AD-A101 673 RADIAN CORP AUSTIN TX F/G 21/4
CHROMATOGRAPHIC SEPARATION OF CONVENTIONAL AND EXPERIMENTAL FUE--ETC(U)
OCT 80 K J BOMBAUGH, D H RODGERS, J C BELTZ F33615-79-C-2083
UNCLASSIFIED RAD-219-030-03 AFWAL-TR-80-2098 NL

1 OF 1
AD
A101673

END
DATE
FILMED
8-81
DTIC

AFWAL-TR-80-2098

CHROMATOGRAPHIC SEPARATION OF CONVENTIONAL AND EXPERIMENTAL FUELS

Karl J. Bombaugh
Donald H. Rodgers
John C. Beltz

Radian Corporation
P. O. Box 9948
Austin, Texas 78766

October 1980

TECHNICAL REPORT AFWAL-TR-80-2098
FINAL REPORT FOR PERIOD SEPTEMBER 1979 - JUNE 1980

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) 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.

Ronald D. Butler

RONALD D. BUTLER
Project Scientist

Arthur V. Churchill

ARTHUR V. CHURCHILL
Chief, Fuels Branch
Fuels and Lubrication Division

FOR THE COMMANDER

Robert D. Sherrill

ROBERT D. SHERRILL
Chief, Fuels and Lubrication Division

If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/POSF, W-PAFB OH 45433 to help us maintain a current mailing list.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AIR FORCE/56780/8 July 1981 — 170

(16) 2303 (17) S1

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(19) REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER: (18) AFWAL-TR-80-2098

2. GOVT ACCESSION NO.: AD-A101673

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): (6) Chromatographic Separation of Conventional and Experimental Fuels.

5. ~~TYPE OF REPORT & PERIOD COVERED~~: (9) Final Technical Report. Sep~~tember 1~~979 – June ~~1~~980

6. ~~PERFORMING ORG. REPORT NUMBER~~: (14) RAD-219-030-03

7. AUTHOR(s): (10) Karl J. Bombaugh
Donald H. Rodgers
John C. Beltz

8. CONTRACT OR GRANT NUMBER(s): (15) F33615-79-C-2083

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Radian Corporation
P. O. Box 9948
Austin, Texas 78766

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
Work Unit 2303S103
Program Element 61102F

11. CONTROLLING OFFICE NAME AND ADDRESS:
Air Force Wright Aeronautical Laboratories, AFSC
Aero Propulsion Laboratory
Wright-Patterson Air Force Base, Ohio 45433

12. REPORT DATE: (11) Oct~~ober 1~~980

13. NUMBER OF PAGES: 49

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (12) 57

15. SECURITY CLASS. (of this report): UNCLASSIFIED

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

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)

Aviation Turbine Fuels
Jet Fuel
Aircraft Fuels
JP-4
JP-7
Liquid Chromatography

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research described in this report was performed in order to develop a chromatographic method for the separation and isolation of the various classes of hydrocarbons present in conventional and experimental aircraft fuels. The objective of such a technique is to provide a convenient means of estimating the relative proportions of the hydrocarbon classes, i. e., normal and branched alkanes, alkylbenzenes, alkenes, etc., and to render the initially complex fuels tractable to conventional methods of analysis and characterization.

The procedure developed consists of a semi-preparative column chromato-

389153

Block 20 (Continued):

graphic method, using spherical particulate silica gel column packing and isobutane as the mobile phase. The fuel samples are fractionated by passing them through the column and collecting the eluting fractions at regular intervals. The volatile isobutane carrier is evaporated from the fractions and the residues are analyzed by techniques such as gas chromatography. Because the isobutane vaporizes quantitatively at low temperatures, the fractions are obtained free of interfering solvent. In this respect, the technique is novel and unprecedented.

Results of the analyses show that the method provides good separation of aliphatic and aromatic hydrocarbons, and partial resolution of aliphatic and olefinic hydrocarbons. Resolution may be improved substantially by optimizing the column temperature and by using low-boiling mobile phases of varying polarity.

FOREWORD

This report describes work performed by Radian Corporation under U. S. Air Force Contract F33615-79-C-2083, to develop an improved technique for the analysis and characterization of aviation turbine fuels.

The work was performed under the technical direction of Mr. Karl J. Bombaugh as Principal Investigator, with support provided by Mr. Donald H. Rodgers and Mr. John C. Beltz.

This contractual effort was funded under Project 2303 (Chemistry), Task 2303S1 (Fuels Chemistry), Work Unit 2303S103, and administered by the Fuels Branch (AFWAL/POSF), Fuels and Lubrication Division, Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. Dr. Ronald D. Butler was the Air Force project scientist.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Concluded)

SECTION I

INTRODUCTION

This report describes work done by Radian Corporation to develop a chromatographic method for the separation of aircraft fuels into the various classes of hydrocarbons of which they are composed.

The report further describes the results of the application of the method to the separation and analysis of six aircraft fuels, both conventional and experimental, supplied by the U. S. Air Force.

The physical and chemical behavior and critical performance parameters of fuels refined from natural sources are determined by the relative proportions of the various classes of hydrocarbons which make up the fuels. Because of the extreme chemical complexity of most fuels, existing methods for their analysis and characterization are not completely satisfactory. The purpose of this investigation was to develop a chromatographic procedure, using a non-interfering mobile phase, which could be used to separate the fuels of interest into several distinct compound classes. This preliminary separation would then facilitate the subsequent analysis of the fractions by more conventional techniques such as gas chromatography.

The method employed here consists of separating the fuels on a semi-preparative column packed with activated spherical particulate silica gel. The unique feature of the procedure is the use of isobutane as the mobile phase: because it has a low boiling point, the isobutane can be easily separated by evaporation from the collected fractions, thereby eliminating solvent interference problems. There is no precedent in the scientific literature for this approach.

The eluted fractions were analyzed by gas chromatographic techniques to determine the separation efficiency of the silica gel column. Calibration of both the separation column and the gas chromatographic analytical columns was achieved by the use of known model compounds, which were chosen as representative of the classes of compounds normally found in the fuels.

SECTION II

EXPERIMENTAL

A. Materials and Equipment

The following instruments, equipment, and reagents were used in this investigation:

Liquid chromatographic column: silica gel (Spherosil XOA-400), 40-100 μ particle size, was packed by the dry/tap fill method into stainless steel tubing 10 mm ID x 600 mm long. The columns were conditioned overnight at 150°C, with a flow of dry nitrogen. A smaller particle size silica gel, Lichrosorb 60, having a mean particle diameter of 30 μ, was also used to pack four 10 x 600 mm columns which were then connected in series.

Isobutane, instrument grade: liquefied isobutane, at a tank pressure of 2.1 bar (20°C) was purchased in cylinders from Phillips Petroleum Company.

Sample introduction valve: a Valco ten-port valve was used for sample injection.

Gas chromatograph: Tracor Model 560 with 3% OV-101 and 10% 1,2,3-tris(2-cyanoethoxy)propane columns.

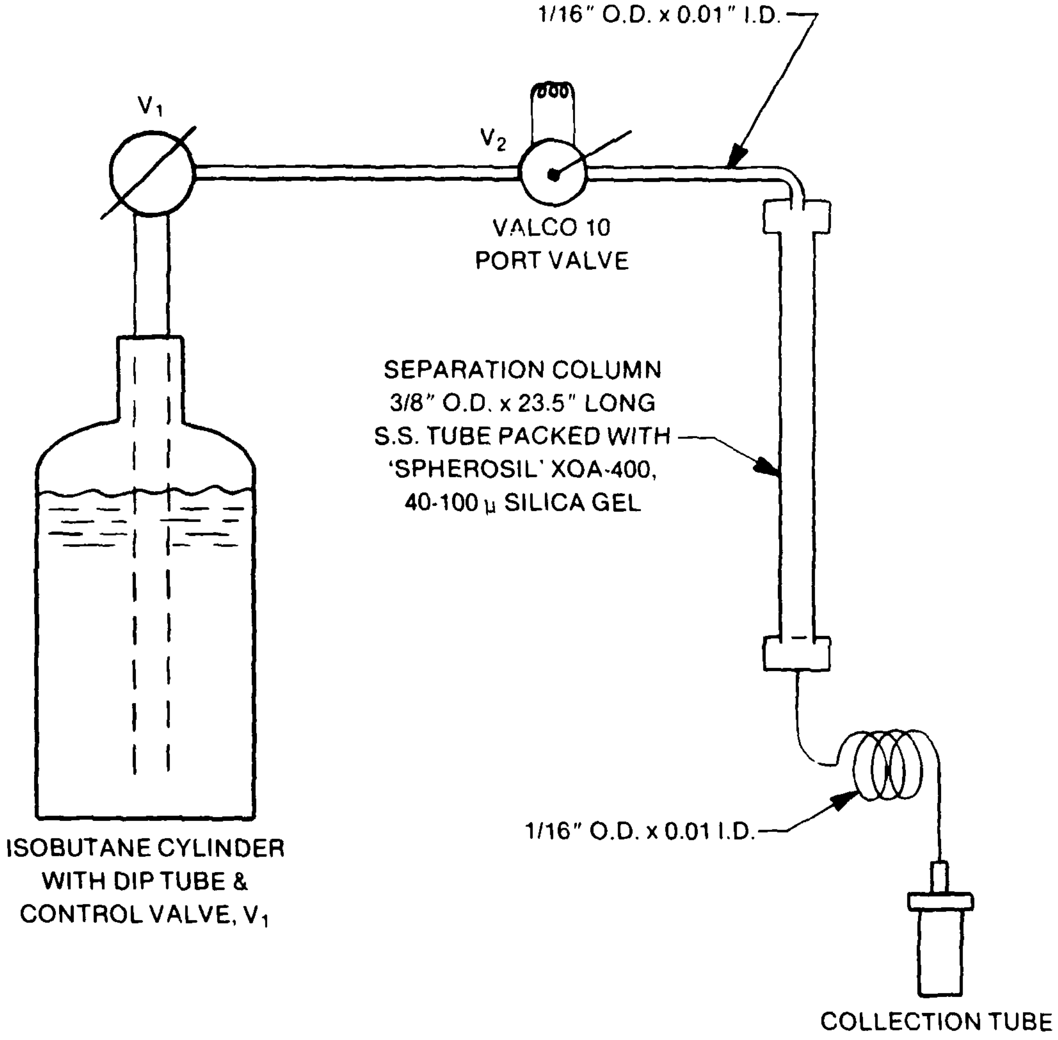
Infrared spectrophotometer: Perkin-Elmer Model 283.

Ultraviolet/visible spectrophotometer: Varian Model 219.

B. Apparatus Configuration

The chromatographic separation system was assembled as shown in Figure 1. The isobutane mobile phase was delivered through the column under its own intrinsic vapor pressure of about 2.1 bar, or at higher pressures with nitrogen pressurization. The flow rate was controlled by the use of metal capillary tubing (0.01 in ID) connected to the column outlet. The flow rate varied slightly over brief periods, but averaged about 2.5 mL/min, as measured by collection of the effluent in a chilled graduated cylinder.

The isobutane cylinder was fitted with a dip tube that passed to the bottom of the cylinder. This enabled the collection of liquid rather than gaseous isobutane. Fuel samples and calibration standards were introduced



70-1836-1

FIGURE 1 DIAGRAM OF SEPARATION APPARATUS onto the column by means of the Valco valve, which was fitted with a sample loop of the desired sample volume.

C. Separation Procedure

In practice, the sample or a standard mixture was introduced onto the separation column via the ten-port valve. The effluent isobutane was then collected at regular intervals in separate chilled containers. The collected fractions were warmed to room temperature and the isobutane carrier allowed to evaporate. The residues were dissolved in carbon disulfide or other appropriate solvents for gas chromatographic, infrared, or ultraviolet measurement. The data obtained from the collected fractions were compared with similar data obtained for the initial neat sample mixture to determine the degree of fractionation.

D. System Calibration

In order to determine the separation efficiency of the system, various calibration mixtures of known compounds were injected onto the column and collected in the effluent. A mixture of hexane, benzene, and naphthalene was chosen as representative of aliphatic and aromatic compounds. Subsequently, mixtures of hexane, cyclohexane, and isopentane were chromatographed and collected. The mixtures were chosen as representative of linear, cyclic, and branched aliphatic hydrocarbons.

Finally, n-octane, 1-octene, *trans*-2-octene, and 2,2,4-trimethylpentane were tested for retention volume in the system. These compounds were chosen as representative of normal, branched, and olefinic hydrocarbons.

In addition to the separation system, mixtures of known hydrocarbons were used as gas chromatography standards to provide retention time data for the identification of various compounds in the liquid chromatographic fractions.

E. Sample Fractionation and Identification

Following calibration of the system, six samples of authentic jet fuels were analyzed by the method. These samples were supplied to Radian by the Air Force project scientist. Separation and fraction collection were carried out as described above. In addition to the isobutane elution, however, a final elution with methylene chloride was carried out on each sample. This final "column wash" was included to remove completely any strongly adsorbed sample components from the column. Four separate fractions were collected, including the final methylene chloride wash. The collected fractions were then analyzed by gas chromatography, and the remaining residues were submitted to the Air Force project scientist for further analysis.

SECTION III

RESULTS AND DISCUSSION

A. System Calibration

The activated separation column was first tested for separation efficiency using standard mixtures of hexane, benzene, and naphthalene as described in Section II. Fractions of the eluate were collected at five-minute intervals and analyzed by gas chromatography for the presence of the three compounds. The results showed that the hexane eluted primarily in the 10-15 minute fraction, benzene in the 20-30 minute fraction, and naphthalene in a broad band from 35 to 115 minutes, with 75% eluting in 40-60 minutes.

The experiment was repeated several times using only hexane and benzene mixtures, resulting in an estimated separation factor >7 for these two compounds. (Separation factor is the ratio of the uncorrected retention times.)

The system was next tested for the separation of normal, branched, and cyclic aliphatic hydrocarbons, using hexane, cyclohexane, and isopentane. Fractions were collected at one-minute intervals and analyzed by gas chromatography. The results showed that these three compounds were poorly separated, and were entirely eluted in the fractions collected between 11 and 15 minutes. Elution profiles of these compounds are shown in Figure 2.

In an attempt to increase resolution, a series of four 600-mm Lichrosorb 60 packed columns were connected in series with the Spherosil column, giving a fivefold increase in column length. To provide adequate carrier flow, the isobutane cylinder was pressurized to 5.4 bar with nitrogen. A mixture of the three test compounds was injected and fractions were collected at five-minute intervals. Analysis of the fractions showed that isopentane eluted first between 100 and 120 minutes, and was almost completely resolved from the hexane and cyclohexane, which were poorly resolved. Repetition of the experiment confirmed these results and suggested that hexane eluted slightly before cyclohexane, but with considerable peak overlap. The elution profiles of the three compounds are shown in Figure 3.

A further attempt to improve the resolution of these compounds was made by lowering the temperature of the three-meter column to 0°C. This was accomplished by immersing the columns in an ice bath. Considerable experimental difficulty was encountered, making the results somewhat ambiguous. However, the results which were obtained appeared to indicate poorer, rather

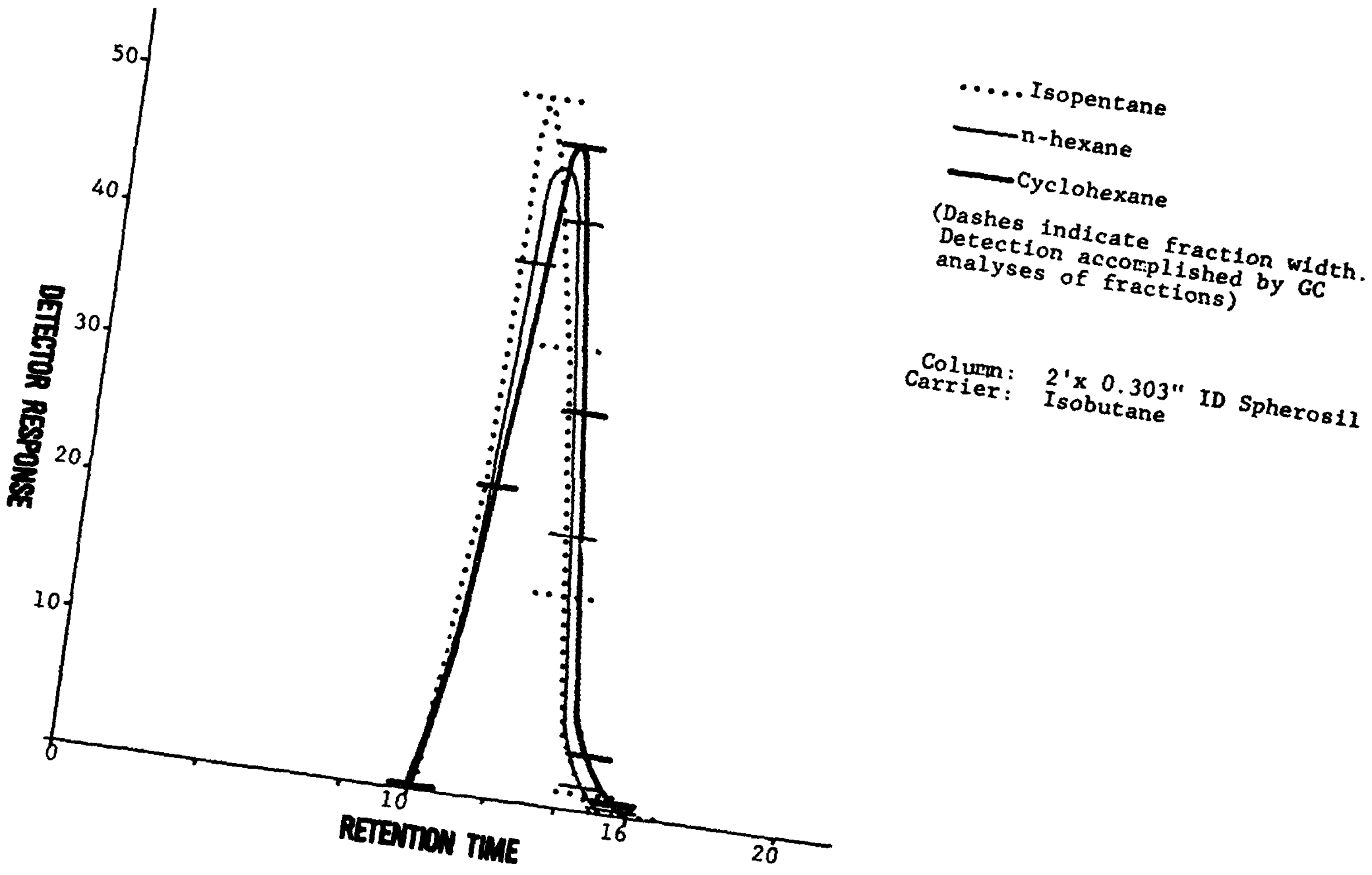


Figure 2. Elution Profile of Paraffins

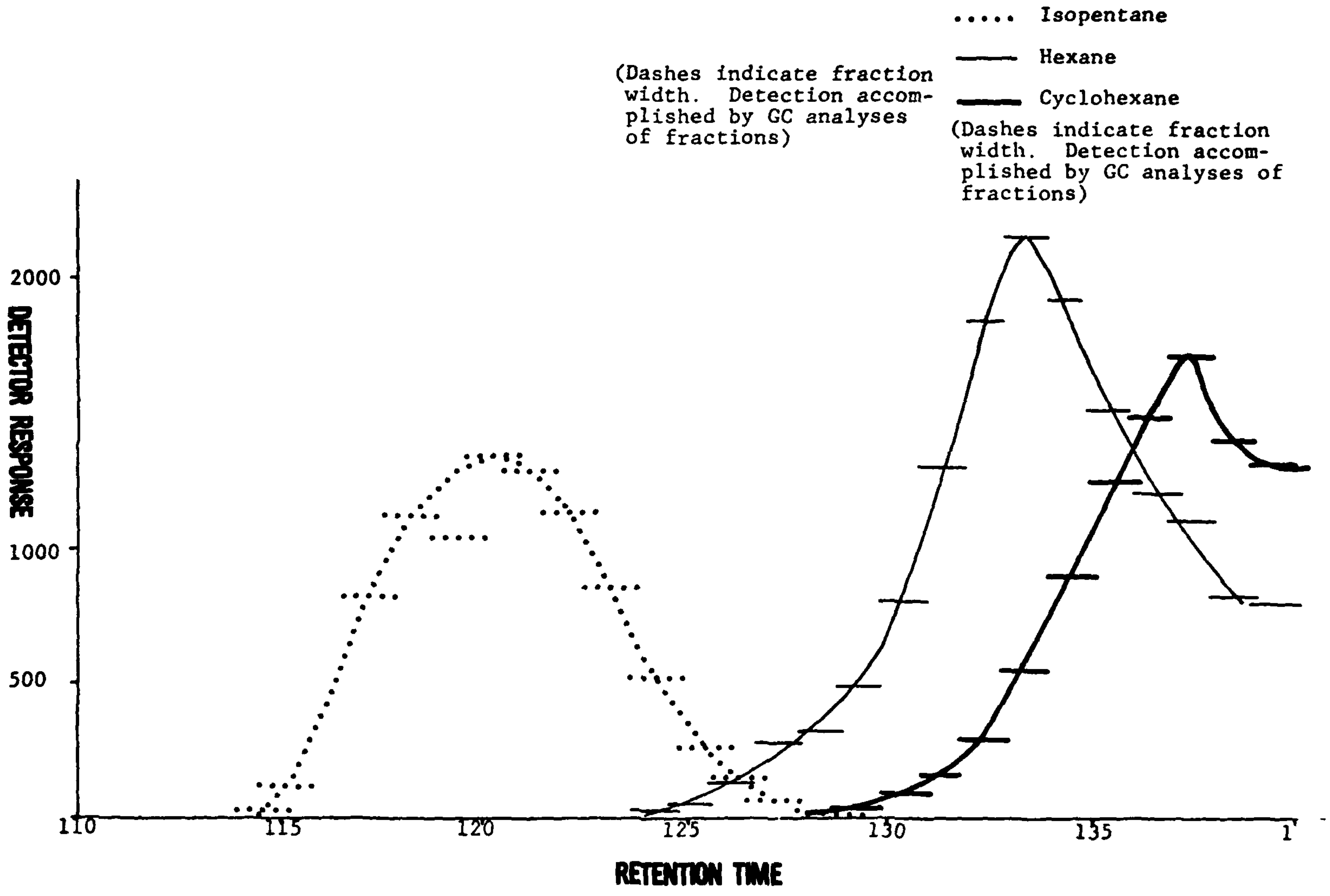


Figure 3. Elution Profiles of Paraffins

than better, resolution of the hexane and cyclohexane. Initially, the data seemed to indicate very long retention times (longer than four hours) with cooling. Repetition of the experiment, however, showed that the components were in fact eluted in the first 100 mL of effluent, or essentially in the solvent front. We are unable to explain these results. No further experiments were performed with column temperature variation.

A final series of calibration tests were made in order to determine the resolution efficiency of the system for saturated and olefinic compounds. n-Octane, 2,2,4-trimethylpentane, 1-octene, and *trans*-2-octene were chromatographed and the fractions analyzed. It was found that the two saturated octanes coeluted in the 10-14 minute fraction (the same as hexane), while the two octene compounds coeluted in 14-16 minutes. Elution profiles of these compounds are shown in Figures 4 and 5.

The gas chromatographic systems were calibrated with the same standards used for the liquid column measurements. In addition, calibration mixtures containing various alkylbenzenes, and also C_{11} to C_{20} hydrocarbons, were chromatographed to obtain retention time data for the identification of column fraction components.

B. Analysis of Fuel Samples

Six jet fuel samples were received from the Air Force for study. The samples as received were examined by infrared and ultraviolet spectrophotometry, and by gas chromatography using both selective and non-selective columns. These preliminary measurements were made to determine the approximate composition of the samples with regard to their aromatic and aliphatic character, and to aid in the later interpretation of the column fraction data. The infrared spectra are shown in Figures 6-11. Sample 3936 was shown to be the most aromatic, and sample 3939 the most paraffinic.

The samples were then subjected to liquid chromatographic separation by the techniques described previously. Four fractions were collected for each sample, and each of the four fractions was analyzed by gas chromatography.

Other intermediate fractions were also collected for most of the samples; however, only those fractions containing hydrocarbon residues (as evidenced by gas chromatographic analysis) were studied and included in this report.

The gas chromatograms obtained for samples 3934 through 3939, and for the respective fractions, are shown in the accompanying figures. The first chromatogram in each set was obtained with the neat sample. A discussion of the individual sample results follows. The assignment of component identities is based primarily on gas chromatographic retention times and their coincidence with known standards.

1. Sample 3934 (JP-4). This sample contains a large fraction of low-boiling, nonpolar substances such as paraffinic hydrocarbons, a comparable amount of higher-boiling hydrocarbons (approximately C_9 to C_{14}), and a smaller amount of strongly retained materials.

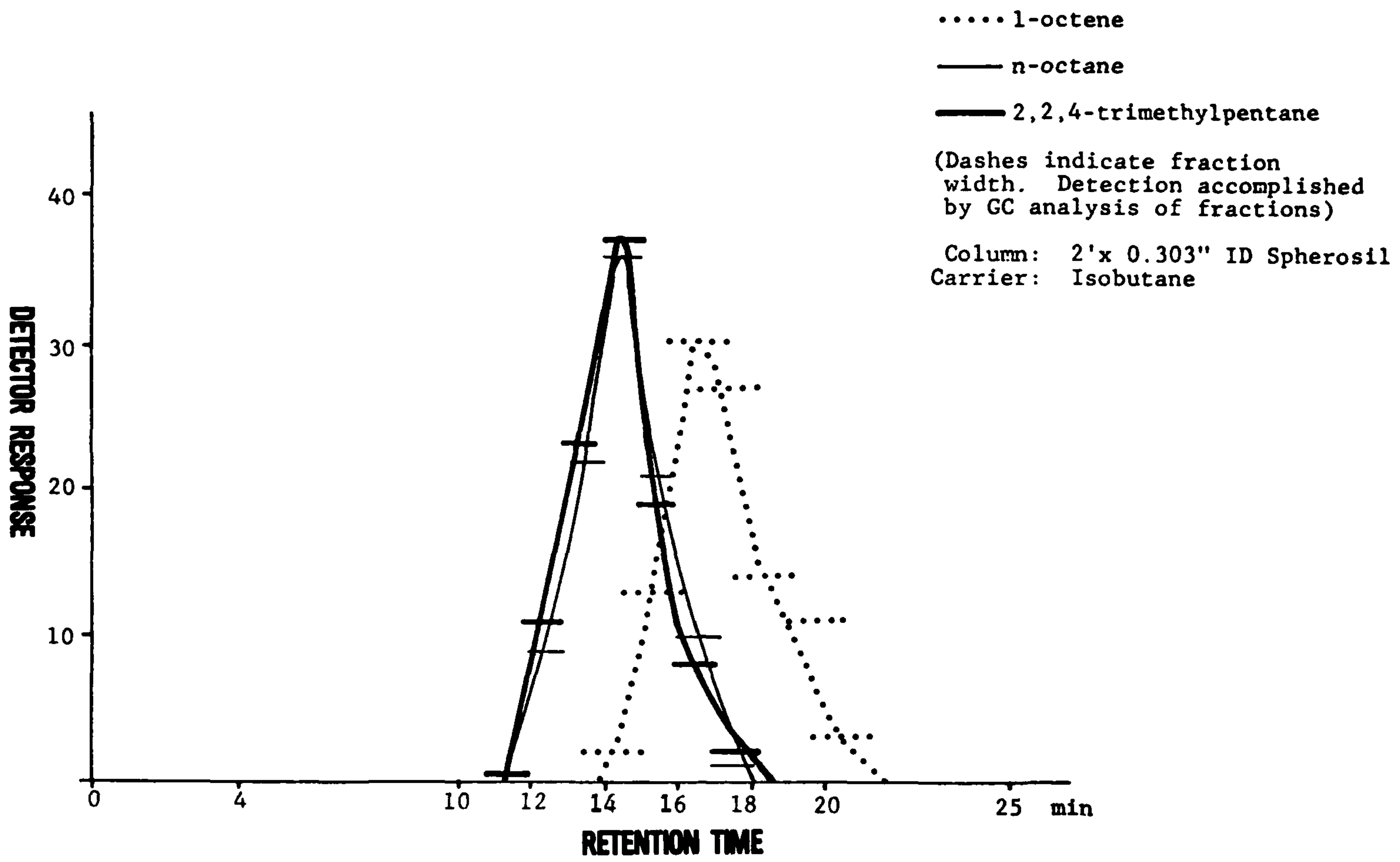
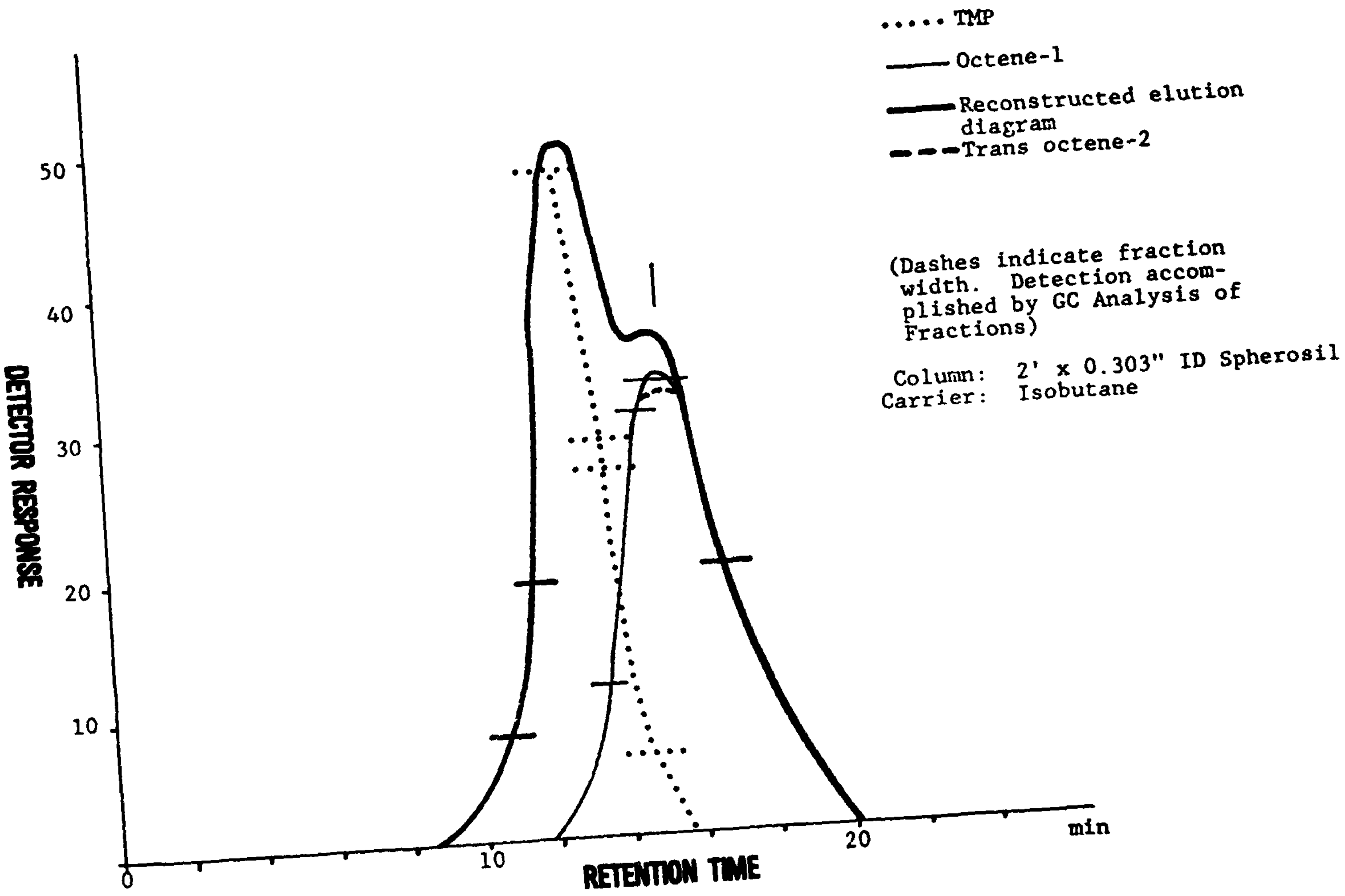


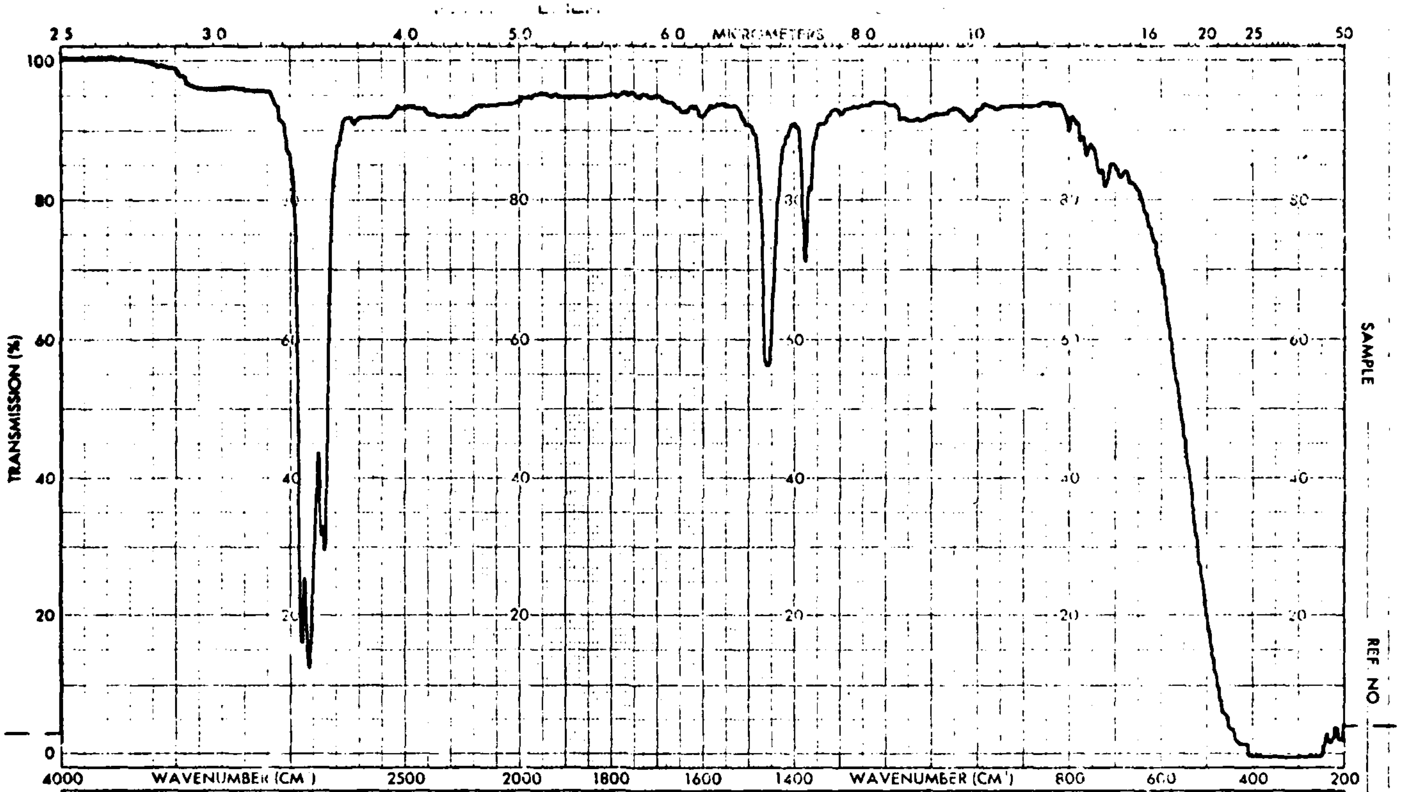
Figure 4. Elution Profile of Octanes and Octene.



(Dashes indicate fraction width. Detection accomplished by GC Analysis of Fractions)

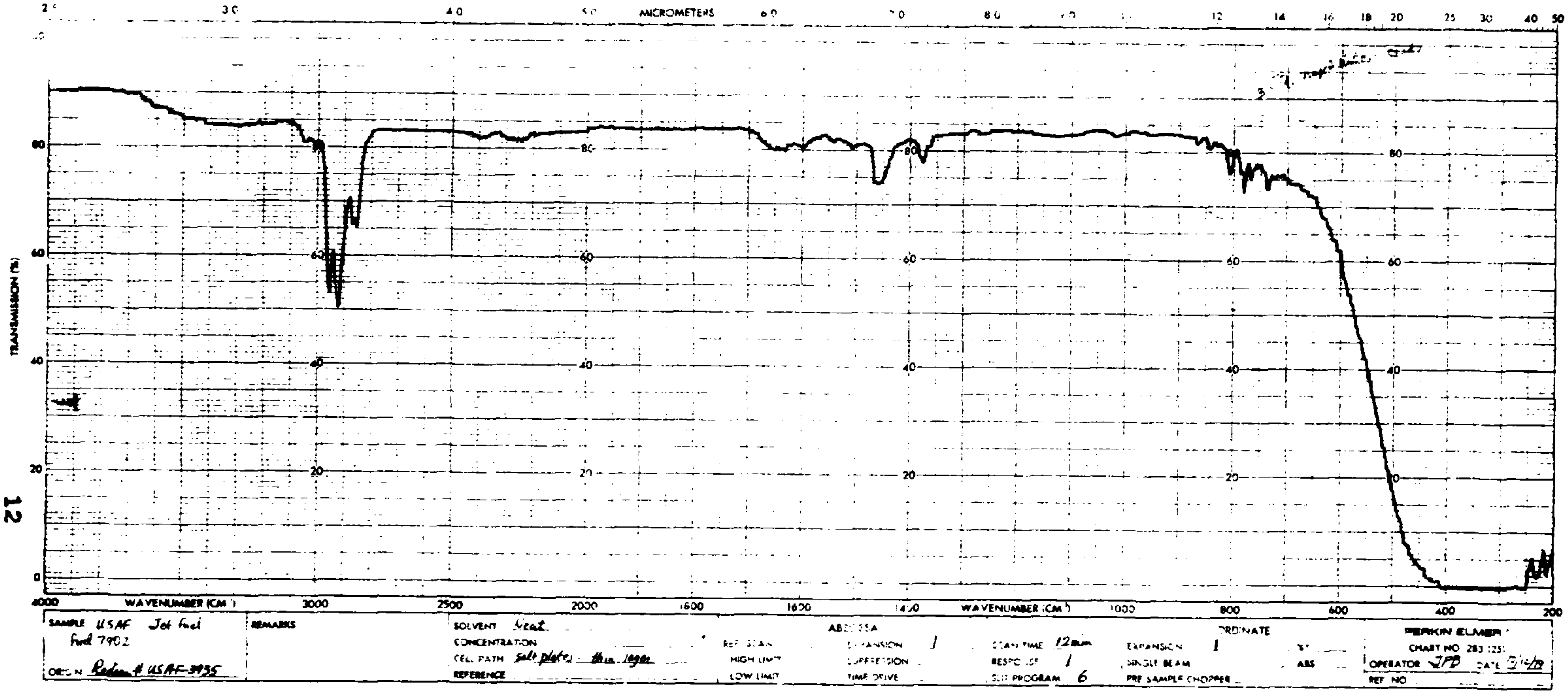
Column: 2' x 0.303" ID Spherosil
Carrier: Isobutane

Figure 5. Elution Profile cf Octene and Octane.



ABSCISSA EXPANSION 1 SUPPRESSION	ORDINATE EXPANSION 1 % T ✓ ABS	SCAN TIME 12 min RESPONSE 1 SLIT PROGRAM 6	REP. SCAN SINGLE BEAM TIME DRIVE PRE SAMPLE CHOP OPERATOR JFB DATE 11/20/79
SAMPLE USAF-3934 ORIGIN	REMARKS	SOLVENT neat CONCENTRATION	CELL PATH Salt Plates REFERENCE

Figure 6. Infrared Spectrum of Sample 3935; JP-4 Fuel



SAMPLE USAF Jet Fuel fuel 7902

ORIGIN Radian # USAF-3935

REMARKS

SOLVENT Neat

CONCENTRATION

CELL PATH salt plates thin layer

REFERENCE

REF. SCAN

HIGH LIMIT

LOW LIMIT

ABSCISSA

EXPANSION 1

SUPPRESSION

TIME DRIVE

SCAN TIME 12 min

RESPONSE 1

SLIT PROGRAM 6

ORDINATE

EXPANSION 1

SINGLE BEAM

PRE SAMPLE CHOPPER

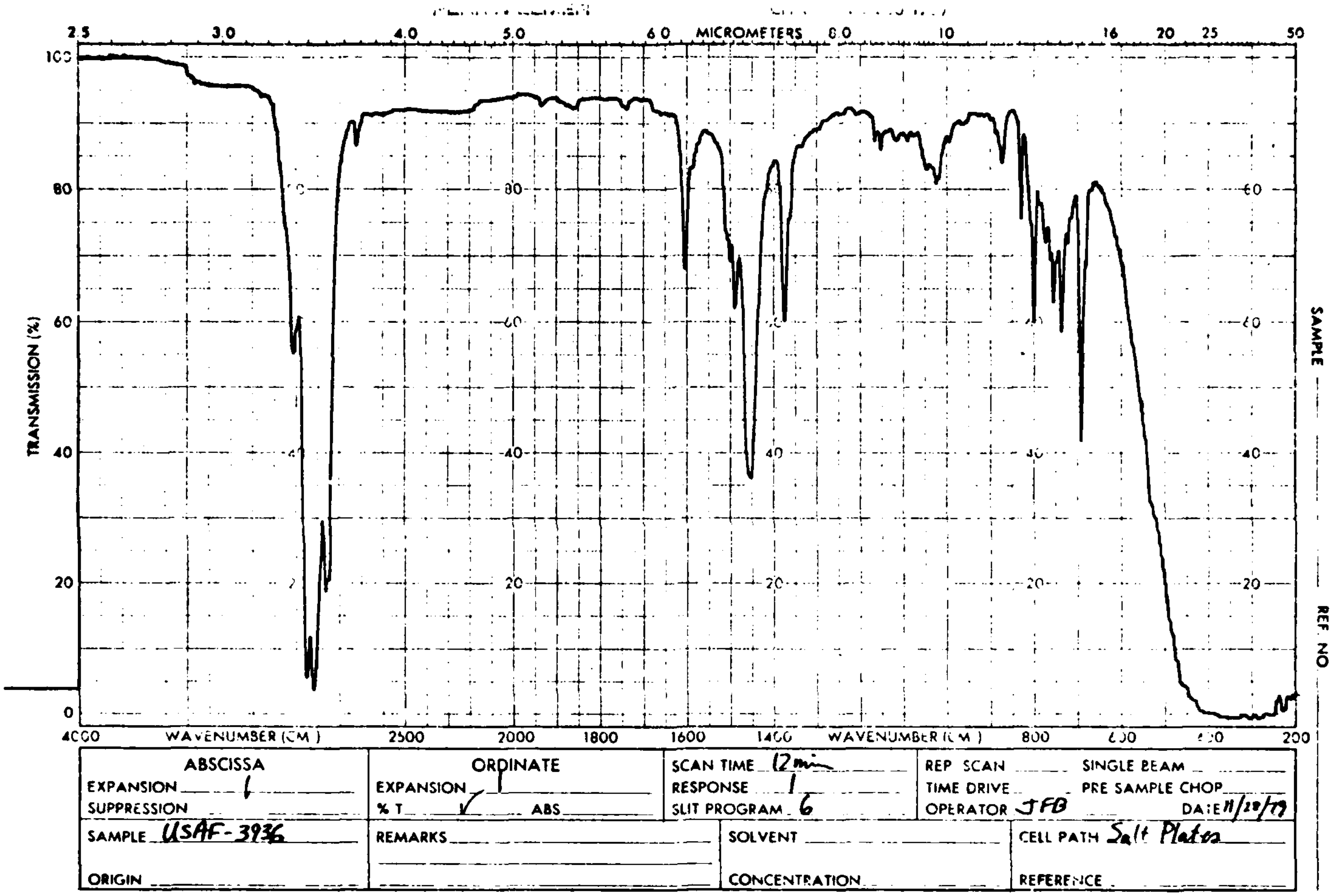
%T

ABS

OPERATOR JPB DATE 3/14/79

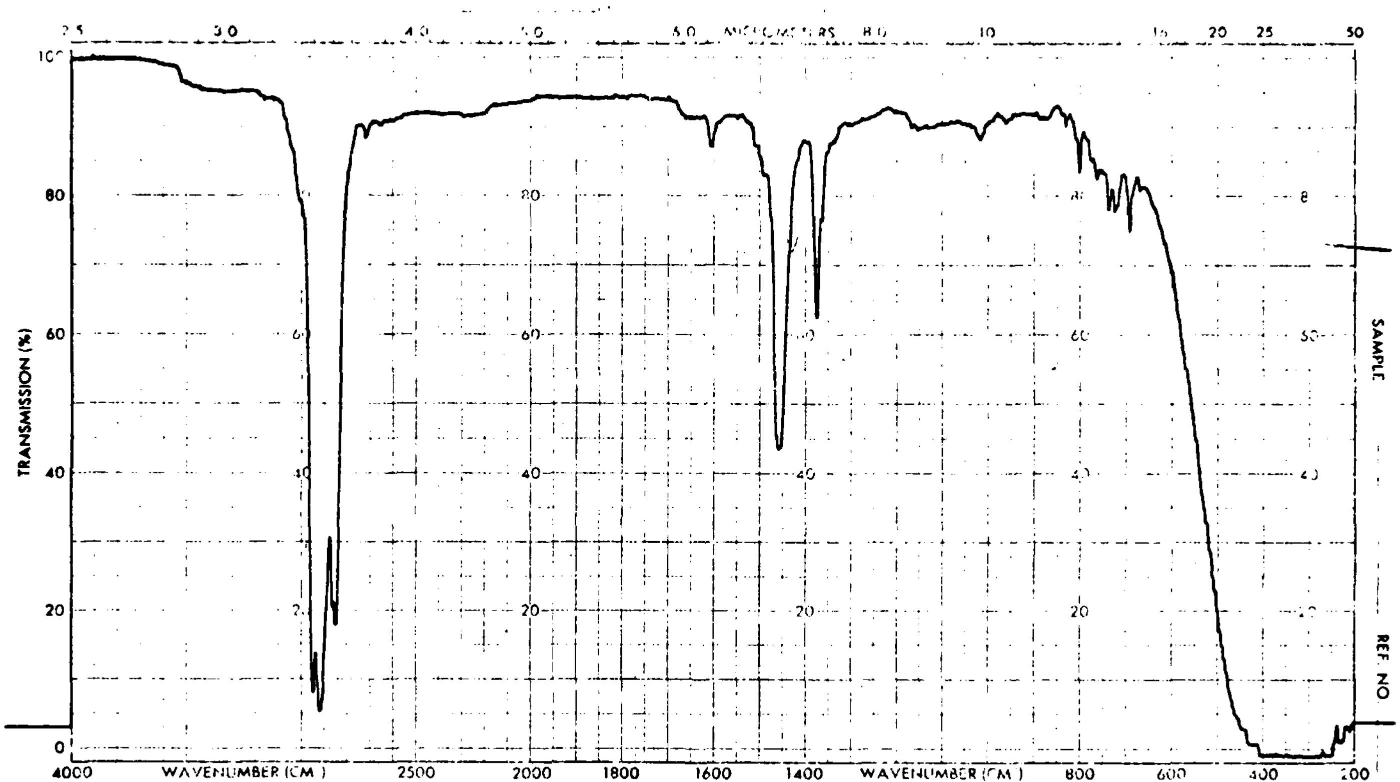
REF. NO.

Figure 7. Infrared Spectrum of Sample 3935; JP-4A2 Fuel



ABSCISSA
EXPANSION 1
SUPPRESSION
ORDINATE
EXPANSION 1
% T ✓ ABS
SCAN TIME 12 min
RESPONSE 1
SLIT PROGRAM 6
REP SCAN
SINGLE BEAM
TIME DRIVE
PRE SAMPLE CHOP
OPERATOR JFB
DATE 11/20/79
SAMPLE USAF-3936
ORIGIN
REMARKS
SOLVENT
CONCENTRATION
CELL PATH Salt Plates
REFERENCE

Figure 8. Infrared Spectrum of Sample 3935; JP-4X2 Fuel



ABSCISSA EXPANSION SUPPRESSION	ORDINATE EXPANSION % T ✓ ABS	SCAN TIME 12 m RESPONSE 1 SLIT PROGRAM 6	REP. SCAN SINGLE BEAM TIME DRIVE PRE SAMPLE CHOP OPERATOR JFB DATE 11/28/79
SAMPLE USAF-3937 ORIGIN	REMARKS	SOLVENT Neat CONCENTRATION	CELL PATH Salt Plates REFERENCE

Figure 9. Infrared Spectrum of Sample 3937; JP-4X/04 Fuel

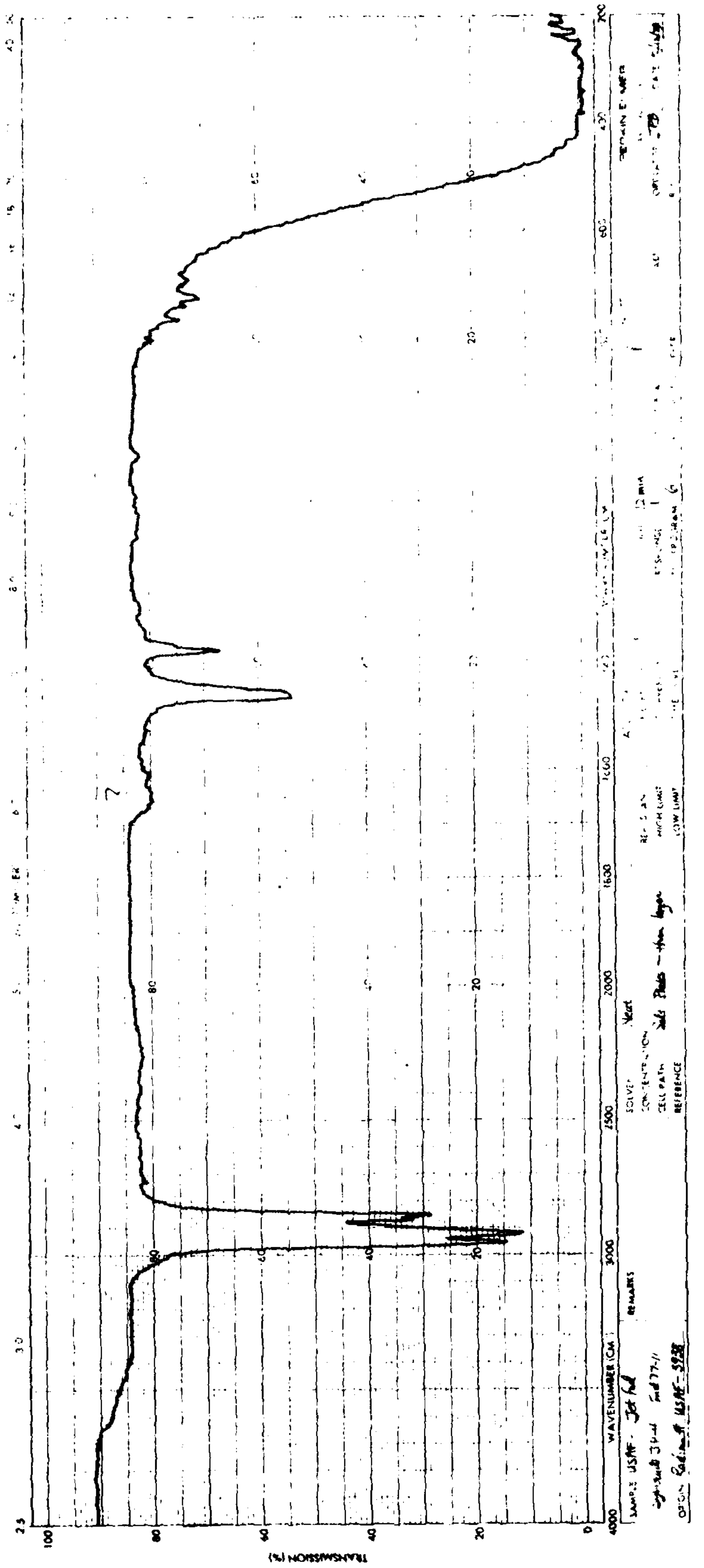
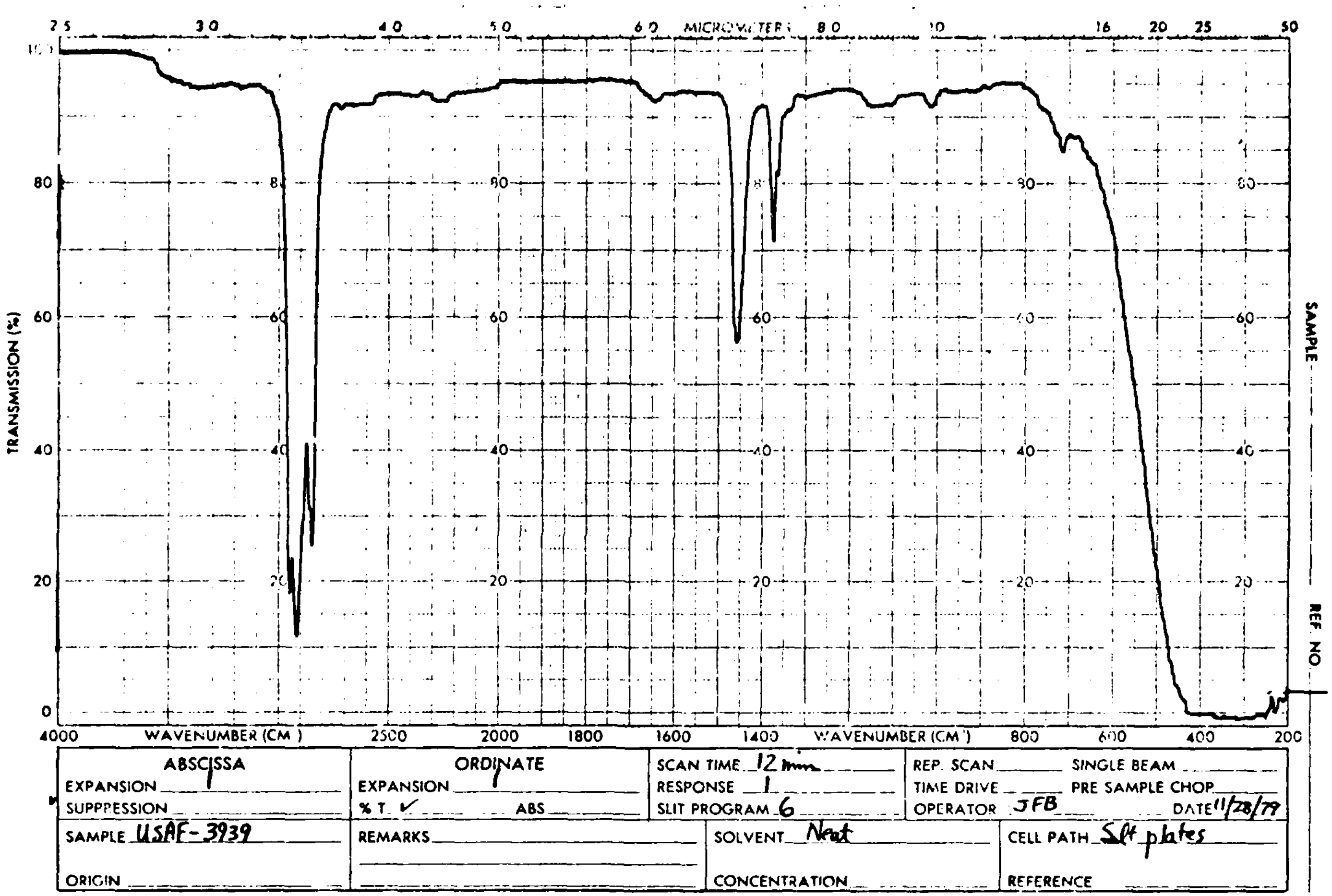


Figure 10. Infrared Spectrum of Sample 3938; Syncrude JP-4 Fuel



ABSCISSA
EXPANSION 1
SUPPRESSION

ORDINATE
EXPANSION 1
% T ✓ ABS

SCAN TIME 12 min
RESPONSE 1
SLIT PROGRAM 6

REP. SCAN
TIME DRIVE
OPERATOR JFB

SINGLE BEAM
PRE SAMPLE CHOP
DATE 11/28/79

SAMPLE USAF-3939
ORIGIN

REMARKS

SOLVENT Neat
CONCENTRATION

CELL PATH Salt plates
REFERENCE

Figure 11. Infrared Spectrum of Sample 3939; JP-7 Fuel

LC fraction 1, collected from 0-10 minutes, contained both the light and intermediate paraffin. Fraction 2, 10-15 minutes, was similar to fraction 1. Fraction 3 (15-22 minutes) contained only a trace of paraffins and some light aromatic compounds. Fraction 4 showed primarily alkylaromatics, and possibly naphthalenes or other bicyclic aromatics. Other polycyclic compounds of higher molecular weight than naphthalene may also have been present; however, we did not attempt to identify these species.

The gas chromatograms of the neat sample 3934 and fractions 1-4 are shown in Figures 12-16.

2. Sample 3935 (JP-4A2). This sample contains a large amount of light hydrocarbon (C_9 to C_{14}), plus a relatively large amount of bicyclic aromatic material.

LC fraction 1 (0 to 7 minutes) contained the light and intermediate paraffins. Fraction 2 (7-14 minutes) contained the paraffins, plus some aromatics. It appeared that some column channeling occurred with this sample since both alkylaromatic and aliphatic compounds are present in fraction 2. Fraction 3 (14-19 minutes) was free of paraffins, and contained both aromatic and bicyclic compounds. Fraction 4 contained only the bicyclic compounds.

Figures 17-21 show the gas chromatograms of the neat sample 3935 and fractions 1-4.

3. Sample 3936 (JP-4X2). Sample 3936 appears to contain two groups of substances, a light paraffin fraction and an alkylaromatic fraction. The paraffin fraction was found to contain primarily C_6 hydrocarbons, with much smaller amounts of C_8 and C_9 compounds. The alkylaromatic fraction is apparently mainly C_3 alkylbenzenes. Lower hydrocarbons, such as C_2-C_4, were probably lost in the isobutane evaporation step; no attempt was made to detect these compounds.

LC fraction 1 (0-10 minutes) contained the C_6 and higher paraffins. Fraction 2 (10 to 25 minutes) contained a mixture of paraffins and alkylaromatics. Fraction 3 contained alkylaromatics, plus a trace of naphthalenes. Fraction 4, eluted with methylene chloride, contained traces of alkylaromatics and the more polar bicyclic compounds. Gas chromatograms of these samples are shown in Figures 22-26.

4. Sample 3937 (JP-4X/04). This sample contains a wide range of aliphatic hydrocarbons, plus some alkylaromatics. LC fraction 1 (0 to 13 minutes) contained the paraffinic compounds, consisting of the normal alkanes to C_{21}. Fraction 2 (14 to 15 minutes) contained some paraffins, from overlap of fraction 1, plus alkylaromatics. Fraction 3 (16 to 20 minutes) contained benzene, toluene, xylenes, and trimethylbenzenes. Fraction 4, the methylene chloride flush, contained both alkylaromatics and bicyclic aromatics.

The gas chromatograms for the neat sample 3937 and the four fractions are shown in Figures 27-31.

5. Sample 3938 (Syncrude JP-4). This sample was found to contain a

narrow distribution of paraffins. In addition to the light paraffins, C_6 to C_8, it contained a relatively large proportion of C_{10} and C_{11} compounds and only a trace of C_{13} to C_{18} paraffins.

LC fraction 1 (10 to 13 minutes) contained only paraffins. Fraction 2 (13 to 16 minutes) was similar to fraction 1. Fraction 3 (16 to 20 minutes) contained alkylaromatics, and fraction 4 contained aromatics plus a trace of bicyclic hydrocarbons.

Although the aromatic naphthalene separation was not as good in this run as in the previous runs, the paraffin separation was superior. This type of inconsistency is probably caused by variations in the activity of the silica gel. Such variations may be corrected by improved procedures for activation of the column and by continuous monitoring of the column effluent.

Figures 32-36 illustrate the gas chromatograms of the neat sample of the four isolated fractions.

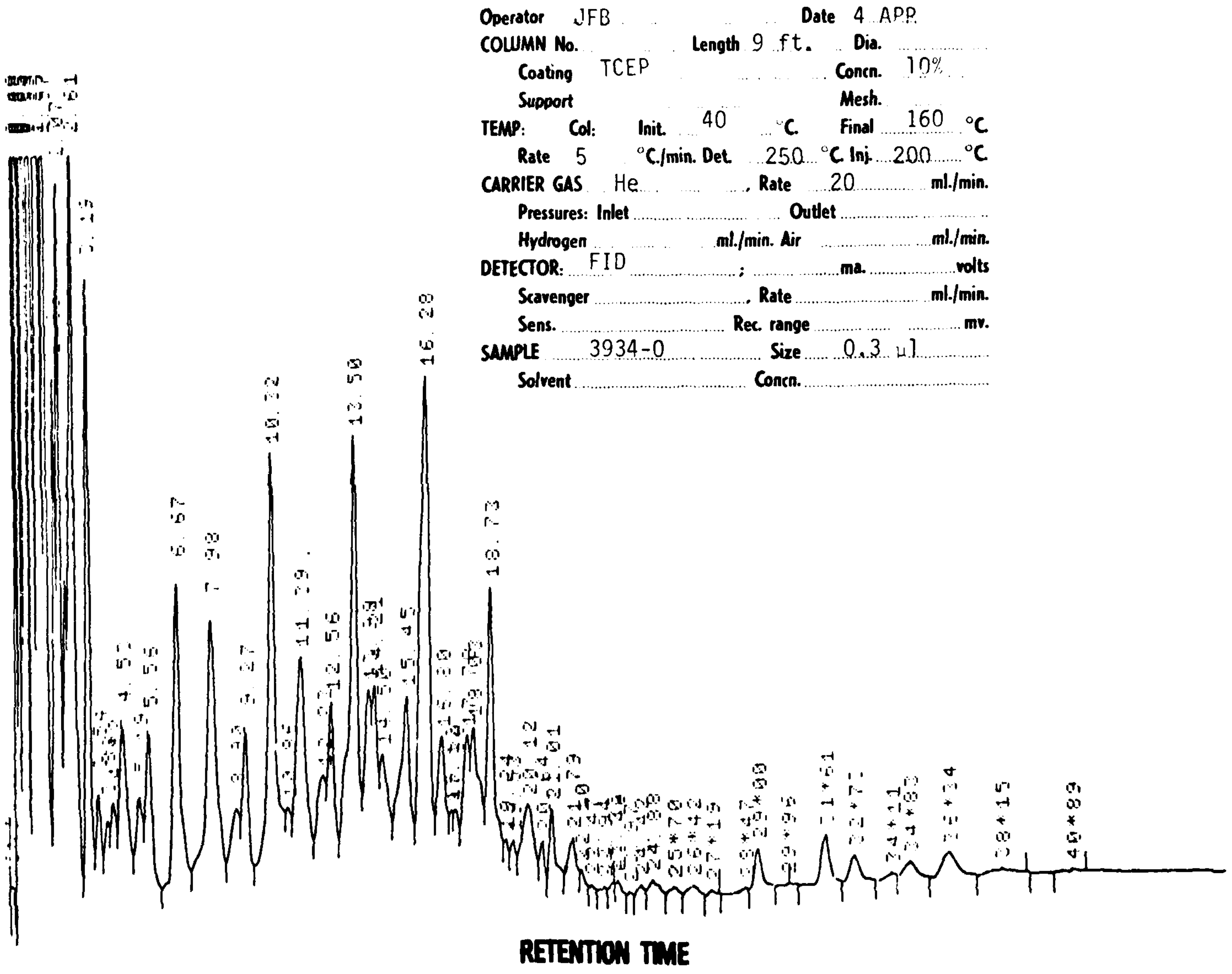
6. Sample 3939 (JP-7). Sample 3939 showed a distinctly different distribution from the other samples. The data indicate that this sample consists of a narrow range, higher-boiling mixture of nonaromatic hydrocarbons.

LC fraction 1 (0 to 10 minutes) contained a small amount of C_{10} to C_{14} compounds. Fraction 2 (10 to 15 minutes) contained a large amount of material which was also C_{10} to C_{14} compounds. Fraction 3 (15 to 20 minutes) gave no measurable residue upon evaporation of the carrier. The methylene chloride flush, fraction 4, contained a small amount of various other compounds.

From the GC retention times of the substances in fraction 4, they appear to be bicyclic. It may be concluded, therefore, that they may be naphthalenic or naphthalene derivatives.

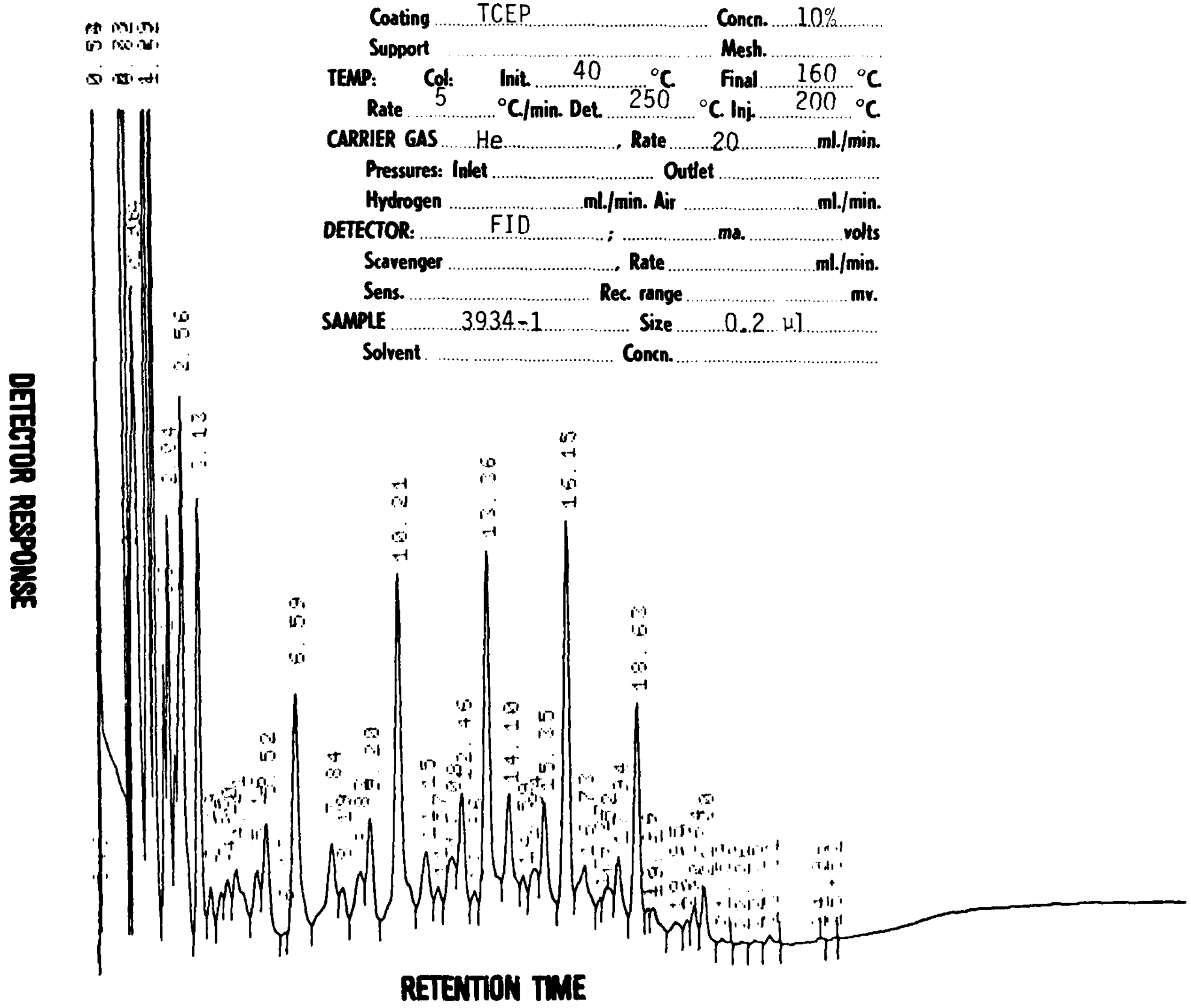
Figures 37-40 show the gas chromatograms for the neat sample and fractions 1, 2, and 4.

Samples of the various fractions obtained from the six fuel samples have been submitted to the Air Force project scientist for further analysis.



Operator JFB **Date** 4 APR
COLUMN No. **Length** 9 ft. **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 **°C. Final** 160 **°C**
Rate 5 **°C./min. Det.** 250 **°C. Inj.** 200 **°C**
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **; ma. volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3934-0 **Size** 0.3 µl
Solvent **Concn.**

Figure 12. Gas Chromatogram of Sample 3934, Neat



Operator	JFB	**Date**	15APR
COLUMN No.	**Length** 9 ft.	**Dia.**	
Coating	TCEP	**Concn.**	10%
Support		**Mesh.**	
TEMP: Col: Init.	40 °C	**Final**	160 °C
Rate	5 °C/min. **Det.** 250 °C	**Inj.**	200 °C
CARRIER GAS	He	**Rate**	20 ml./min.
Pressures: Inlet		**Outlet**	
Hydrogen	ml./min.	**Air**	ml./min.
DETECTOR:	FID ; ma.	volts	
Scavenger		**Rate**	ml./min.
Sens.		**Rec. range**	mv.
SAMPLE	3934-1	**Size**	0.2 μl
Solvent		**Concn.**	

Figure 13. Gas Chromatogram of Sample 3934, LC Fraction 1

Operator JFB **Date** 15 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 °C **Final** 160 °C
Rate 5 °C/min. **Det.** 250 °C **Inj.** 200 °C
CARRIER GAS He, **Rate** 20 ml./min.
Pressures: Inlet **Outlet**
Hydrogen ml./min. **Air** ml./min.
DETECTOR: FID ; ma. volts
Scavenger , **Rate** ml./min.
Sens. **Rec. range** mv.
SAMPLE 3934-2 **Size** 0.2 μl
Solvent **Concn.**

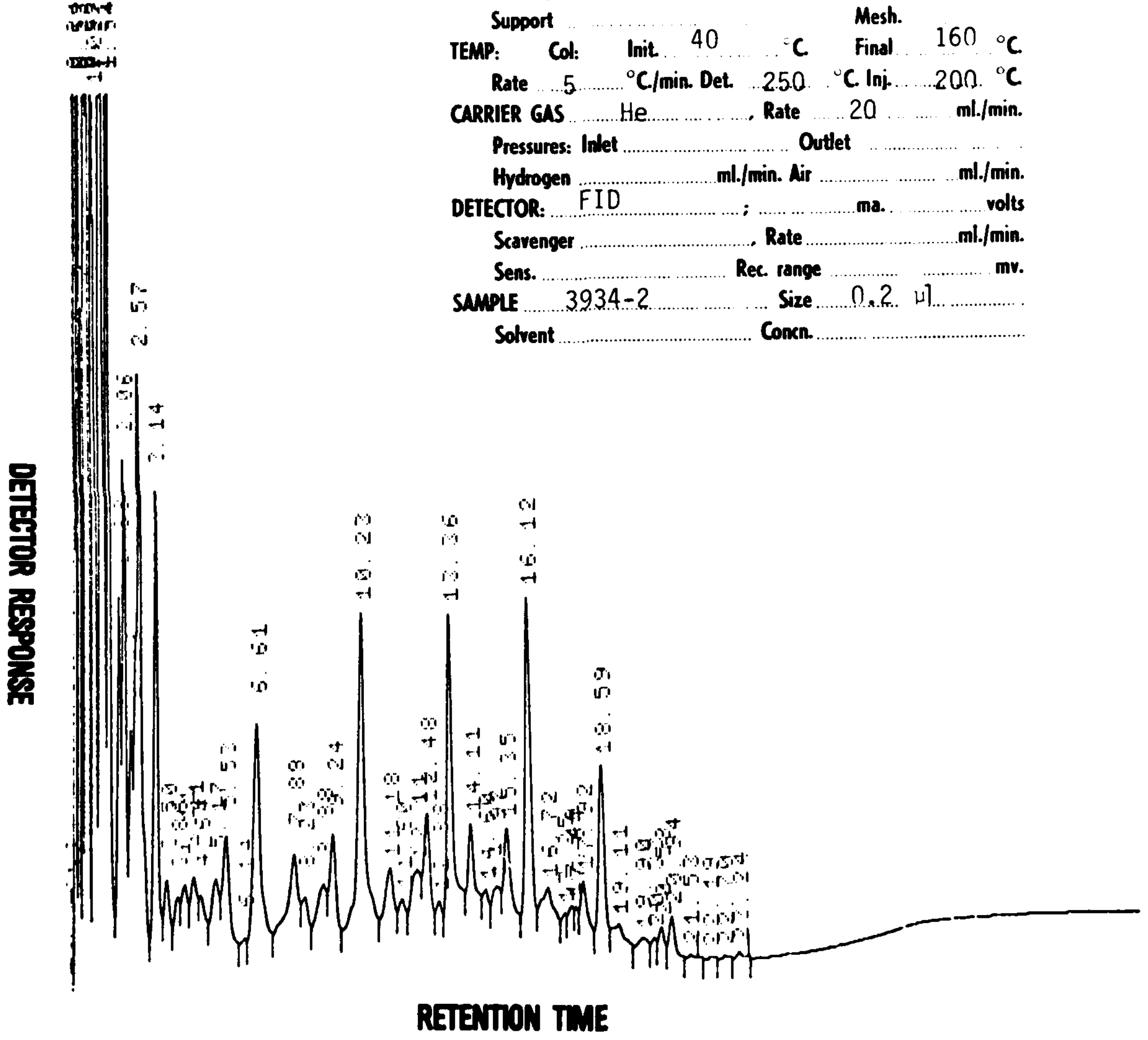
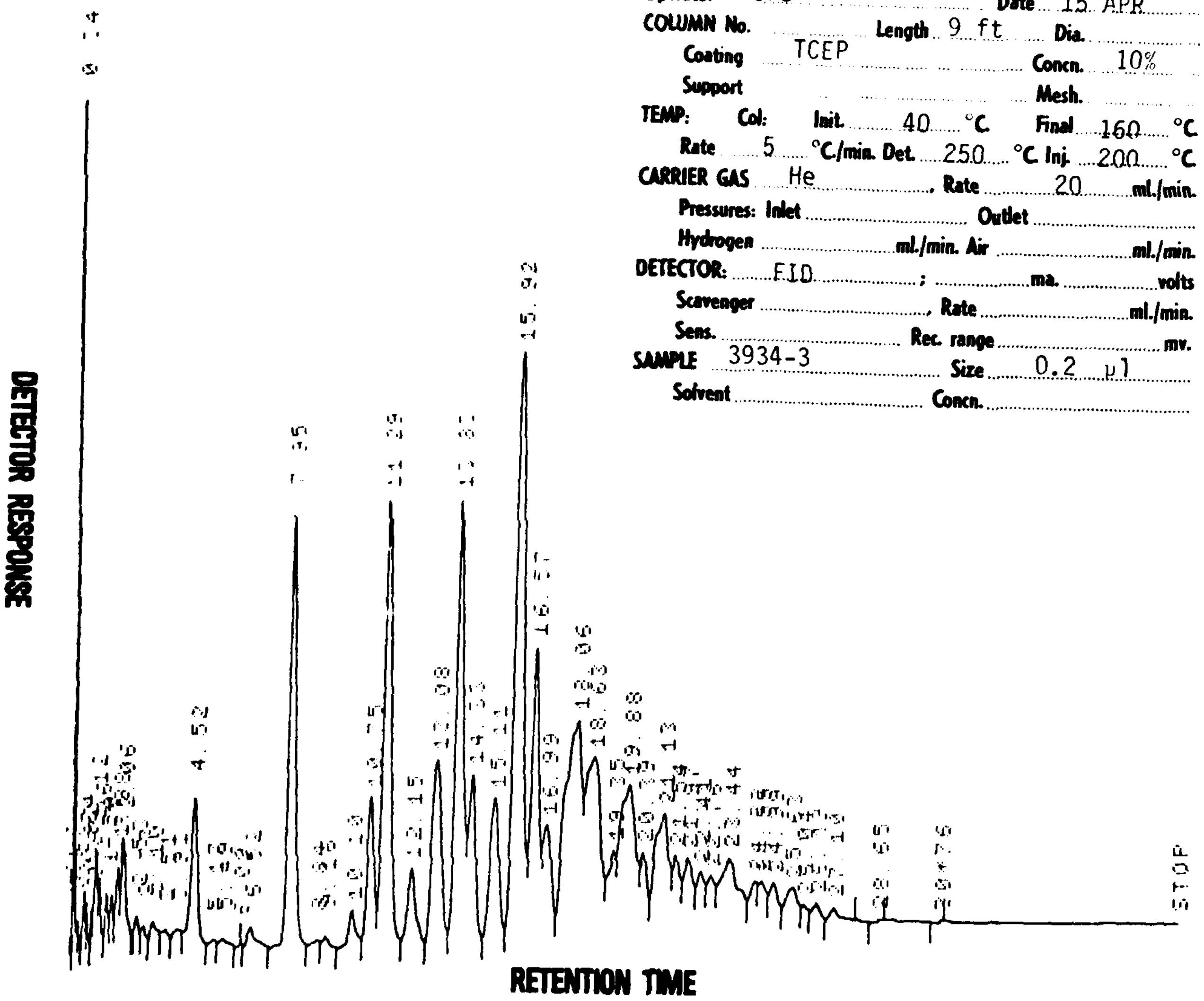
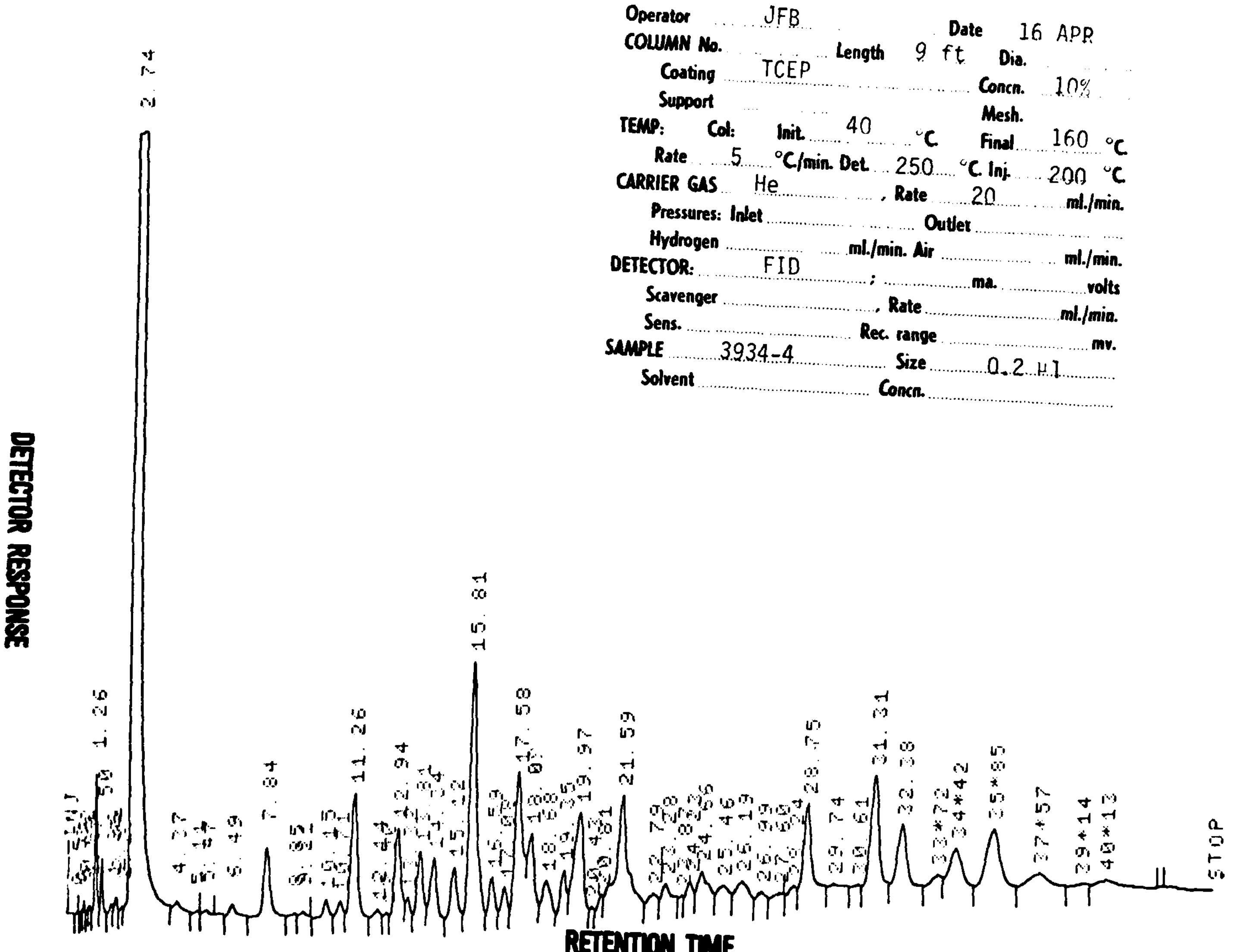


Figure 14. Gas Chromatogram of Sample 3934, LC Fraction 2



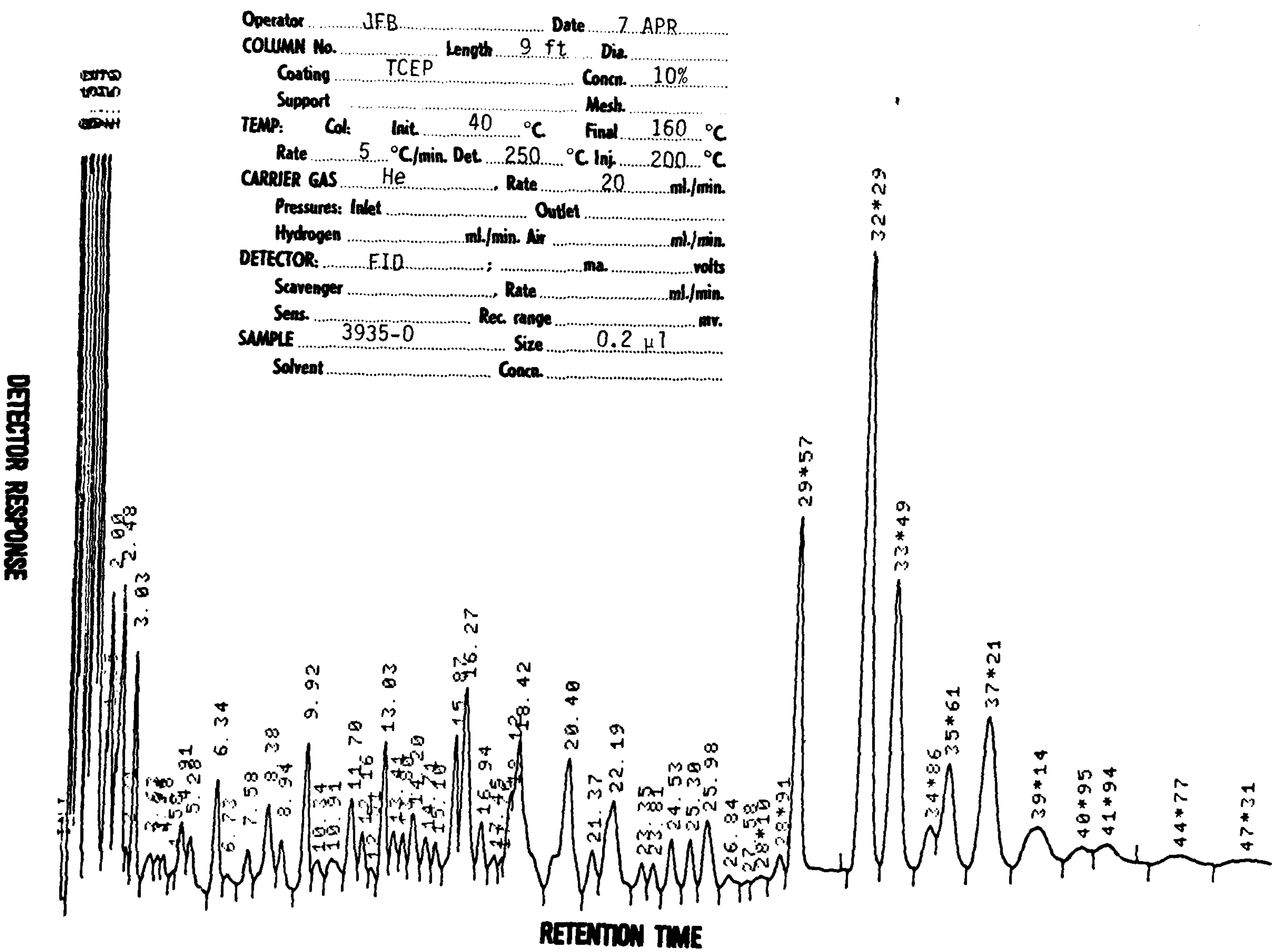
Operator JFB Date 15 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3934-3 Size 0.2 µl
Solvent Concn.

Figure 15. Gas Chromatogram of Sample 3934, LC Fraction 3



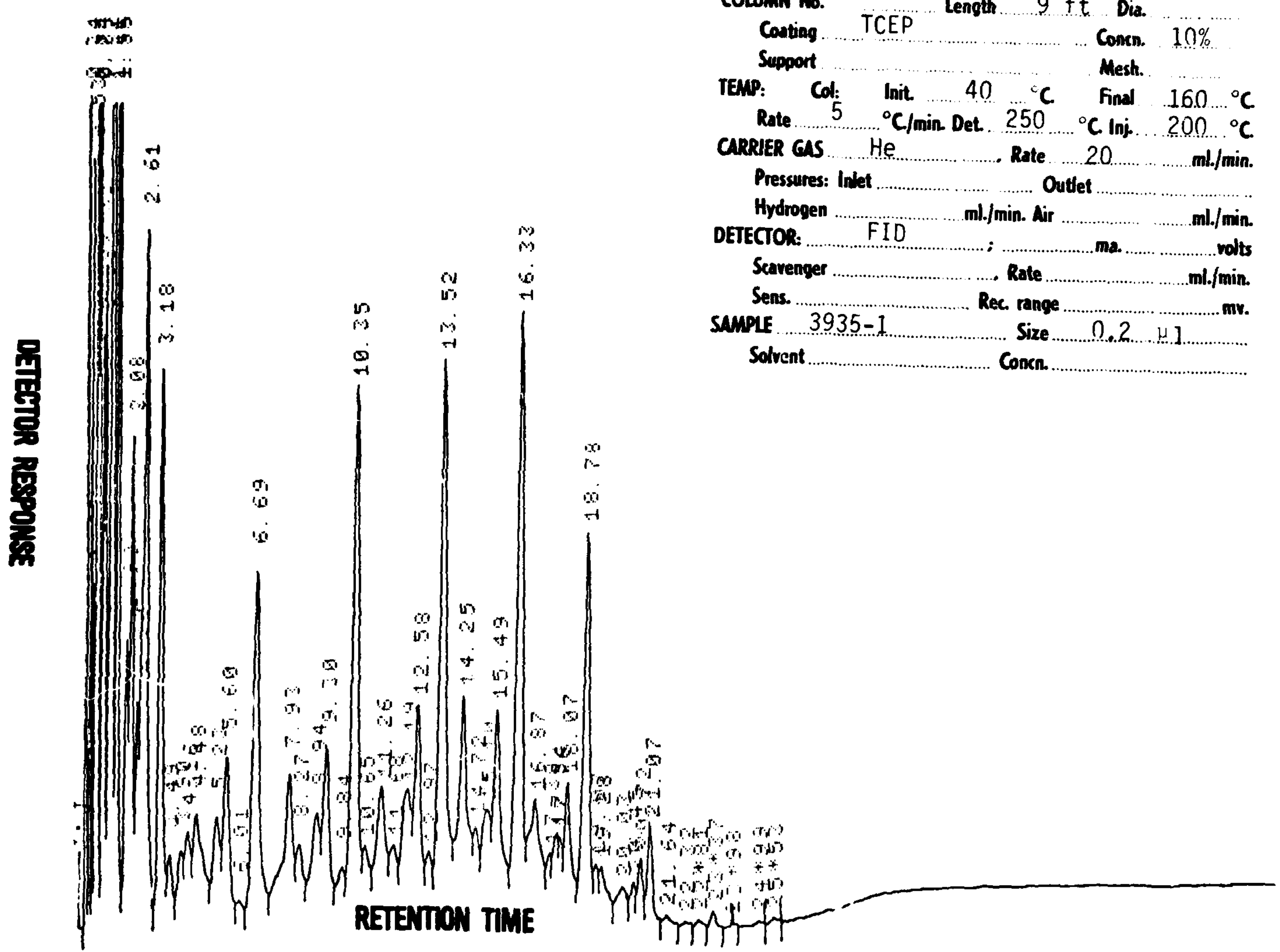
Operator JFB **Date** 16 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 °C **Final** 160 °C
Rate 5 °C/min. **Det.** 250 °C **Inj.** 200 °C
CARRIER GAS He , **Rate** 20 ml./min.
Pressures: Inlet **Outlet**
Hydrogen ml./min. **Air** ml./min.
DETECTOR: FID ; ma. volts
Scavenger , **Rate** ml./min.
Sens. **Rec. range** mv.
SAMPLE 3934-4 **Size** 0.2 µl
Solvent **Concn.**

Figure 16. Gas Chromatogram of Sample 3934, LC Fraction 4



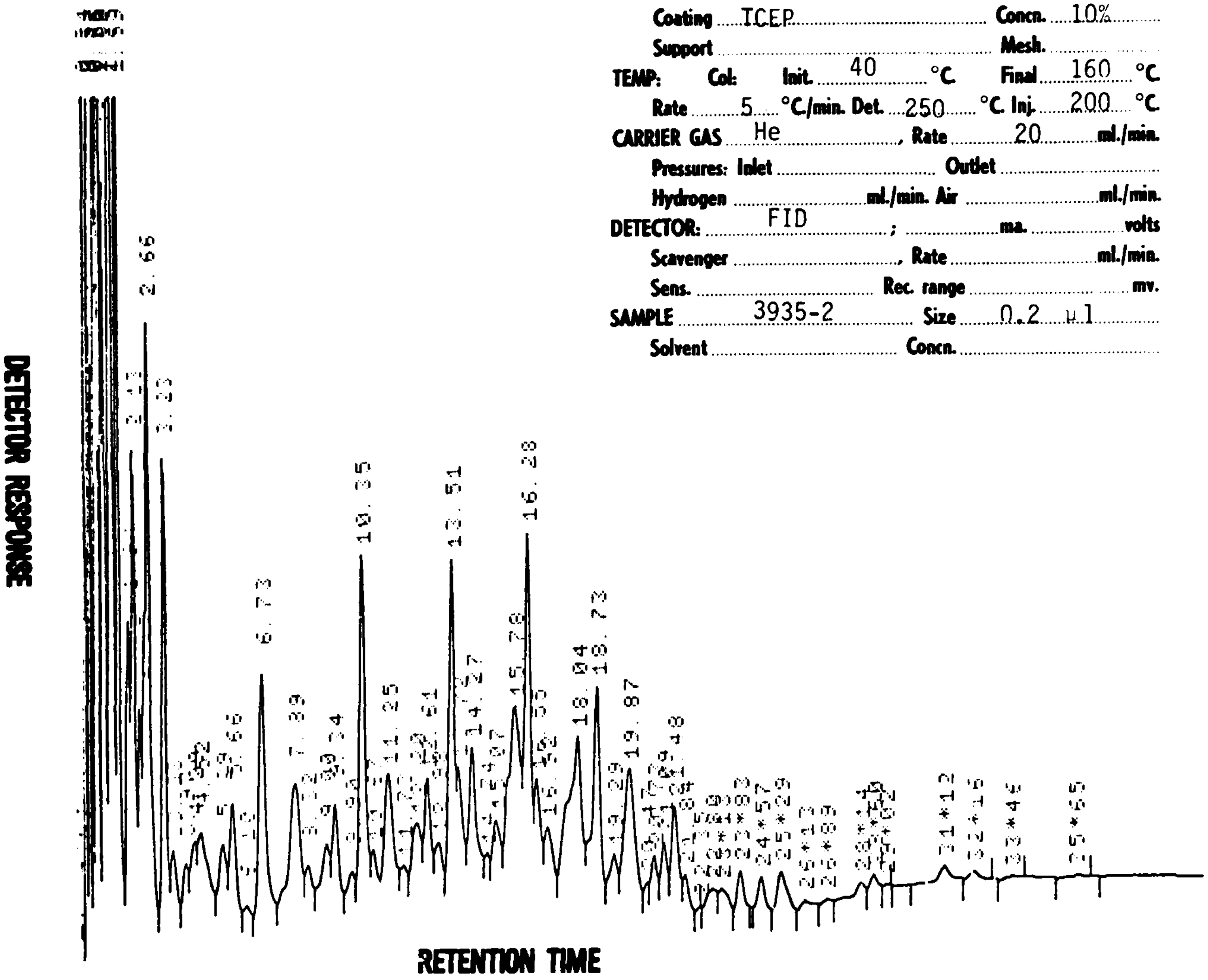
Operator JFB Date 7 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3935-0 Size 0.2 µl
Solvent Concn.

Figure 17. Gas Chromatogram of Sample 3935, Neat



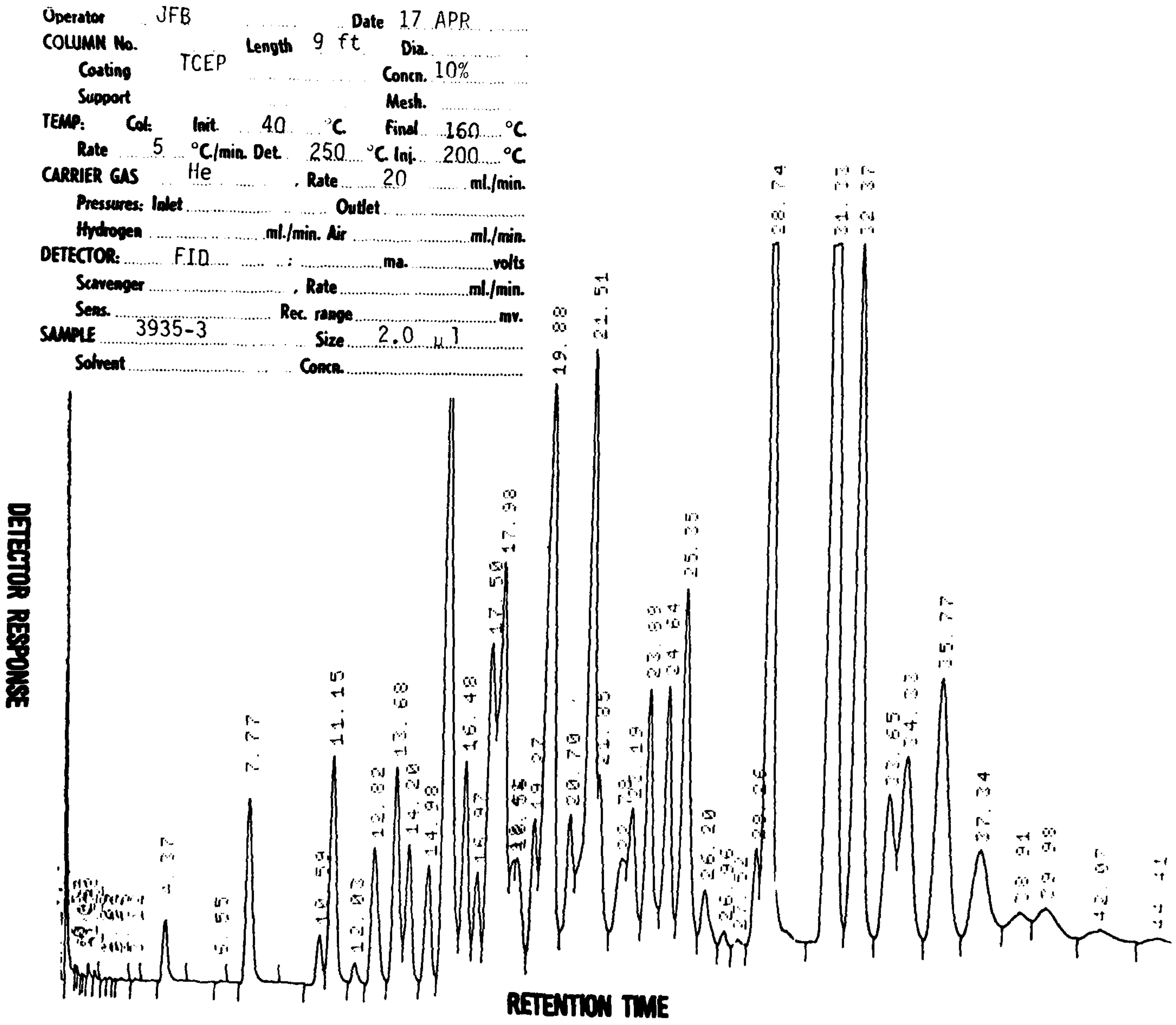
Operator JFB Date 17 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3935-1 Size 0.2 µl
Solvent Concn.

Figure 18. Gas Chromatogram of Sample 3935, LC Fraction 1



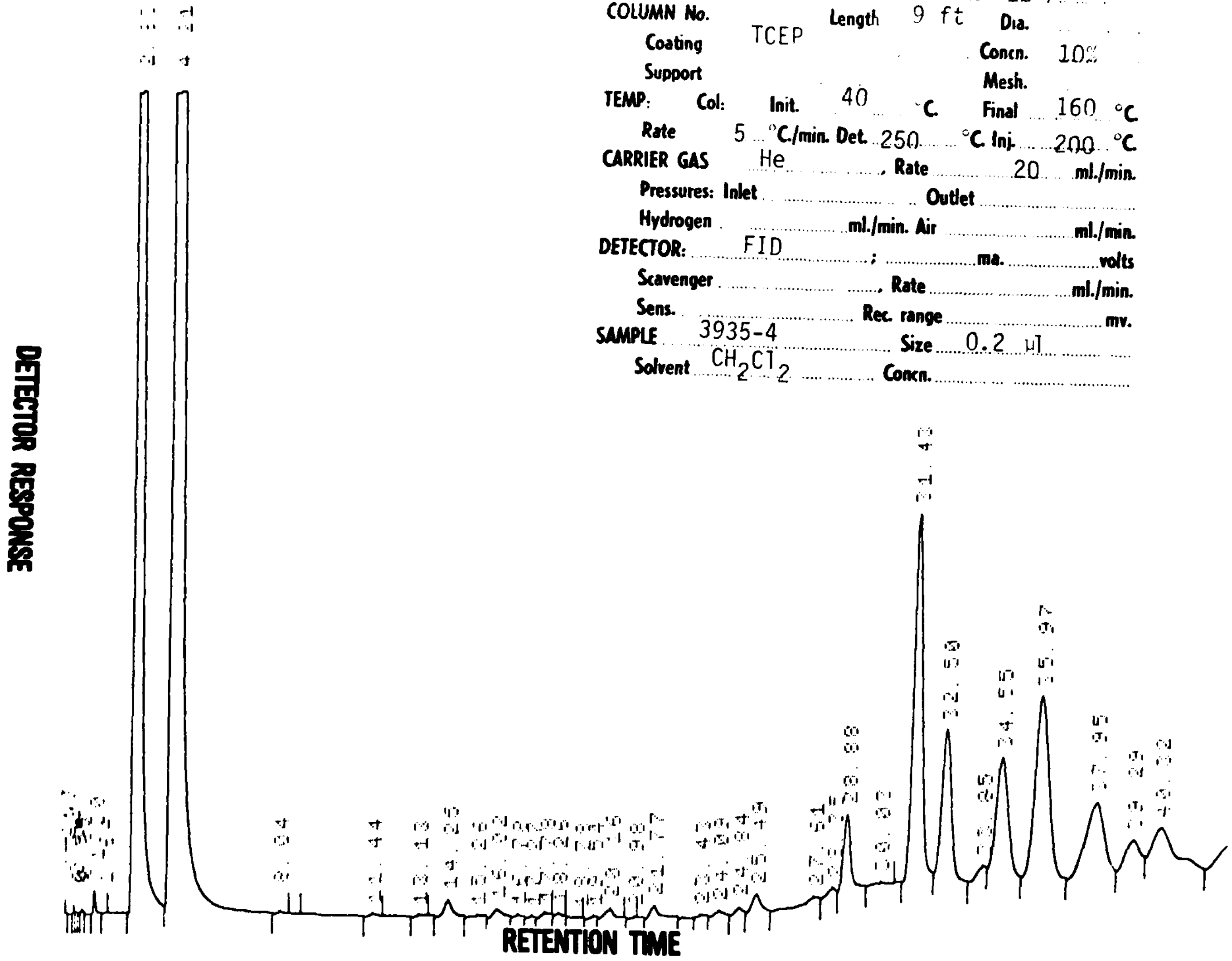
Operator JFB Date 17 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID; ma. volts
Scavenger, Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3935-2 Size 0.2 μl
Solvent Concn.

Figure 19. Cas Chromatogram of Sample 3935, LC Fraction 2



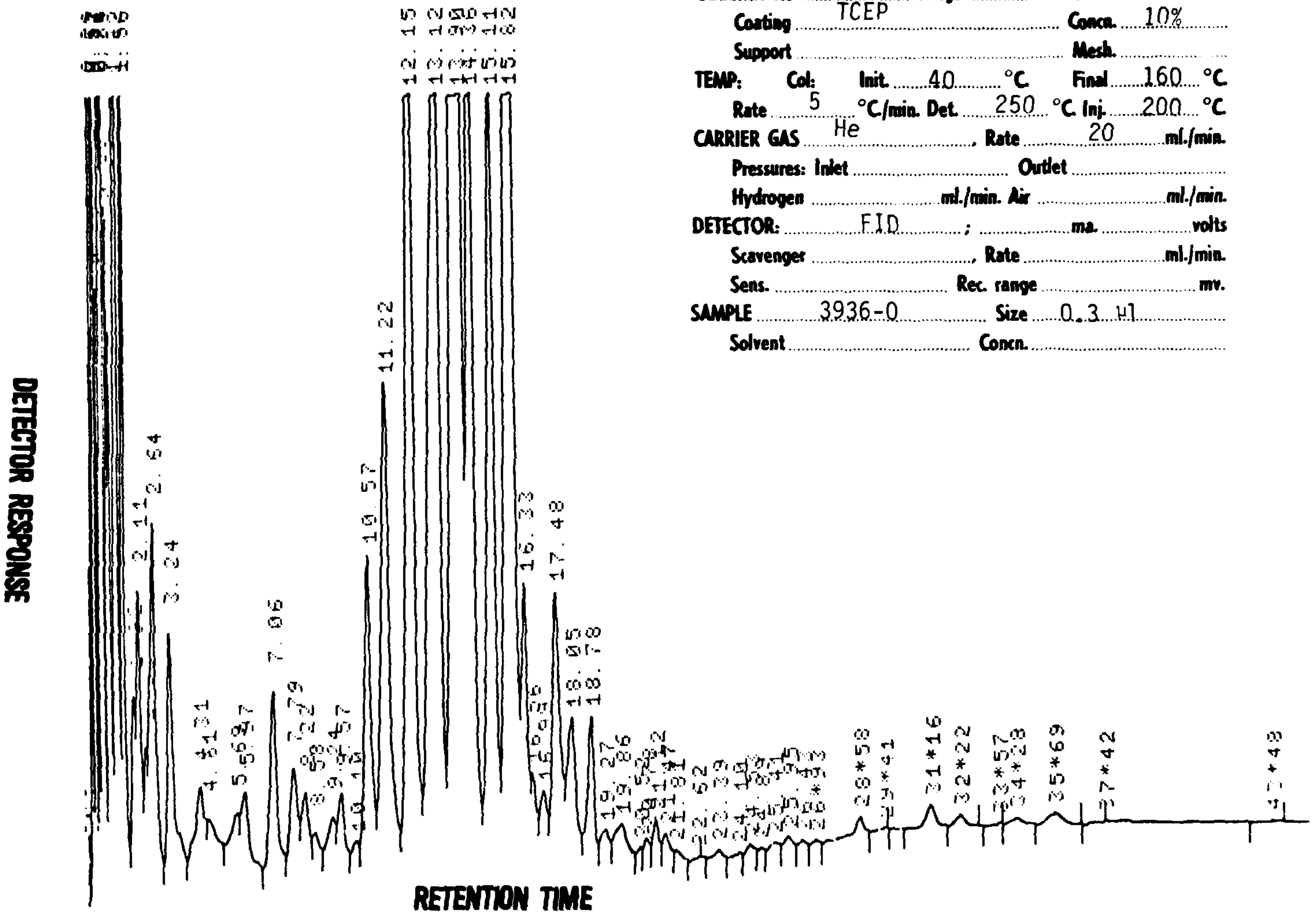
Operator JFB Date 17 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He , Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID : ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3935-3 Size 2.0 μl
Solvent Concn.

Figure 20. Gas Chromatogram of Sample 3935, LC Fraction 3



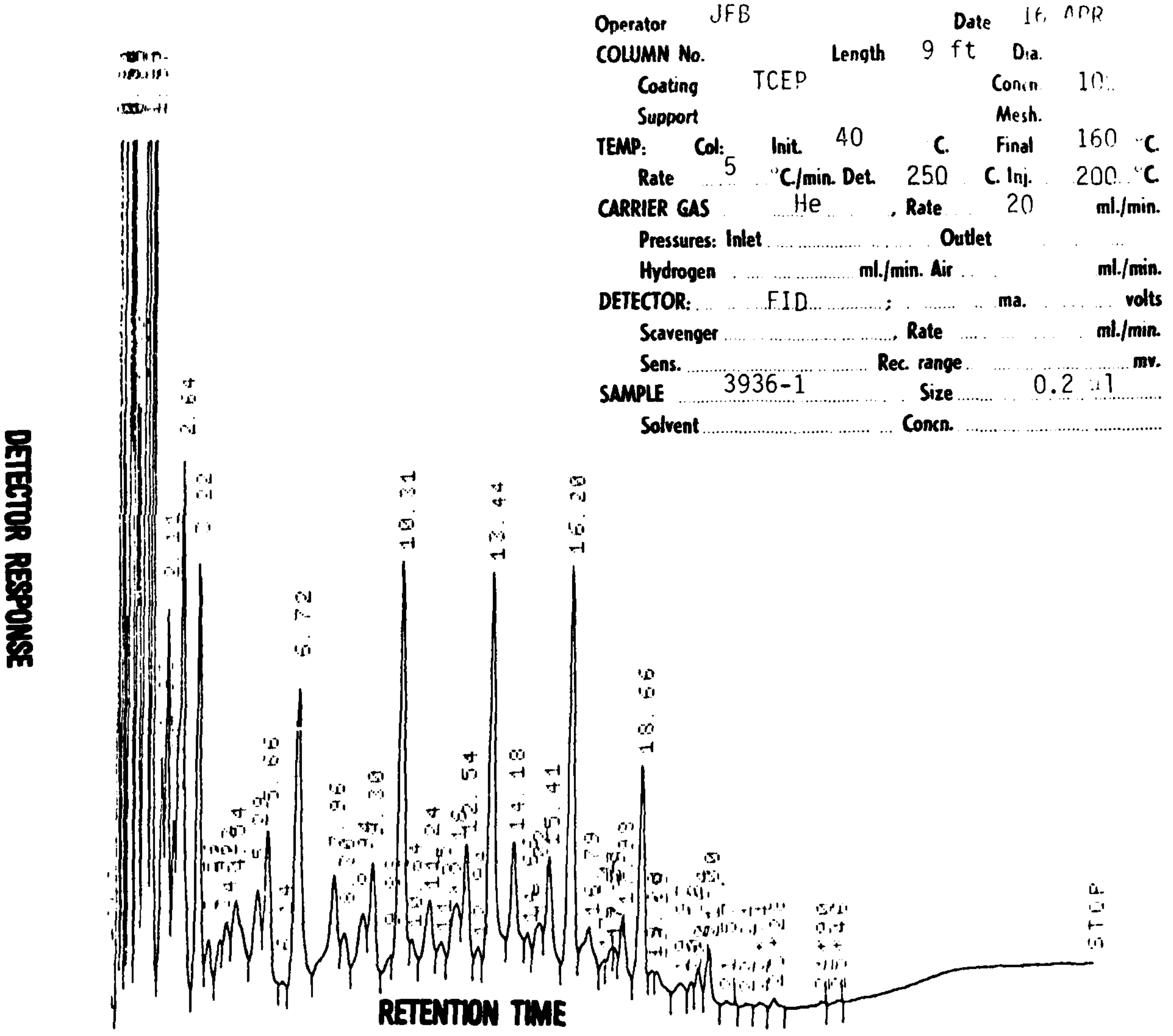
Operator JFB Date 16 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3935-4 Size 0.2 μl
Solvent CH_2Cl_2 Concn.

Figure 21. Gas Chromatogram of Sample 3935, LC Fraction 4



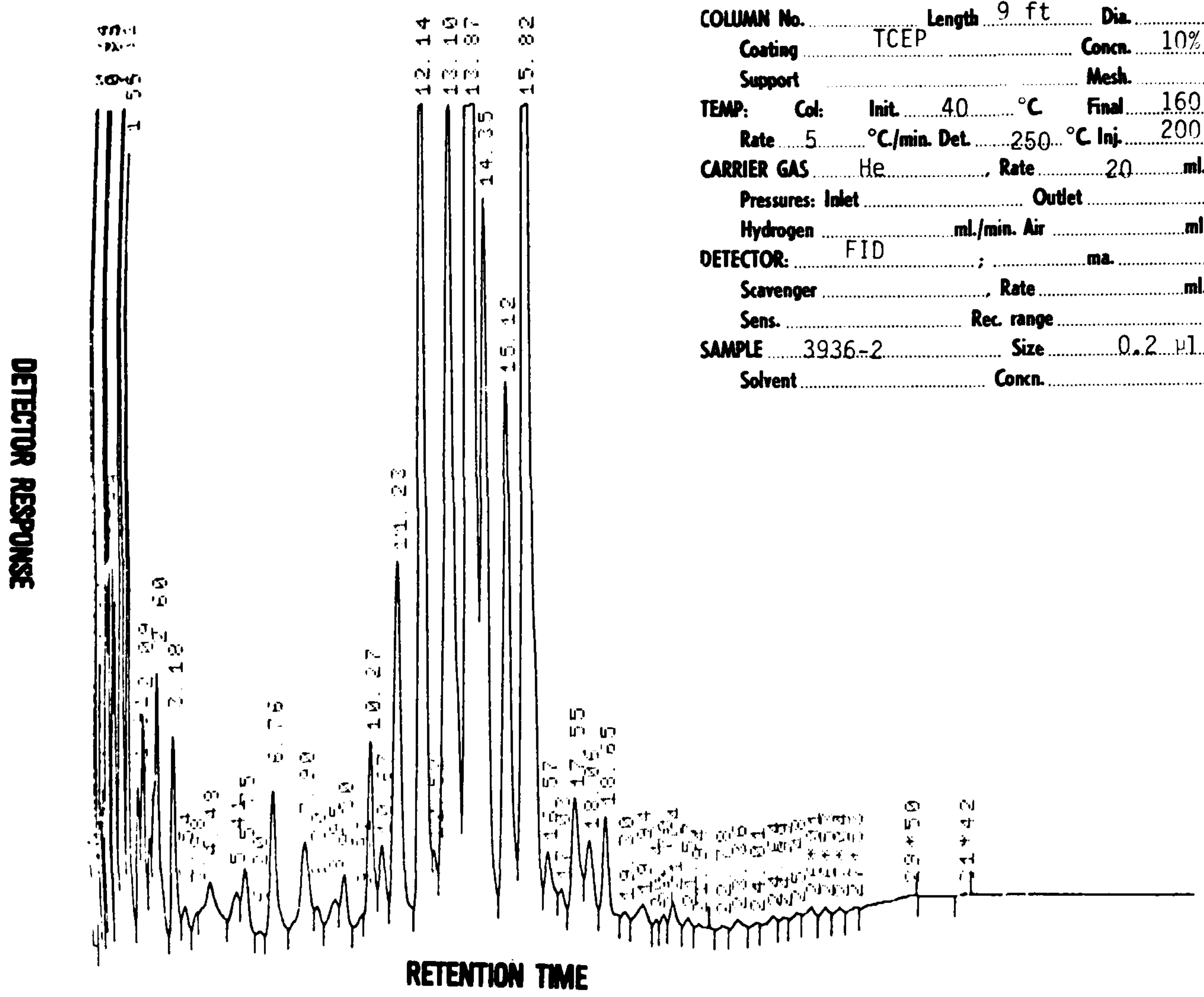
Operator JFB Date 18 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3936-0 Size 0.3 µl
Solvent Concn.

Figure 22. Gas Chromatogram of Sample 3936, Neat



Operator JFB Date 16 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn 10
Support Mesh.
TEMP: Col: Init. 40 C. Final 160 °C
Rate 5 °C/min. Det. 250 C. Inj. 200 °C
CARRIER GAS He , Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3936-1 Size 0.2 µl
Solvent Concn.

Figure 23. Gas Chromatogram of Sample 3936, LC Fraction 1



Operator JFB Date 16 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3936-2 Size 0.2 µl
Solvent Concn.

Figure 24. Gas Chromatogram of Sample 3936, LC Fraction 2

Operator JFB Date 16 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10
Support Mesh.
TEMP: Col: Init. 40 C. Final 160 C.
Rate 5 C./min. Det. 250 C. Inj. 200 C.
CARRIER GAS He , Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3936-3 Size 0.2 µl
Solvent Concn.

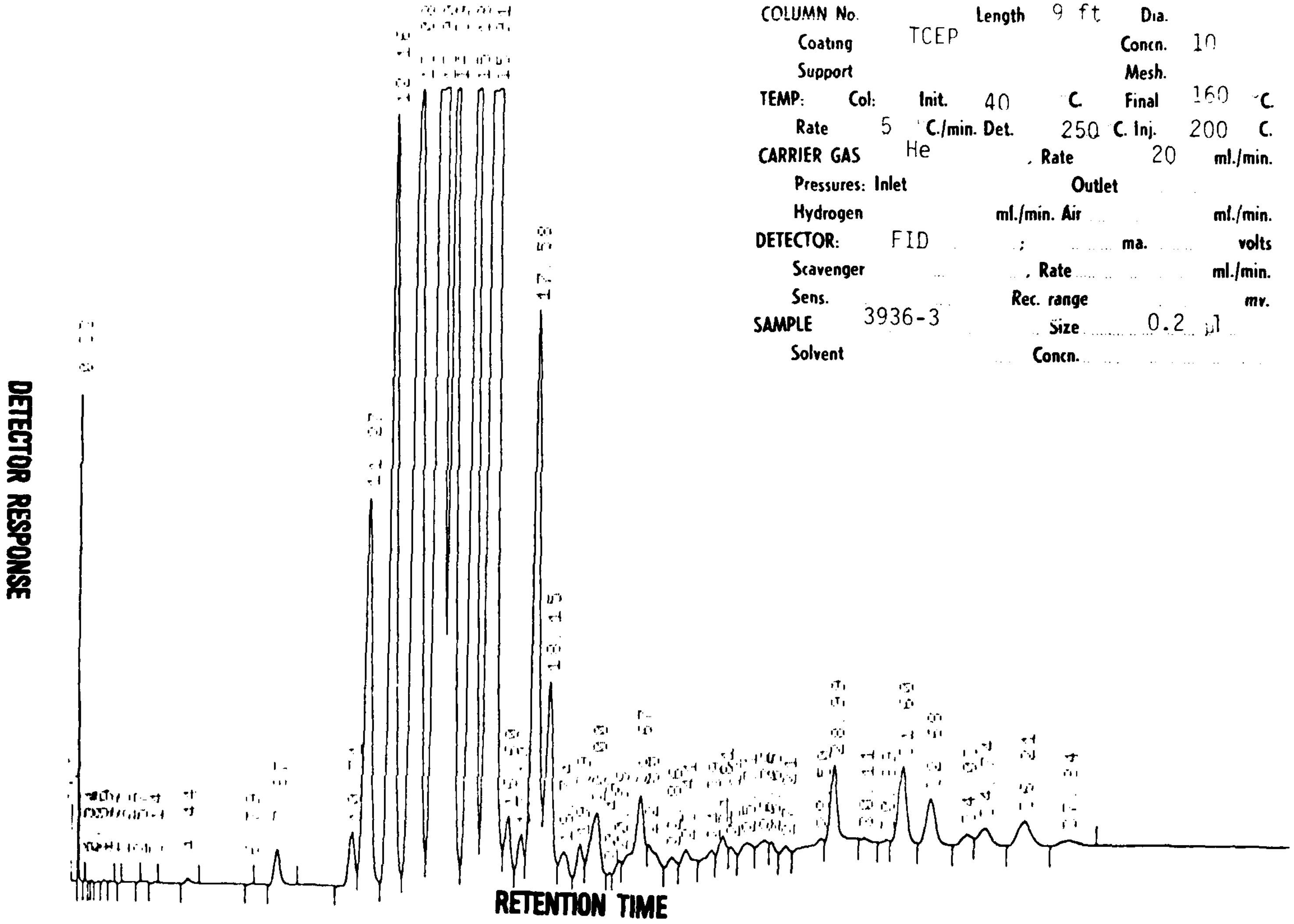


Figure 25. Gas Chromatogram of Sample 3936, LC Fraction 3

Operator JFB **Date** 16 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 **°C Final** 160 **°C**
Rate 5 **°C/min. Det.** 250 **°C Inj.** 200 **°C**
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **;** **ma.** **volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3936-4 **Size** 0.2 μl
Solvent CH_2Cl_2 **Concn.**

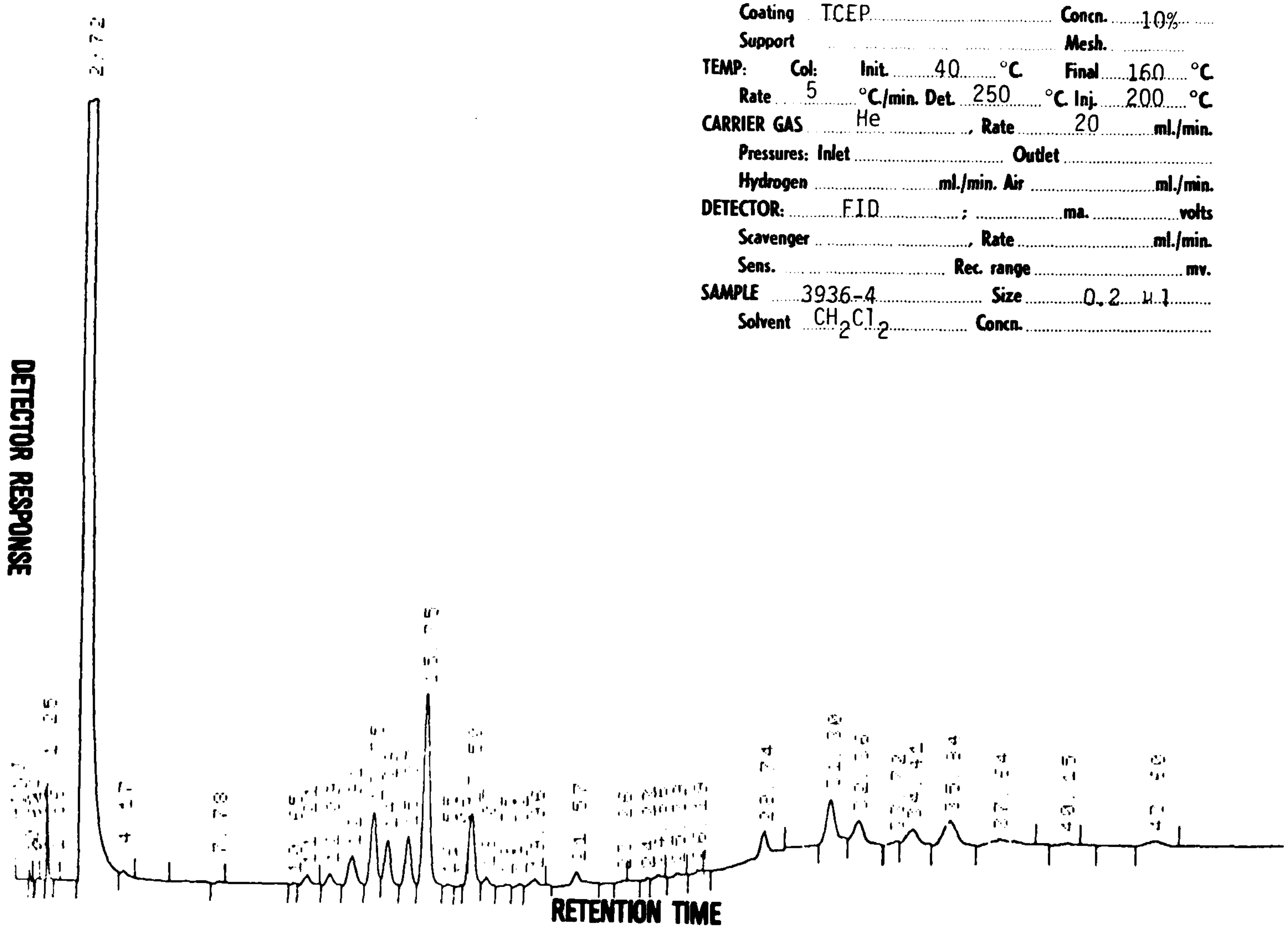
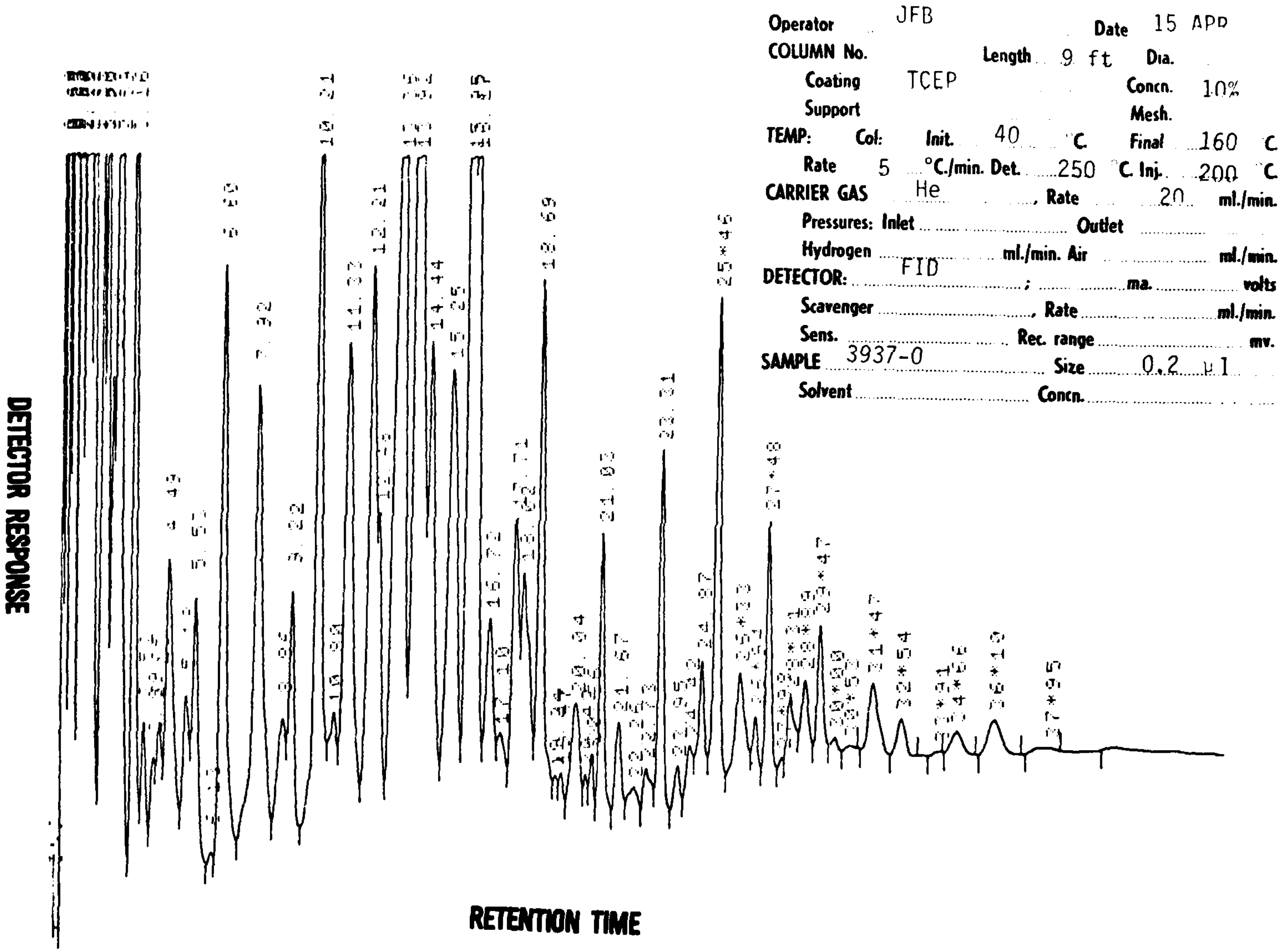


Figure 26 Gas Chromatogram of Sample 3936, LC Fraction 4



Operator JFB Date 15 APR

COLUMN No. Length 9 ft Dia.

Coating TCEP Concn. 10%

Support Mesh.

TEMP: Col: Init. 40 °C. Final 160 °C

Rate 5 °C./min. Det. 250 °C. Inj. 200 °C

CARRIER GAS He , Rate 20 ml./min.

Pressures: Inlet Outlet

Hydrogen ml./min. Air ml./min.

DETECTOR: FID ; ma. volts

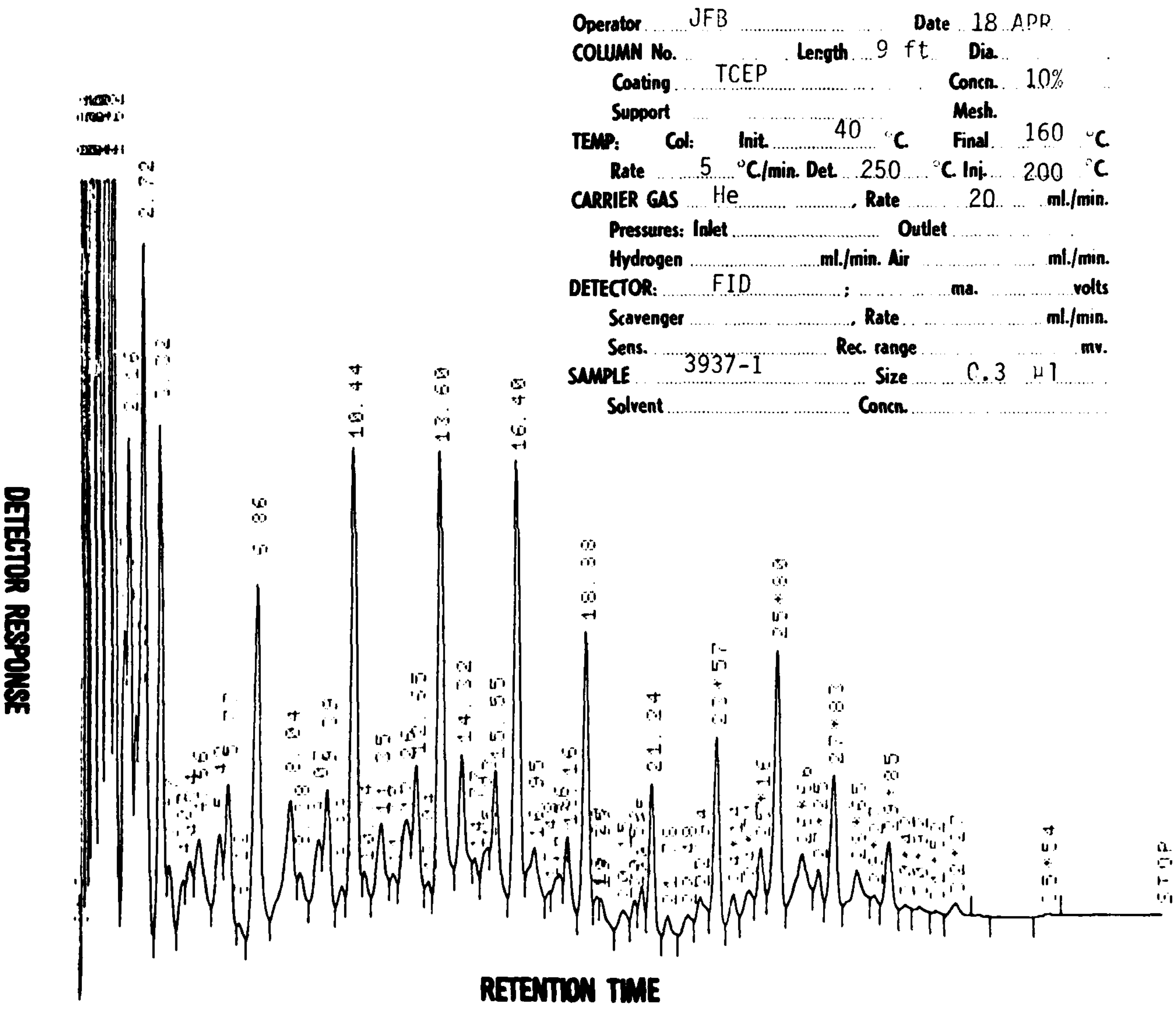
Scavenger , Rate ml./min.

Sens. Rec. range mv.

SAMPLE 3937-0 Size 0.2 µl

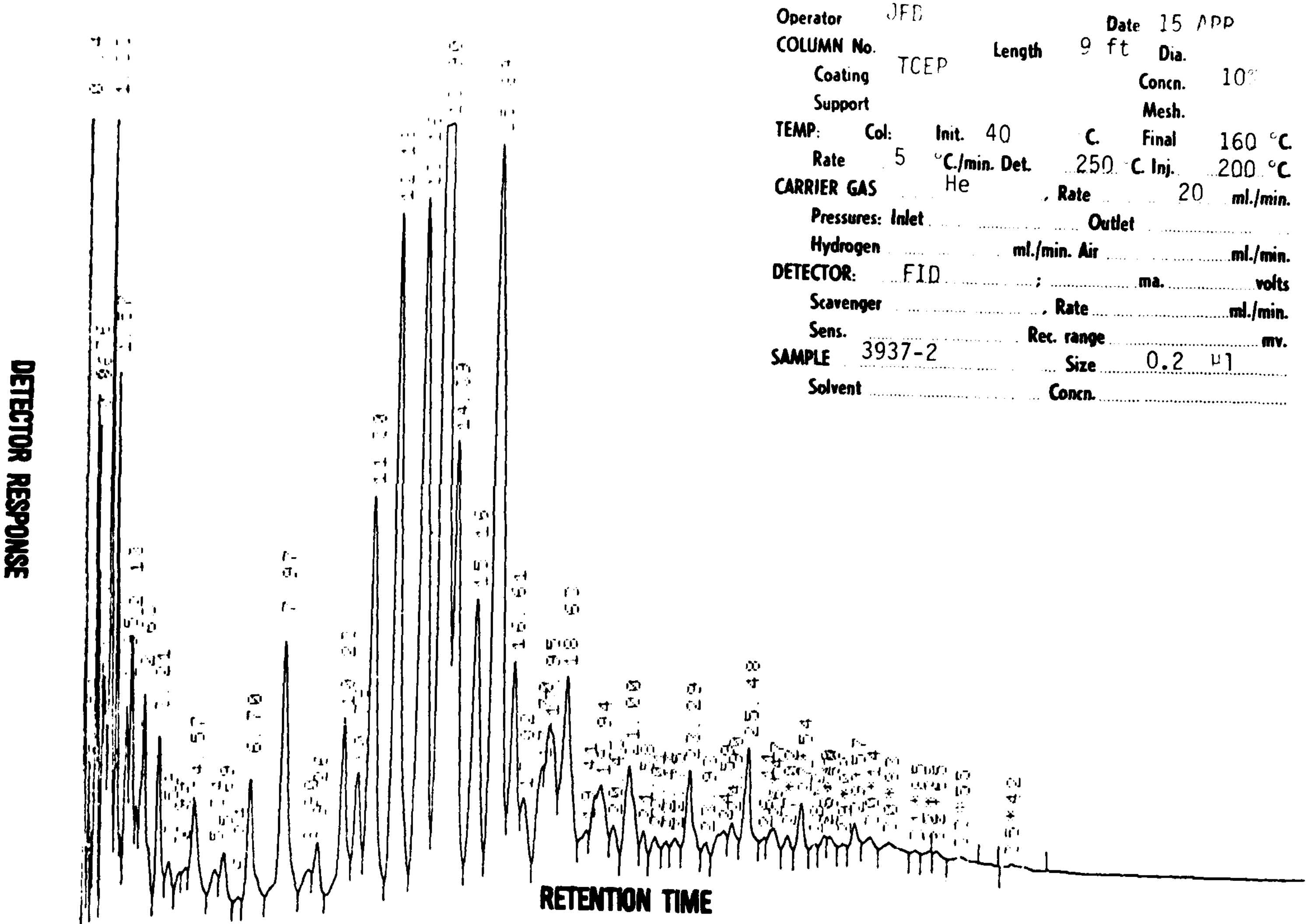
Solvent Concn.

Figure 27. Gas Chromatogram of Sample 3937, Neat



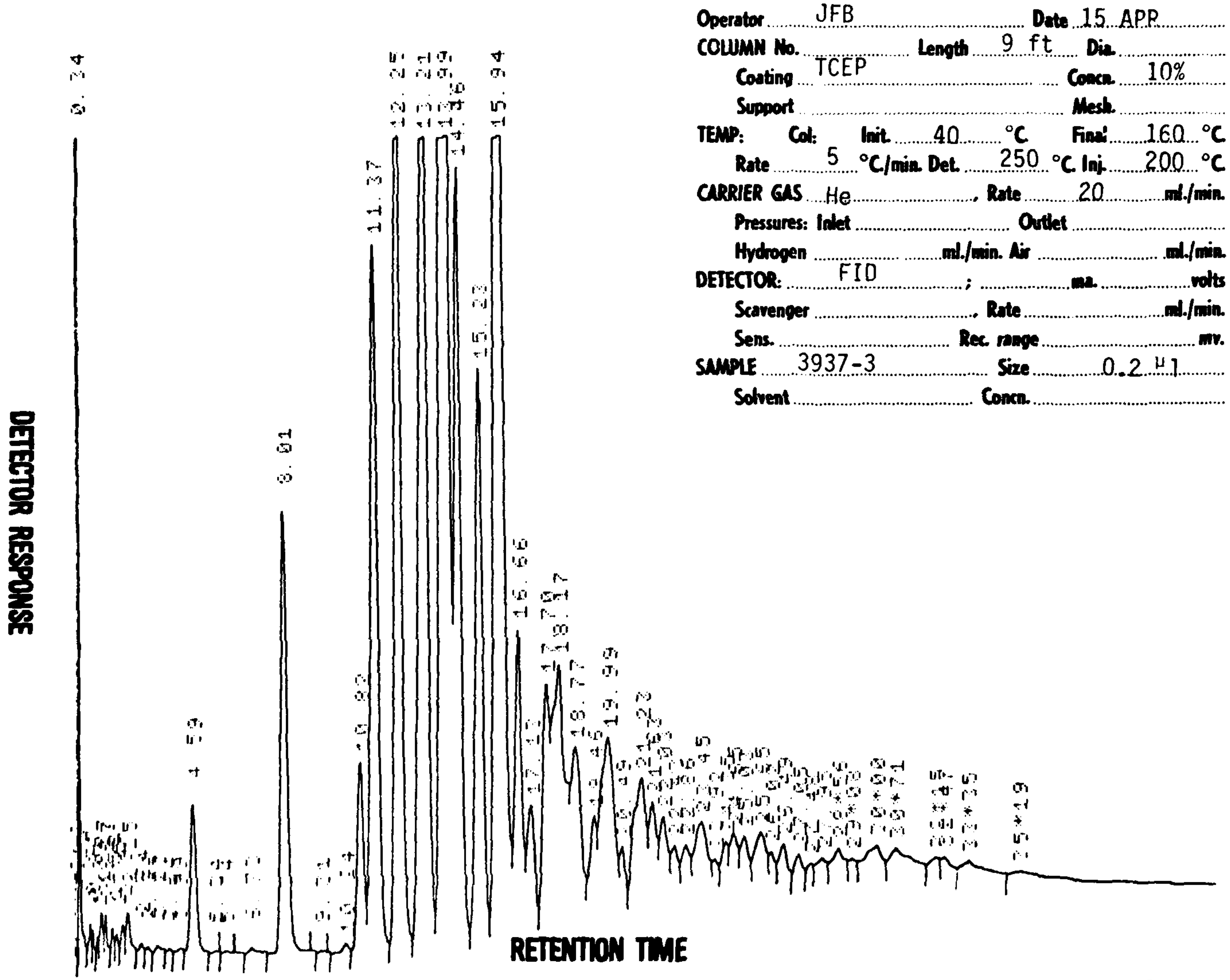
Operator JFB **Date** 18 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 °C **Final** 160 °C
Rate 5 °C/min. **Det.** 250 °C **Inj.** 200 °C
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **;** **ma.** **volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3937-1 **Size** 0.3 µl
Solvent **Concn.**

Figure 28. Gas Chromatogram of Sample 3937, LC Fraction 1



Operator JFD Date 15 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 C. Final 160 °C.
Rate 5 °C./min. Det. 250 C. Inj. 200 °C.
CARRIER GAS He , Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3937-2 Size 0.2 μl
Solvent Concn.

Figure 29. Gas Chromatogram of Sample 3937, LC Fraction 2



Operator JFB Date 15 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger, Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3937-3 Size 0.2 µl
Solvent Concn.

Figure 30. Gas Chromatogram of Sample 3937, LC Fraction 3

Operator JFB **Date** 16 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 °C **Final** 160 °C
Rate 5 °C/min. **Det.** 250 °C **Inj.** 200 °C
CARRIER GAS He, **Rate** 20 ml./min.
Pressures: Inlet **Outlet**
Hydrogen ml./min. **Air** ml./min.
DETECTOR: FID ; ma. volts
Scavenger , **Rate** ml./min.
Sens. **Rec. range** mv.
SAMPLE 3937-4 **Size** 0.2 µl
Solvent CH_2Cl_2 **Concn.**

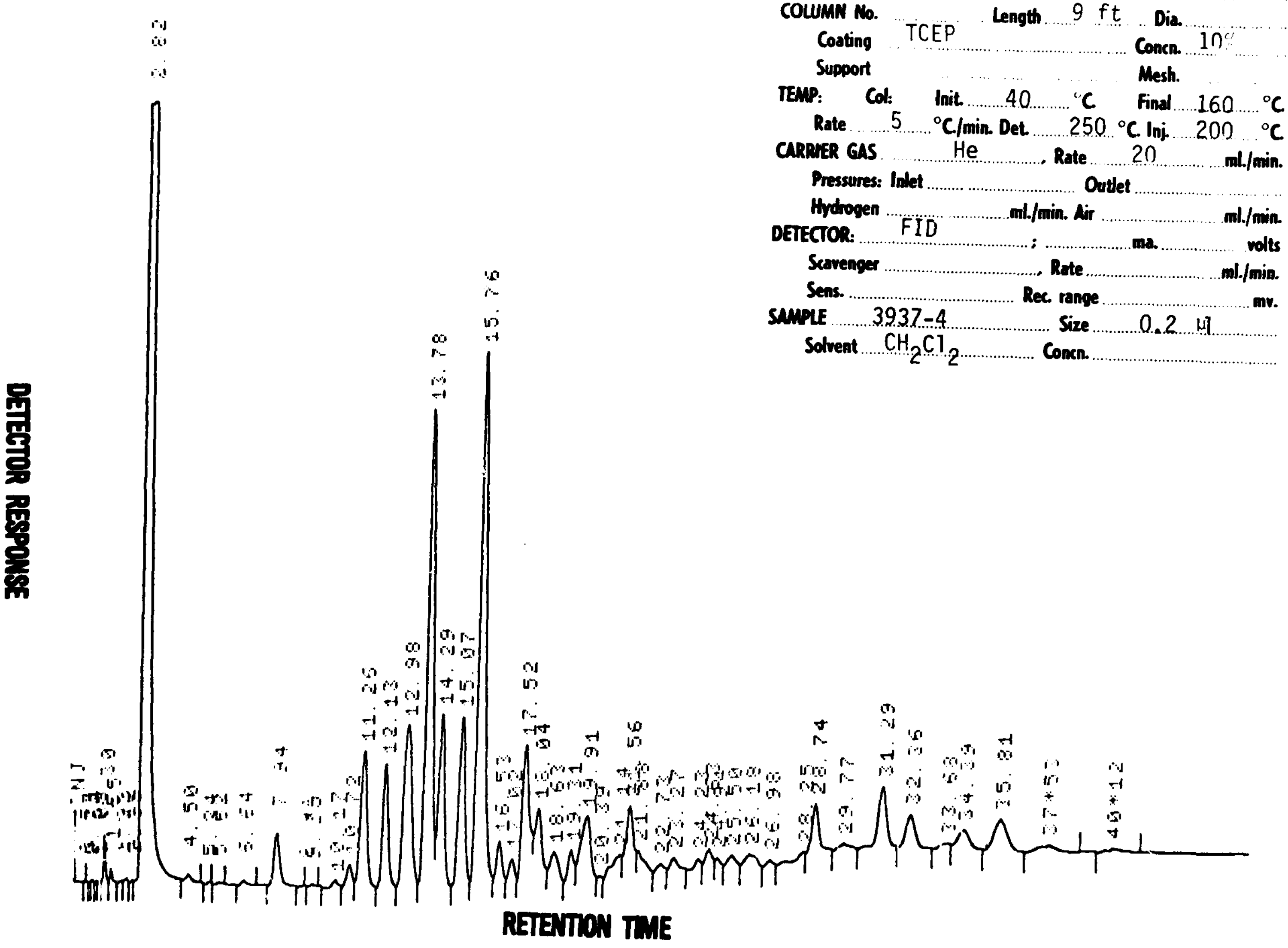
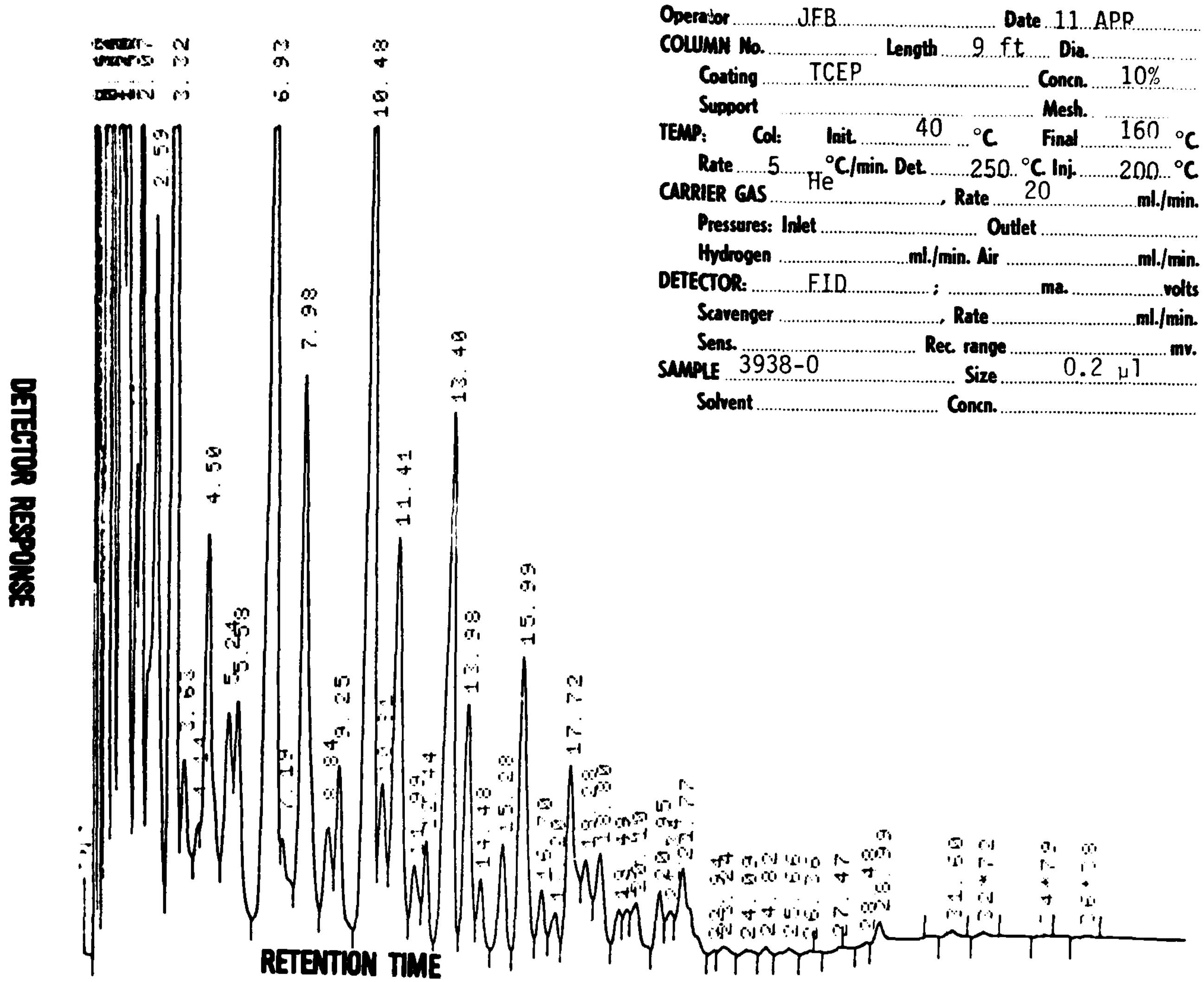
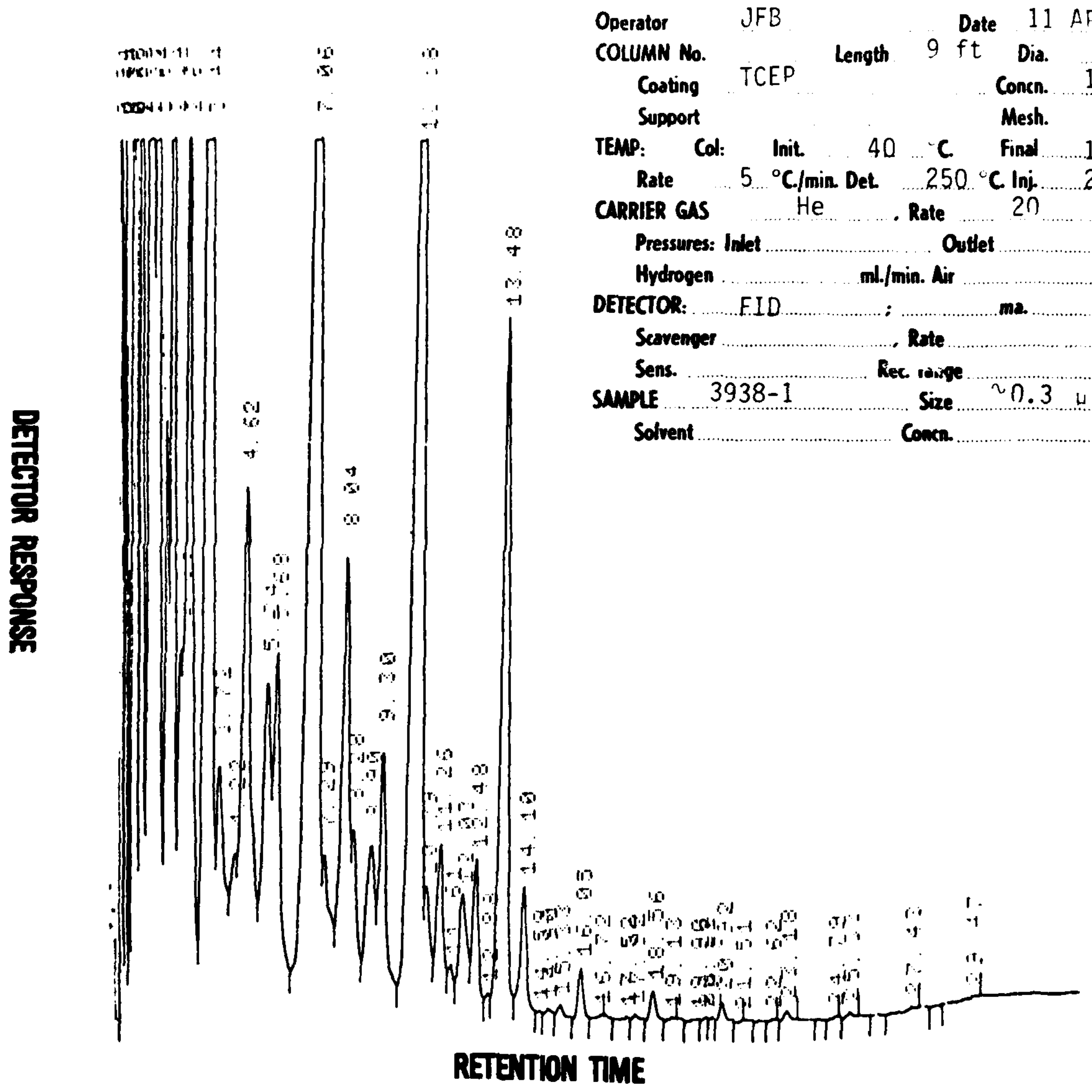


Figure 31. Gas Chromatogram of Sample 3937, LC Fraction 4



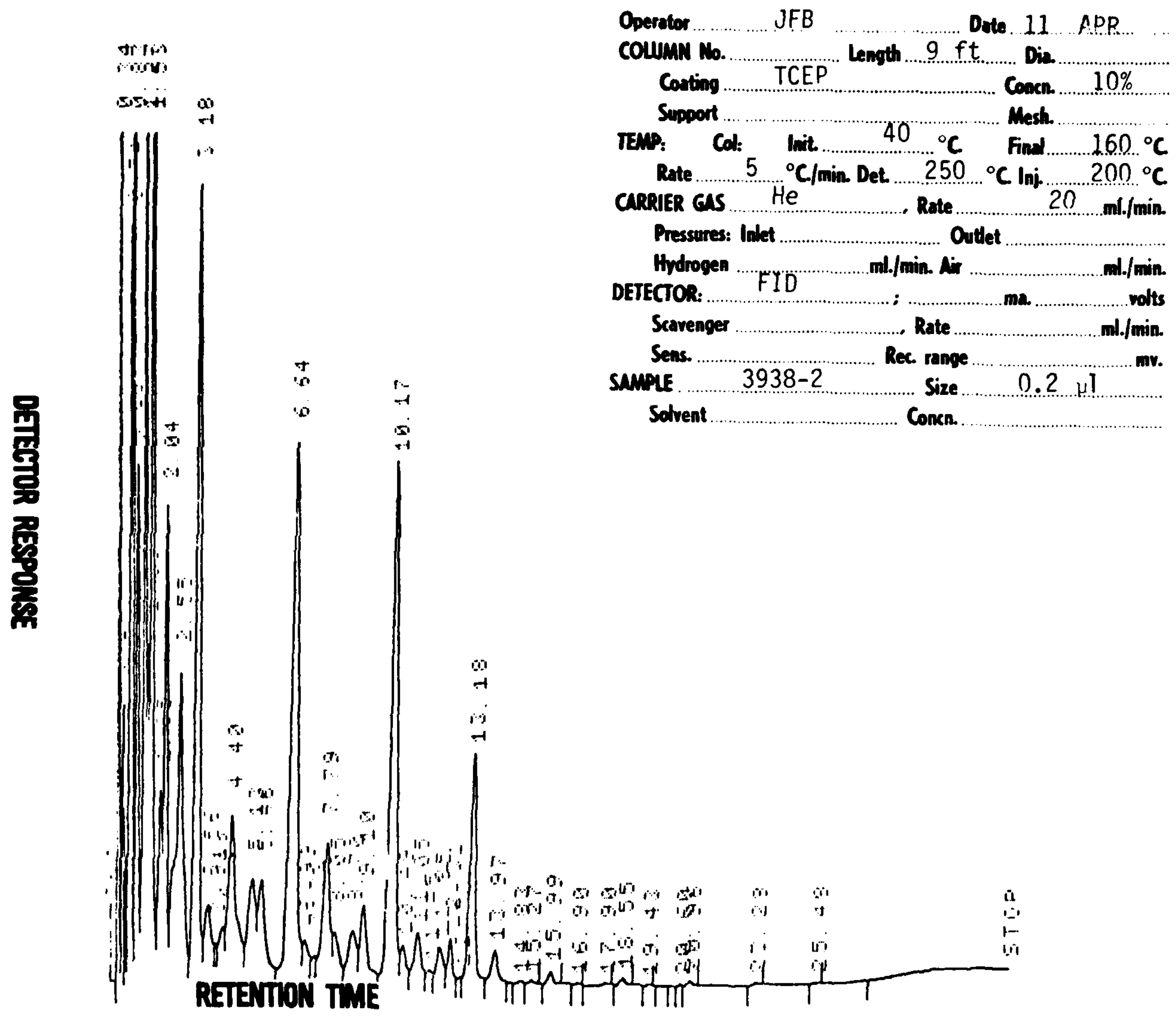
Operator JFB Date 11 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3938-0 Size 0.2 µl
Solvent Concn.

Figure 32. Gas Chromatogram of Sample 3938, Neat



Operator JFB **Date** 11 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 °C **Final** 160 °C
Rate 5 **°C./min. Det.** 250 **°C Inj.** 200 °C
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **;** **ma.** **volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3938-1 **Size** ~0.3 μl
Solvent **Concn.**

Figure 33. Gas Chromatogram of Sample 3938, LC Fraction 1



Operator JFB **Date** 11 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 **°C Final** 160 **°C**
Rate 5 **°C/min. Det.** 250 **°C Inj.** 200 **°C**
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **; ma. volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3938-2 **Size** 0.2 µl
Solvent **Concn.**

Figure 34. Gas Chromatogram of Sample 3938, LC Fraction 2

Operator JFB **Date** 11 APP
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 **°C. Final** 160 **°C.**
Rate 5 **°C./min. Det.** 250 **°C. Inj.** 200 **°C.**
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **;** **ma.** **volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3938-3 **Size** 0.2 µl
Solvent **Concn.**

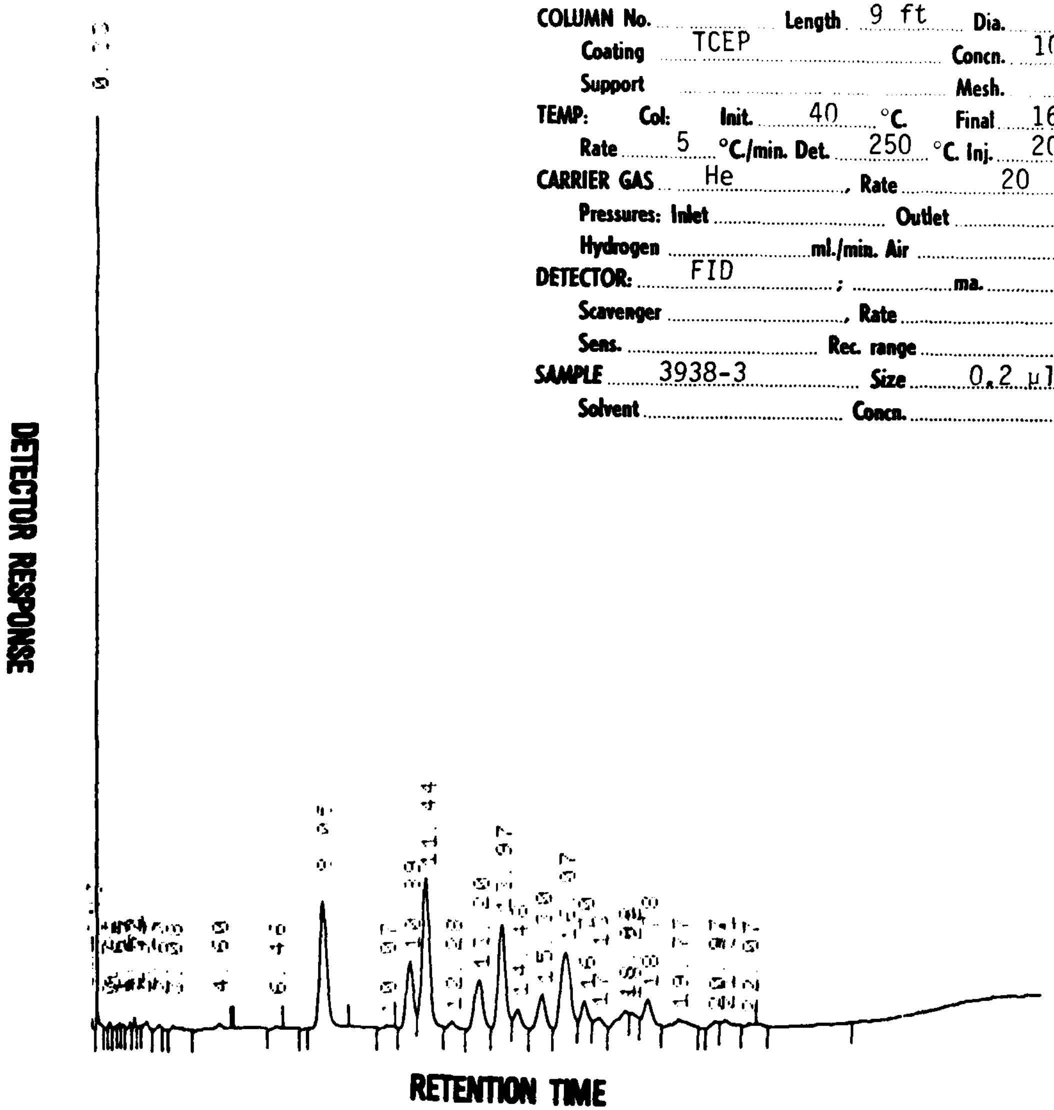
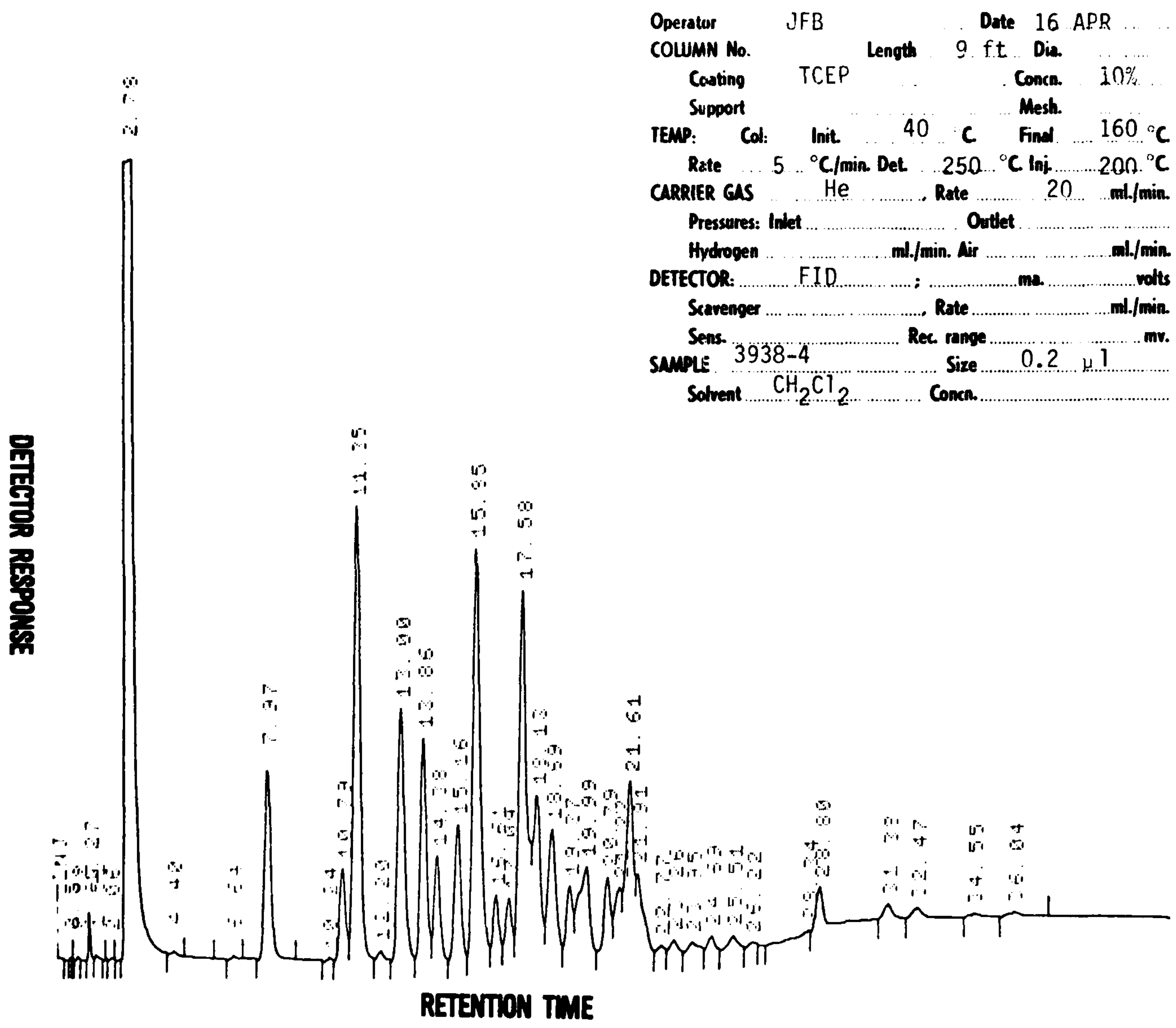
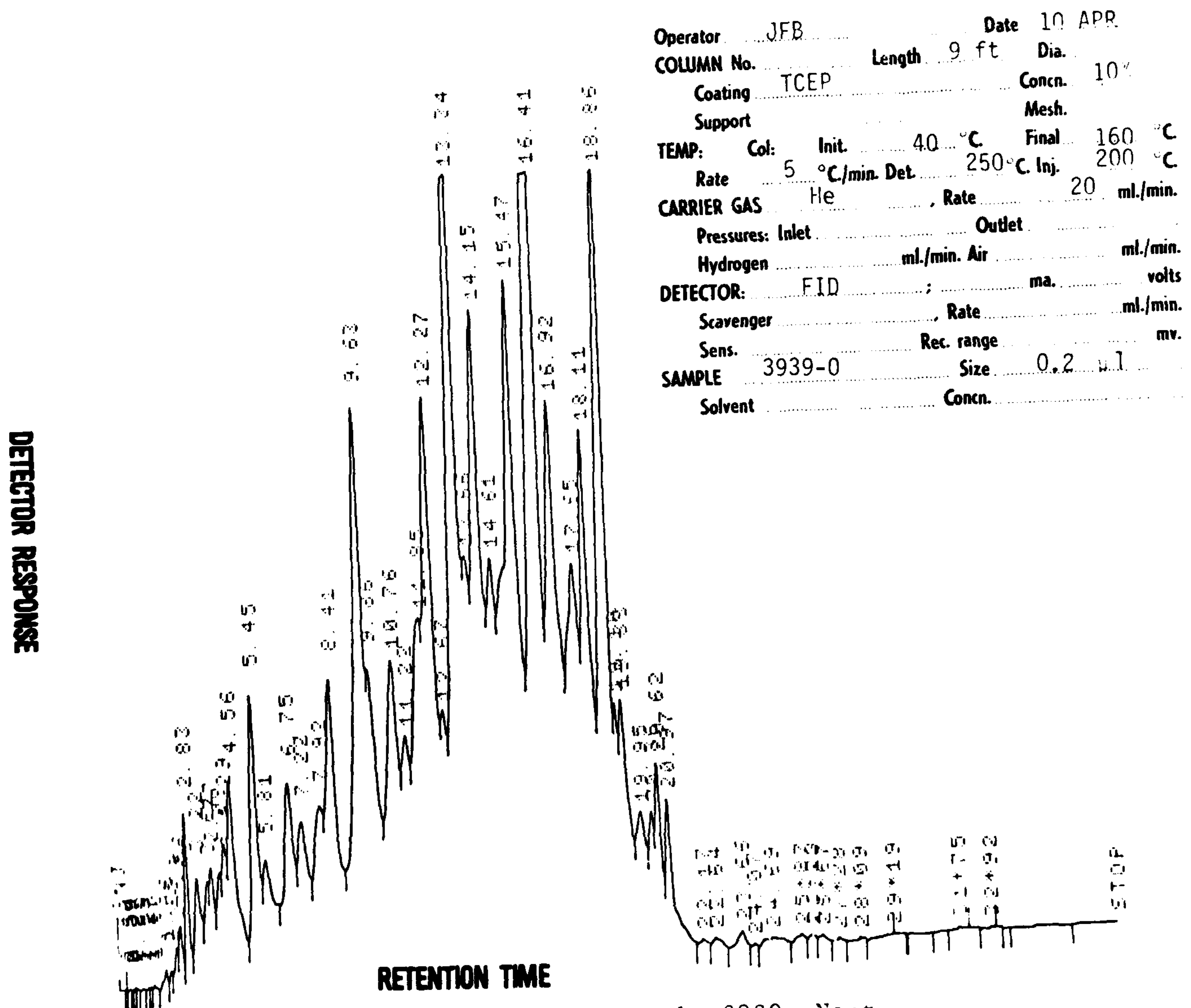


Figure 35. Gas Chromatogram of Sample 3938, LC Fraction 3



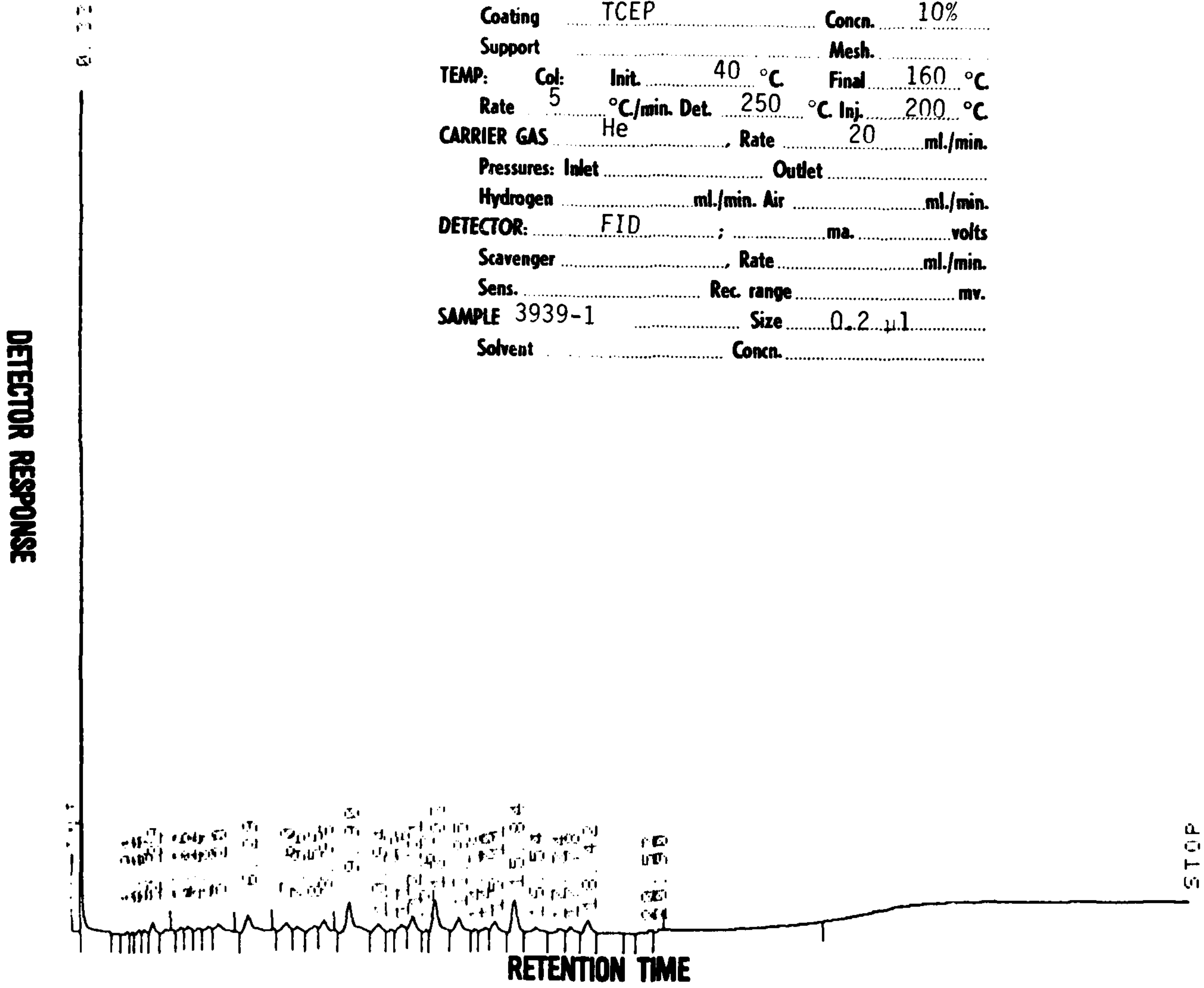
Operator JFB **Date** 16 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 **C Final** 160 **°C**
Rate 5 **°C/min. Det.** 250 **°C Inj.** 200 **°C**
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **;** **ma.** **volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3938-4 **Size** 0.2 µl
Solvent CH_2Cl_2 **Concn.**

Figure 36. Gas Chromatogram of Sample 3938, LC Fraction 4



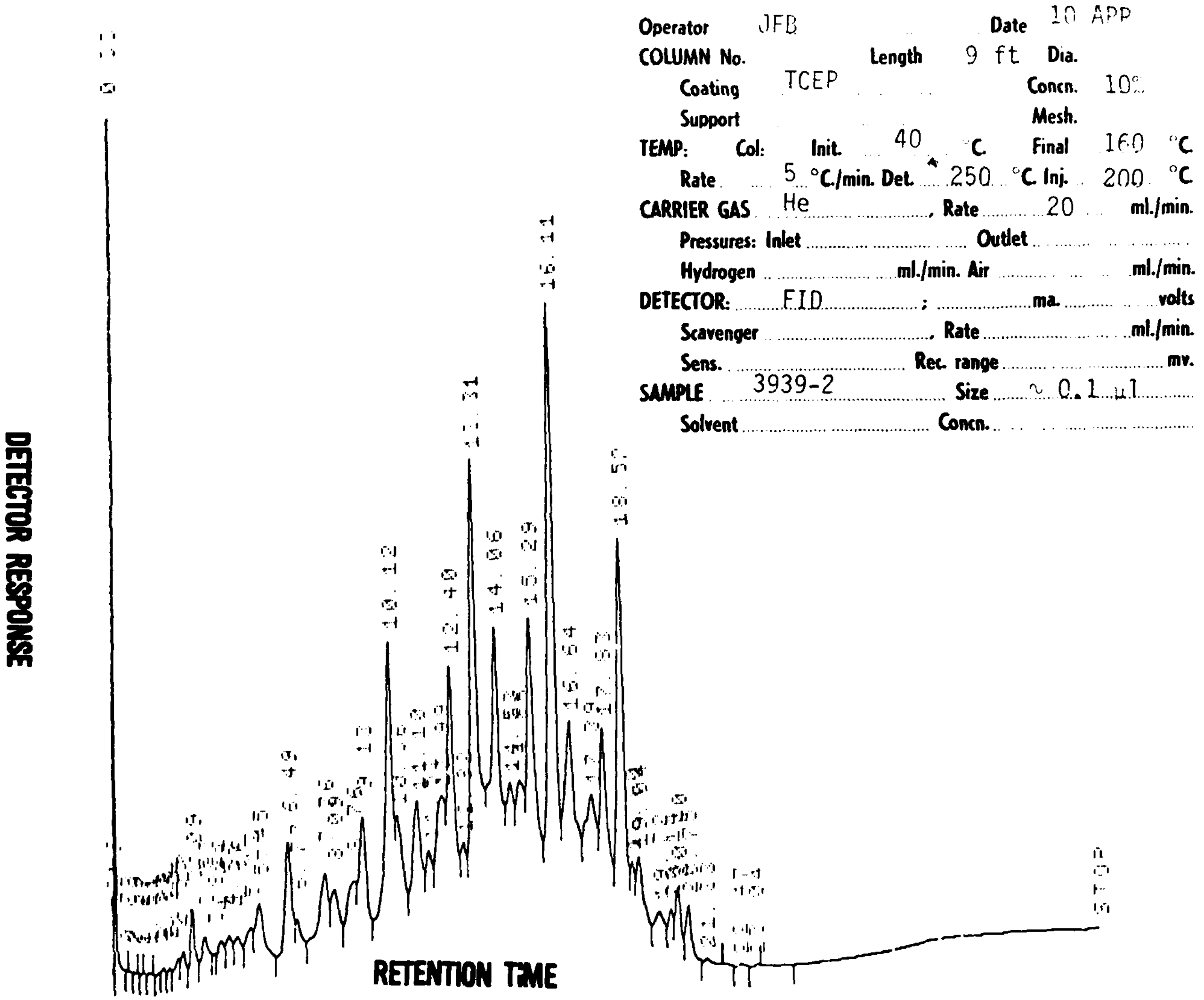
Operator JFB Date 10 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C. Final 160 °C.
Rate 5 °C./min. Det. 250 °C. Inj. 200 °C.
CARRIER GAS He , Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger , Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3939-0 Size 0.2 µl
Solvent Concn.

Figure 37. Gas Chromatogram of Sample 3939. Neat



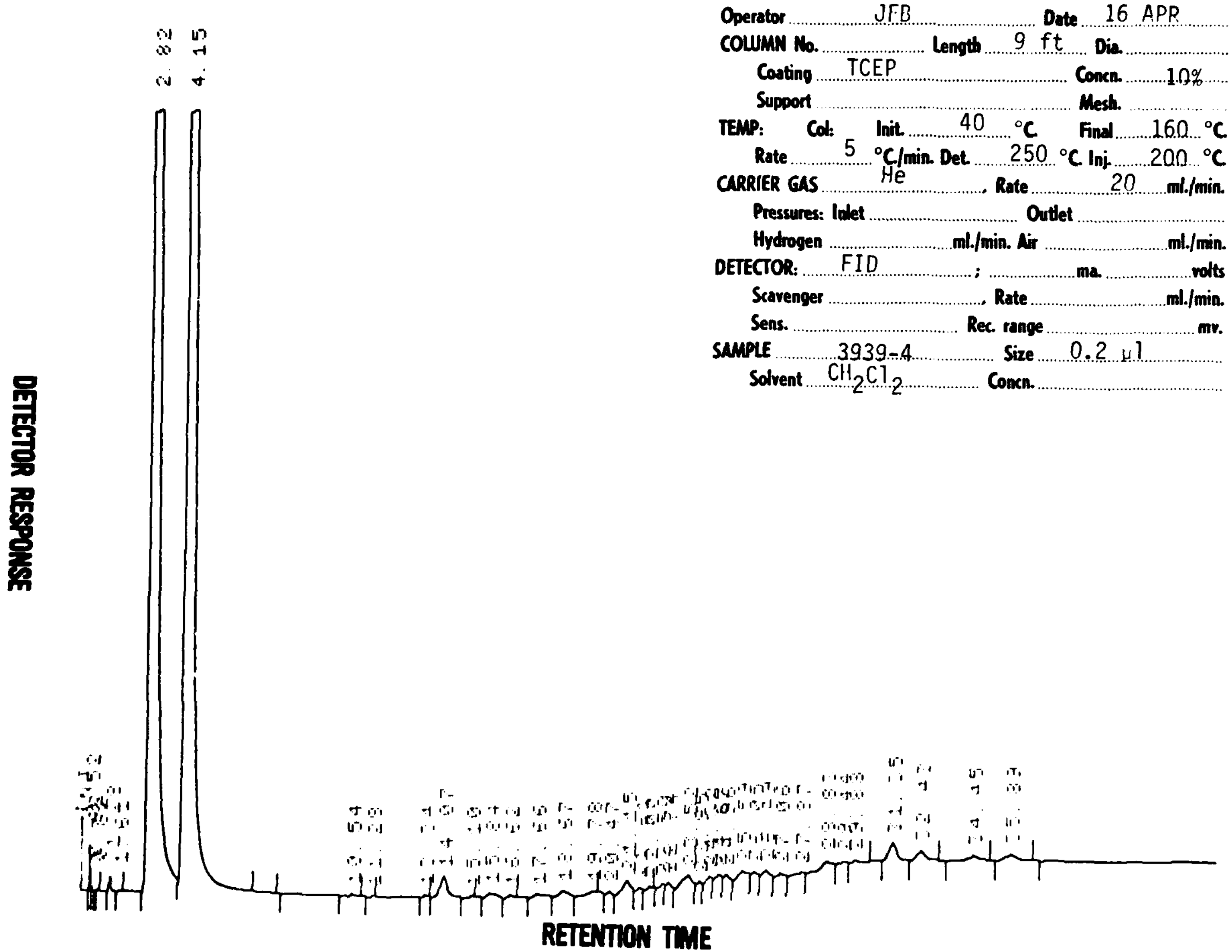
Operator JFB **Date** 10 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 **°C Final** 160 **°C**
Rate 5 **°C/min. Det.** 250 **°C Inj.** 200 **°C**
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **;** **ma.** **volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3939-1 **Size** 0.2 μl
Solvent **Concn.**

Figure 38. Gas Chromatogram of Sample 3939, LC Fraction 1



Operator JFB Date 10 APR
COLUMN No. Length 9 ft Dia.
Coating TCEP Concn. 10%
Support Mesh.
TEMP: Col: Init. 40 °C Final 160 °C
Rate 5 °C/min. Det. 250 °C Inj. 200 °C
CARRIER GAS He, Rate 20 ml./min.
Pressures: Inlet Outlet
Hydrogen ml./min. Air ml./min.
DETECTOR: FID ; ma. volts
Scavenger, Rate ml./min.
Sens. Rec. range mv.
SAMPLE 3939-2 Size ~ 0.1 µl
Solvent Concn.

Figure 39. Gas Chromatogram of Sample 3939, LC Fraction 2



Operator JFB **Date** 16 APR
COLUMN No. **Length** 9 ft **Dia.**
Coating TCEP **Concn.** 10%
Support **Mesh.**
TEMP: Col: Init. 40 **°C Final** 160 **°C**
Rate 5 **°C/min. Det.** 250 **°C Inj.** 200 **°C**
CARRIER GAS He **, Rate** 20 **ml./min.**
Pressures: Inlet **Outlet**
Hydrogen **ml./min. Air** **ml./min.**
DETECTOR: FID **;** **ma.** **volts**
Scavenger **, Rate** **ml./min.**
Sens. **Rec. range** **mv.**
SAMPLE 3939-4 **Size** 0.2 µl
Solvent CH_2Cl_2 **Concn.**

Figure 40. Gas Chromatogram of Sample 3939, LC Fraction 4

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

The accumulated data from the separation and analysis of the various fuel samples, as well as the model compounds, indicate that the method developed is feasible for the intended purpose. Good separations were achieved for aliphatic and aromatic compounds. Fairly good separation of olefinic compounds was also realized. However, relatively poor or no separation occurred between linear, branched, and cyclic aliphatic compounds.

Experiments with the use of longer columns suggest that partial separation of the various aliphatic hydrocarbon classes might be at least feasible.

The results also indicate that the plate efficiencies of the silica gel columns used in this system were rather poor. This fact may have been partly due to channeling resulting from bubble formation in the low-boiling solvent. The use of a totally pressurized system with continuous monitoring of the eluate, rather than intermittent fraction collection, should alleviate this problem.

Isobutane was selected as the mobile phase because of its reasonable cost, its low boiling point, and its generally innocuous nature. This compound was found, in fact, to be easily separable from the collected sample fractions. However, better resolution of compound classes might be achieved by using a low-boiling perfluorinated solvent. Compounds of this type are generally less polar than hydrocarbons, and should therefore provide better selectivity for the different aliphatic compound classes. Indeed, a dual solvent system employing both fluorocarbons and hydrocarbon mobile phases might be devised which could greatly enhance the separation of the fuel components.

In summary, we believe that the general objectives of this exploratory project were accomplished. Although the desired degree of separation was not obtained for all the compound classes, further work along the lines suggested above should greatly improve the separation efficiency of the method.

SECTION V

ADDITIONAL CONSIDERATIONS

A. Environmental Impact

It is conceivable that the separation method, as devised, could help in the ultimate development of fuel formulations having better air pollution properties than existing fuels. The environmental impact of the experimental method itself, however, is negligible. In the event that other mobile phases, particularly any of the various fluorocarbons, were used as suggested previously in this report, measures would have to be taken to recover them rather than venting them to the atmosphere. Such recovery would also be desirable from an economic standpoint, since such compounds are relatively costly.

B. Suggestions For Method Scale-Up

The method as developed, using 10-mm ID columns, is applicable to samples up to a maximum of a few hundred microliters. In order to provide the capacity for sample volumes up to about 10 mL, the column diameter would have to be increased to about 50 mm. This larger column diameter would necessitate mobile phase flow rates up to 50 mL per minute in order to maintain the same solvent linear velocity, and therefore preserve the separation patterns observed in the present method. Such large flow rates would necessitate the use of relatively large quantities of mobile phase, and for safety purposes would no doubt require the design of some type of solvent recovery system.

The separation of even larger amounts of fuel, e. g., 100 mL, could be achieved using a 50-mm preparative column, and running repetitive injections of 10 mL samples. The fractions would then be combined from successive runs. This system would, of course, be rather tedious and would require good control of flow rates, temperature, and other chromatographic parameters.

Scale-up to liter quantities seems unfeasible using the system described in this report. In order to separate one liter of fuel in a single run, column diameters up to 130 cm would be necessary. Such columns are very difficult to pack and generally provide low efficiencies. Furthermore, the mobile phase flow rates and volumes required would be prohibitive. A better technique would probably involve fractional distillation of the fuels.

U.S.Government Printing Office: 1981 -- 757-002/623