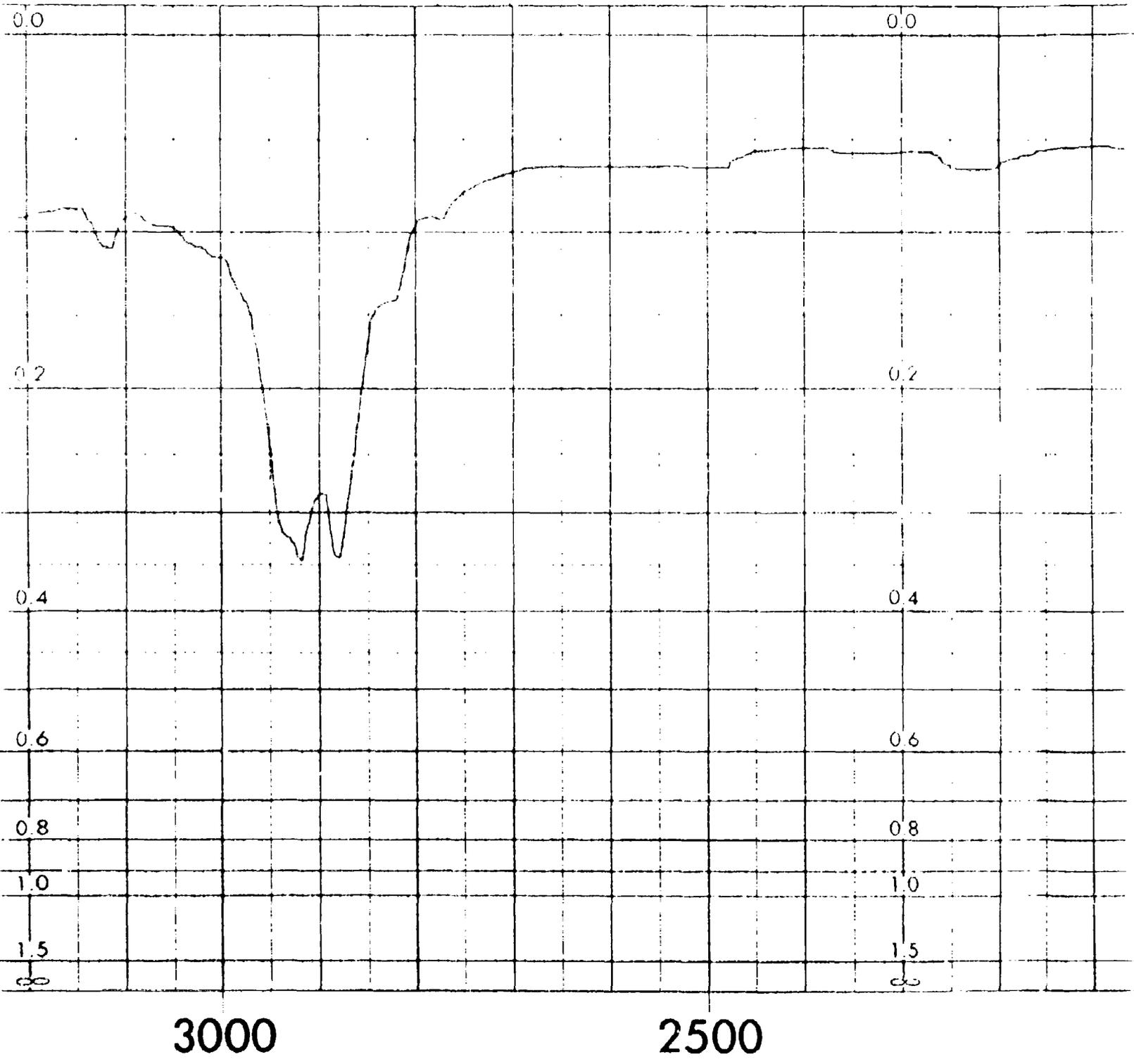
SAMPLE 5411

15118
276 23 20/51

ABSORBANCE



WAVELENGTH (MIC
4



3000

2500

FREQUENCY (CM

Figure B-13. Shell DEPECH Lot I

2

(MICRONS)

5

6

7

8

9

10

0.0

0.2

0.4

0.6

0.8

1.0

1.5

∞

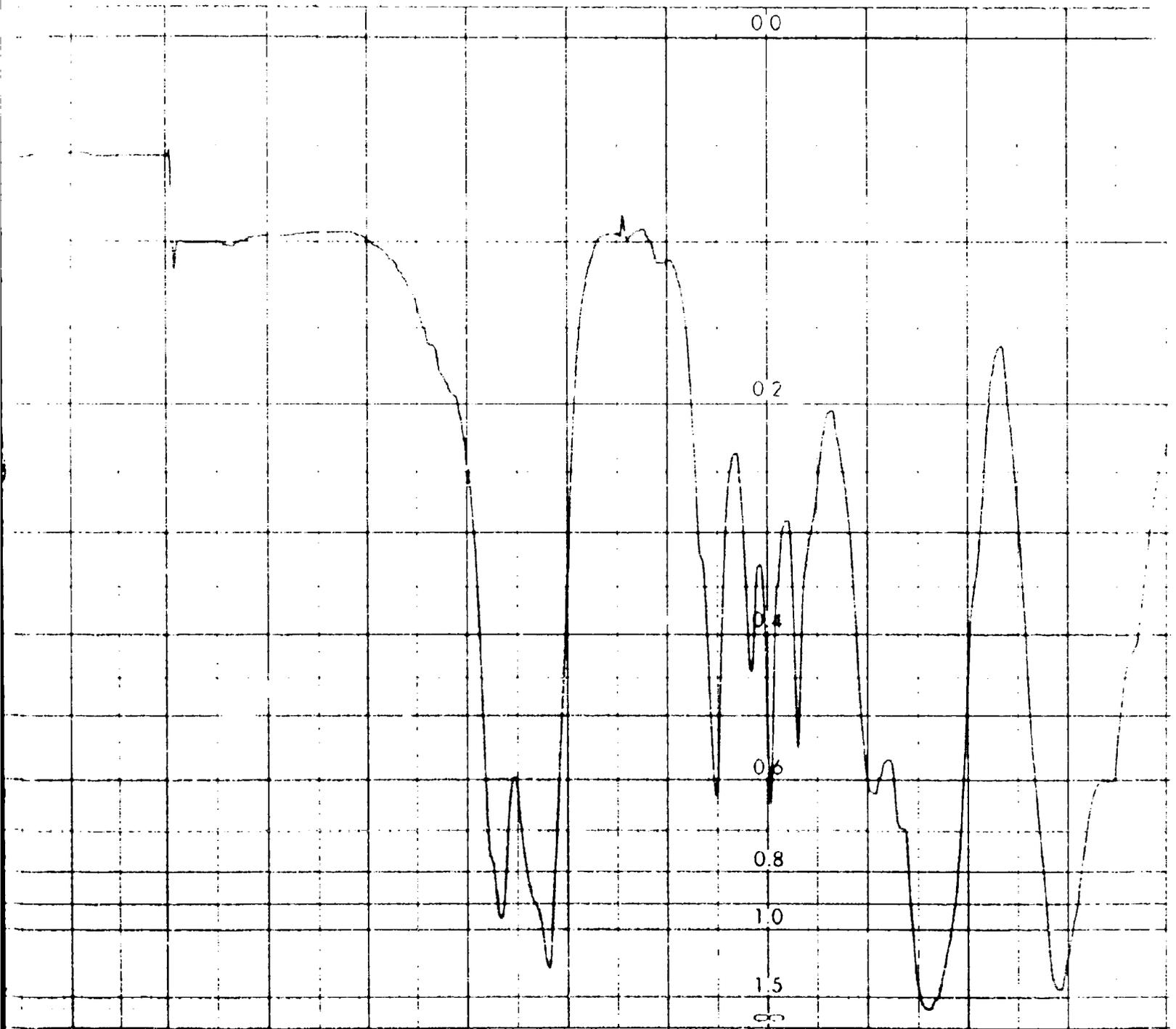
2000

1500

1000

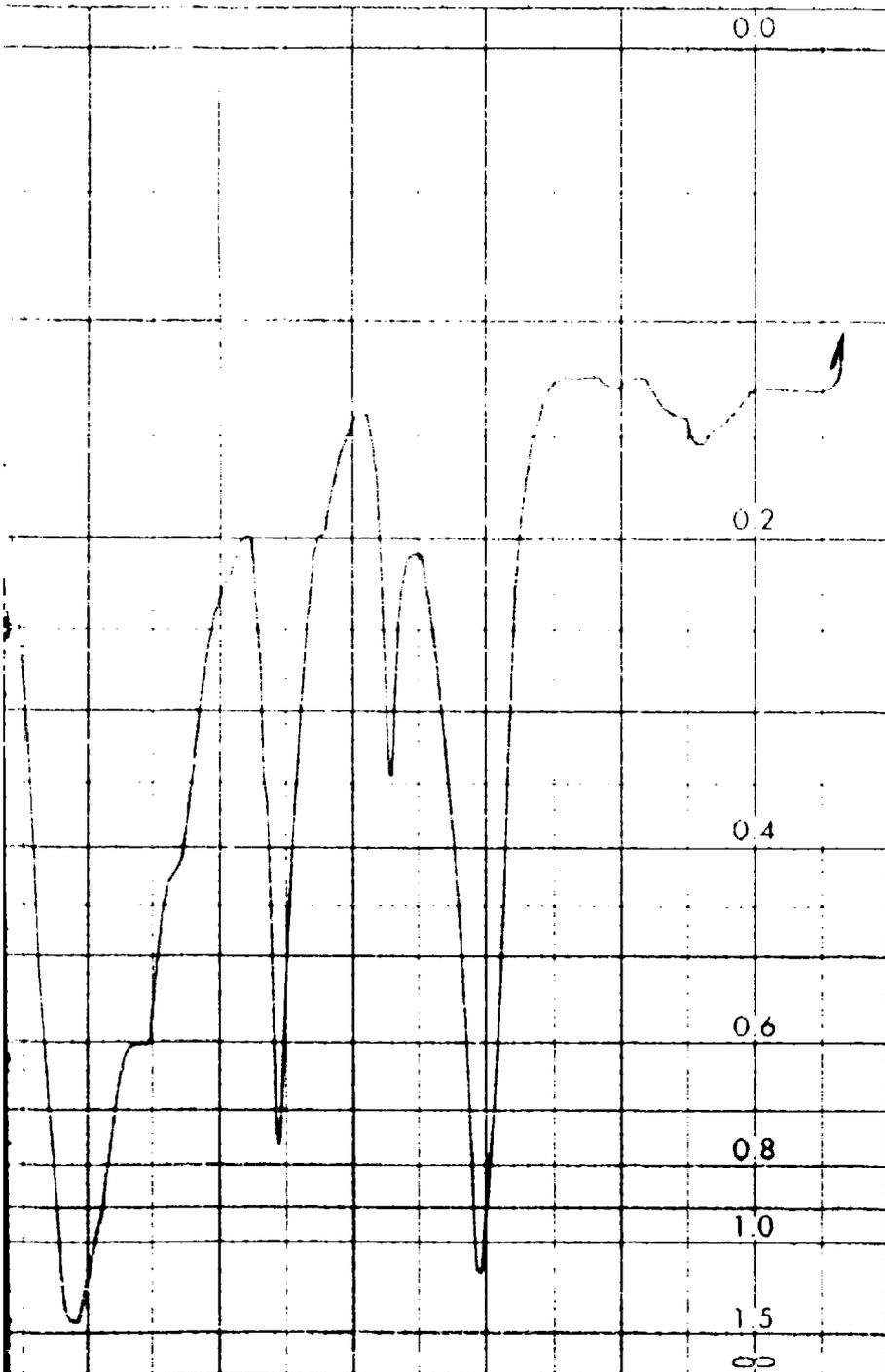
(CM^{-1})

H Lot 16P3D151



9 10 12 15 20

4/8/76



SPECTRUM NO.

SAMPLE SHELL DEPECH
IGP3D151

ORIGIN

PURITY

PHASE S.P.1

THICKNESS K8

1.

2.

3.

DATE April 8, 1976

OPERATOR

REMARKS

INTERCHANGE

SLIT PROGRAM

GAIN

ATTENUATOR SPEED

SCAN TIME

SUPPRESSION

SCALE

SOURCE CURRENT

1000

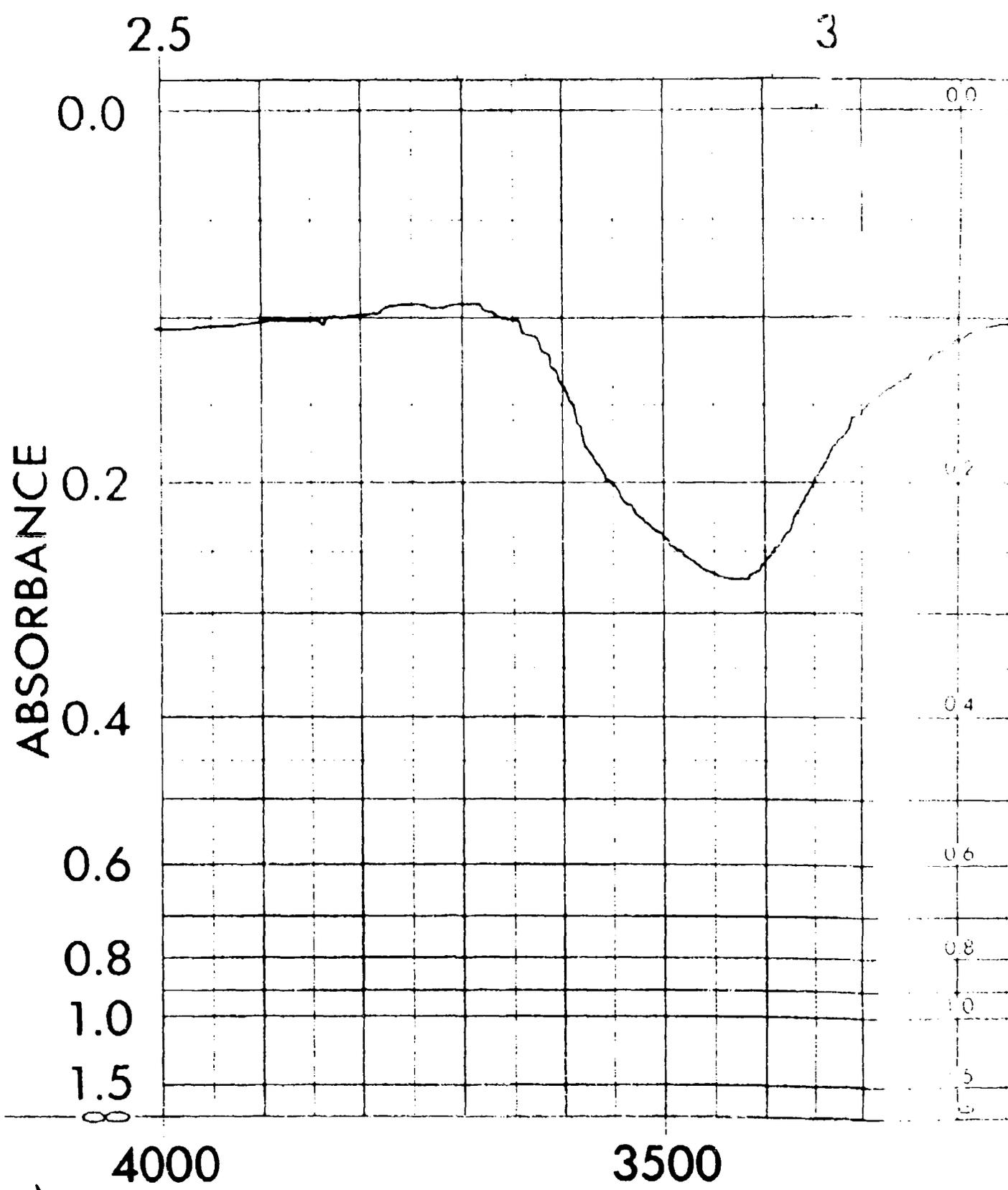
500

RECORDING CHART
MADISON AVENUE, NEW YORK, N.Y.
PR 1131
(221-1600)

B-23

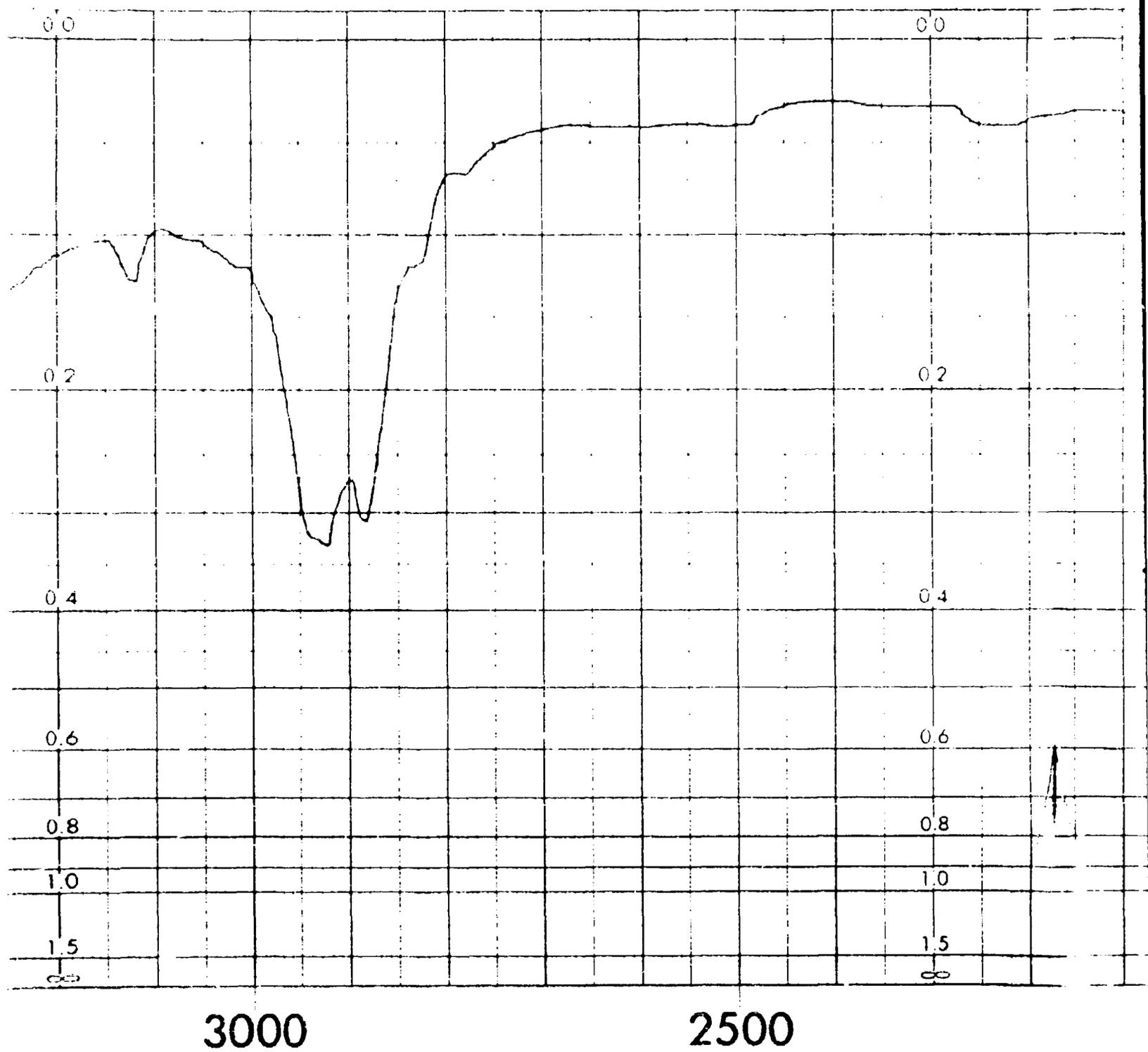
4

SAMPLE 753.12



WAVELENGTH (MI

4



3000

2500

FREQUENCY (CM

Figure B-14. ABL DEPECH Lot

2-

H (MICRONS)

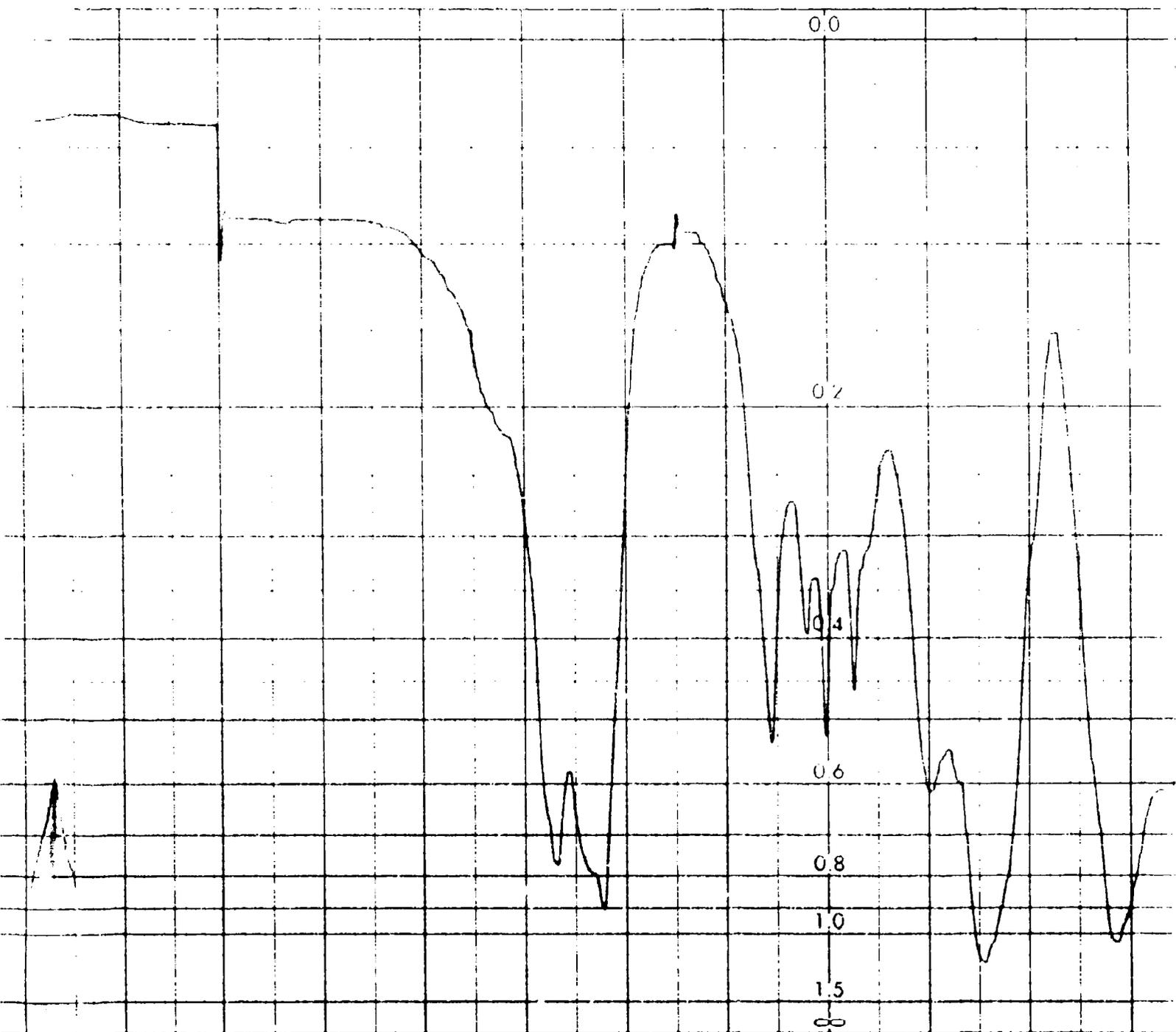
5

6

7

8

9



2000

1500

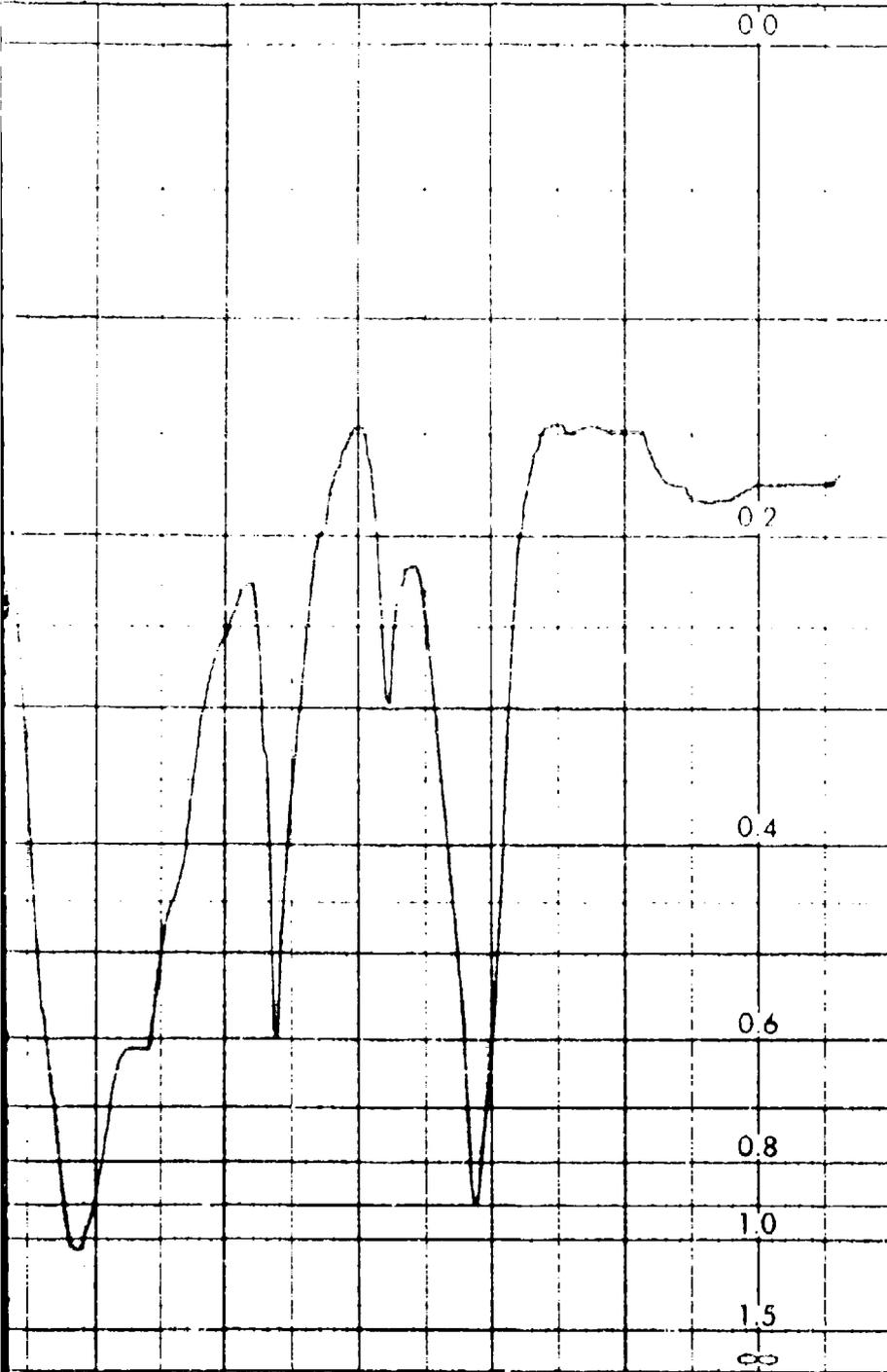
CM⁻¹

EPECH Lot 983-12

3

9 10 12 15 20

4/8/77



SPECTRUM NO.

SAMPLE *ABL DEPECH*
983-12

ORIGIN

PURITY

PHASE *solid*

THICKNESS *KBr*

1.

2.

3.

DATE *APRIL 8, 1977*

OPERATOR

REMARKS

INTERCHANGE

SLIT PROGRAM

GAIN

ATTENUATOR SPEED

SCAN TIME

SUPPRESSION

SCALE

SOURCE CURRENT _____

RECORDING CHARTS
BUFFALO, NEW YORK
PR 1131
(221-1600)

1000

500

B-24

Handwritten mark

4000Hz 200 ppm
2000 100
1000 50
800 40
600 30

3000
1500
750
600
450

2000
1000
500
400
300

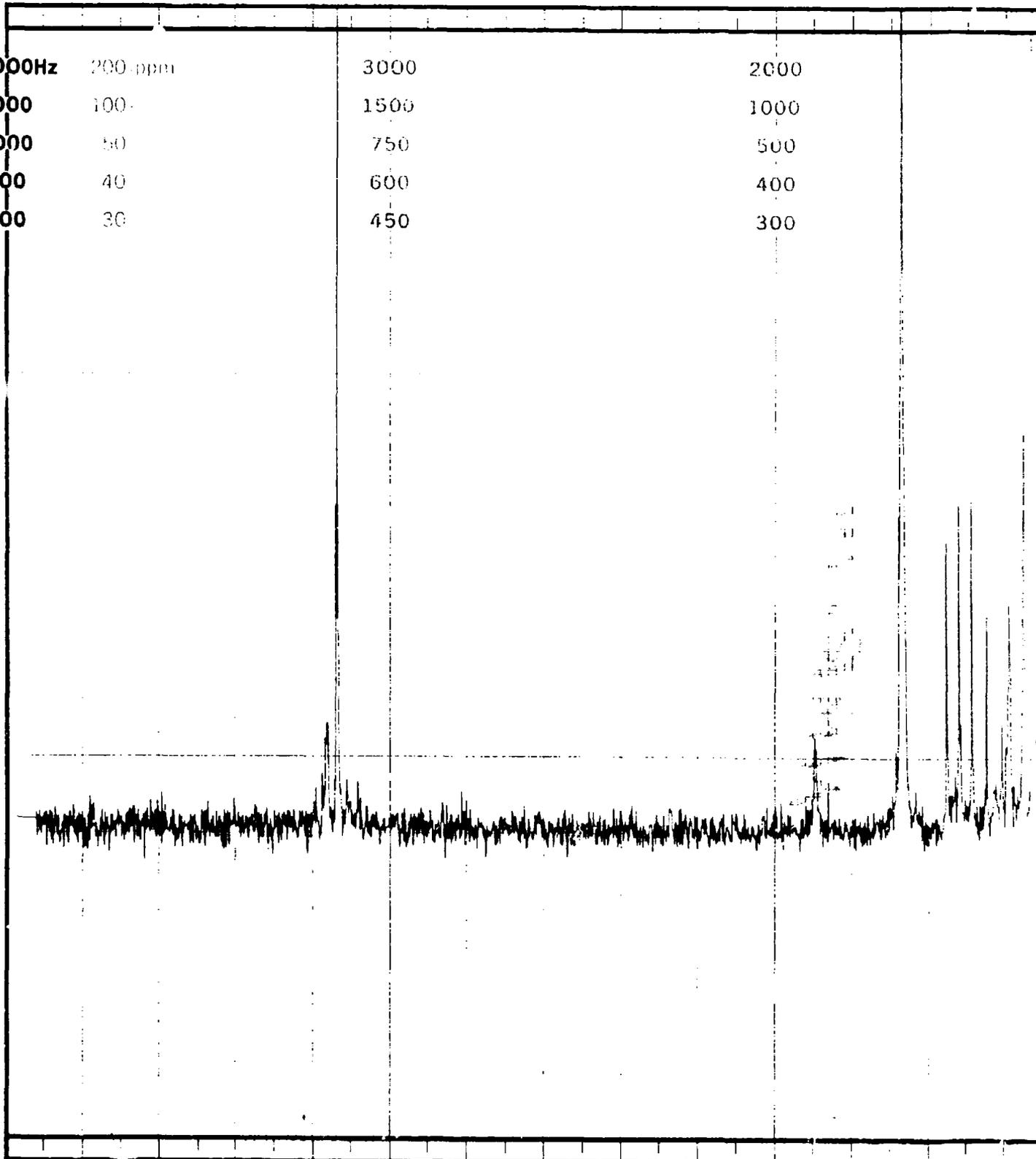
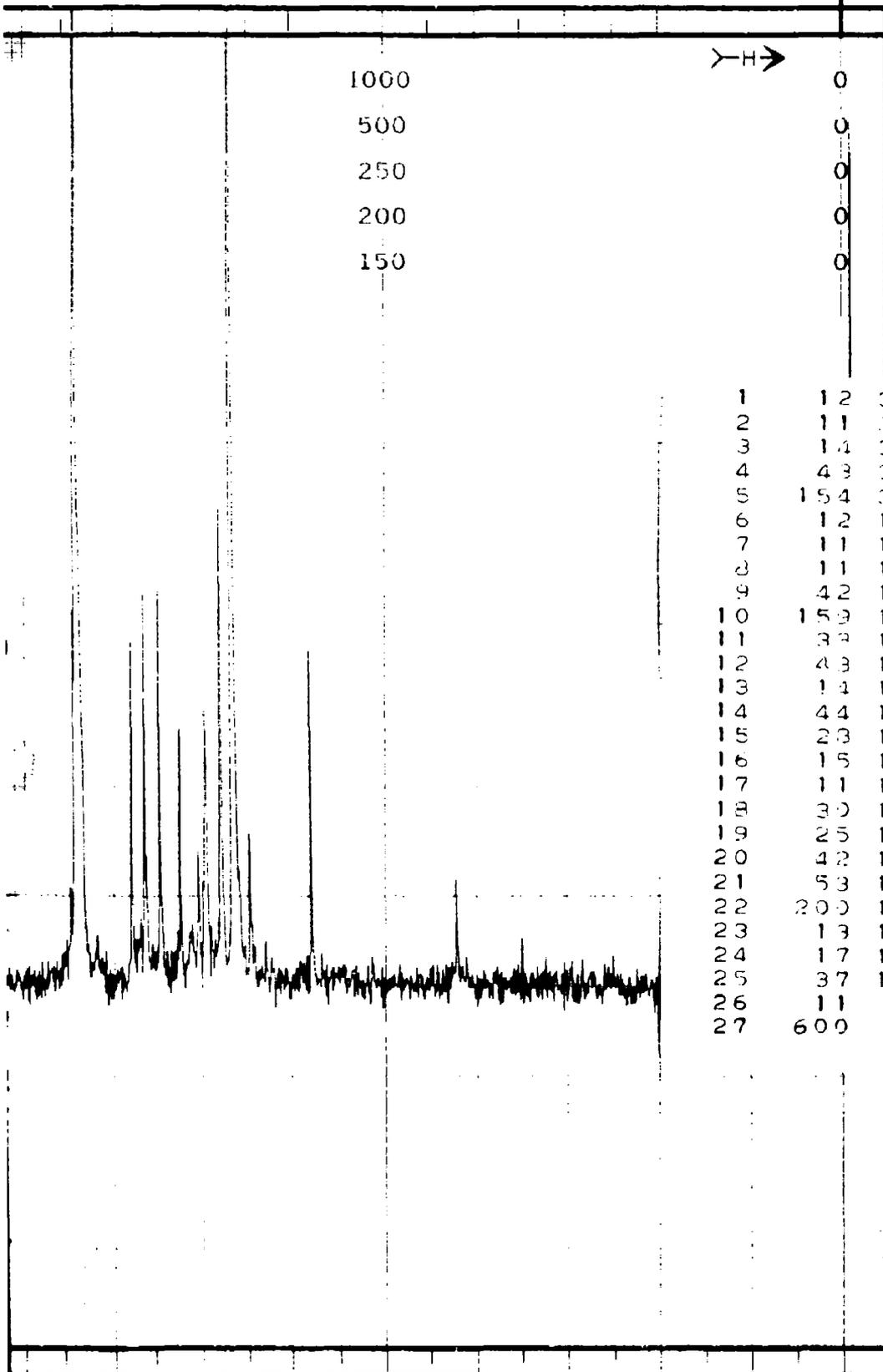


Figure B-15. NMR ABL DEPECH 983-12

CFT-20 SPECTRUM NO.
 OPERATOR Haas DATES 12-20

SAMPLE DEPECH ARB
983-12
dried



1	12	3179.5	158.97
2	11	3176.7	158.93
3	14	3174.4	158.71
4	43	3171.2	157.55
5	154	3147.6	157.37
6	12	1908.2	95.40
7	11	1905.5	95.27
8	11	1701.0	85.04
9	42	1693.2	84.66
10	153	1635.3	84.29
11	32	1572.6	78.67
12	43	1541.7	77.08
13	14	1537.3	76.46
14	44	1503.7	75.46
15	23	1472.2	73.50
16	15	1430.6	71.53
17	11	1418.2	70.91
18	30	1412.2	70.61
19	25	1410.3	70.51
20	42	1375.5	63.82
21	53	1374.4	63.72
22	200	1351.3	67.56
23	13	1340.1	67.00
24	17	1319.0	65.95
25	37	1184.6	59.23
26	11	859.3	43.46
27	600	0.0	0.00

TEMP °C
 4000 Hz
 T) 9000
 1.02 sec.
 8 sec.
 8/92 sec.
 (TO) 50
 IW FIELD
 3
 0) 52

NOISE BANDWIDTH (NB) kHz

DISPLAY
 SENS. ENHANCEMENT (SE) -8 sec.
 WIDTH OF PLOT (WP) 4000 Hz
 END OF PLOT (EP) -20 Hz
 WIDTH OF CHART (WC) 4000 Hz
 END OF CHART (EC) 0 Hz
 VERTICAL SCALE (VS)
 REFERENCE LINE (RL) THS

DEPECH 983-12 (Dried)

B-25



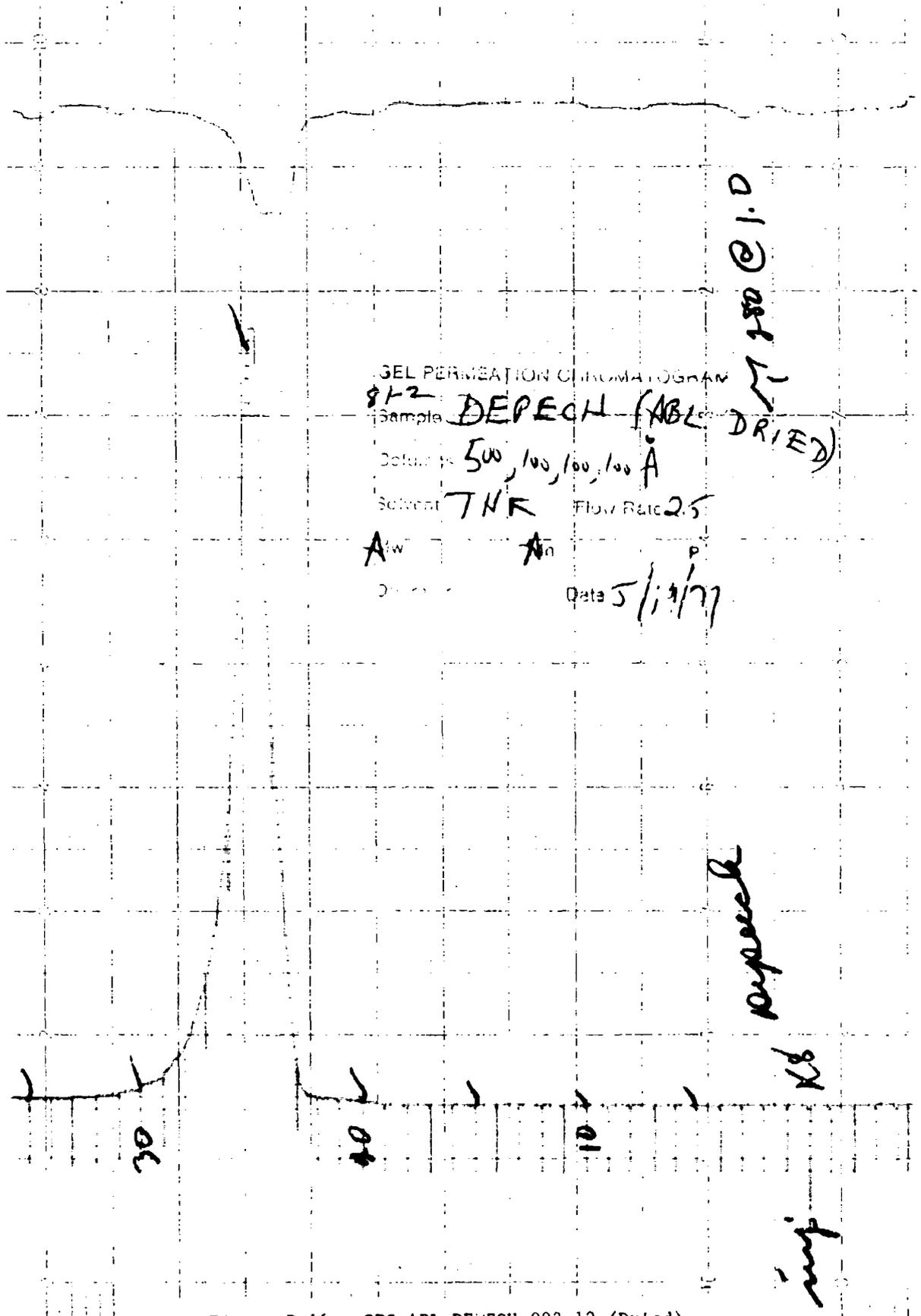


Figure B-16. GPC ABL DEPECH 983-12 (Dried)

APPENDIX C
DEPECH PRODUCTION REPORT FROM ABL



HERCULES INCORPORATED

ALLEGANY BALLISTICS LABORATORY P O BOX 210 • CUMBERLAND, MARYLAND 21502
TELEPHONE RIDGELEY WEST VIRGINIA AREA CODE 304-726-4500

March 2, 1977

FINAL CONTRACT REPORT

Investigator: N. F. Stanley
Work Period: September 20, 1976 - February 28, 1977
Mill Order: ROO-98
Report No.: A09690-790-01-006

DEPECH PRODUCTION

This is the final report issued under A09690 for Air Force Contract F04611-75-C-0024.

Objective

The objective of this work was to define and examine methods for producing DEPECH (dehydrochlorinated polyepichlorohydrin) of satisfactory quality for PCDE production at HI/Bacchus.

Summary

Laboratory- and pilot-scale equipment were set up and operated to produce PECH prepolymer, PECH, and DEPECH for source qualification testing at Hercules/Bacchus. No significant processing problems were apparent in the prepolymer and PECH syntheses steps, but DEPECH handling (precipitation/leaching, filtration, and drying) requires further development.

Preliminary process evaluation results are presented in this report. Product evaluation results will be reported by Hercules/Bacchus.

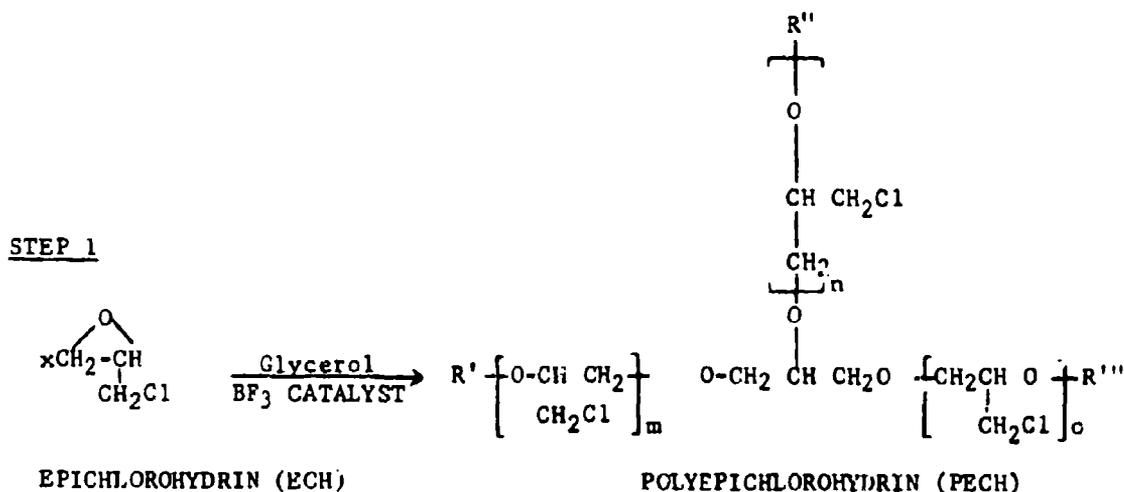
Twenty-five pounds of DEPECH were shipped to Bacchus for product evaluation. No significant conclusions can be made until the product evaluation is completed. Despite some problems in DEPECH handling, the Shell-developed process appears to be feasible for DEPECH production if the quality is satisfactory.

Introduction

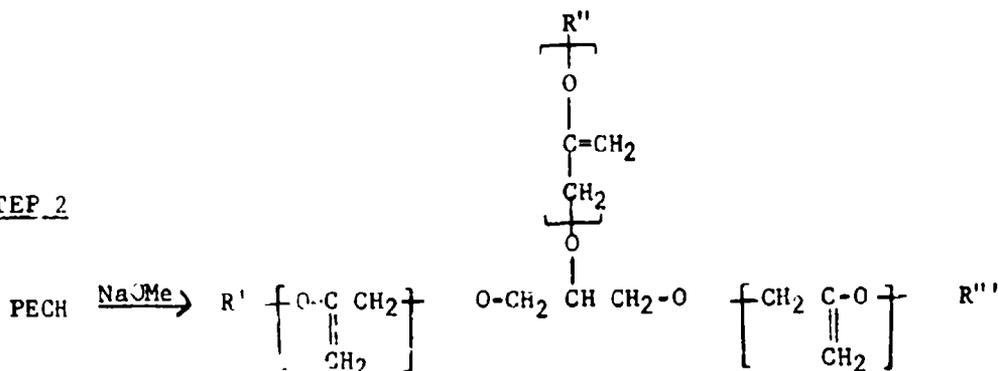
Shell Development Company (SDC) has been supplying DEPECH for PCDF synthesis and evaluation by HI/Bacchus. However, Shell is no longer interested in the small production of this polymer. Under Air Force contract, Hercules/ABL has examined the process and supplied 25 pounds of DEPECH for source qualification testing at Bacchus. The limited work scope (6 months) included laboratory- and pilot-scale process examination to facilitate both product and process verification.

Based on the reported SDC results and preliminary laboratory-scale testing by Hercules, a small pilot plant was operated to produce DEPECH for the source qualification. Detailed SDC pilot plant results are given in SDC's Technical Report AFML-TR-74-153, July, 1974. Major unit operations in the process are the chemical reaction steps, solvent recovery, solids precipitation, separation, and drying as shown in Figure C-1.

The Shell-developed process is based on the following chemistry.



STEP 2



POLY (2,3-EPOXYPROPANE), (DEPECH)

In the Shell process step 1 consists of coordinating gaseous BF₃ with glycerol to prepare a prepolymer by partially reacting ECH with the activated glycerol before combining the prepolymer with additional ECH to produce PECH. The PECH is then dehydrochlorinated with sodium methylate, precipitated in water, centrifuged, and dried.

Discussion of Results

1. Process Description

The Shell process was examined initially in laboratory equipment in preparation for pilot-scale production of the polymer. The laboratory effort was directed primarily toward verifying the materials handling features reported by Shell. Polymerization and dehydrochlorination processing methods developed by Shell are summarized briefly below.

The PECH was prepared by polymerizing epichlorohydrin (ECH) in methylene chloride solution in the presence of activated prepolymer acting as an initiator complex. In this work, the complex consisted of glycerin, ECH, and boron trifluoride gas as the catalyst source rather than the BF₃ etherate used by Shell in their early work. For the prepolymer preparation, the BF₃ gas was sparged into a glycerin/MeCl₂ mixture, ECH was added as shown in Table C-1, and the initiator complex subsequently combined with ECH to produce PECH.

Polymerization of ECH to PECH consisted of dissolving prepolymer mixture in methylene chloride and adding ECH slowly while maintaining a 10°C. reaction temperature. Following the reaction, the mixture was held at low temperature overnight to complete the reaction and then sparged with ammonia to quench the reaction. The solvent was then stripped from the product in a thin film evaporator.

Dehydrochlorination to produce DEPECH consisted of slowly combining the PECH with sodium methylate, DMSO, and THF and refluxing for 4 hours following the combination. The PECH was added as a 50/50 mixture of PECH/THF to produce the final mixture shown in Table C-1.

In summary, the three reaction steps presented no particular processing problems and evaporation of methylene chloride from the PECH intermediate, although slow, was satisfactory in a Rodney Hunt thin film evaporator. The major pilot-scale processing difficulties arose in the DEPECH handling steps following the dehydrochlorination reaction. Significant details concerning DEPECH handling are included in the pilot plant test discussion. Laboratory-scale handling of DEPECH presented no problems except in the initial test.

2. Laboratory-Scale Tests

The initial work consisted of assembling and operating standard laboratory equipment for preliminary examination of the Shell process. The equipment tested was a 5-liter, 4-neck, batch reflux reactor for the prepolymer, PECH, and DEPECH synthesis steps and a 12-liter set-up for the precipitation step.

Prepolymer, PECH, and DEPECH were prepared from the recipe shown in Table C-1, as specified in the Shell reports.

There were no important materials handling problems apparent in the prepolymer and PECH steps, but the DEPECH step was more difficult. The initial evaluation (IR and molecular weight) showed satisfactory results for the PECH synthesis, but the DEPECH product did not precipitate as a solid. The result was interpreted as inadequate dehydrochlorination attributed to low grade sodium methylate used in the reaction. Subsequent testing with fresh sodium methylate, however, produced qualitatively satisfactory product.

Since there were no significant materials handling problems, it was decided to go ahead with the pilot-scale tests based on minimal product characterization of the laboratory-scale product.

Essentially, preliminary product characterization test difficulties at ABL suggested that the characterization should be conducted later at Hercules/Bacchus. The limited ABL analyses consisted of molecular weight determinations and comparative infrared (IR) analyses. Molecular weight

determinations showed an average of about $2000 \pm 10\%$ for the early samples of PECH. The IR spectra are given in Figures C-2 and C-3 to show the similarity of Hercules/ABL samples with the Shell product supplied by Bacchus.

3. Pilot Plant

The Hercules/ABL PECH/DEPECH pilot plant was similar to Shell's pilot plant (Figure C-4), but the plant did not include the THF recovery capability. The plant was installed and operated to demonstrate and assess processing features described by SDC and to provide 20 pounds of DEPECH to Hercules/Bacchus for source qualification. Although THF recovery is required for a production process, solvent recovery is not needed for small pilot-scale production of DEPECH.

The pilot facility included the following major pieces of equipment:

	<u>Capacity</u>
1. Pfaudler Reactor, glass-lined	30-gallon
2. Thin film Evaporator (Rodney Hunt)	1 ft. ²
3. Pfaudler Reactor, stainless steel	100-gallon
4. Batch Filter, Ceramic	7 ft. ²
5. DeVine Tray Dryer, vacuum	4 ft. ² /tray
6. Barrel Dryer, vacuum	3-ft. diameter

A major effort in the pilot plant program was installation and modification of a Rodney Hunt thin film evaporator (TFE) required for solvent removal from the PECH. The other equipment listed was available at ABL and was operated satisfactorily for batch prepolymer, PECH, and DEPECH syntheses at the 10- to 20-pound scale. A rotating barrel dryer (Item 6) was added to the original pilot plant capability because tray drying of DEPECH was accomplished with difficulty.

Operation of the plant to produce PECH consisted of purging the reactor with nitrogen, manually charging the methylene chloride and prepolymer mixture, preconditioning and holding the reactor contents at $10^{\circ}\text{C.} \pm 5^{\circ}\text{C.}$ while slowly feeding ECH (about 25 cc/minute in run 983-10)

over a 4-6 hour period. The low temperature was maintained for 16 hours to complete the reaction. There were minimal vapor losses via the reflux condenser (\approx 0.5 gallon MeCl_2 estimated). Following the reaction, ammonia was sparged via a dip tube for 30-45 minutes to stop the reaction.

It is noteworthy that even with such a slow feeding rate, there was one reaction temperature excursion to about 27°C . for 2-3 minutes, attributed to an induction time effect.

Product was then pumped directly to the thin film evaporator (TFE) operated at \sim 1400 rpm, 10 mm Hg (absolute), and 90°C . TFE through-put was 40 cc/minute to give a bottom product essentially solvent-free [i.e., no further weight loss overnight at 5 mm Hg (absolute) and 95°C .]

Operation of the reactor for DEPECH production consisted of again purging with nitrogen, charging THF, DMSO, and NaOCH_3 , heating to reflux temperature ($\sim 60^\circ\text{C}$.), and pumping a 50/50 PECH/THF mixture into the mildly refluxing reactor at about 200 cc/minute. The reaction exotherm nearly produced a mild reflux but periodic heating was required to maintain the reflux condition. Following the PECH/THF addition, the reaction was held at reflux for 4 hours.

Transfer of the DEPECH reaction product mixture from the 30-gallon (glass-lined) reactor to the 100-gallon reactor utilized as the precipitation/leaching vessel was accomplished with some difficulty because the two reactors were not in close physical proximity. In a more efficient operation, DEPECH slurry would simply be pumped to a precipitation/leaching vessel. (Refer to Table C-2.)

Raw material specifications, defined by SDC, are included as Table C-3. All of the liquids were sieve dried (Linde 4A) prior to use to ensure a minimal moisture level in the reactions.

4. Process Analysis

Pilot-scale production of DEPECH via the Shell-developed process is considered satisfactory despite DEPECH recovery problems associated with the precipitation/leaching, filtration, washing, and drying steps. As already discussed, the reaction steps are relatively simple and process control is largely a matter of equipment capability. Regardless of operating scale, the simple sequence of three batch reaction steps requires charging ingredients to the reactor, maintaining reaction conditions and emptying and cleaning the reactor following each step.

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Labor requirements are reasonably high for the present pilot capability, but additional temperature control features could be added to the plant to minimize operating labor, if desirable. One particular equipment feature required is additional cooling capacity for the low temperature PECH reaction step. Addition rate of ECH to the reactor is essentially determined by reactor cooling capacity. Inadequate capacity requires a very slow ECH addition to maintain the low temperature.

As reported by Shell, substantial reflux condenser capacity is required for the dehydrochlorination step due to the apparent induction time before the reaction exotherm (142 BTU/pound PECH) commences. Apparently, some minimum PECH concentration is required for initiation of the reaction. The induction effect is obvious in the temperature/time profiles for the three batches of DEPECH produced.

DEPECH solids handling is difficult. The DEPECH reaction product is a solution of the DEPECH in THF/DMSO/methanol with suspended insoluble salts of NaOCH_3 and NaCl . DEPECH recovery steps developed by Shell consist of adding the mixture to a mildly agitated tank of water (20 pounds H_2O /pound DEPECH) to precipitate the DEPECH and then filtering and washing the filter cake. The precipitation/leaching, filtration and washing steps were performed with difficulty largely because the DEPECH solids, initially soft and tacky, harden as solvent is leached from the precipitate. The precipitation/leaching step, in particular, requires further development. In one ABL run (Figure C-5), the physical form of the DEPECH was significantly improved by operating at a higher precipitation/leach temperature. The nearly spherical product obtained in run 983-11 shown in the figure is considered to be much superior from a materials handling viewpoint.

In the ABL tests, filter cake was displacement washed three times to remove absorbed or occluded salts and residual solvent, but chloride content and other DEPECH properties were not measured. Hercules/Bacchus analyses are required to assess the ABL washing technique.

Since DEPECH drying was so difficult and the yield in run 983-12 was higher than anticipated, it is speculated that some of the absorbed or occluded salts may have remained with the DEPECH and contributed to the drying problem.

Although the effort in this brief program was mainly directed toward producing DEPECH for the source qualification testing at Hercules/Bacchus, a preliminary operating cost appraisal is included to identify the important cost elements for planning purposes.

Cost estimating is basically an art, based on both empirical and factual relationships. One purpose of cost estimating is to permit economic evaluation of manufacturing processes at various stages of development. There are various types of cost estimates differing in detail and accuracy, depending on the amount of information available concerning the particular process. New processes, such as the DEPECH process, generally lack the detailed information needed to prepare a cost estimate of high accuracy (i.e., $\pm 10\%$), nor is it generally in the interest of time or money to prepare such an estimate.

The primary basis for economic evaluation of a manufacturing process is the development of a flow sheet for the process. Such a diagram includes material and energy balances for the process and enables determination of equipment capacities, requirements, utility consumption, etc. In this preliminary process analysis, only the direct and indirect operating costs of producing DEPECH were projected to show that DEPECH cost will be almost totally defined by production scale.

Raw material costs are given in Table C-4. The costs reflect mid 1976 prices when ECH and NaOCH_3 appeared to be escalating rapidly. As evident in the table, glycerin and BF_3 costs are small and were excluded. The THF cost was also excluded from the summation because its recovery would be essential for a production process. The \$2.12 total ingredient cost without the THF could rise to around \$2.75/pound DEPECH (allowing about 10¢/pound for THF recovery and minimal solvent losses to the process).

The basis of the raw material estimate is stoichiometric conversion of ECH to PECH and 84% of stoichiometric conversion of PECH to DEPECH based on one pilot-scale run (run 983-11). Stoichiometric conversion of PECH to DEPECH is $257/366.4 = 0.7$ $\frac{\text{pound DEPECH}}{\text{pound PECH}}$. As already noted, THF recovery is essential for process economy and was excluded from the analysis.

Generally, operating costs would be projected in terms of direct labor, supervision at 12.5% of operating labor, maintenance as a fraction of fixed capital/year, etc. as shown in Table C-5. For this simplified analysis, however, the total operating cost was simply estimated based on a representative composite (Hercules/ABL) figure of \$25/hour to illustrate production-scale dependence of the operating cost estimate. The figure should be accurate to within 15% or so and is escalating at about 7%/year.

The primary basis for the direct labor estimate is 55 man-hours/batch of DEPECH in the existing pilot plant. The labor breakdown is five man-hours for prepolymer, 20 man-hours for PECH, and 30 man-hours for DEPECH preparation. This amounts to 2.75 man-hours/pound DEPECH (\sim \$70/pound) at the 20-pound scale. Increasing the batch size to 50 pounds would

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probably increase the labor to 65 man-hours or so for a direct labor cost of 1.3 man-hours/pound DEPECH. Even at the 50-pound scale, DEPECH would be expensive due to the high labor requirements.

If the process were scaled to 1,000-pound batches, however, labor requirements for material handling and minimal reactor operation might only double to give a resultant direct labor figure of 0.13 man-hours/pound DEPECH, or about \$3.25/pound plus the \$2.75/pound for raw materials. Thus, an optimistic price for DEPECH might be ~ \$6.00/pound (based on 1976 raw materials and current labor rates), plus amortization of the fixed operating cost required for larger scale equipment.

Recommendations

It is recommended that the DEPECH product be evaluated by Hercules/Bacchus before additional process development is considered. If the product is chemically satisfactory, process improvement studies are recommended for the DEPECH handling operations. In particular, DEPECH precipitation/leaching, filtration, and drying steps require improvement for production of the polymer.

Personnel

Mr. J. C. Farber is the Bacchus program manager, and Mr. T. C. Rissell is the ABL program manager for this investigation. Mr. N. F. Stanley is the principal investigator.


N. F. Stanley

NFS:lr
Attachments

Approved by Mr. T. C. Rissell

TABLE C-1. REACTANT PROPORTIONS FOR LABORATORY-SCALE DEPECH SYNTHESIS

Step 1 - Prepolymer Preparation (2 moles ECH/mole G)

<u>Ingredient</u>	<u>Lb/Lb ECH</u>	<u>Weight (Gms)</u>
Glycerin	0.5	357
BF ₃	0.0462	33
MeCl ₂	1.546	1104
ECH	1.0	714.3

Step 2 - PECH Preparation (42 moles ECH/mole G)

<u>Ingredient</u>	<u>Lb/Lb Mixture</u>	<u>Weight (Gms)</u>
Prepolymer Mixture	1.0	75
MeCl ₂	4.434	333
ECH	6.93	520

Step 3 - DEPECH Preparation

<u>Ingredient</u>	<u>Lb/Lb PECH</u>	<u>Weight (Gms)</u>
PECH	1	300
THF	3	900
DMSO	0.19	57
NaOCH ₃	0.87	261

TABLE C-2. REACTANT PROPORTIONS

1. Prepolymer Preparation - Laboratory-Scale (983-2 and 983-9)

<u>Ingredient</u>	<u>Lb/Lb Mixture</u>	<u>Weight (Gms)</u>
Glycerin	0.5	357
BF ₃	0.041	29-33
MeCl ₂	1.546	1104
ECH	1.0	714.3

2. PECH Preparation - Pilot-Scale

<u>Ingredient</u>	<u>Lb/Lb Mixture</u>	<u>983-10 Weight (Lbs.)</u>	<u>983-7 Weight (Lbs.)</u>
Prepolymer Mixture	1.0	3.00	4.80
MeCl ₂	4.434	13.30	21.28
ECH	6.93	20.79	33.27

3. DEPECH Preparation - Pilot-Scale

<u>Ingredient</u>	<u>Lb/Lb PECH</u>	<u>983-8 Weight (Lbs.)</u>	<u>983-11 Weight (Lbs.)</u>	<u>983-12 Weight (Lbs.)</u>
PECH	1	10.0	17.25	10.0
THF	3	30.0	51.75	30.0
DMSO	0.19	1.9	3.27	1.9
NaOCH ₃	0.87	<u>8.7</u>	<u>15.00</u>	<u>8.7</u>
Total		50.6	87.27	50.6

TABLE C-3. RAW MATERIAL SPECIFICATIONS

<u>Ammonia</u>		
	Assay	98%
<u>BF₃</u>		
	Assay	99% W
<u>Dimethylsulfoxide</u>		
	Assay	99%
	Water	<3000 ppm
<u>ECH</u>		
	Assay	99%
<u>Sodium Methylate</u>		
	Assay	95% W
	Sodium Hydroxide	<1.8% W
	Sodium Carbonate	<0.4% W
<u>Tetrahydrofuran</u>		
	Specific Gravity 20/4°C.	0.886-0.889
	Water	<300 ppm
	Peroxide (as THF hydroperoxide)	<150 ppm
<u>Methylene Chloride</u>		
	Nonvolatile Residue	<10 ppm
	Acidity	<5 ppm
	Water	<100 ppm
<u>Glycerin</u>		
	Specific Gravity 60/60°F.	1.264
	Acidity	<0.001 eq/100g
	Chloride	<5 ppm
	Ash	<0.01% (sulfate)
	Water	<800 ppm

TABLE C-4. RAW MATERIAL COSTS (1976)

<u>Ingredient</u>	<u>\$/Lb</u>	<u>Lb/Lb DEPECH</u>	<u>\$/Lb DEPECH</u>
DMSO	0.52	0.323	0.17
ECH	0.47 ↑	1.70	0.80
MeCl ₂	0.20	1.156	0.23
THF	0.71	5.1	(3.62)
NaOCH ₃	0.62 ↑	1.479	<u>0.92</u>
			\$2.12

- NOTES: (1) ECH and NaOCH₃ costs are escalating significantly.
- (2) Glycerin and BF₃ costs are relatively trivial and were excluded.

TABLE C-5. GENERAL FORMAT FOR COST ANALYSIS

I Direct Operating Cost

Raw Materials
Steam
Utilities
Operating Labor
Supervision
Maintenance
Maintenance Material

TOTAL D.O. COST

II Indirect Operating Cost

Analytical Support
Plant (Area) Overhead
Labor Overhead
G&A/Fringe Benefits
G&A Basic

TOTAL I.O. COST

III Fixed Operating Cost
(Depreciation & Interest)

IV Total Cost - I + II + III

GLOSSARY

BF_3	Boron trifluoride
ECH	Epichlorohydrin
DMSO	Dimethyl sulfoxide
G	Glycerin
MeCl_2	Methylene chloride
NaOCH_3	Sodium methylate
THF	Tetrahydrofuran

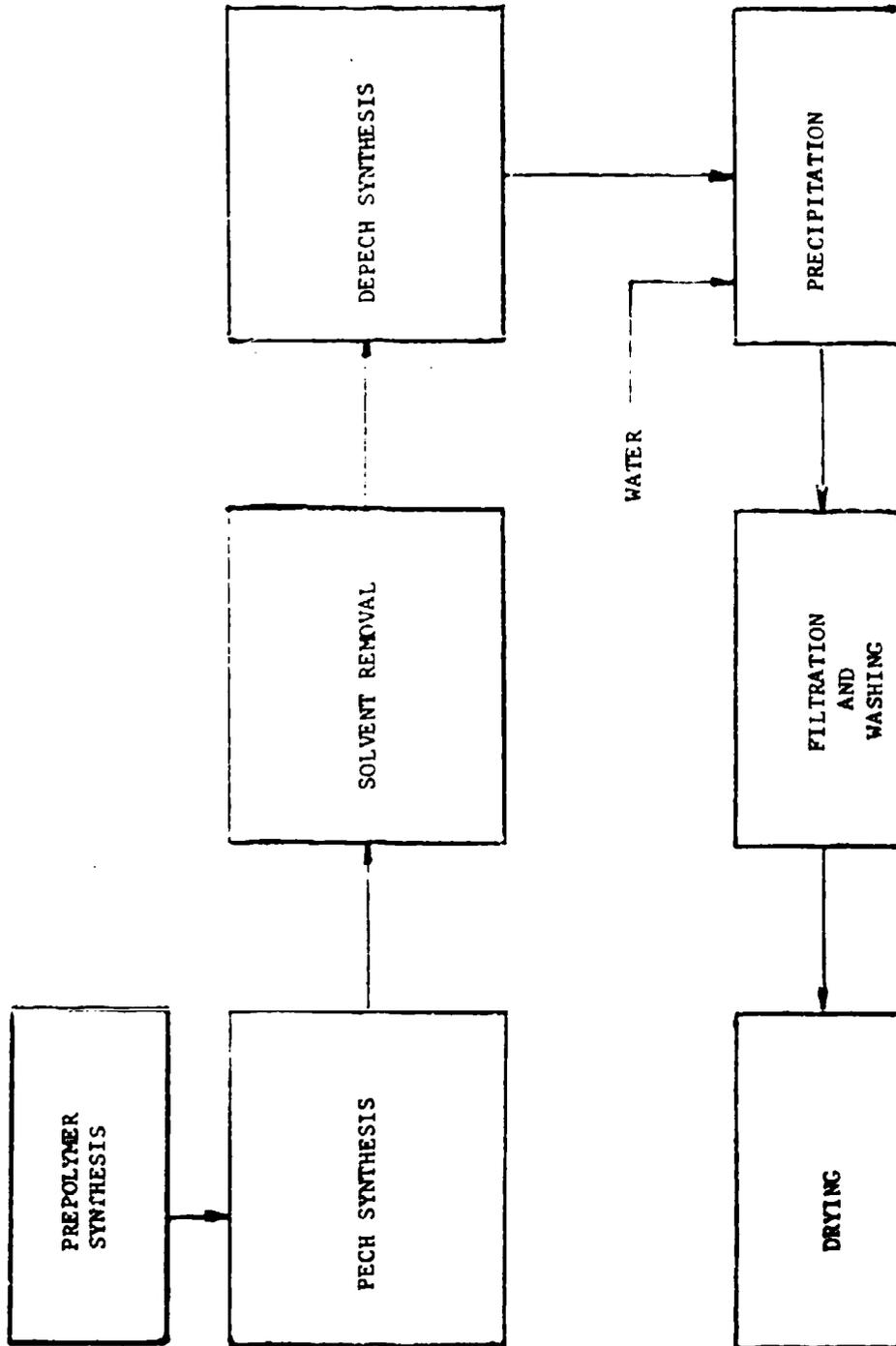
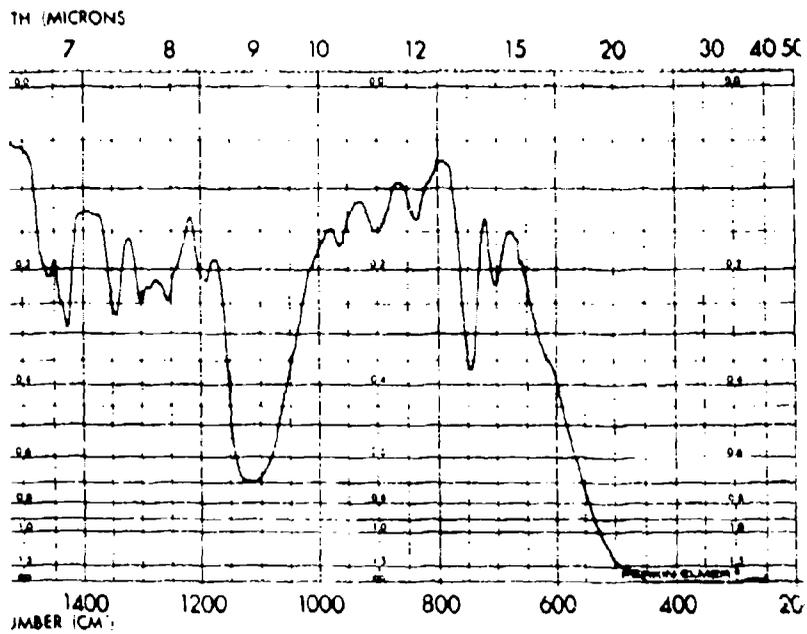
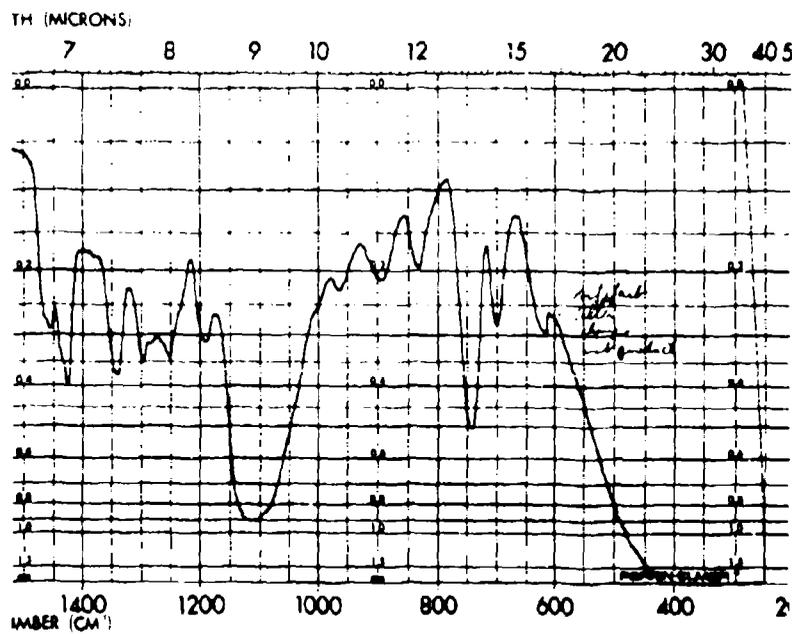


Figure C-1. Block Diagram of Processing Operations



983-3 (Lab Run)



983-10 (Pilot Plant Run)

Figure C-2. Infrared Spectra for PECH

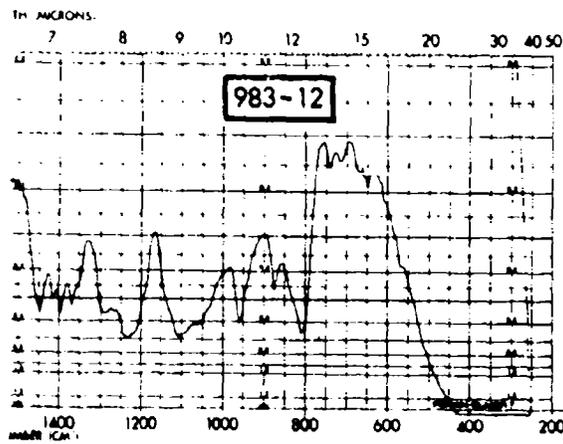
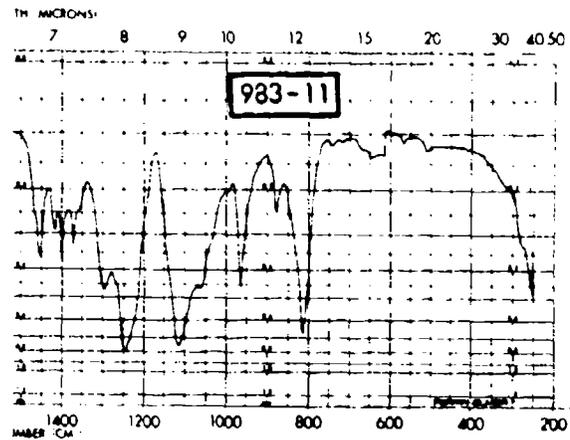
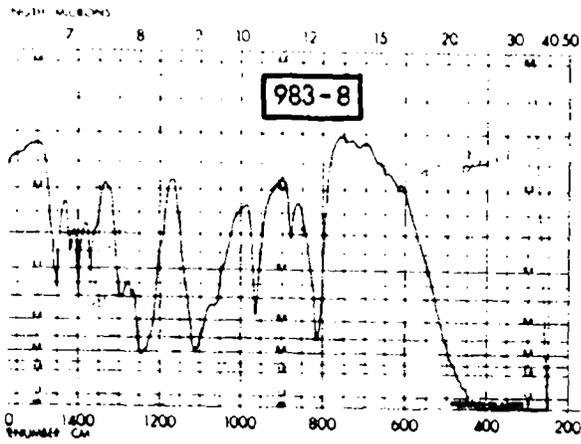
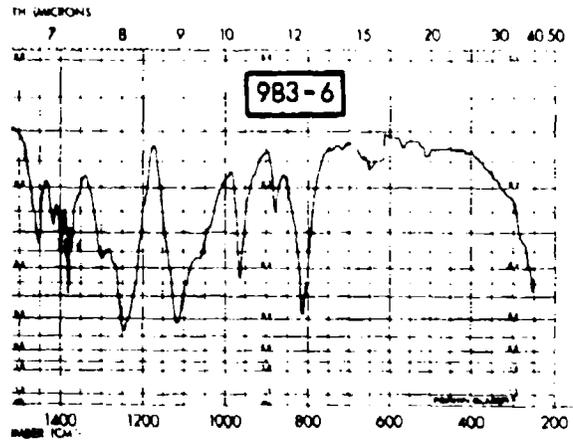
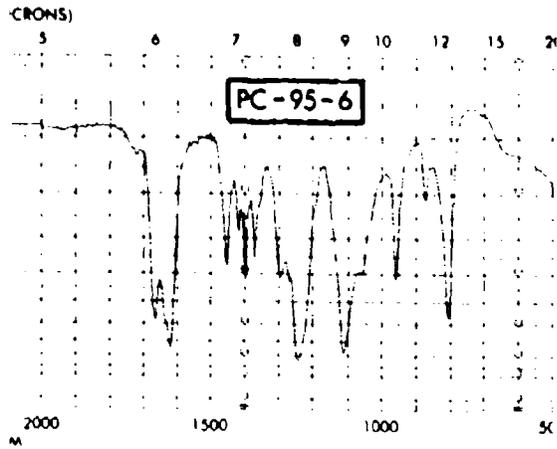


Figure C-3. Infrared Spectra for DEPECH

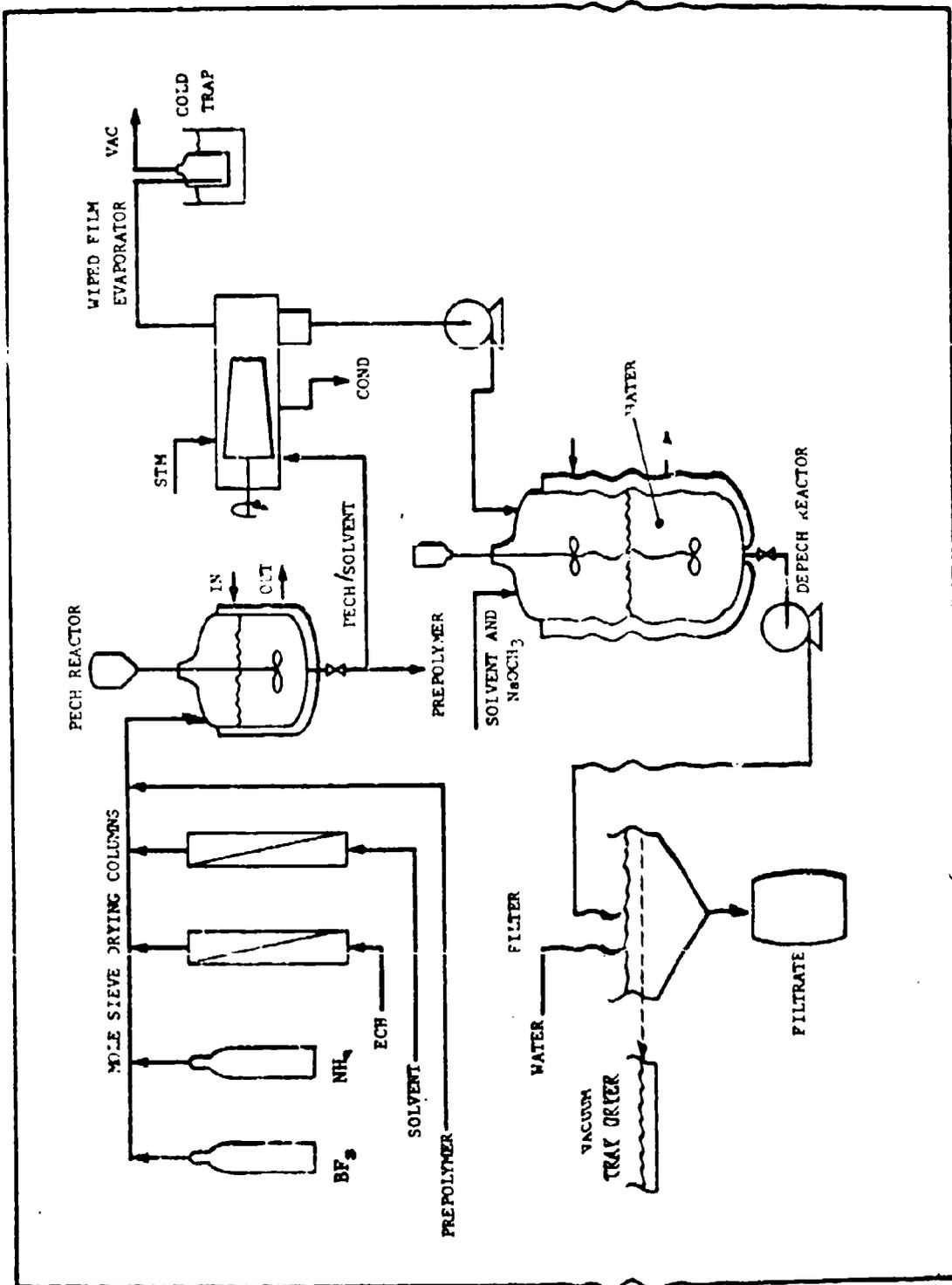


Figure C-4. Schematic Flow Diagram of DEPECH Pilot Plant

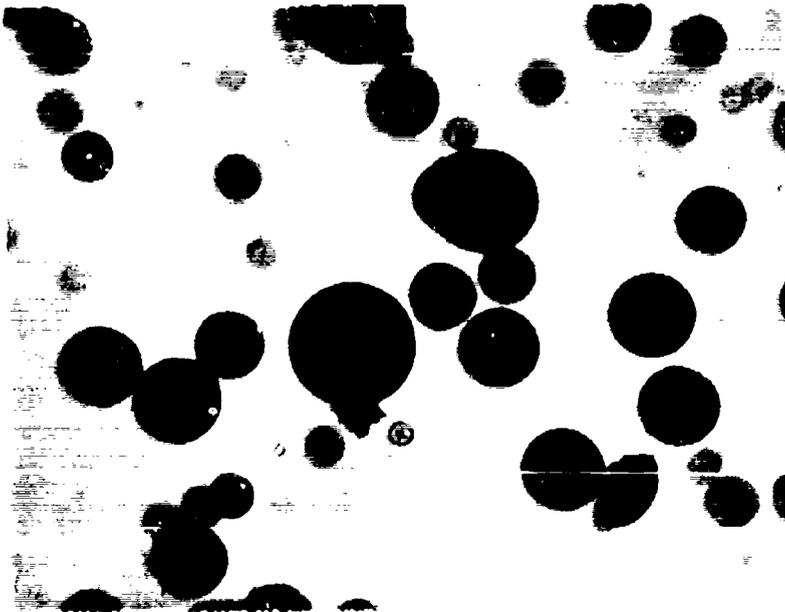


Figure C-5. DEPECH Photomicrographs (100X)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1 REPORT NUMBER 18 AFRPL TR-77-45	2 GOVT ACCESSION NO	3 RECIPIENT'S CATALOG NUMBER
4 TITLE (and Subtitle) 9 MANUFACTURE OF PCDE PREPOLYMER.	5 TYPE OF REPORT & PERIOD COVERED 7 Final report. January 1973 - May 1973	6 PERFORMING ORG. REPORT NUMBER
7 AUTHOR(s) 10 S. M. Nielson	8 CONTRACT OR GRANT NUMBER(s) 15 F04611-73-C-0051 F04611-75-C-0024	9 PERFORMING ORGANIZATION NAME AND ADDRESS Hercules Incorporated, Bacchus Works Magna, Utah 84044
10 CONTROLLING OFFICE NAME AND ADDRESS Air Force Rocket Propulsion Laboratory/MKPA Edwards AFB, CA 93523	11 REPORT DATE 11 October 1977	12 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS JON 3059081X JON 305908FE
13 MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 284p	14 SECURITY CLASS (of this report) UNCLASSIFIED	15 DECLASSIFICATION/DOWNGRADING SCHEDULE
16 DISTRIBUTION STATEMENT (of this Report) APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED		16 3451 17 43
17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18 SUPPLEMENTARY NOTES		
19 KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Process chemistry	DEPECH	Drying
Tubular reactors	Trimethylamine	Waste Disposal
PBEP	Fluorine	Product quality
PCDE	Equilibrium stages	Thermal Stability
PECH	Washing	Functionality
20 ABSTRACT (Continue on reverse side if necessary and identify by block number)		
Under Air Force Contract F33615-68-C-1568, Shell Development Company developed and evaluated a process for making PCDE, progressing through the intermediate steps of PECH, DEPECH, and PBEP. Hercules Incorporated, under Shell Contract SDNO 84723, for Air Force Contract F33615-72-C-1446, successfully demonstrated the PBEP and PCDE processes at rates of 6 lb/hr and provided other data pertinent to designing a large scale PCDE manufacturing plant.		

402 250

LB

20. Abstract (Cont)

Study was made of two methods for increasing the molecular weight and functionality of PCDE by improving the qualities in the PECH. The first method was to subject "standard" PECH to treatment that would retain only the higher molecular weight fraction. The second method used was to vary the PECH process to increase the molecular weight and functionality. The latter approach, a low temperature process, was chosen as the best method for making improved product.

As of August 1976, the two PCDE production contracts have been completed. A total of 1450 lb of PCDE have been shipped; 992 lb under F04611-73-C-0051 and 458 lb under F04611-75-C-0024. In addition to the specification material shipped, 63.3 lb of poor quality PCDE (Runs 14 and 20) were shipped to Naval Weapons Center, China Lake, California. Also, approximately 90 lb of material containing N-fluorazoxy contaminant were destroyed.

ACCESSION IN	
NTIS	Write Section <input checked="" type="checkbox"/>
DDC	Diff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	AVAIL. OR W/ SPECIAL
A	

APPENDIX D

SHIPPING CLASSIFICATION OF PCDE



J. Roads

DEPARTMENT OF THE NAVY
NAVAL ORDNANCE SYSTEMS COMMAND
NAVAL PLANT BRANCH REPRESENTATIVE OFFICE
HERCULES, INCORPORATED
POST OFFICE BOX 157
MAGNA, UTAH 84044

IN REPLY REFER TO
SPLB-64:BLB:rh
4610
Ser 425

JUN 6 1974

From: Naval Plant Branch Representative Office, Magna, Utah
To: Manager, Safety, Hercules Incorporated, Bacchus Works, Magna, Utah
(Mr. J. F. Cross)

Subj: PCDE (35%); classification of

Ref: (a) HI ltr MISC/14/0-2311 of 17 May 1974 (same subject)
(b) Title 49 CFR parts 170-189

1. Reference (a) recommends that 35% PCDE in Methylene Chloride be assigned a classification of "Propellant Explosives (liquid), Class B".

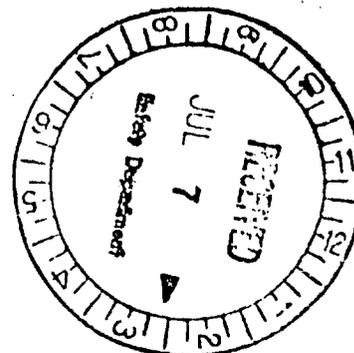
2. After witnessing the tests and reviewing the test data on PCDE (produced by Hercules Inc.) in a 35% PCDE 65% methylene solution, a tentative classification of Class B explosives is assigned.

3. The subject material should be described for shipment as "Propellant Explosives (liquid), Class B".

4. Packaging for shipment must be in accordance with reference (b) Section 173.93(c) or Bureau of Explosives approved container BA1721.

B. L. Bingham
B. L. BINGHAM
Transportation Officer

cy
KLADIS
PALMER
DANIELLE
FARBER



Hercules Incorporated
Bacchus Works
Magna, Utah

May 13, 1974

Ref. No. C4/5/74-182

cc: B. Bingham
J. Cross
J. Thacher
R. L. Keefe
J. Farber
S. Neilson
J. Duppell

TO: J. Rhoads

FROM: G. H. Lafferty/W. D. Bath

G. H. Lafferty, W. D. Bath

Reference to your request for Hazards Analysis-DOT Hazard Classification,
dated 4-8-74. Tests have been completed, results are summarized on the
attached form.

GHL/WDB/jg

Date 10 APR 1974

Sponsoring Agency USAF

Contract No. _____

Propellant Identity (Type No.) 35% PCDE IN METHYLENE CHLORIDE

Propellant Spec. _____ Batch _____

Mfg. Date _____

Detonation Test

	pevl	Exploded		Burned		SPARKED	
		Yes	No	Yes	No	Yes	No
7) No. 8 Blasting Cap Test I	300 ml	---	✓	---	✓	---	---
10 Gms. COTTON Test II	250 ml	---	✓	---	✓	---	---
" " " Test III	125 ml	---	✓	---	✓	---	---
" " " Test IV	150 ml	---	✓	---	✓	---	---
" " " Test V	100 ml	---	✓	---	✓	---	---

(1)

Samples: Five 2-inch cubes.

Test: One blasting cap per sample.

Ignition & Unconfined Burning Test

	Exploded		Average Burning Time	
	Yes	No	MIN	Seconds
One 2-inch cube (225 ml in container)	---	✓	3	15
One 2-inch cube	---	---	---	---
Four 2-inch cubes	---	---	---	---

(2)

Samples: Six 2-inch cubes.

Test: Ignite & burn unconfined - vigorously after 3 min

Thermal Stability Test

	Explosion		Ignition		Change in Configuration	
	Yes	No	Yes	No	Yes	No
One 2-inch cube	---	✓	---	✓	---	✓

Samples: One 2-inch cube

Test: 48 hours at 75° C. in vented oven @ 67.5% loss

Card Gap Test NOT RUN

60% Value (No. of Cards) _____

Impact Sensitivity Test

Bureau of Explosives Impact Apparatus

Ten 3 3/4" (± 1/16") Drop Test
10 Trials

4 Kg

Ten 10" (± 1/16") Drop Test
10 Trials

No. of Trials Exhibiting			No. of Trials Exhibiting		
Explosion Flame and Noise	Decomposition Smoke No Noise	No Reaction No Smoke No Noise	Explosion Flame and Noise	Decomposition Smoke No Noise	10 No Reaction 10 No Smoke 10 No Noise

Approved:

Test Director G. W. Dufferty

Test Department Head _____

Assigned Classification	
ICC Forbidden	_____
ICC Restricted*	_____
ICC Class A	_____
ICC Class B	_____

DOD Approval

Signature _____
Title _____
Organization _____

*Shipping Instructions are to be requested from ICC (para 3-12a(2)).

Figure 1. Sample summary data sheet.

Red. Raymond
W. D. B. 1/12
(Key Office)
Raymond
Dufferty

5
3. D-4
1
12

J. H. Hoads

SOCIATION OF
AMERICAN RAILROADS
OPERATIONS AND MAINTENANCE DEPARTMENT · BUREAU OF EXPLOSIVES
AMERICAN RAILROADS BUILDING · WASHINGTON, D.C. 20036 · 202/293 4048

R. R. MANION
Vice-President

R. M. GRAZIANO
Director

BA 1.21

15-145

SLP-RM

January 9, 1974

Mr. J. F. Cross, Mgr. - Safety
Hercules Incorporated
P.O. Box 98
Magna, Utah 84044

Dear Mr. Cross:

Reference my letter of December 19, 1973 and your letter of August 28, 1973, concerning "PCDE".

Be advised that the packaging in 5-gallon containers (DOT 17E) overpacked in DOT 15A wooden boxes detailed in your letter of 8-28-73 is approved pursuant to Section 173.93(c)(4) of the DOT Regulations.

Any incident involving this material and/or packaging must be reported to the Bureau of Explosives.

If we may be of further service, please advise.

Very truly yours,

R. M. Graziano
R. M. Graziano

cc: C. W. Schultz

KLADIS
FARBER
BINGHAM
HARDY
TILSON/PALMETO

ASSOCIATION OF

AMERICAN RAILROADS

OPERATIONS AND MAINTENANCE DEPARTMENT · BUREAU OF EXPLOSIVES
AMERICAN RAILROADS BUILDING · WASHINGTON, D.C. 20036 · 202/293-4048

R. R. MANION
Vice-President

R. M. GRAZIANO
Director

BA 1721

15-145

SLF-DC

December 19, 1973

Mr. J. F. Cross, Mgr. - Safety
Hercules Incorporated
P. O. Box 98
Magna, Utah 84044

Dear Mr. Cross:

The material described in your letter of August 28, 1973
and our attached laboratory report No. (s) 63011, September 18, 1973
is properly described as Propellant Explosive (Liquid), Class B
in accordance with Section 172.5 and classified as
Class B Explosive in accordance with Section 173.88(f) of
the DOT Hazardous Materials Regulations.

Required packaging, marking and labeling for surface transportation
(rail and highway) may be found in Sections as follows:

- A. Packaging - Section 173.93
- B. Marking - Section 173.93(f)
- C. Labeling - Section 173.405

Section 173.86 requires that, except for shipments of sample quantities, a written notification of the classification and approval accompanied by a supporting laboratory report or equivalent data must be filed with the Department of Transportation before any new explosive device is offered for shipment.

If we may be of further service, please advise.

Very truly yours


R. M. Graziano
Director

**KLADIS
FARBER
C1 BINGMAN
HARDY**

Attachment - Invoice BEL 001248 & BEL 001251
cc: C. W. Schultz, Chief Chemist

ASSOCIATION OF

AMERICAN RAILROADS

OPERATIONS AND MAINTENANCE DEPARTMENT · BUREAU OF EXPLOSIVES
RARITAN CENTER · BUILDING 817 · EDISON, NEW JERSEY 08817 · 201/225-1618

CHEMICAL LABORATORY REPORT

R. M. GRAZIANO
Director and Chief Inspector

File Number _____

C. W. SCHULTZ
Chief Chemist

Laboratory Number 63011

Laboratory Date September 18, 1973

Propellant Explosives (Liquid), Class B 9.9% PCDE in Methylenechloride Hercules Incorporated

A sample of material identified as 9.9% PCDE in methylenechloride was received from Hercules Inc. of Magna, Utah.

The material was a orange color, clear liquid containing 9.9% PCDE.

A portion of the sample was maintained at 75° C for 48 hours, under an Air reflex Condenser. It did not ignite or decompose. Methylenechloride was evaporated showing 90% loss of weight.

Portions of the sample as received and when absorbed in cotton were initiated with Number 8 electric blasting caps. In all of these tests the materials were contained in waxed paper cylinders 3" in diameter.

<u>Material tested</u>	<u>Test Result</u>
10 grams of absorbent cotton plus 250 ml of liquid	No explosion
10 grams of absorbent cotton plus 175 ml of liquid	"
10 grams of absorbent cotton plus 150 ml of liquid	"
10 grams of absorbent cotton plus 100 ml of liquid	"
200 ml of head liquid	"

A portion of the material was placed on a bed of kerosene soaked sawdust, which was ignited. When the fire reached the test portion it burned rapidly without explosion.

Small portions of the liquid, both as received and absorbed in filter paper were subjected to 10" drops in the Bureau of Explosives Impact Apparatus (Liquid modification). Six trials were made with paper and six without. In none of the trials was there any sign of explosion or decomposition.

Material represented by this sample is properly described as propellant explosive (liquid), Class B and classed as Class B Explosive under the DOT Regulations.

D-7 C. W. Schultz
Chief Chemist



HERCULES INCORPORATED

INDUSTRIAL SYSTEMS DEPARTMENT • SYSTEMS GROUP
P. O. BOX 98, MAGNA, UTAH 84044 • TELEPHONE: 297-5911

May 18, 1973

Ref: MISC/14/0-2004

Mr. Stanley Fastenau
Bureau of Explosives
Association of American Railroads
Washington, D. C. 20036

Dear Mr. Fastenau:

We have been shipping a liquid explosive known as PCDE (35%) in methylene chloride in one gallon quantity 17E containers per special BE permit No. 588. This material is properly classed as Class B explosives and is marked as propellant explosives (liquid) Class B for shipping purposes.

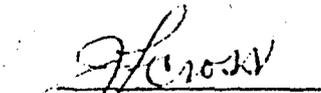
Bureau of Explosive special permit No. 588 was originally issued to Shell Development Company in 1966 and updated in 1969 to ship PBEP and PCDE in one gallon and 1.25 gallon DOT specification 17E, 24 gauge drums lined with phenolic base resin (Code R-801 or R-819) and provided with all polyethylene gaskets. One such drum is to be overpacked in a DOT specification 15-A wooden box. The space between the drum and the box is to be filled with incombustible packing material (Vermiculite) and be of such quantity that any spillage of the solution will be absorbed.

The question has arisen as to whether or not Hercules should apply for a BE special permit to ship PCDE, based on a new set of sensitivity tests run on material manufactured at Bacchus; or can we legally continue shipping this material on BE special permit No. 588?

Hercules (Bacchus) is presently manufacturing and shipping small amounts of PCDE on a contract with Edwards Air Force Base. The contract specifically spells out the use of the special permit No. 588 to ship this PCDE.

Please advise us of your opinion on this matter at your earliest convenience.

Yours very truly,


J. F. Cross
Manager of Safety

JFC/EWGivens/slv

cc: J. C. Farber
B. L. Bingham
Safety File

HERCULES INCORPORATED

(Date)

PCDE ANALYSIS REPORT

LOT: _____

<u>ITEM</u>	<u>DETERMINATION</u>	<u>ANALYSIS</u>
1	Nitrogen, percent weight	_____
2	Fluorine, percent weight	_____
3	Hydroxyl equivalent per 100 gms	
3.1	By chemical reactivity method	_____
3.2	By effective gellation method	_____
4	Molecular weight by VPO	_____
5	Hydroxyl functionality	
5.1	By chemical reactivity method	_____
5.2	By effective gellation method	_____
6	Thermal stability, 110° C	_____
7	Solids content, weight percent	_____
8	Moisture, ppm	_____
9	Acetone, weight percent	_____
10	Infrared scan	Attached

ANALYSIS CERTIFIED BY*

Dr. R. J. DuBois,
R&D Laboratory Supervisor

APPENDIX E
OPERATING AND LABORATORY PROCEDURES
(Report Form)

HERCULES INCORPORATED

(Date)

PCDE ANALYSIS REPORT

LOT: _____

<u>ITEM</u>	<u>DETERMINATION</u>	<u>ANALYSIS</u>
1	Nitrogen, percent weight	_____
2	Fluorine, percent weight	_____
3	Hydroxyl equivalent per 100 gms	_____
3.1	By chemical reactivity method	_____
3.2	By effective gellation method	_____
4	Molecular weight by VPO	_____
5	Hydroxyl functionality	_____
5.1	By chemical reactivity method	_____
5.2	By effective gellation method	_____
6	Thermal stability, 110° C	_____
7	Solids content, weight percent	_____
8	Moisture, ppm	_____
9	Acetone, weight percent	_____
10	Infrared scan	Attached

ANALYSIS CERTIFIED BY*

Dr. R. J. DuBois,
R&D Laboratory Supervisor

* For product shipment only

Laboratory Procedure
Water in PBEP and PCDE

APPARATUS (Cont'd)

(2) Volumetric Flasks - 25 cc volumetric flask with ground glass stopper, dried at 110°C and stored in a dessicator. Prior to use, the flasks are blown out with dry nitrogen.

PROCEDURE

(1) Standardization

Weigh to the nearest 0.1 mg, 50 mg of water into a tared dry 25 ml volumetric flask. Make up to volume with dioxane previously dried with mole sieves overnight. Inject 15 µl aliquots into the chromatograph, setting the attenuator to insure the water peak remains on scale. Also run a 15 µl solvent blank. Measure the peak area using triangulation. After each run increase the column temperature to 150°C to remove the solvent.

(2) Sample run.

Inject 40 µl aliquots of the "as received" sample into the chromatograph, setting the attenuator to insure the water peak remains on scale. Measure the peak area using triangulation. After each run increase the column temperature to 150°C to remove the solvent. Determine the density of the sample solution at 25°C.

CALCULATION

The response factor (F) for water is calculated using the following relationship:

$$F \text{ } \mu\text{g}/\text{cm}^2 = \frac{S \times V}{25 \times (A-B)}$$

where: V = volume sample injected in µl.
S = weight of water added in mg.
A = area of water peak in standard in cm².
B = area of water peak in blank in cm².

The concentration of water present in PBEP or PCDE is calculated as follows:

$$\% \text{ H}_2\text{O} = \frac{F \times (A) \times 100}{V \times D}$$

where: A = area of water peak in sample in cm².
V = volume of sample injected in µl.
D = specific gravity of PCDE solution in mg/ml.

Laboratory Procedure

Determination of Water in PBEP and PCDE

SCOPE

A gas chromatographic method for the determination of water in methylene chloride solutions of PBEP or PCDE has been developed. To avoid interferences and decomposition a "low temperature inlet or on-column injection" technique is employed.

SAFETY

Lab coats, safety shoes and safety glasses will be required as a minimum. The Laboratory Procedure for working with fluorinated compounds, Bacchus Laboratory Manual, Section XI, Method I, will be followed for all sample handling and disposal.

REAGENTS

- (1) Dioxane - reagent grade.
- (2) Molecular sieves - 5A, Union Carbide Company.

APPARATUS

- (1) Gas Chromatograph - FM 720 or an instrument capable of using on-column injection.

Instrumental Conditions:

Column - 2' x 1/4" SS Porapak Q.
Temp. - 100°C.
Current - 130 ma.
Detector - 250°C.
Inlet - 110°C.
Chart Speed - 30"/hr.
Flow - 60 cc/min.

HERCULES INCORPORATED
Bacchus Works
Magna, Utah

Initiated by: L. B. Jones

Revision: _____

Approved: R. J. La Bois

Date: _____

Approved: _____

Approved: _____

Approved: _____

Approved: _____

Best Available Copy

Procedure
Water in PBEP and PCDE

APPENDIX (Cont'd)

(1) Volumetric Flasks - 25 cc volumetric flask with ground glass stopper, dried at 110°C and stored in a desiccator. Prior to use, the flasks are blown out with dry nitrogen.

PROCEDURE

(1) Standardization

Weigh to the nearest 0.1 mg, 50 mg of water into a tared dry 25 ml volumetric flask. Make up to volume with dioxane previously dried with mole sieves overnight. Inject 15 μ l aliquots into the chromatograph, setting the attenuator to insure the water peak remains on scale. Also run a 15 μ l solvent blank. Measure the peak area using triangulation. After each run increase the column temperature to 150°C to remove the solvent.

(2) Sample run.

Inject 40 μ l aliquots of the "as received" sample into the chromatograph, setting the attenuator to insure the water peak remains on scale. Measure the peak area using triangulation. After each run increase the column temperature to 150°C to remove the solvent. Determine the density of the sample solution at 25°C.

CALCULATION

The response factor (F) for water is calculated using the following relationship:

$$F \mu\text{g}/\text{cm}^2 = \frac{S \times V}{25 \times (A-B)}$$

Where: V = volume sample injected in μ l.
S = weight of water added in mg.
A = area of water peak in standard in cm^2 .
B = area of water peak in blank in cm^2 .

The concentration of water present in PBEP or PCDE is calculated as follows:

$$\% \text{H}_2\text{O} = \frac{F \times (A) \times 100}{V \times D}$$

Where: A = area of water peak in sample in cm^2 .
V = volume of sample injected in μ l.
D = specific gravity of PCDE solution in mg/ml.

Best Available Copy

AREA: Building 8115, Room 6

TASK:

TITLE: Infrared Analysis of PCDE-PLEP Solutions

PROCEDURE NO. 2E-4003 REVISION 0

TYPE I

Total number of pages is 11

Hercules Incorporated
Industrial Systems Department
Systems Group

BACCHUS WORKS
MAGNA, UTAH

APPROVED BY	
	DATE
<i>Alonso T. Sauer</i>	7-8-74
<i>P. H. Bennett</i>	7-5-74
SAFETY DEPARTMENT	DATE
<i>J. Bryant</i>	7-8-74
Date <u>July 8, 1974</u>	Copy No. _____

Laboratory Procedure
Area - Building 8115, Room 6
Procedure No. 2R-4093

Infrared Analysis of PCDE-PBEP Solutions

I. Summary

- A. Scope - This procedure covers the infrared analysis of PBEP or PCDE solutions.
- B. Principle - Infrared analysis provides information on reaction stoichiometry and a first indication of product purity.
- C. Limitations and Interferences - None.

II. Reagents

1. Molecular sieves, 3A, any vendor.
2. Acetone, technical grade, any vendor.

III. Apparatus

1. Infrared spectrometer, Perkin-Elmer 237 or equivalent.
2. NaCl windows, any source.
3. Eyedroppers, any source.

General Procedure

IR Scans PCDE-PBEP

Sample Preparation

All samples are typically received in 4oz. polyethylene bottles. PCDE may arrive in a two phase system (water wash/PCDE solution). The aqueous phase may be decanted from the PCDE solution or the PCDE solution may be removed from under the aqueous phase with the aid of a medicine dropper.

1. Dry NaCl plates at 100^o C for at least one hour (overnight if possible).
2. Place ~ 20 ml of solution in small polyethylene vial. Dry with ~ 1/3 volume of 3A molecular sieves. Allow to dry with swirling ~ 5 minutes.
3. Assuming 10% solutions, place 15-20 drops of solution on a warm salt plate.
4. Place salt plate in oven at 100^o C for 10-15 minutes or until acetone is completely removed. (This can be checked by scanning through 2000-1500 cm⁻¹.) The absence of a shoulder on the $\overset{\curvearrowright}{\text{C}} = \text{O}$ band (see scan No. 1) indicates no acetone is present. If acetone is present, return the sample to the oven until the band at 1750 cm⁻¹ is well rounded. (See scan No. 2.) When no acetone is evident in the IR scan, proceed to scan.

IR Scan

1. Place sample in sample holder.
2. Adjust 100% control to 75% at 4000 cm⁻¹.
3. Adjust sample thickness to get 25-30% reading at 2950.
(Do not change 100% adjust to adjust percent transmittance at 2950 cm⁻¹. To adjust sample thickness, either remove or redistribute material on the salt plate with a wooden spatula.)
4. Return carriage to 4000 cm⁻¹ and record scan at fast speed.

Scan Analysis

A. To check for conversion of PBEP to PCDE

The band at $\sim 1420 \text{ cm}^{-1}$ (Scan No. 2) is indicative of the primary difluoramine group ($-\text{CH}_2-\text{NF}_2$). During conversion to PCDE, this group is transformed to a nitrile, $-\text{C}\equiv\text{N}$, which absorbs at 2260 cm^{-1} . Absence of a band or any hint of a band at 1420 cm^{-1} (see Scan No. 3) indicates that the PBEP has successfully been converted to PCDE.

B. To check for conversion of DEPECH to PBEP

Unconverted DEPECH will show up in the infrared scan at 1650 cm^{-1} . (See Scan No. 4.) This band has been assigned to the double bond of DEPECH ($\text{C}=\text{C}$) which has not been totally converted.

C. N-fluorazoxy check.

A band in the spectrum at 1520 cm^{-1} is indicative of an N-fluorazoxy moiety, $\begin{matrix} \text{O} \\ | \\ -\text{N} = \text{NF} \end{matrix}$. This presumably is due to NO in the difluoramination process. NO most likely would be formed from hydrolysis of N_2F_4 during reaction.

	-O-H	3450-3650 cm^{-1}	
	-CH	2930-3050 cm^{-1}	
	-C \equiv N	2260 cm^{-1}	
	>C=O	1740 cm^{-1}	
	acetone C=O	1720 cm^{-1}	Should not be there
	<C=C	1655 cm^{-1}	DEPECH only
	$\begin{matrix} \text{O} \\ \\ -\text{N} = \text{NF} \end{matrix}$	1520 cm^{-1}	NO present in reactor
PCDE	-NF ₂ (tertiary)	1460 cm^{-1}	
		1380 cm^{-1}	
PBEP	NF ₂ (primary)	1425 cm^{-1}	
		1360 cm^{-1}	

Approved By

L. W. Haas

L. W. Haas

R. J. DuBois

R. J. DuBois

G. M. Daurelle

G. M. Daurelle

Initiated By Dennis T. Sauer

Dennis T. Sauer

Safety Department

Nitrogen Content of PBEP and PCDE

SCOPE

This method is to be used for determining the nitrogen content of PBEP and PCDE using a C,H,N Analyzer. This method consists of combusting the sample at 1000°C in an inert atmosphere and reducing the nitrogen containing functional groups to nitrogen. The nitrogen is separated from the other gasses using a Porapak Q column, which has been calibrated using acetanilide as a standard.

SAFETY

Lab coats, safety shoes and safety glasses will be required as a minimum. The Laboratory Procedure for working with fluorinated compounds, Bacchus Laboratory Manual, Section XI, Method I, will be followed for all sample handling and disposal.

REAGENTS

(1) Acetanilide - National Bureau of Standards 141A, Contains 10.363% N.

APPARATUS

(1) C,H,N Analyzer:

Instrumental Conditions:

Combustion furnace temp. - 1000°C
Reduction furnace temp. - 570°C
Column - 4' x 1/4" SS Porapak Q
Column temp. - 60°C
Column flow - 25 cc/min.
Splitter flow - 200 cc/min.
Filament voltage - 7 volts

HERCULES INCORPORATED

Bacchus Works
Magna, Utah

Initiated by: D.W. Naas Revision: _____

Approved: R.J. Davis Date: _____

Approved: _____ Approved: _____

Laboratory Procedure - Tentative

APPARATUS - Con't.

- (2) Balance - Cahn gram electrobalance.
- (3) Aluminum sample boats - Hewlett Packard Co. Cat. # 5080-5045.

PROCEDURE

Accurately weigh out four to seven milligram neat PBEP or PCDE to the nearest 0.001 mg into a tared aluminum boat. Place the boat containing the sample into the push rod. Insert the rod into the cold zone of the furnace and allow the system to be purged with helium. When equilibrium is obtained insert the push rod into the combustion furnace for a static burn period of 20 seconds. Set the attenuator to ensure that the nitrogen peak remains on scale. Measure the peak area using triangulation.

Using the same procedure described for the sample determine the response factor for nitrogen using four to seven milligrams acetanilide weighed to the nearest 0.001 mg.

CALCULATION

- (1) Standardization using acetanilide.

The response factor (F) in terms of mg/cm² is calculated using the following equation:

$$F = \frac{S \times .10363}{A_{st}}$$

Where: S = wt. of acetanilide in mg.
A_{st} = area of N₂ peak in cm² of acetanilide.

- (2) Samples.

The nitrogen content of PBEP or PCDE is calculated using the following equation:

$$\%N = \frac{F \times A_s \times 100}{W}$$

Where: A_s = area of N₂ peak of sample in cm².
W = weight of sample in mg.

FLUORINE CONTENT OF PBEP AND PCDE

SCOPE

This method is to be used for determining the fluorine content of PBEP and PCDE. The perfluoramine groups of PBEP and PCDE are base hydrolyzed to fluoride ion in an alcohol solution of the sample. The alcohol is evaporated on a steam bath which also assures complete conversion to fluoride ion. The fluoride is diluted to a known volume in a manner which provides a resultant pH of 8.3 and a constant ionic strength of 0.1000 M. The solutions are then subjected to a standard addition titration with 0.1000 M NaF (having an ionic strength of 0.1000 M also) using a fluoride ion-calomel electrode pair in conjunction with a precision pH meter. At least five incremental additions of the titrant are made and the resultant solution potentials are recorded to a tenth of a millivolt. The data are treated via the Gran's plot concept.

SAFETY

Lab coats, safety shoes and safety glasses will be required as a minimum. The Laboratory Procedure for working with fluorinated compounds, Bacchus Laboratory Manual, Section XI, Method I will be followed for all sample handling and disposal.

REAGENTS

- (1) Sodium fluoride, 99.3% Baker Analyzed Reagent. Dry at 105°C for two hours before use.
- (2) Sodium fluoride, 0.1000 M. Dissolve 4.1991 g in a liter of distilled water.
- (3) Constant Ionic Strength -pH Buffer. Prepare a solution 0.807 M in sodium bicarbonate by dissolving 67.89 g of the material in distilled water and diluting it to one liter.
- (4) Sodium hydroxide, 50%
- (5) Nitric acid, concentrated.
- (6) Alcohol, reagent, specially denatured.

HERCULES INCORPORATED

Bacchus Works
Magna, Utah

Initiated by: *L. W. Adams* Revision: _____
 Approved: *R. J. Bair* Date: _____
 Approved: _____ Approved: _____

Laboratory Procedure - Type I

APPARATUS

(1) Fluoride Ion Electrode, Orion Model 9409 or equivalent, Orion Research Inc., Cambridge, Mass.

(2) Calomel reference electrode, saturated.

(3) Research Model pH Meter, Corning Model 12 or equivalent, capable of reading to 0.1 mv.

(4) Gran's Plot paper, 10% volume corrected, Orion Research Inc., Cat. # 90-00-90 or computer facility, capable of performing a relative least squares evaluation of the Gran's plot data.

PROCEDURE

Accurately weigh neat PBEP or PCDE samples, containing three to five millimoles of fluorine into 250 ml polyethylene beakers. Add ten milliliters of reagent alcohol and stir the samples into solution, taking care not to splash the samples on the walls of the beaker. Add exactly 1.00 ml of 50% sodium hydroxide by pipette buret and continue to stir while the samples heat up, hydrolyzing the perfluoramine. Cover the samples with a watch glass and continue stirring ten minutes or so. Place the samples on a boiling steam bath, remove the watch glasses, washing them with alcohol, and evaporate the solvent to dryness or near dryness. When the residues appear dry (white) remove the beakers and add about 100 ml of distilled water. Adjust the pH of the solution to 8.0 to 8.5 with nitric acid. Add 100 ml of the 0.807 M buffer and dilute the contents of the flask to one liter with distilled water. (At this point the samples will be at a pH of 8.3 and the total ionic strength will closely approximate 0.1000 M).

Prepare standard runs by accurately weighing 100 to 200 mg reagent grade sodium fluoride into polyethylene beakers and process these in a manner identical to the samples above.

Empty the liter dilutions into two liter beakers without washing, but taking care to drain the contents well. Add a stir bar and immerse the fluoride ion calomel electrode pair into the stirring solution. Record the initial millivolt reading using the expanded scale of the instrument. Add incrementally 10.00, 20.00, 30.00, 40.00, and 50.00 ml of 0.1000 M sodium fluoride and record the potential responses to each addition to the nearest 0.1 mv.

Plot the data from the standard run on Gran's plot paper and determine the initial concentration of fluoride present in the sample. An alternative and preferred treatment of this data can be obtained by programming the Gran's plot into a computer such as an IBM 370, utilizing a relative least squares program for reduction of the data.

Laboratory Procedure - Type I

NOTES

Adjust all data for the purity of sodium fluoride reported on the label.

CALCULATION

The fluorine content of PBEP and PCDE is calculated in the following manner:

$$\%F = \frac{M \times 18.998 \times 1000}{W}$$

Where: M = the molar concentration of fluoride determined by the Gran's Plot technique.

W = the weight of the sample in grams.

Removal of Solvent From PBEP and PCDE

SCOPE

Prior to the analysis of PBEP and PCDE it is necessary to remove the solvent in which the materials were prepared.

PROCEDURE

- 1) A sample of PBEP and PCDE solution containing approximately two grams of the desired product is placed in a 50 cc round bottomed flask along with a one inch Teflon covered magnetic stirring bar.
- 2) Remove the solvent from the sample using a Rinco evaporator with the sample immersed in a 50-60° water bath.
- 3) After sufficient solvent has been removed such that a vacuum of one to two Torr may be applied without causing the product to foam out of the flask, release the vacuum and add about 30 cc of dry ethylene dichloride.
- 4) Rotate the flask in warm water until the polymer has redissolved.
- 5) Remove the solvent as previously described then repeat the process for two additional aliquots of ethylene dichloride.
- 6) For final complete solvent removal the heated rotating flask is subjected to a vacuum of 0.1-0.2 Torr for two hours.

SAFETY

Provisions have been made to shield the entire operation with plexiglass shields. Lab coats, safety shoes and safety glasses will be required as a minimum. The Laboratory Procedure for working with fluorinated compounds, Bacchus Laboratory Manual, Section XI, Method I will be followed for all sample handling and disposal.

HERCULES INCORPORATED
Bacchus Works
Magna, Utah

Initiated by: L. W. Neas Revision: _____
Approved: R. J. Quinn Date: _____
Approved: _____ Approved: _____

Effective Functionality

SCOPE

Functionality is normally defined as the ratio of the molecular weight to the equivalent weight of a compound. Functionalities described in this manner are often quite meaningless in that they contain monofunctional or nonfunctional impurities which do not enter into the binder network. These impurities do, however, effect the GPC or VPO results.

Now if only those chains which contain functional groups capable of reacting with an alcohol and taking part in the formation of a binder network are considered, what is known as an "effective" functionality is obtained.

Experimentally, the isocyanate/hydroxyl (NCO/OH) equivalents ratio at incipient gelation is determined and the "effective" functionality (fe) calculated according to the following equation:

$$(NCO)/(OH) = 2/fe$$

This equation predicts that a triisocyanate will gel when 2/3 of its functions are reacted when mixed with a diol.

Reagents and Apparatus

- 1) Glass Vials - 3 dram, snap cap vials, dried at 110°C and stored in a desiccator.
- 2) PGA - difunctional Ruccoflex S1011-115.
- 3) Cyclohexanone - reagent grade.
- 4) Iron(III) acetylacetonate (Fe (AAA)₃) - reagent grade, 5% in dimethyl phthalate.
- 5) Dimethyl phthalate - reagent grade.

HERCULES INCORPORATED
Bacchus Works
Magna, Utah

Initiated: J. W. Haas *J.W. Haas*

Revision: 2

Approved: *R.A. Ober*
R&D Superintendent

Date: 21 December 1976

Laboratory Procedure - Type III
Effective Functionality

Standards and Solutions

- 1) PGA standard - Accurately weigh 24.5 grams PGA and 25.5 g cyclohexanone and mix.
- 2) N-100 solution - Use the % NCO value obtained for the particular lot to be tested and determine the grams of N-100 per NCO equivalent (equivalent weight (eq. wt.)).

$$\text{Eq. Wt.} = \frac{42}{\% \text{ NCO}} \times 100$$

From this, prepare the N-100 solution as follows:

- a) N-100, g = $\frac{\text{Eq. Wt.}}{10}$
- b) Cyclohexanone, g = (100 g - g N-100)

Mix well.

Procedure

- 1) Into each glass vial accurately weigh exactly 5.00 g of the PGA solution (3 vials should suffice).
- 2) Into each individual vial accurately weigh 2.40, 2.60, 2.80 g of the N-100 solution.
- 3) Add 5 drops of $\text{Fe}(\text{AAA})_3$ catalyst, shake and put into a 120°F oven overnight to gel.
- 4) Determine the point at which the sample gels. A gel occurred if the sample does not flow upon turning the vial upside down.
- 5) Establish the exact gel point by preparing four more vials with 5.00 g PGA solution and accurately weighing in N-100 solutions at 50 mg intervals between the gel sample and the one below it which did not gel.

Example: If gel occurred at 2.6 g N-100, weigh out for the second set 2.450, 2.500, and 2.550 g of N-100 solution.

Calculation

Calculate "effective" functionality as follows:

$$f_e = \frac{2}{A}$$

Where: A = grams of N-100 solution used in step 5 to effect gel.

UNIT OPERATING PROCEDURE

PROGRAM

RESEARCH AND DEVELOPMENT

AREA

PILOT PLANT

TASK

PC-300 PBEP MANUFACTURE

TITLE

PBEP SYNTHESIS & PURIFICATION - PC-300 SECTION

PROCEDURE NO.
UOP 2R-PC31

REV. LTR.
2

TOTAL NO. PAGES
21

TYPE I

HERCULES INCORPORATED
CHEMICAL PROPULSION DIVISION

PLANT

BACCHUS WORKS - PLANT 1

APPROVED BY

	SIGNATURE	DATE
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1. SCOPE

1.1 This document describes the procedure for synthesizing and preliminary purification of PBEP in a liquid phase flow reactor system.

2. REQUIREMENTS

2.1 Personnel working in this operation are responsible for knowing and following this procedure.

2.2 This procedure may be redlined with approvals by building supervision and Safety.

2.3 No person will conduct a live run unless he has conducted at least two inert runs with nitrogen and solvent, or a live run within the previous 90-day period.

2.4 Handle volatile solvents per GOP 2-G20-55.

2.5 Dispose of waste material per GOP 2-G15-10.

2.6 Observe building and personnel limits specified in GOP 2R-TV01.

2.7 All applicable safety rules specified in GOP 2R-TV01 shall be adhered to.

3. APPLICABLE DOCUMENTS

GOP 2-G20-55	Handling and Use of Volatile Solvents
GOP 2-G15-10	Waste Disposal
GOP 2R-TV01	Building Limits, Safety Rules, and Building and Equipment Inspection
GOP 25-12	TVOFA, PBEP, and PCDE Spill Cleanup
Operating Orders	Bound Shift Log Book

4. MATERIALS AND EQUIPMENT

4.1 MATERIALS	DESCRIPTION
Acetone	NR
Methylene Chloride	NR
TA	Triacetin
Ethylene Glycol	Approved for use in pilot plant
High Pressure Nitrogen	Nitrogen gas in cylinders, full pressure 2200 psi.
Low Pressure Nitrogen	Liquid nitrogen available as gas at 125-150 psig, furnished in bulk storage tank
Methanol	NR
Wood Pulp	NR

4.1 MATERIALS (Cont'd)	DESCRIPTION
Cloth	Clean, untreated
Wipes	Reticulon, Industrial Wipes
Olefin	DEPECH
N ₂ F ₄	NR
Halocarbon 18CS/100 or Fluorolube MO-10B	Positive displacement pump oil
4.2 EQUIPMENT	DESCRIPTION
Reaction System	Defined on process flow sheet 083-2354-11001-5BU as modified
Respirator	Vapor type, air line, or mask with type N cartridge
Slum Pot	Clean, seamless aluminum container
Ion exchange feed pump hose	3/8" OD x 1/16" wall, Nordell Rubber
Pinch Clamps	Hose clamp
Liquid explosive sample bottles	Polypropylene sample bottles, 4 oz.
Sample Carrier	Drawing 08H00094
Product bottles	5-gallon polyethylene
Jug	1-, 2-, 5- and 7-gallon polyethylene translucent, heavy wall
Trays	Plastic or aluminum, approximately 1-1/2 ft x 2 ft x 6 inches deep
Transfer Boxes	Wood with polyethylene foam liner
Beaker	Polyethylene, 1000 cc
Funnel	Polyethylene, 3 in. to 6 in.
Shoes	Safety, non-conductive
Strap	Shoe, conductive
Glasses	Safety, prescription or plain lenses
Liquid explosive sampler	Plastic pi-pump and polyethylene pipette or syringe and air bulb

4.2	EQUIPMENT (Cont'd)	DESCRIPTION
	Gloves	Neoprene
	Hard Hat	With face shield
	Hand truck	two-wheel flat bed with sides
	Scale	Dial, 0-75 pounds

5. SAFETY

5.1 Eye protection shall be worn when within the confines of the pilot plant, including all areas of TV100, TV200, and PC300 sections.

5.2 Avoid exposure to and inhalation of acetone or N_2F_4 .

5.3 During transfer of acetone from drum to solvent vessel, the hose is to be positioned to allow the acetone to run down the side of the vessel. The acetone should not be allowed to fall free when filling the vessel due to possible static electricity buildup. During acetone transfer, all personnel in the solvent room or area will wear a face shield. Acetone drums will be grounded during acetone transfer.

5.4 N_2F_4 is a highly toxic gas, and personnel exposure to even low concentration of N_2F_4 should be limited. Anyone working in an area where a faint odor of N_2F_4 exists should leave the area if the situation cannot be corrected within 30 minutes. If the odor becomes pungent, the area should be evacuated immediately. Also, it should be remembered that continued exposure to N_2F_4 has been reported to deaden the olfactory nerve, so it is important to have a fresh observer occasionally check an area where N_2F_4 may be present even though personnel working in the area cannot detect any odor. The operator can do this by going to a fresh air area for a few minutes and then return to the suspected area. N_2F_4 is a strong oxidizer and should not be allowed to contact hydrocarbon greases or solvents or other reducing chemicals. Moisture and all gases except dry nitrogen or dry helium must be excluded from the system. For this reason, all equipment used with N_2F_4 must be degreased prior to use. The reactions of N_2F_4 with other materials may be catalyzed by the presence of air (oxygen). Therefore, air should be rigorously excluded from systems containing N_2F_4 , and these systems should be maintained in a leak-free condition. All N_2F_4 valves must be operated by remote means.

5.5 Once the doors to the reactor bay to the PC-300 reactor area have been closed, do not open them until the entry shutdown has been performed. The control room door to the PC-300 area is not considered closed until the latch has been secured.

5.6 Before operating an N_2F_4 valve, be sure that (1) all personnel are in the control room, and (2) building compressed air is on before any remote valves are operated. Do not approach the N_2F_4 storage area if the red light is turned on.

5.7 Before opening the N_2F_4 manifold, be sure that the remote control valves nearest the storage tanks (MPC-211 and MPC-212) are closed.

5.8 PBEP solutions will be treated as explosive material since if a spill occurs or sufficient solvent evaporated, an explosive hazard could exist. Undiluted PBEP is highly sensitive.

5.9 Once the reaction has started, the solvent must continue flowing until either the reactors are cleared of explosive material (3 gallons of solvent), or the temperature of both reactors is below 50° C.

WARNING

Failure to keep solvent flowing may result in an explosion within the reactor.

5.10 All bottles containing PBEP are to be placed in trays during operations where spill may occur. Place PBEP bottles in aluminum or plastic trays during storage.

5.11 All PBEP processing waste is to be placed in TA wet pulp in explosive waste container and disposed of as liquid explosive per GOP 2-G15-10.

5.12 PBEP solution will never be permitted in any area of building 2354 other than the reactor bay and purification bay.

5.13 Before process gas is allowed to flow through valves MPC-314 or -315, the heaters of the fluoride traps shall be locked in "off" position. The key shall be held by the supervisor.

5.14 Because N_2F_4 is a strong oxidizer, N_2F_4 - acetone vapor mixtures can spontaneously detonate with (1) improper purging of air from the system, (2) improper passivation of the system, or (3) out-of-control high reboiler conditions. Therefore, the process must be vigorously adhered to during (1) the N_2 purging operations, (2) the N_2F_4 passivation operations, and (3) high temperature alarm testing.

6. OPERATIONS

6.1 PRELIMINARY OPERATIONS AND CHECK-OFFS

6.1.1 All operating personnel will perform at least one simulated emergency shutdown before start-up or at the beginning of each shift if operations are continuous.

6.1.2 Verify instrument air is on.

6.1.3 Make sure there are 1-1/2 bottles of high pressure nitrogen and sufficient liquid nitrogen to supply low pressure nitrogen gas.

6.1.4 Make sure electricity is on at the panel board and lights are on in the reaction area.

6.1.5 Pumps P-301 and P-302 will have previously been set to deliver the required feed rates.

6.1.6 If air has been in system:

- 6.1.6.1 If air has been introduced either to the compressor or the reactor system, purge the reactor and compressor system as follows, otherwise, go to Step 6.1.7.
- 6.1.6.2 Isolate 200 gas feed system from the compressor system by closing feed valves MPC-314 and -315, as well as the manifold selector valves if the TV-200 section is down. Close MPC-334.
- 6.1.6.3 Place collection vessels T-303A & B under drain valves MPC-318 and MPC-319. Use T-303A (MPC-318) for product and T-303B (MPC-319) for scrap collection. At the same time, visually check tubing in pump P-303 to be sure it is in good condition.
- 6.1.6.4 Drain valves MPC-317 and MPC-319 should be open.
- 6.1.6.5 Switch compressor K-301 speed control PRC-305 to manual. Then adjust PRC-305. Set point to 6 to 9 psi on air loader.
- 6.1.6.6 Switch Compressor K-302 flow controller FRC-307 to manual and open control valve FRC-307D.
- 6.1.6.7 Adjust reactor back pressure controller PRC-303 to a low level (below 25 psig).
- 6.1.6.8 Purge the compressor suction lines.
- 6.1.6.8.1 Pressurize the suction lines to 16 to 20 psig with nitrogen feed through MPC-306. Close MPC-306.
- 6.1.6.8.2 Turn on Compressors K-301 and K-302. Open discharge valve MPC-311 and evacuate the suction lines to 1 to 2 psig.
- 6.1.6.8.3 Repeat the pressurization and evacuation steps five more times.
- 6.1.6.9 Purge the reactors.
- 6.1.6.9.1 Place Controller PRC-305 on automatic and carefully pressurize the suction lines to full nitrogen pressure through MPC-306. Leave MPC-306 open. Set PRC-305 air loading at 70 ± 5 psig.
- 6.1.6.9.2 Adjust reactor back pressure valve PRC-303 to 100 psig.
- 6.1.6.9.3 Place K-302 on automatic at 12 ± 3 SCFH. Continue to purge for at least two minutes after the reactor system reaches 100 psig.
- 6.1.6.9.4 Place Compressor Controllers PRC-305 and FRC-307 on manual control. Then reduce PRC-303 setting to below 25 psig and bleed off nitrogen.
- 6.1.6.9.5 Repeat Steps 6.1.6.9.2 through 6.1.6.9.4 five more times. It is not necessary to place controllers PRC-305 and FRC-307 on automatic control for the cycling operations.
- 6.1.6.10 Shut down compressors.
- 6.1.6.10.1 Verify Compressor Controllers PRC-305 and FRC-307 are still on manual control. Verify reactor bulk pressure setting is still set below 25 psig back pressure.

- 6.1.6.10.2 Slowly reduce K-301 speed controller FRC-305 pressure to 30 psig setting.
- 6.1.6.10.3 Adjust K-302 flow controller setting as required to hold 30 psig suction pressure.
- 6.1.6.10.4 Close MPC-306.
- 6.1.6.10.5 When suction pressure drops to 0 psig or below, shut off compressors K-301 and K-302.
- 6.1.6.11 Raise pressure setting on PRC-303 to 400 - 500 psi to close valve.
- 6.1.6.12 Dispose of any liquid and explosive scrap and close drain valves MPC-317 and MPC-321 from C-302 and vent trap V-303.
- 6.1.7 If TVOPA or other contaminant has been in system
- 6.1.7.1 Verify that tubing in pinch valves and P-303 is acceptable for PBEP operations. Replace tubing if necessary.
- 6.1.7.2 Verify the R-301 reactor pressure drop monitoring system has been disconnected from (1) the R-301 inlet mixer, and (2) R-301 outlet line.
- 6.1.7.3 Verify that the 3/8 tempered water system is connected to E-301 (absorber) and E-306 (Freon chiller) exchangers. Also, verify that the spectacle flange will permit brine flow through the by-pass line. (The closed side of the flange is out).
- 6.1.7.4 Drain tanks T-301, T-302, and T-302A. Pump 1 to 2 gallons of methanol from T-301 into reactors. Flush out all four tanks with several small washes of acetone.
- NOTE: When filling tanks with acetone, position fill hose so acetone runs down side of tank to minimize static electricity buildup.
- 6.1.7.5 Partially fill tanks T-301, T-302, and T-302A with acetone.
- 6.1.7.6 Pump 6 gallons of acetone through system. Pump at least one gallon out of T-302A and at least two gallons each from tanks T-301 and T-302.
- 6.1.7.7 Recalibrate pumps P-301 and P-302 while pumping acetone in Step 6.1.7.6.
- 6.1.8 Verify reactor system has been pumped full of solvent by appearance of solvent at seal leg between colums C-301 and C-302. System checkout can be continued while filling reactor system.
- 6.1.9 Start up hot water circulation system by following steps:
- 6.1.9.1 Ensure that adequate water (70% \pm 5 %) level is in hot water drum V-306. Add water if necessary with level indicator controller LIC-306.
- 6.1.9.2 Bring water to required temperature by opening steam valve TRC-303; use automatic controller. Set back pressure valves BPV-304 and BPC-305 as required by instructions in Operating Log Book.

6.1.9.3 Turn on hot water pump P-304. Open manual valves to provide steam to TRC-302D. Open TRC-302D on manual instrument control and then switch to automatic control, or use automatic control.

6.1.10 Mixing Olefin

6.1.10.1 Verify that tank T-302 temperature is below 45° C.

6.1.10.2 Purge tank T-302 with N₂.

6.1.10.2.1 Set purge N₂ system pressure at 6 psig.

6.1.10.2.2 Pressure and vent tank T-302 three times. Vent tank through rupture disk by-pass valve.

6.1.10.2.3 Leave a small N₂ bleed going after purging tank (0.1 setting on purge rotometer). Also leave rupture disk by-pass valve open.

6.1.10.3 Verify that tank T-302 pressure has been relieved. Then carefully unbolt and open 4-inch port.

6.1.10.4 Verify that all valves under Tank T-302 are closed and that filter housings are full of acetone.

6.1.10.5 Fill Tank T-302 with acetone to specified level. Record volumes on transfer log.

NOTE: When filling tanks with acetone, position fill hose so acetone runs down side of tank to minimize static electricity buildup.

6.1.10.6 Start agitator in Tank T-302.

6.1.10.7 Add specified amount of olefin to Tank T-302. Record weight on transfer log.

6.1.10.8 Close and bolt 4-inch port.

6.1.10.9 Close rupture disk by-pass valve.

6.1.10.10 Adjust purge N₂ system pressure to 20 psig.

6.1.10.11 Using the 3/8-inch tempered water system and steam, heat the acetone in tank T-302 to 75° C. The tempered water from Tank T-302 should go to the drain.

6.1.10.12 Maintain a 75°C acetone temperature in Tank T-302 for 90 minutes.

6.1.10.13 Using 3/8-inch tempered water system, cool acetone in tank T-302 to specified temperature. Send cool water to drain line.

6.1.10.14 Realign the tempered water systems as follows:

6.1.10.14.1 Set the 3/8 tempered water system to maintain T-302 temperature as specified in the operating orders (normally between 55 and 65° C).

6.1.10.14.2 Start the 1/4" tempered water system to heat the traced lines and to exchangers E-306 and E-301. Send water back to the recirculation system.

6.1.11 Prepare other tanks as follows:

6.1.11.1 Fill Tank T-301 to level specified in operating orders. Record volumes on transfer log.

NOTE: When filling tanks with acetone, position fill hose so acetone runs down side of tank to minimize static electricity buildup.

6.1.12 Fill shutdown Tank T-302A with acetone. Record volumes on transfer log. Observe note after Step 6.1.11.1.

6.1.13 Observe feed tank level records LRA-301 and LRA-302 to be sure they are operating.

NOTE: Alarms are activated automatically at 13% low level.

6.1.14 Ensure that suction lines from pumps P-301 and P-302 are full of solvent by closing discharge valves, opening circulation valves, starting pumps, and operating them until lines are filled. Pump out of Tank T-301 for both pumps.

6.1.15 Turn on water to back flash preventor column when it is installed.

CAUTION: 200 process gas lines to back flash preventor column should be disconnected and plugged.

6.1.16 Valve Checks

6.1.16.1 Fill in hand valve check-off sheet.

6.1.16.2 Verify that following MPC valves are closed.

- (a) MPC-314 - 200 gas manifold
- (b) MPC-315 - 200 gas manifold
- (c) MPC-301 - Compressor suction
- (d) MPC-310 - Compressor vent valve
- (e) MPC-311 - Compressor discharge
- (f) MPC-312 - Reactor N₂ back pressure
- (g) MPC-306 - N₂ to compressors
- (h) MPC-330 through MPC-340 and MPC-342 - N₂F₄ recovery system

6.1.16.3 Verify that following MPC valves are open.

- (a) MPC-308 - Feed rate bomb

6.1.16.4 Verify that nitrogen flow valves for FI-304, FI-305 and FI-306 are open and flow rates are set as specified.

6.1.16.5 Close the following control valves:

FPC-303
PRC-306
LRC-303
FRC-305
PRC-304
PRC-301
FRC-307

6.1.16.6 Set regulator on high pressure nitrogen at 600-650 psi unless otherwise specified. Set one bottle to regulate about 25 psi below other bottle.

6.1.16.7 Set MPC-307 to flow through the recovery system.

6.1.17 Leak-check following items of equipment for a minimum of 15 minutes. (It is possible to perform the leak check during an overnight shutdown).

6.1.17.1 Leak-check process lines from 200 gas manifold through compressor to compressor discharge valves MPC-311. If 200 gas was left in system on shutdown, perform leak-check with 200 gas. Otherwise use nitrogen from feed valve MPC-206 to pre-pressurize system to 30 psig. Do not operate Compressor K-301. Do not waste 200 gas.

6.1.17.2 Pressurize recovery system to 15 psig, as follows:

6.1.17.2.1 Align valves as follows:

Open MPC-332
Open PRC-304D
Open PRC-306D

Verify that the following valves are closed:

LRC-303D
MPC-333
MPC-335
MPC-334
FRC-305D

6.1.17.2.2 Carefully pressurize recovery system to 15 ± 3 psig through reactor back pressure valve PRC-303D. Then close PRC-303D.

6.1.17.3 Leak-check reactor system at desired operating pressure between compressor discharge valve MPC-311 and back pressure valve PRC-303. Use solvent from P-301 to establish back pressure or admit nitrogen through back pressure valve MPC-312, then close.

6.1.17.4 If no pressure drop is observed in any part of system for 15 minute period, proceed. If leaks are indicated, consult with supervisor; further procedure will be made at his direction.

6.2 Start Up

6.2.1 Perform the following checklist before starting:

- (a) Solvent present in line from T-301 through solvent pump P-301 into first stage reactor R-301.
- (b) Pump oil in both P-301 and P-302.
- (c) The compressor line from TV-200 gas manifold to compressor discharge valve pressurized with from 2 to 15 psig of nitrogen.
- (d) The olefin line contains solvent from olefin feed tank T-302 through pump P-302 check valve near reactor R-301. Also, that the olefin feed line has been heated to 40 to 45° C.
- (e) The reactor system pressurized and pressure recorder controller PRC-303 set at reactor back pressure given in operating order book.
- (f) The reactor hot water system operating at temperatures given in operating order book.
- (g) The hand valve check-off list has been completed.
- (h) N₂ is flowing to C-301, C-302, and vent bottle.
- (i) Process gas vent lines from 300 section are connected.
- (j) Collection jugs T-303A and B are empty and in position in trays. Never remove one of the jugs without replacing it with a clean vessel.
- (k) The brine system is on and circulating through the 300 section.

6.2.2 Recovery Column Startup

6.2.2.1 Align control valves as follows:

LRC-303D - closed
FRC-305D - closed
PRC-306D - closed
PRC-304D - open

6.2.2.2 Align MPC valves as follows:

MPC-331 - open	MPC-337 - closed
MPC-332 - open	MPC-338 - closed
MPC-333 - closed	MPC-339 - closed
MPC-334 - closed	MPC-340 - closed
MPC-335 - open	MPC-341 - for system flow
MPC-336 - closed	MPC-342 - closed

6.2.2.3 Purge column with N₂.

6.2.2.3.1 Purge through rotometer FI-305 at a 50% setting.

6.2.2.3.2 After five minutes, close MPC-335 and observe pressure rise on PRC-304. Record pressure at which high pressure alarm sounds and then open MPC-335 again.

NOTE: If alarm does not sound below 25 psig,
terminate alarm test and notify supervisor.

- 6.2.2.3.3 Close MPC-335 and pressurize system to 20 psig and then open MPC-335 and vent system to 5 psig.
- 6.2.2.3.4 Repeat Step 6.2.2.3.3. five times.
- 6.2.2.3.5 Close valves opened in Steps 6.2.2.1 and 6.2.2.2. Open MPC-342.
- 6.2.2.4 Fill system with acetone.
- 6.2.2.4.1 Set PRC-306 on a 4 psig air loading on manual control.
- 6.2.2.4.2 Set LRC-303 on a 20% scale setting on automatic control.
- 6.2.2.4.3 Verify that brine valves to E-310, and C-301 are open.
- 6.2.2.4.4 Verify that valve MPC-332 is closed.
- 6.2.2.4.5 Pump acetone through system using pump P-301.
- 6.2.2.4.6 Set rotometer FI-310 to give an E-302 product outlet temperature of 100° F.
- 6.2.2.4.7 Verify that water to E-309 is turned on.
- 6.2.2.4.8 When level in the column (C-304) is sufficient for LRC-303 to start controlling, carefully close control valve LRC-303D and observe level rise on LRC-303. Record level at which alarm sounds.

NOTE: If the alarm does not sound below the 50%
level, terminate the test and notify supervisor.

- 6.2.2.4.9 Slowly open control valve LRC-303D with LRC-303 on automatic control and allow column to return to specified level.
- 6.2.2.5 Start heating the column.
- 6.2.2.5.1 Place FRC-303 on manual control and open control valve FRC-303D.
- 6.2.2.5.2 Open MPC-330 and slowly open hand valve in hot water line and record temperature at which tempered water alarm sounds.

NOTE: If the alarm does not sound below 200° F.
terminate test and notify supervisor.

- 6.2.2.5.3 Set reboiler tempered water temperature at 180° F.
- 6.2.2.5.4 Slowly adjust rotometer FI-310 to increase E-302 product outlet temperature to 140° F.
- 6.2.2.5.5 Record temperature at which column high temperature alarm sounds.

NOTE: If alarm does not sound below 70° F. notify supervisor.

6.2.2.5.6 When reboiler temperature reaches 140° F. and alarm test is completed, start P-302 using bypass line from shutdown tank.

6.2.2.5.7 Then slowly reduce E-302 product outlet temperature to 70° F. by adjusting FI-310.

6.2.2.5.8 With FRC-303 still on manual control, adjust central valve FRC-303D to maintain specified reboiler temperature.

6.2.2.5.9 When column lines out, put TRC-304 on automatic control and FRC-303 on automatic cascade control.

6.2.3 Reactor Startup

6.2.3.1 Start Compressors.

6.2.3.1.1 Verify that temperature on the traced line through compressor heads to the absorber is between 105 and 125° F.

6.2.3.1.2 Align MPC valves as follows:

- MPC-301 - closed
- MPC-306 - closed
- MPC-308 - open
- MPC-310 - closed
- MPC-311 - closed
- MPC-332 - open
- MPC-333 - closed
- MPC-334 - closed
- MPC-335 - open
- MPC-336 - closed
- MPC-337 - closed

6.2.3.1.3 Verify that FRC-305 is closed.

6.2.3.1.4 Verify that PRC-301 is closed and then open MPC-306 and MPC-301.

6.2.3.1.5 Slowly open PRC-301 on automatic control until a 5 psig suction pressure is achieved.

6.2.3.1.6 Set FRC-307 on automatic control with control valve FRC-307D closed.

6.2.3.1.7 Set PRC-305 at 9 psi air loading on automatic control and start compressor K-301.

6.2.3.1.8 When PRC-305 indicates 50 psig, start compressor K-302.

6.2.3.1.9 When PR -303 indicates a K-302 discharge pressure higher than reactor pressure, open MPC-311.

6.2.3.1.10 Adjust FRC-307 to specified startup flow rate. Adjust PRC-305 to a 70 psig setting.

6.2.3.1.11 Make a final check of 300 bay and lock 300 bay door.

- 6.2.3.1.12 Turn on red operating light.
- 6.2.3.1.13 Have the 200 operator open valves from specified 200 gas feed cylinders.
- 6.2.3.1.14 Close MPC-306 and when pressure on PR-301 is slightly lower than N_2F_4 pressure, open either MPC-314 or MPC-315 as specified. Record the time.
- 6.2.3.1.15 After N_2F_4 has been flowing for 15 minutes, slowly adjust FRC-307 to specified startup rate.
- 6.2.3.1.16 After specified startup N_2F_4 flow rate has been achieved, run a feed rate bomb test using procedure 6.3.9.
- 6.2.3.2 Switch pump P-302 to DEPECH feed.
- 6.2.3.2.1 Three minutes after specified N_2F_4 startup flow rate has been achieved, switch P-302 to DEPECH feed. Record the time.
- 6.2.3.2.2 Verify calibration of P-302.
- 6.2.3.2.3 Verify calibration of P-301.
- 6.2.3.2.4 When PBEP appears in plastic line under column C-302, close MPC-319 and open MPC-318.
- 6.2.3.2.5 Slum material in plastic jug under MPC-319.
- 6.2.3.3 Start Gas Chromatograph.
- 6.2.3.3.1 Verify helium gas is flowing and that the cylinder contains sufficient gas for the run.
- 6.2.3.3.2 Verify that calibration gas cylinder contains sufficient gas for run.
- 6.2.3.3.3 Turn on power and timer switches.
- CAUTION: Power without helium flow may burn out detector elements.
- 6.2.3.3.4 Obtain a readout on calibration gas.
- 6.2.3.3.5 When satisfied, stop analyzer at 90-100% cycle by turning off timer switch.
- 6.2.3.3.6 When ready for a reading, open MPC-336.
- 6.2.3.3.7 Then close calibration gas valve and open N_2F_4 sample valve from 300 section on the west wall of 200 bay hood. Open MPC-336.
- 6.2.3.4 When GC printouts indicate that acetone content of recycle N_2F_4 is below specified maximum limit, start N_2F_4 recirculation.
- 6.2.3.4.1 Place FRC-305 on manual control and open control valve FRC-305D to indicated bleed rate.
- 6.2.3.4.2 Place PRC-301 on manual control maintaining same flow rate.

6.2.3.4.3 Close MPC-335 and open MPC-334.

6.2.3.4.4 If a K-301 compressor suction pressure change is indicated, manually adjust PRC-301 to compensate. When suction pressure has stabilized, place PRC-301 back on automatic control.

6.2.3.4.5 Then place FRC-305 on automatic control and adjust, as required, until specified bleed rate has been achieved.

6.3 While Running -

6.3.1 Adjust FRC-307 setting as required to maintain TV-200 gas feed rate designated in operating orders.

6.3.2 Record items listed on operating log sheet at intervals specified or during any sudden changes in system.

6.3.3 Observe pressure and behavior of system and if flow should stop for any reason, immediately follow emergency shutdown procedure.

6.3.4 If reaction temperature should suddenly rise, check solvent feed pump P-301 to be sure it is pumping. If pump is operating properly, perform emergency shutdown procedure at once. (If pump is not operating properly, attempt to bring reaction under control by adjusting pump).

6.3.5 If seal leg between column C-301 and C-302 does not run full, notify supervisor. Do not shut down.

6.3.6 If seal leg from column C-302 blows, reduce gas flow to strippers at once to re-establish seal. Shut down if seal is not re-established within 3 minutes.

6.3.7 Maintain an adequate level in feed tanks T-301 and T-302. If tank level is too low, level alarm will sound.

WARNING

Do not let pumps suck air; explosion could result.

6.3.8 To switch from nearly empty gas feed vessel to full feed vessel:

6.3.8.1 Close valve(s) on nearly empty vessel (MPC-314 or MPC-315) and switch TV-200 section valve as required.

6.3.8.2 Immediately open for a short time (about 3-10 seconds) the valves from full vessel. Observe action of suction pressure controller PRC-301 so that suction pressure is maintained nearly constant.

6.3.8.3 Continue to open and close valve MPC-314 (or MPC-315) until full storage pressure is read on PR-302, then leave valve open.

6.3.9 At designated intervals, verify N_2F_4 flow rate using calibrated feed rate bomb V-301.

6.3.9.1 Leave MPC-308 open during normal operations.

- 6.3.9.2 Close MPC-314 or MPC-315 as applicable. Also close MPC-334.
- 6.3.9.3 Time by using a stop watch and record pressures from PR-301.
- 6.3.9.4 Open MPC-334 and MPC-314 or MPC-315 for short intervals until suction pressure is back under control.
- 6.3.9.5 Using the measured pressure drop over timed interval and charts, determine feed rate and compare to rate indicated on FR-301.
- 6.3.9.6 Adjust FR-301 setting as required to maintain specified feed rate.

6.4 Normal Shutdown Procedure

- 6.4.1 Shut down the reactor feed.
 - 6.4.1.1 Switch pump P-302 from DEPECH feed to acetone feed through bypass line. Wait 10 minutes.
 - 6.4.1.2 Place FRC-305 on manual control and maintain same bleed rate.
 - 6.4.1.3 Open MPC-335, close MPC-334, and close FRC-305.
 - 6.4.1.4 Adjust FRC-307 controller to 12 ± 3 SCFH setting and continue N_2F_4 flow for 45 minutes.
 - 6.4.1.5 Close MPC-314 or MPC-315 and carefully open MPC-306.
 - 6.4.1.6 Have 200 operator close storage bank valves.
 - 6.4.1.7 Purge compressors with N_2 for 30 minutes. Then close MPC-306.
 - 6.4.1.8 When compressor suction pressure, as measured on PRC-301, is below 30 psig, stop K-301.
 - 6.4.1.9 When PRC-305 pressure is below 30 psig, stop K-302.
 - 6.4.1.10 Close MPC-310 and MPC-332.
- 6.4.2 Shut down recovery column.
 - 6.4.2.1 When color in plastic line under column C-302 starts to lighten up, close MPC-318 and open MPC-319.
 - 6.4.2.2 Continue to pump acetone until through with Step 6.4.2.1.
 - 6.4.2.3 Then close hand valve in hot water line to reboiler.
 - 6.4.2.4 Flush the DP cells.
 - 6.4.2.4.1 Open hand valve on flush line near pump P-301 discharge.
 - 6.4.2.4.2 Open MPC-339 and flush for 5 minutes. Close MPC-339.
 - 6.4.2.4.3 Open MPC-338 and flush for 5 minutes. Close MPC-338.

- 6.4.2.4.4 If explosive has gotten into overhead system, flush through MPC-340 for 5 minutes with MPC-333 open. Otherwise, ignore this step.
- 6.4.2.5 Continue to pump acetone through column for 10 minutes. Then stop pumps P-301 and P-302.
- 6.4.2.6 When reboiler temperature drops below 45° C, close hand valve in cold water line to reboiler. Close MPC-330.
- 6.4.2.7 Unlock 300 bay door.

NOTE: This step may be performed anytime after Step 6.4.2.2.

- 6.4.2.8 Close hand valves in condenser overhead brine system.
- 6.4.2.9 Close hand valves in E-309 cooler water system.
- 6.4.3 Flush the DEPECH System.
- 6.4.3.1 Start cooling down tank T-302.
- 6.4.3.2 Set pump P-302 to pump from bypass line from tank T-301 and pump to tank-302. Start pump P-302.
- 6.4.3.3 When tank T-302 temperature is below 45°C., open port on top of tank.
- CAUTION: Be sure tank pressure has been relieved before unbolting cover.
- 6.4.3.4 Drain tank T-302 through drain line.
- 6.4.3.5 Flush acetone from tank T-302A back into tank T-302 through pump suction line.
- 6.4.3.6 Close drain valves under tank T-302 and add 2 gallons of Methylene Chloride to tank T-302.
- 6.4.3.7 Switch valves to feed acetone through DEPECH system from tank T-302A.
- 6.4.3.8 Switch pump P-302 suction back to DEPECH system. Continue to pump to tank T-302.
- 6.4.3.9 Verify that tank T-302 sight glass is empty. If not, pump it out at this time.
- 6.4.3.10 Increase pump P-302 to full pumping rate. Wait 15 minutes.
- 6.4.3.11 Switch to clean DEPECH filter. Wait 15 minutes.
- 6.4.3.12 Flush tank T-302 sight glass for 5 minutes minimum.
- 6.4.3.13 Shut down pump P-302.
- 6.4.3.14 Close valves under tanks T-301 and T-302.
- 6.4.3.15 Clean tank T-302.

- 6.4.3.15.1 Drain tank T-302 through drain line.
- 6.4.3.15.2 Rinse tank with 1 gallon of Methylene Chloride.
- 6.4.3.15.3 Rinse tank with 2 gallons of acetone.
- 6.4.3.16 Clean DEPECH filter housings.
- 6.4.3.17 Cool down reactors.
- 6.4.3.17.1 Turn off hot water circulating pump P-304.
- 6.4.3.17.2 When reactor temperature is below 45° C., close hand valves to FI-310.
- 6.4.3.18 Turn off tempered water systems.
- 6.4.3.19 Shut off brine cooling system to PC-300 unit.

CAUTION: Do not stop brine flow to TV-V-104 and V-105 unless they are empty. Loss of cooling to V-104 and V-105 will cause DFU to decompose.

- 6.4.3.20 Shut down hot water circulating pump. Turn off nitrogen valves to the stripper. Turn off nitrogen supply to TV-300 unit. Turn off recorders. Close MPC-317, MPC-318, and MPC-319.
- 6.4.3.21 If this is an overnight shutdown, apply leak check per Paragraph 6.1.17. Record each pressure and bay temperature.
- 6.4.3.22 Turn off bay lights and operating warning lights.

6.5 300 Bay Entry Shutdown for Maintenance

- 6.5.1 If shutdown is for entry into reactor bay for maintenance, follow normal shutdown procedure with following exception:
 - 6.5.1.2 Pump an additional 5 gallons of solvent through the reactors R-301 and R-302.
- 6.5.2 Purge the compressor and TV-200 gas lines by the following procedure:
 - a. Open nitrogen feed valve MPC-306 to pressurize compressor system and turn on compressors K-301 and K-302.
 - b. When compressor K-302 discharge reaches 200 psig, close nitrogen feed valve MPC-306 and open vent valve MPC-310 to TV-R-203.
 - c. When suction pressure reaches one to two psig, repeat previous two items five times, and then pressurize suction lines to 5 psig.
 - d. Close MPC-310. Stop compressor K-301. Close MPC-306.

6.5.3 Continue with normal shutdown procedure.

6.6 Emergency Shutdown Procedure

6.6.1 If reaction needs to be stopped quickly due to fire, explosion, plugging, or some general emergency, follow this procedure immediately:

NOTE: Red markers are beside each of the following stop buttons or valves.

- a. Stop compressors K-301 and K-302.
- b. Stop olefin feed pump P-302.
- c. Close compressor discharge valve MPC-311.
- d. Push emergency nitrogen purge button, if required.
- e. Open emergency cooling water valve if required and stop hot water circulation pump P-304.

WARNING

Extreme care should be used in considering this step. Disruption of the hot water flow will probably cause the olefin to gel in tank T-302 and in the feed lines.

- f. Close compressor feed valve MPC-301.

NOTE: Do not turn off the solvent feed pump P-301 unless the system is plugged or the main line has been ruptured.

- g. Close MPC-332, MPC-330, and MPC-334.

6.6.2 If time permits, do the following, preferably in order listed:

- a. Close all process gas block valves in TV-300 and TV-200 sections including MPC-314 and MPC-315.
- b. Close TRC-302 to stop steam flow to R-302.
- c. Move set point on TRC-301 to 50^o C. to obtain maximum cooling water flow. Note warning after Step 6.6.1.e.

6.6.3 If product material is spilled onto the floor, turn on red warning light.

6.6.4 Switch product collection MPC-318 or MPC-319 to jug containing lowest quantity of material.

6.6.5 Clear immediate area of all personnel, notify supervisor, and wait for further instructions.

6.6.6 When 10 gallons of solvent have been pumped into reactor system, turn off solvent pump P-301.

6.6.7 In the event it is not possible to pump acetone through the reactors in an emergency, the following steps are to be taken:

6.6.7.1 Notify the supervisor.

6.6.7.2 Pump acetone through MPC-339 (FRC-304A acetone flush valve) and control the C-304 cleaning by using level control valve LRC-303D.

NOTE: If MPC-339 is not suitable for this flushout at the time, the flushing could be carried out using MPC-338 (LRC-303A acetone flush valve).

6.7 Disassembly or Tightening of Joints

6.7.1 Turn on red light and reduce building personnel to absolute minimum required.

6.7.2 No joint in the process line shall be disassembled or tightened unless the supervisor is standing by.

6.7.3 Before disassembly begins, a bay entry shutdown, in accordance with Paragraph 6.6 of this procedure, will be performed. If it is not possible to perform bay entry procedure 6.6 and clear the reactor system of all explosive material, proceed to Step 6.8.

6.7.4 The individuals disassembling the joint shall wear the following as a minimum:

- a. Safety glasses.
- b. Hard hat and face shield.
- c. Blast protective gloves.

6.7.5 The individuals working on disassembly shall be shielded by a 1/4-inch thick plexiglass shield or equivalent.

6.7.6 No more than two persons shall be in the reactor area during disassembly.

6.7.7 Proceed with disassembly or tightening.

6.8 Plugged reactor procedure

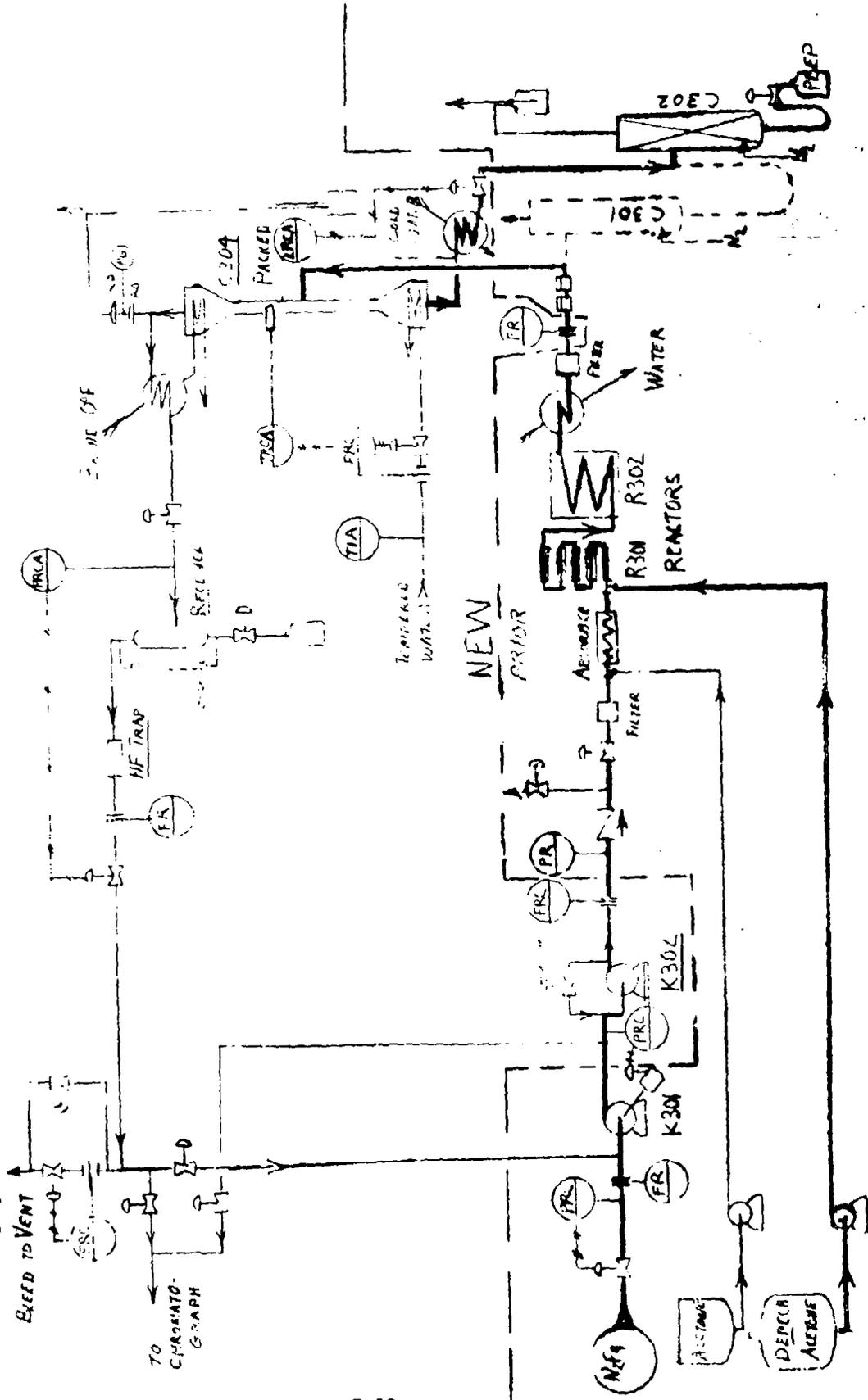
6.8.1 Attempt to clear both reactors R-301 and R-302 by pumping acetone through the remote solvent purge valves located at the entrance and exit of reactor R-301.

6.8.1.1 If reactor R-302 is cleared but reactor R-301 is still plugged, pump against the entry of reactor R-301 and close the remote purge valve. Disassemble the fitting between the purge valve at the reactor R-301 inlet and the check valve immediately upstream of the valve per Steps 6.8.1. Then attempt to back flush reactor R-301 by pumping acetone through the remote purge valve located at the R-301 outlet. Collect any material collected from R-301 backflush operation and treat as exotic explosive waste.

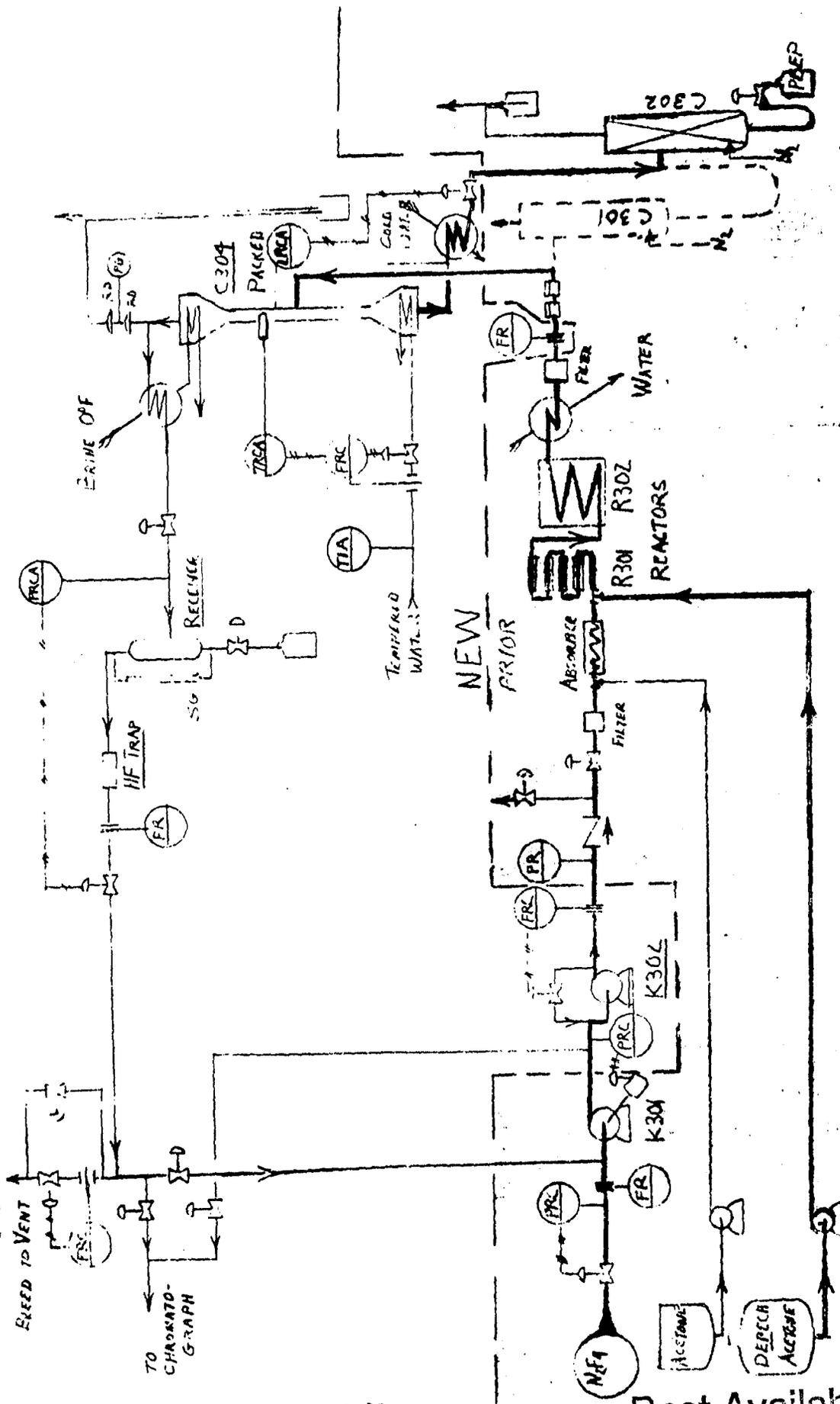
6.8.1.2 If reactor R-301 or the feed line remain plugged, disassemble any necessary fittings using remote operated hydraulic jacks.

END

BY JLM DATE 11/17/79 SUBJECT PC-300 SHEET NO. OF
CHECKED BY DATE RE-CYCLE GAS SYSTEM JOB NO.



BY J.M. DATE 1/11/54 SUBJECT PC-300 SHEET NO. OF
CHECKED BY DATE RECYCLE GAS SYSTEM JOB NO.



UNIT OPERATING PROCEDURE

PROGRAM
RESEARCH AND DEVELOPMENT
AREA
PCDE PLANT - BUILDING 2284
TASK
PC-400 PCDE MANUFACTURE

TITLE	PROCEDURE NO	REV. LTR.
PCDE MANUFACTURE - PC-400 SECTION	UOP 2R-PC60	1
	TOTAL NO. PAGES	18

TYPE I

HERCULES INCORPORATED
CHEMICAL PROPULSION DIVISION

PLANT
BACCHUS WORKS - PLANT 1

APPROVED BY		
Research and Development	SIGNATURE <i>M. J. [unclear]</i>	DATE 22 May 1974
Safety Department	SIGNATURE <i>J. E. [unclear]</i>	DATE 23 May 1974
Cognizant Engineer	SIGNATURE <i>A. M. [unclear]</i>	DATE 22 May 1974
	SIGNATURE	DATE

1. SCOPE

1.1 This document describes the procedure for synthesizing and preliminary purification of PCDE in a liquid phase flow reactor system.

2. REQUIREMENTS

2.1 Personnel working in this operation are responsible for knowing and following this procedure. This procedure can be redefined.

2.2 No person will conduct a live run unless he has conducted at least two inert runs with solvent, or a live run within the previous 90-day period.

2.3 Handle volatile solvents per GOP 2-G20-55.

2.4 Dispose of waste material per GOP 2-G15-10.

2.5 Observe building and personnel limits specified in GOP 2R-PC01.

2.6 All applicable safety rules specified in GOP 2R-PC01 shall be adhered to.

3. APPLICABLE DOCUMENTS

GOP 2-G20-55	Handling and Use of Volatile Solvents
GOP 2-G15-10	Waste Disposal
GOP 2R-PC01	Building Limits, Safety Rules, and Building and Equipment Inspection
GOP 2-G25-12, Rev. 1	TVOPA/PBEP/PCDE Spill Cleanup
Operating Orders	Bound Shift Log Book

4. MATERIALS AND EQUIPMENT

4.1 MATERIALS

	DESCRIPTION
DMK	Acetone
Lime	NR
NaOH	NR
H ₂ SO	NR
TA	Triacetin
Molecular Sieve	See Appendix A
High pressure Nitrogen	Nitrogen gas in cylinders, full pressure 2200 psi
Low pressure Nitrogen	Liquid nitrogen available as gas at 125-150 psig, furnished in LS 156 cylinders or equivalent

4.1 MATERIALS (Cont'd)

	DESCRIPTION
Wood Pulp	NR
Cloth	Clean, untreated
MDC	Methylene Chloride
TMA	Trimethylamine
Halocarbon 18CS/100 or fluorolube MO-10B or turbine 15	Positive displacement pump oil

4.2 EQUIPMENT

	DESCRIPTION
Injection System	Defined on flow sketch
Respirators	Vapor type, air line, or mask with Type N cartridge
Slum Pot	Clean seamless aluminum container
Ion exchange feed pump hose	Viton, 3/8 OD x 3/32 wall
Pinch Clamps	Hose clamp
PCDE Sampler	Plastic pi-pump and polyethylene pipette
Tubing	Nordel, Viton, gum rubber, assorted sizes
PCDE Sample Bottles	Polyethylene sample bottles, 200 cc's
Sample Carrier	Drawing 08H00094
Sampling Assembly	Rubber stopper fitted with a squeeze bulb pressurizing plastic tube and discharge plastic tube and with a venting bulb or a third "venting" tube
Bottles	5 gallon polyethylene with nylon harness
Jug	5 gallon, 7 gallon polyethylene, trans- lucent, heavy wall
Trays	Plastic or aluminum, approximately 1-1/2 ft x 2 ft x 6" deep
Transfer Boxes	Wood with polyethylene foam liner
Beaker	Polyethylene, 1000 cc
Funnel	Polyethylene, 3" to 6"
Refrigerator	NR

4.2 EQUIPMENT (Cont'd)	DESCRIPTION
Shoes	Safety, conductive
Glasses	Safety, prescription or plain lenses
Gloves	Neoprene
Hard Hat	with face shield
Hand Truck	2 wheel flat bed with sides
Scale	Dial, 100

5. SAFETY

5.1 Eye protection shall be worn within the confines of Building 2284 including all areas of operation and storage.

5.2 Avoid exposure to and inhalation of solvent or TMA.

5.3 Acetone is a volatile, flammable liquid. During any transfer it shall be allowed to flow down the side of receiving vessel or discharge hose shall be at bottom of receiving vessel. During operations hood safety doors will be closed.

5.4 TMA is a flammable, alkaline, colorless gas at room temperature and pressure. It has a characteristic fishy odor in lower concentrations. In higher concentrations (100-500 ppm) the fishy odor is no longer detectable and odor is more like ammonia. It is readily liquified and is shipped in steel cylinders as a liquified gas under its own vapor pressure. It is very soluble in water and in various organic solvents. A threshold limit value of 10 ppm is suggested. Inhalation of higher concentrations of TMA will produce moderate to severe irritation of upper respiratory tract and lungs (suitable gas masks should, therefore, be provided for exposed workers). Workers who are exposed continuously to trimethylamine (TMA) should wear eye protective devices to prevent injury in case of spillage. Bronchitis and conjunctivitis may result from exposure to vapors. Direct contact of TMA with skin and mucous membranes may cause burns; dermatitis and conjunctivitis occur occasionally after prolonged exposure to vapors but sensitization has not been observed. Both liquid and vapor TMA are highly irritating to eyes, and injury to eyes may occur if proper care is not given at time of exposure. However, odor is detectable at low concentrations to give adequate warning of its presence and no bad effects have been observed on persons exposed for long periods of low concentrations.

5.5 During operations yellow light on top of Building 2284 will be turned on.

5.6 PBEP and PCDE solutions will be treated as explosive material since if a spill occurs or sufficient solvent evaporated, an explosive hazard could exist. Undiluted PBEP and PCDE is highly sensitive.

5.7 All bottles containing PBEP or PCDE are to be placed in trays during operations where spill may occur. Place PBEP and PCDE bottles in aluminum or plastic trays during storage.

5.8 All PBEP or PCDE processing waste is to be placed in TA wet pulp in explosive waste container and disposed of as liquid explosive per GOP 2-G15-10.

5.9 Process solvents attack all plastics. Inspect hoses and plastic containers for evidence of damage.

6. OPERATIONS

6.1 PRELIMINARY OPERATIONS AND CHECK OFF

NOTE: As the hoods contain flammable materials it will be necessary to keep the hood doors closed except to adjust pump rates, remove hose clamps, and normal maintenance. The doors act as a flash shield. The doors will be kept closed whenever any pump is operating in the hood.

6.1.1 Verify that instrument air is on.

6.1.2 Make certain electricity is on at panel board and lights are on in reaction room.

6.1.3 Ascertain that pumps P-401, P-403, P-404, and P-405 have been set to deliver required feed rates.

6.1.4 Verify that columns C-403 and C-404 has been prepared in accordance with Appendix A.

6.1.5 Check to make certain following valves and pinch clamps are in their proper position.

- (a) Reactor drain line HC-404, HC-405, HC-406, HC-407 all closed
- (b) Back pressure control valve BPC-401 closed at proper setting.
- (c) Drain lines HC-409, HC-410, HC-411, HC-412, HC-413, HC-414 all closed.

6.1.6 Prepare acid mixture in accordance with directions given in Appendix A.

6.1.7 Turn on cooling water to reactor R-401 at proper flow rate and temperatures as directed in operating log book.

6.2 START UP

6.2.1 Perform following checklist before starting:

- (a) Valve and clamps set as noted in 6.1.5.
- (b) Pump oil in both P-403 and P-404.
- (c) Cooling water to reactors on at proper rate and temperature.
- (d) Check water level control system on feed to P-408 to make certain float valve is working.

- (e) Make certain temperature recorder is turned on and operating.
- (f) Make certain T-401 contains enough solvent to start run. Record weight.

6.2.2 Start up pumps and flows in following manner.

6.2.2.1 Start P-403 feeding MDC.

6.2.2.2 Using FRC-401 bring flow of TMA to flow setting indicated in operating log.

6.2.2.3 Turn on acid pump P-404.

NOTE: Inspect tubing and pumps for any leaks.

6.2.2.4 Start pump P-404 and inspect system for leaks.

NOTE: Monitor temperature carefully during start up to make certain feed is flowing properly.

6.3 RUNNING-REACTION

6.3.1 Allow product to collect in T-404 for approximately two hours. The water phase will overflow into T-405 as needed.

6.3.2 Empty T-405 to waste tank in following manner.

6.3.2.1 Make certain T-406 has sufficient capacity to hold contents of T-405.

6.3.2.2 Inspect T-405 for evidence of product phase. If there is no product phase or product phase is below pump suction outlet, proceed with next step. If product phase is sufficient to be near or above pump suction, go to Step 6.3.2.6. Do not pump to T-406.

6.3.2.3 Position clamps to route waste from T-405 to T-406.

6.3.2.4 Start P-407 and empty T-405.

6.3.2.5 Stop P-407. Go to Step 6.3.3.

6.3.2.6 Determine source of product stream and whether it is still entering T-405.

6.3.2.7 Shut down using normal shutdown procedure if leak cannot be stopped.

6.3.2.8 Pump product phase to T-403 using following steps:

(a) Place P-407 discharge hose to pump to T-404.

(b) Start P-407. Pump until product phase has been pumped to T-404 then pump an additional 2 gallons of water.

NOTE: This clears pump of any product

(c) Stop P-407.

(d) Replace P-407 discharge hose to T-406.

6.3.2.9 Start up process again using start-up procedure. Begin extraction start-up as instructed in log book.

6.3.3 At designated intervals make feed rate checks on feed solution P-401 speed, solvent flow (T-401), and acid flow (T-402).

6.3.3.1 Use dip stick to measure content of T-402.

6.3.3.2 Record level of T-401 and T-402.

6.3.3.3 With time and level information calculate flow rates of feed solution and acid flow.

6.3.3.4 Periodically check rotometers to make certain water flows are at proper rates.

6.3.3.5 Periodically check rubber tubing for leaks and signs of deterioration.

6.4 EXTRACTION SYSTEM START-UP

NOTE: Sufficient material must have accumulated in T-404 from reactor hood or feed material must have been transferred into T-404 from another source (see Section 6.15).

6.4.1 Turn on water to C-401 (FI-402) and C-402 (FI-403) at settings specified in operating log. Pump P-408 must be on.

NOTE: This water will overflow to T-405 making necessary more frequent transfers of waste to T-406.

6.4.2 When water begins to overflow to T-405 from C-401, position clamps to route P-405 discharge to extraction column C-401.

6.4.3 Start P-405.

6.4.4 Check P-406 discharge and suction lines to make sure lines are not clamped.

6.4.5 Watch C-401 for evidence of product and when product phase has reached desired level start P-406.

NOTE: Adjust pump rates on P-406 to maintain interface on both C-401 and C-402.

6.4.6 Take care to maintain interface in C-401 and C-402 between limits indicated on columns. This is done by controlling the pump rates of P-406.

6.5 NORMAL SHUTDOWN - REACTION

NOTE: Extraction section may still be operating.

6.5.1 Stop P-401.

6.5.2 Wait three minutes then turn off TMA flow using FRC-401.

6.5.3 Continue to pump solvent (P-402) for 5 more minutes.

- 6.5.4 After pumping solvent (6.4.3) for 5 minutes, stop P-402.
- 6.5.5 Stop P-404.
- 6.5.6 If extraction step is not in operation stop P-408.
- 6.5.7 When extraction step is completed, perform a maintenance system flush (6.7).
- 6.6 NORMAL SHUTDOWN - EXTRACTION

NOTE: Normally the reaction step will be complete and all product will be in either T-404 or T-403.

- 6.6.1 Monitor interface level on T-404 and note when interface is at bottom of T-404.
- 6.6.2 When product phase has been pumped from T-404, continue to pump until approximately one gallon of aqueous phase has been pumped also.
- 6.6.3 Stop P-405 and stop water flow FI-402.
- 6.6.4 Stop P-406 when interfaces are at minimum contact marks.
- 6.6.5 Make certain T-405 will hold aqueous phase in T-404. If necessary pump T-405 to T-406.
- 6.6.6 Pump contents of T-404 to T-406 as follows:
 - (a) Place P-407 pump suction in T-404.
 - (b) Start P-407.
- 6.6.7 When T-404 is empty, stop P-405.
- 6.6.8 Wait for several minutes to allow C-401 interface to stabilize.
- 6.6.9 Change pump head and tubing in pump P-404. Use 7015 head and viton tubing.

NOTE: Anytime MDC is to be pumped a 7015 head and viton tubing must be used in P-404.
- 6.6.10 Add 1 gallon of MDC to T-404.
- 6.6.11 Start P-405 and pump MDC to C-401.

NOTE: Do not turn on water.
- 6.6.12 When MDC has been removed from T-404, stop P-405 and wait until interface stabilizes again.
- 6.6.13 Start P-406 and pump product phase to C-402 and T-403.
- 6.6.14 If necessary to recover additional product in C-401, repeat Steps 6.5.6 through 6.5.13.

- 6.6.15 Drain the contents of T-403 into T-404 by opening clamp HC-417.
- 6.6.16 Close clamp HC-417 when T-403 is drained.

NOTE: The product is now ready for settling prior to drying step or recycle through extraction step.

6.6.17 If recycle through extraction step is necessary, start up extraction step per procedure, Step 6.3 making certain the proper pump head and tubing are used in P-405.

6.6.18 If recycle is not necessary, allow product phase to settle for time indicated by supervisor.

6.6.19 Empty T-405 to T-406.

6.7 DRYING

6.7.1 Complete this portion of procedure only after approval of supervisor.

6.7.2 Set pump speed as indicated in operational log book.

6.7.3 Set clamps to route from T-404 to dry columns.

(a) Open HC-419

(b) Close HC-418

6.7.4 Make certain C-403 and C-404 have been prepared according to Appendix A.

6.7.5 Place a product receiver in position.

6.7.6 Place column discharge hose in T-407 and remove HC-413.

6.7.7 Close hood doors to hoods 2 and 3.

6.7.8 Start P-405.

6.7.9 Pump until interface on T-404 is just at tank bottom.

NOTE: Do not pump any aqueous phase into column.

6.7.10 Stop P-405.

6.7.11 Change P-405 suction and pump MDC from bucket.

6.7.12 Start P-405 and pump MDC until discharge for C-404 has cleared.

6.7.13 Stop P-405.

6.7.14 Carefully stir product in T-407 and sample.

6.7.15 Load out product from T-407 to product cans when directed by supervision using procedure in Appendix C.

6.8 PROCESS FLUSH

6.8.1 Reactor System

6.8.1.1 Place a 5 gallon jug containing 3 gallons MDC or DMK in position T-304.

6.8.1.2 Place 7015 head and viton tubing on P-401 if MDC is used.

6.8.1.3 Pump flush solution through system to T-404.

6.8.1.4 Drain system to slum bag from HC-404, HC-405, HC-406 and HC-407.

6.8.2 Extraction System

6.8.2.1 Pour 5 gallons of MDC into T-404.

6.8.2.2 Set clamps as follows:

- (a) Close HC-415
- (b) Close HC-419
- (c) Open HC-416
- (d) Open HC-418

6.8.2.3 Set P-405 pump rate at maximum flow.

6.8.2.4 Start P-405.

6.8.2.5 When level of MDC in C-401 is within 1 or 2 inches of top, start P-406 setting pump rate to hold MDC level within 1 inch of the top of C-401. Clamp C-402 discharge to D-406 so C-402 will fill.

6.8.2.6 When C-402 is filled stop P-405.

6.8.2.7 Pump from C-401 to C-402 to T-403 until C-401 and C-402 are empty.

6.8.2.8 Stop P-406.

6.8.2.9 Slum contents of T-403 directly to a prepared slum pot using drain to T-404 and opening HC-417.

6.9 EMERGENCY SHUTDOWN

6.9.1 If reaction needs to be stopped quickly due to fire, explosion, plugging, or some general emergency, follow this procedure immediately.

- (a) Turn off pumps P-401, P-403, P-404, P-408, P-405, P-406, and P-407.
- (b) Stop TMA flow FRC-401.

6.9.2 If time permits, do following:

- (a) Turn off reactor cooling water system.
- (b) Close TMA cylinder valve.
- (c) Close water rotometer valve to FI-401.

6.9.3 Clear immediate area of all personnel, notify supervisor, and wait for further instructions.

6.10 DISASSEMBLY OR TIGHTENING OF METAL JOINTS

6.10.1 Turn on building warning light and reduce building personnel to absolute minimum required.

6.10.2 No joint in process line shall be disassembled or tightened, unless supervisor is standing by.

6.10.3 Before disassembly begins, a system flush with Paragraph 6.8 of this procedure will be performed.

6.10.4 The individuals disassembling the joint will wear the following protective gear as a minimum.

- (a) Safety glasses.
- (b) Hard hat and face shield.
- (c) Blast protective gloves.

6.10.5 The individuals working on disassembly shall be shielded by a 1/4 inch thick Plexiglas shield, or equivalent.

6.10.6 No more than two persons shall be in reactor room during disassembly.

6.10.7 Proceed with disassembly or tightening.

6.11 WASTE DISPOSAL

6.11.1 Inspect the bottom of T-406 for evidence of product phase.

6.11.2 Remove product phase by draining or by using long stem sample pump. Collect product in 5 gallon drums.

6.11.3 Start T-406 agitator, M-401.

6.11.4 Very slowly add 1# of lime per 100 gallons of waste.

6.11.5 Place pH meter probes into liquid phase and measure pH.

6.11.6 Slowly add 50% NaOH to T-406 until pH of solution exceeds 11.0.

NOTE: Use rubber gloves and face mask in handling NaOH.

- 6.11.7 Stir for 20 minutes.
- 6.11.8 Slowly add H_2SO_4 to T-406 until the pH is between 5.5 and 6.5.
- 6.11.9 Stir for 10 minutes to make certain pH has stabilized.
- 6.11.10 Drain T-406 to waste pond.
- 6.11.11 Stop agitator when tank is emptied.

6.12 PROCESS LINE PLUG REMOVAL

- 6.12.1 Isolate the position of the plug using various drain positions.
- 6.12.2 Pump back through the appropriate drain valves using one of the pumps in hood and a temporary line hookup.

NOTE: Obtain supervisors approval before any pumping is started.

- 6.12.3 If plug cannot be broken loose, remove the section of line which is plugged making certain that any part of the line disconnected or cut has been flushed.

NOTE: Use normal disassembly procedure 6.10.

6.13 CLEANUP OF PRODUCT

NOTE: PCDE product may need further treatment using amberlyst.

- 6.13.1 Collect all product to be cleaned in T-404.
- 6.13.2 Using Appendix A, clean C-402 and refill with amberlyst resin instead of mole sieves.
- 6.13.3 Using procedure for drying (6.7), pass product through amberlyst column.
- 6.13.4 Flush line from T-404 to C-402 with MDC using procedure 6.8.
- 6.13.5 Refill C-402 with molecular sieves using procedure outlined in Appendix A.

6.14 PRODUCT CONCENTRATION

NOTE: Product can be PCDE or PBEP in containers through which the product level can be seen. The product must be in methylene chloride.

- 6.14.1 Start hood fan.
- 6.14.2 Place product jug in position in hood #3.
- 6.14.3 Mark product jug with a piece of tape at final liquid level desired as instructed by supervisor.

- 6.14.4 Open air needle valve on dry air supply line and allow entrapped moisture to purge to hood floor.
- 6.14.5 Insert sparge hose in container of product.
- 6.14.6 Tape hose in position to keep hose end near bottom of product container.
- 6.14.7 Adjust needle valve on dry air line to give desired agitation in container.

NOTE: Product solution should be agitating but not splashing.

- 6.14.8 Continue agitating (concentrating) until liquid reaches the desired level.
- 6.14.9 Remove sparge hose being careful to wipe with cloth dampened with methylene chloride.
- 6.14.10 Sample product, if required, then remove from hood.
- 6.14.11 Rinse sparge hose with methylene chloride, wipe dry and store in plastic bag taped around top.

6.15 SPECIAL T-404 FILL

NOTE: This procedure is used for filling T-404 in order to process material through the extraction system without using the reaction system.

- 6.15.1 Disconnect P-401 from Hood #1 and place in Hood #3. The power connection will be made outside of hood using an extension cord.
- 6.15.2 Route a 5/8" Nordel rubber hose from Hood #3 to T-404 in Hood #3 through holes provided in front side of hood.
- 6.15.3 Connect P-401 discharge to the Nordel tubing.
- 6.15.4 Place 5 gallon drum containing solution to be pumped in place in Hood #3.
- 6.15.5 Put P-401 suction into 5 gallon drum.
- 6.15.6 Close Hood #3 down.
- 6.15.7 Start P-401 and empty 5 gallon drum.
- 6.15.8 Remove drum from Hood #3.
- 6.15.9 Repeat Steps 6.15.4 through 6.15.8 until T-404 is full or all material has been transferred.

NOTE: If T-404 will not hold all material to be transferred start extraction system and repeat Steps 6.15.4 through 6.15.8 during extraction operation.

- 6.15.10 When all material has been transferred place 5 gallon drum containing 2 gallons acetone and repeat Steps 6.15.5 through 6.15.8.
- 6.15.11 Remove P-401 and put in place in Hood #1.
- 6.15.12 Remove Nordel tubing and store in plastic bag in utility room.

END

APPENDIX A

CHANGING MOLECULAR SIEVE COLUMN PC-C-402

1. Pump MDC through C-402 using the following steps if column has not been previously flushed with MDC.
 - 1.1 Pour 3-4 gallons MDC into T-404.
 - 1.2 Position switch to open MDC-402 and close MPC-401.
 - 1.3 Place a 5 gallon container in position T-407 to catch MDC.
 - 1.4 Remove HC-413.
 - 1.5 Start P-405 and collect MDC in T-407.
2. Clamp the hose connecting C-402 top and bottom.
3. Drain the line from P-405 into a jug by removing HC-412. Replace HC-412 when drained.
4. Disconnect C-402 leaving the hose clamps on.
5. Remove the column from the unistrut brackets.
6. Unload column as follows:
 - 6.1 Open top flange on C-402 and empty molecular sieves into slum pot bag.
 - 6.2 Tag and dispose of molecular sieves per GOP 2-G15-10 as exotic waste.
7. Load column as follows: (Load only if it is to be used within 24 hours).
 - 7.1 Pour molecular sieves into column until full (~ 15 pounds).

NOTE: If 13x sieves are used they must be carefully prewetted with MDC.
 - 7.2 Replace screen support and screen and tap flange and tighten bolts to 75 ft.lbs.
 - 7.3 Tighten bottom flange bolts also.
 - 7.4 Replace column.
8. Connect hose to top and bottom of column and remove hose clamps.
9. Pour 2 gallons of MDC into T-404.

10. Position switch to open MPC-402 and close MPC-401.
11. Place a jug in T-407 position.
12. Pump MDC through column into T-407.

APPENDIX B

ACID MAKEUP

NOTE: Whenever handling H_2SO_4 , wear rubber suit and face mask and Neoprene gloves.

CAUTION: Add acid very slowly to prevent over heating and spattering.

1. Check level in T-402 and determine gallons of acid in tank.
2. Add sufficient water to bring liquid level to at least 40 gallon level.
3. Determine water added.
4. For every gallon of water added, slowly add the amount of 96 percent H_2SO_4 designated in operating log book.
5. Stir with stirring rod for approximately 5 minutes.

PCDE PRODUCT LOADOUT

22 May 1974

NOTE: Use Masterflex pump with type 7015 head and viton tubing. Make certain pump is in plastic tray and tubing is in good shape for pumping.

1. Prepare mole sieves by soaking 13x sieves in MDC. Keep wet until used.
2. Tare 5 gallon shipping cans and mark tare weight on can.
3. Place can in tray on scale and put funnel into opening.
4. Place pump suction tubing into product tank.
5. Place pump discharge tube into can opening.
6. Hold pump discharge tubing and turn on pump. Hold tubing while pumping.
7. Fill can to 50 pounds net product.
8. Add 300 cc mole sieves to can.
9. Replace can lid and torque to 120 ft.lbs.
10. Repeat for each can. Record can No. and weight in log book.

UNIT OPERATING PROCEDURE

PROGRAM	RESEARCH AND DEVELOPMENT
AREA	PILOT PLANT
TASK	PC-400 PCDE MANUFACTURE

TITLE	PROCEDURE NO.	REV. LTR.
PCDE SYNTHESIS - PC-400 SECTION BUILDING 2354	UOP 2R-PC41	2
	TOTAL NO. PAGES	8

TYPE I

HERCULES INCORPORATED
CHEMICAL PROPULSION DIVISION

UNCONTROLLED
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PLANT	BACCHUS WORKS - PLANT 1
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APPROVED BY		
Research & Development	SIGNATURE <i>[Signature]</i>	DATE 18 Sept 1974
Safety Department	SIGNATURE <i>[Signature]</i>	DATE 19 Sept 1974
Cognizant Engineer	SIGNATURE <i>[Signature]</i>	DATE July 31, 1974

1. SCOPE

1.1 This document describes the procedure for synthesizing PCDE in Building 2354 per the following sections:

- (a) 6.1 Preparations
- (b) 6.2 Reaction
- (c) 6.3 Cleaning and Disassembly
- (d) 6.4 Test for Explosive
- (e) 6.5 Acid Makeup
- (f) 6.6 Emergency Shut Down

2. REQUIREMENTS

2.1 Personnel working in this operation are responsible for knowing and following this procedure.

2.2 No person will conduct a live run unless he has conducted at least two inert runs with inert materials and solvent, or a live run within the previous 90-day period.

2.3 Handle volatile solvents per GOP 2-G20-55.

2.4 Dispose of waste material per GOP 2-G15-10.

2.5 Observe building and personnel limits specified in GOP 2R-TV01.

2.6 All applicable safety rules specified in GOP 2R-TV01 shall be adhered to.

2.7 This procedure may be redlined.

3. APPLICABLE DOCUMENTS

GOP 2-G20-55	Handling and Use of Volatile Solvents
GOP 2-G15-10	Waste Disposal
GOP 2R-TV01	Building Limits and Safety Rules
GOP G-25-22	Fluoro Chemical Spill Cleanup
Operating Orders	Bound, Shift Log Book

4. MATERIALS AND EQUIPMENT

4.1 MATERIALS	DESCRIPTION
DMK	Acetone
MDC	Methylene Chloride
TA	Triacetin

4.1 MATERIALS (Cont'd)	DESCRIPTION
Low Pressure Nitrogen	Liquid nitrogen available as gas at 125-150 psig, furnished in bulk storage tank
Wood Pulp	NR
Cloth	Clean, untreated
H ₂ SO ₄	Reagent Grade
PBEP	NR
TMA	NR
TVOPA detector	Bottles, 1,2, and 3
4.2 EQUIPMENT	DESCRIPTION
Reaction System	Defined on process flow sheet, sketches PC-400-10 and PC-400-11
Respirator	Vapor type, air line, or mask with type N cartridge
Slum Pot	Clean, seamless aluminum container
Feed pump P-303 Hose	3/8" OD x 1/16" wall, Viton
Circulating Pump Hose, P-401	Viton, TAT Pump Co.
Pinch Clamps	Hose clamp
Liquid explosive sampler	Polyethylene pipette or syringe and air bulb
Liquid explosive sample bottles	Polypropylene sample vials, 4 oz.
Sample Carrier	Drawing 08H00094
Product container	5-gallon polyethylene bottle, grey
Jug	1-2,2-, and 7-gallon polyethylene translucent, heavy wall
Trays	Plastic or aluminum, approximately 1-1/2 ft x 2 ft x 6 inches deep
Transfer Boxes	Wood with polyethylene foam liner
Beaker	Polyethylene, 1000 cc
Washing waste drum	55 gal, hi density, polyethylene, closed head

4.2 EQUIPMENT (Cont'd)	DESCRIPTION
Funnel	Polyethylene, 3 in. to 6 in.
Refrigerator	NR
Shoes	Safety, non-conductive
Strap	Shoe, conductive
Glasses	Safety, prescription or plain lenses
Safety Suit	Two piece rubberized suit
Gloves	Neoprene
Hard Hat	with face shield
Hand truck	two-wheel flat bed with sides
Scale	Dial, 0-75 pounds
Scale	Over-under 300 lbs.

5. SAFETY

5.1 Eye protection shall be worn when within the confines of the pilot plant, including all areas of TV-100, TV-200, PC-300, and PC-400 sections.

5.2 Avoid exposure to and inhalation of solvents or TMA.

5.3 During transfer of solvent and solutions, the hose is to be positioned to allow the solvent and solutions to run down the side of the vessel. The solvent and solutions should not be allowed to fall free when filling the vessel due to possible static electricity buildup.

5.4 TMA is a flammable, alkaline, colorless gas at room temperature and pressure. It has a characteristic fishy odor in lower concentrations. In higher concentrations (100-500 ppm) the fishy odor is no longer detectable and the odor is more like ammonia. It is readily liquified and is shipped in steel cylinders as a liquified gas under its own vapor pressure. It is very soluble in water and in various organic solvents. A threshold limit value of 10 ppm is suggested. Inhalation of higher concentrations of TMA will produce moderate to severe irritation of the upper respiratory tract and the lungs (suitable gas masks should, therefore, be provided for exposed workers). Workers who are exposed continuously to trimethylamine should wear eye protective devices to prevent injury in case of spillage. Bronchitis and conjunctivitis may result from exposure to the vapors. Direct contact of TMA with skin and mucous membranes may cause burns; dermatitis and conjunctivitis occur occasionally after prolonged exposure to vapors, but sensitization has not been observed. Both the liquid and vapor TMA are highly irritating to the eyes, and injury to the eyes may occur if proper care is not given at the time of exposure. However, the odor is detectable at low concentrations to give adequate warning of its presence and no bad effects have been observed on persons exposed for long periods to low concentrations.

- 5.5 Once the doors to the reactor bay to the PC-400 reactor area have been closed, do not open them until the entry shutdown has been performed.
- 5.6 During operations the yellow light on top of the pilot plant will be turned on.
- 5.7 PBEP and PCDE solutions will be treated as explosive material since if a spill occurs or sufficient solvent evaporated, an explosive hazard could exist. Undiluted PBEP and PCDE are highly sensitive.
- 5.8 All bottles containing PBEP or PCDE are to be placed in trays during operations where spill may occur. Place PBEP and PCDE bottles in aluminum or plastic trays during storage. This requirement does not apply to 55-gal polyethylene drum.
- 5.9 All PBEP and PCDE processing waste is to be placed in wood pulp in explosive waste container and disposed of as liquid explosive per COP 2-G15-10.
- 5.10 PBEP or PCDE solution will never be permitted in any area of Building 2354 other than the reactor bay and purification bay.
- 5.11 Process solvents attack all plastics. Inspect hoses and plastic containers for evidence of damage.
- 5.12 Sulfuric acid is a corrosive and dehydrating agent. During dilution with water it gets hot. Spattering and/or boiling may result. Avoid sulfuric acid contact with eyes, skin or clothing. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes and call extension "2114" for medical aid.

6. OPERATIONS

6.1 PREPARATIONS

6.1.1 TMA Cylinders Hook-Up and Makeup

- 6.1.1.1 Place a TMA cylinder next to TMA acetone feed drum.
- 6.1.1.2 While wearing face shield and neoprene gloves, remove the cylinder cap and the valve cap. Connect the TMA solution tubing to the TMA cylinder. Do not open cylinder at this time.
- 6.1.1.3 Weigh the acetone TMA feed tank and determine the amount of acetone in the tank.
- 6.1.1.4 Add dry ice to plastic bucket to cool the coil thru which TMA will be added to the acetone and add approximately one quart acetone to dry ice in bucket.
- 6.1.1.5 Set scale to read the proper weight for TMA acetone mixture as provided by supervisor.
- 6.1.1.6 Make certain acetone TMA tank is vented to hood.
- 6.1.1.7 Slowly open cylinder valve and then open ball valve and allow TMA to bubble into acetone. Continue until proper weight of TMA has been added, then close TMA valve and cylinder valve.

6.1.2 Reactor Room Preparation

- 6.1.2.1 Rate check pump P-303 by pumping acetone from 5-gallon drum on 75 pound scale to a second 5-gallon drum. Set pump rate as directed by supervisor.
- 6.1.2.2 Ensure that vent fan is on.
- 6.1.2.3 Start cooling water flowing through mixer jacket.
- 6.1.2.4 Set back pressure on PCDE Grove valve.

NOTE: This must be done before the PBEP reaction has started in 300 bay.

- 6.1.2.5 Place pinch clamp to divert reactor system discharge to desired wash drum.

6.2 REACTION

6.2.1 Start Up

NOTE: Before starting PCDE step, the PBEP unit should be started. Allow enough time to make certain the PBEP process has leveled out and enough PBEP has accumulated to start.

- 6.2.1.1 Start dilute acid pump P-402.
- 6.2.1.2 Start TMA acetone pump, P-401.
- 6.2.1.3 Wait for the approved time as defined in following note, then start PBEP feed, P-303 and MDC, P-403.

NOTE: On initial start up or with an empty line from TMA-acetone tank, wait for at least three (3) minutes before starting PBEP and MDC, otherwise wait for two minutes before starting P-303 and P-403.

- 6.2.1.4 Observe the temperatures of the mixer and pre-cooler outlet (respectively, points 9 and 6 on TI 301/302/303) for reaction and/or unusual heating. Record at timed intervals.
- 6.2.1.5 Observe the system back pressure. If pressure exceeds 20 psi, shut down immediately.

6.2.2 Shut Down

- 6.2.2.1 Temporary shut down for PBEP drum change or switch wash drum.
 - 6.2.2.1.1 Stop P-303.
 - 6.2.2.1.2 Wait one minute then stop P-401, P-402, and P-403.
 - 6.2.2.1.3 Open PC-400 bay door and enter.
 - 6.2.2.1.4 Change P-303 suction line to full PBEP drum. Catch any drops with clean cloth.

- 6.2.2.1.5 If needed switch pinch valve and use second wash drum.
- 6.2.2.1.6 Shut door and return to control room.
- 6.2.2.2 Normal shutdown.
- 6.2.2.2.1 Stop P-303.
- 6.2.2.2.2 Wait two minutes then enter PC-400 bay and place P-303 pump suction in a bucket containing acetone return to control room.
- 6.2.2.2.3 Start P-303 and pump for five minutes.
- 6.2.2.2.4 Stop P-401, P-402 and P-404.
- 6.2.2.2.5 Wait five minutes then stop P-303.
- 6.2.2.2.6 Enter PC-400 bay and place P-303 suction in tray. Remove acetone bucket from bay.

6.3 CLEANING AND DISASSEMBLY

- 6.3.1 Flush process tubing with DMK and/or MDC by placing P-303 suction in bucket containing solvent and pumping into 55 gallon wash drum.
- 6.3.2 Wet and wipe clean the external surface of any fitting to be disassembled.
- 6.3.3 Before disassembly of compression fittings at the TMA check valves and downstream of that point, the system will be flushed with at least two volumes of DMK and/or MDC.
- 6.3.4 A face shield and gloves will be worn and the operation must be observed by supervisor.
- 6.3.5 All tubing sections, when removed, will be immediately cleaned with DMK and/or MDC.

6.4 TEST FOR EXPLOSIVE

- 6.4.1 When cleaning is complete or there is otherwise need to test for presence of explosive, the TVOPA detector will be used.
- 6.4.2 Test freshness of detector by putting a drop of solution 3 (cyanide) on a methanol dampened towel or cloth. Add a drop of solution 1 and wait about 30 seconds. Add a drop of solution 2. If a red color does not develop, discard detector solutions and obtain fresh material from chemical laboratory.
- 6.4.3 To test a suspected area, blot it with a methanol dampened cloth or towel. Move to the control room. Add several scattered drops of solution 1 (yellow) to the towel or cloth. Wait about 30 seconds. Add a drop of solution 2 (green) over each drop of solution 1. A red color indicates the presence of TVOPA, PCDE, or PBEP.

6.5 ACID MAKEUP

- 6.5.1 Use safety equipment including goggles, face shield and rubberized suit.

- 6.5.2 For every 100 lbs. of water to be added to acid drum add 2 lbs. H_2SO_4 .
- 6.5.3 Add water to drum, using hose. Do not fill drum more than 4 inches below top of drum.
- 6.5.4 After adding water then add the calculated amount of H_2SO_4 from 9 lb. acid bottles.

CAUTION: Add the acid slowly to avoid spattering.

- 6.5.5 Stir the acid with piece of 3/4" stainless steel tubing provided.

6.6 EMERGENCY SHUT DOWN

- 6.6.1 Stop P-303.
- 6.6.2 Stop P-401, P-402, and P-403.
- 6.6.3 In the event a leak or plug occurs in the reactor area, shut down per 6.6.1 and 6.6.2.
- 6.6.4 Wait at least 10 minutes then with the supervisor in attendance enter reactor bay and decontaminate any spill outside the steel drum and wash tank.
- 6.6.5 First add MDC to the spill, then blot with clean cloth. Wear gloves and also face shield where practical and safe.
- 6.6.6 Wet down spill with MDC and blot.
- 6.6.7 Perform test for explosive 6.4. If positive, repeat 6.6.6.
- 6.6.8 If spill is in steel drum, remove water by dipping or siphoning. Slum, then remove spill by method 6.6.5 and 6.6.6.
- 6.6.9 If plug occurs, remove clamp from rubber hose at end of distribution tube and add a long hose to a bucket. Replace PBEP drum on 75 pound scale with drum containing solvent. Leave bay and pump solvent through reactor with P-303.
- 6.6.10 If solvent cannot be pumped, remove hose at pump and remove all solution possible from line by gravity.
- 6.6.11 From control room pass nitrogen at 1 to 5 psi through TMA line backwards thru PBEP feed line to clean the feed line.
- 6.6.12 Stop water and disconnect water lines and TMA line at check valve. Seal the ends of the reaction system with bags, then remove it from the wall.
- 6.6.13 Remove as much material as possible from the system by gravity.
- 6.6.14 Using 1/4 inch minimum acrylic shielding and stapled gloves, disassemble the tubing. Start at the joint between the reactor and distributor. Wet the joints with Freon containing TA. Next disconnect the PBEP feed line at the mix "T". Parts can now be inspected and sent to the decontamination oven as required.

END