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SYNTHESIS OF p-TRIFLUOROMETHYL-TOLUENE AND 3,6-BIS(TRIFLUOROMETHYL)PHENANTHRENE USING SULFUR TETRAFLUORIDE

FINAL COMPREHENSIVE REPORT

Andrew J. Woytek, James F. Tompkins (Investigators)

David R. Latshaw, Barton Milligan
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U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
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Contract No. DADA-17-70-C-0007

Air Products and Chemicals, Inc.
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I. Summary

The object of this work was to investigate, on a laboratory scale, the individual reactions of SF_4 with p-toluic acid to produce p-trifluoromethyl toluene and of 3,6-phenanthrene dicarboxylic acid to produce 3,6-bis(trifluoromethyl)phenanthrene. This laboratory data was to serve as a basis for scaleup of this reactions to a commercial process.

A total of 46 runs were conducted during this investigation with 16 runs performed with p-toluic acid in a 300 ml autoclave, 10 runs with p-toluic acid in a 1750 ml autoclave, and 20 runs with 3,6-phenanthrene dicarboxylic acid in the 300 ml autoclave. The parameters investigated were temperature over the range of 20°C to 225°C, pressure over the range of 140 to 3,000 psig, reaction times from one to 18 hours, SF_4 concentrations at 50% to 4,500% excess, catalysis with hydrogen fluoride and the use of inert solvents for the 3,6-phenanthrene dicarboxylic acid runs.

The p-toluic acid reaction was initially studied in a 300 ml hastelloy autoclave and a 78% p-trifluoromethyl toluene conversion was obtained at reaction conditions of 160°C, 1600 psig, 16 hour reaction time with a 50% molar excess of SF_4. Recycle of the p-toluic acid fluoride generated during this reaction would increase the yield of p-trifluoromethyl toluene to over 95% for these conditions. This reaction was scaled to a 1750 ml stainless steel autoclave in which a total of ten runs were made. The conversion to p-trifluoromethyl toluene using similar reaction conditions averaged 72% (57 to 85% range) for these runs and the yield averaged 87% (77 to 100% range) including recycle of the p-toluic acid fluoride. Purification of the crude reaction product by distillation gave a 90% recovery of >99% purity p-trifluoromethyl toluene from the reaction mixture. From this series of reactions, two 1500 grams samples of p-trifluoromethyl toluene was delivered to the Walter Reed Medical Center.

Twenty reactions of 3,6-phenanthrene dicarboxylic acid or its derivative 3,6-phenanthrene dicarbonyl fluoride were performed in the 300 ml autoclave. Relatively pure (>95%) 3,6-phenanthrene dicarbonyl fluoride was produced in quantitative yields from 3,6-phenanthrene dicarboxylic acid by reaction with SF_4 at temperatures of 110 to 160°C. The highest conversion (22.5%) of 3,6-bis(trifluoromethyl)phenanthrene was obtained by suspending the 3,6-phenanthrene dicarboxylic acid in benzotrifluoride and reacting at a temperature of 210 to 220°C, pressure of 1950-2150 psig, reaction time of 16 hours with a 1100% excess of SF_4. In addition, a 17.5% yield of 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 2.4% yield of 3,6-phenanthrene dicarbonyl fluoride was obtained. A similar reaction performed at a lower temperature gave a lower conversion (8.1%) to 3,6-bis(trifluoromethyl)phenanthrene but a higher yield of the intermediates (48% 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 26% 3,6-phenanthrene dicarbonyl fluoride). This yield data is based on an analysis of the crude reaction mixture by quantitative GLC and TLC analysis. These analytical tools were developed during the course of this study and can be now routinely used for analysis of 3,6-bis(trifluoromethyl)phenanthrene directly. The major intermediates (3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 3,6-phenanthrene dicarbonyl fluoride) can be quantitatively determined by reacting the crude reaction mixture with methanol and determining their concentrations based on the response of the corresponding methyl esters. A purified sample of 3,6-bis(trifluoromethyl)phenanthrene was not obtained from these reactions but studies on the soxhlet extractors showed promise that separation and isolation is possible.

A sample of purified 3,6-bis(trifluoromethyl)phenanthrene was obtained by decarboxylating the 3,6-bis(trifluoromethyl)phenanthrene-9-carboxylic acid. Identification of this compound (section V-A) was confirmed by IR, melting point, NMR, UV and elemental analysis. This sample served as a standard for GLC and TLC analysis of the crude reaction product.

Corrosion data gathered during the course of the p-toluic acid reactions showed a corrosion rate of <0.002 inches per year on 316 stainless steel under reaction conditions.

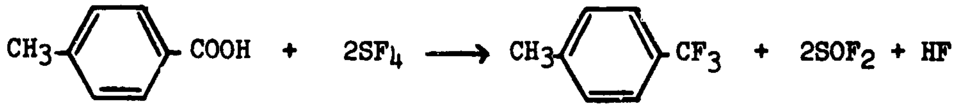
An economic evaluation of the production of 3,6-bis(trifluoromethyl) phenanthrene based on a 20% conversion to 3,6-bis(trifluoromethyl) phenanthrene plus an additional 30% yield of recycleable intermediates showed that a selling price (excluding 3,6-phenanthrene dicarboxylic acid costs) of ~ $15/pound could be achieved at 30,000 to 50,000 lbs per year 3,6-bis(trifluoromethyl)phenanthrene. For smaller requirements (~3,000 lbs/yr), the selling price (excluding 3,6-phenanthrene dicarboxylic acid costs) would be ~$40/lb. These figures reflect an expected SF_4 selling price of $10 per pound at the lower production rate and $3 per pound at the higher production rate.

II. Foreword

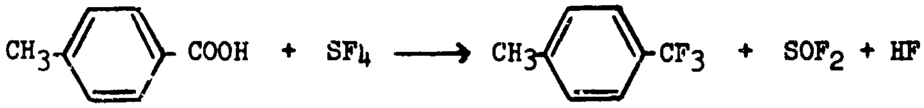
This work was performed for the Walter Reed Army Institute of Research, Washington, D. C. 20012 under Contract No. DADA-17-70-C-0007 as issued by the U.S. Army Medical Research and Development Command, Washington D.C. 20315. The program was conducted between July 1, 1969 and February 1, 1970 by Air Products and Chemicals, Inc. under the direction of J. F. Tompkins, (215-395-7261) principle investigator, at its Research and Development Department located at Trexlertown, Pennsylvania.

The program consisted of studying the individual reactions of SF_4 with p-toluic acid and 3,6-phenanthrene dicarboxylic acid to produce the corresponding trifluoromethyl function in place of the carboxylic acid function. The p-toluic acid reactions were performed in a 300 ml and 1750 ml autoclave while the phenanthrene reactions were performed only on the 300 ml scale. The overall reactions under study are detailed below in I and II, with the major intermediate reactions indicated in Ia, Ib, II(a), IIb, IIc.

I.

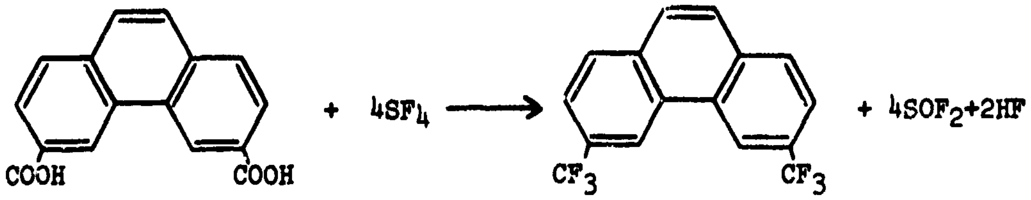


Ia.

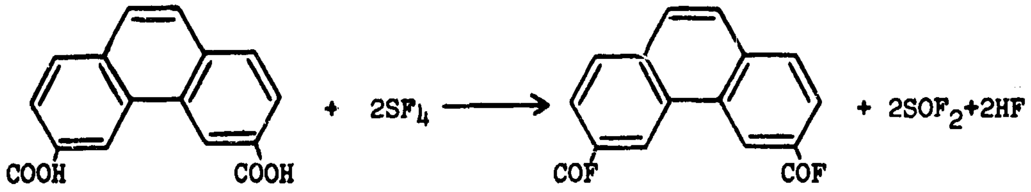


Ib.

II.



IIa.



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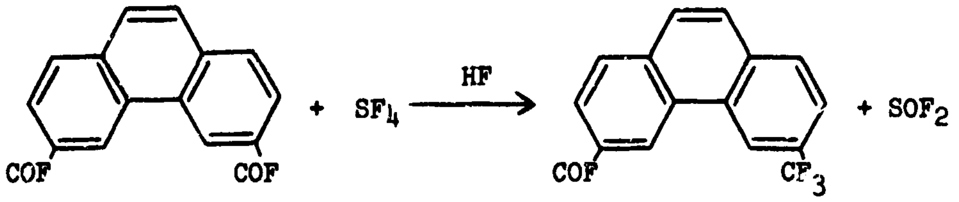
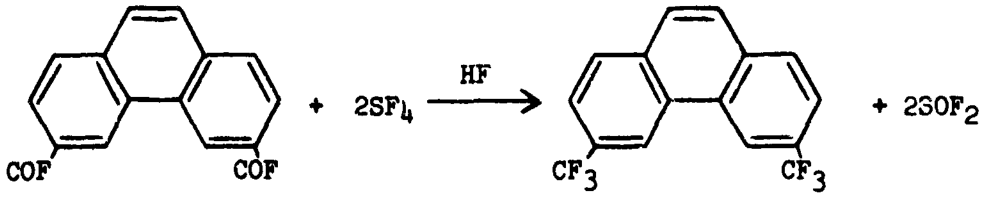


IIc.



The basis of this study was unpublished work previously performed by the Air Products and Chemical's Research and Development Department and open literature publications on the reactions of SF_4.

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III. Experimental Procedure

Figure 1 is a flow diagram of the 300 ml autoclave used in these experiments. For the p-trifluoromethyl toluene runs made in the 1750 ml autoclave, the equipment and experimental procedure is the same except that the 300 ml hastelloy rocking autoclave is replaced by a 1750 ml stirred stainless steel autoclave. The following basic procedure was followed for both the p-toluic acid and 3,6-phenanthrene dicarboxylic acid runs with variations in time and temperatures for the different runs.

1. The 300 ml hastelloy pressure vessel is purged with N_2 and then pressure tested to 2,000 psig @ room temperature.

2. The reactor is vented, evacuated to 1 mm Hg and vented to the atmosphere.

3. A charge of dry acid is immediately added to the vessel. For the p-toluic acid runs this was normally 57 grams (0.42 moles) of acid while for the 3,6-phenanthrene dicarboxylic acid runs this was normally 10 grams (0.037 moles).

4. The vessel is again evacuated to 1 mm Hg and is cooled to -40°F in a dry ice - acetone bath.

5. A weighed amount of gaseous SF_4 is condensed in the reaction vessel. For the p-toluic acid runs this was normally 157 grams (1.43 moles), while for the 3,6-phenanthrene dicarboxylic acid runs SF_4 charges from 24 to 356 grams (0.2 to 3.3 moles) were used.

6. The reactor is allowed to warm to room temperature with the pressure increasing to approximately 140 psig.

7. The reactor is placed in the heating furnace and heated to the desired temperature over a one to two hour period and allowed to react at this temperature for the predetermined time (usually 16-20 hours).

8. At the end of the reaction time, the reactor is cooled to room temperature and vented to a caustic solution.

9. The reactor is opened after the pressure reaches atmospheric and the contents are poured into a polyethylene bottle. In the case of the 1750 ml reactor, the material is removed through a dip tube.

10. The crude reaction mixture is then analyzed. For the p-toluic acid runs, the analysis is performed on the gas chromatograph to determine p-toluic acid, p-toluic acid fluoride, p-trifluoromethyl toluene content and the material is processed as indicated below. For the 3,6-phenanthrene dicarboxylic acid runs, the gas chromatograph is used to determine the 3,6-bis(trifluoromethyl) phenanthrene content and the material is further worked up through extractions, TLC analysis, and mass spectrograph analysis detailed in subsequent sections of the report.

The following procedure was used to work up the reaction mixture from the p-toluic acid runs to purified p-trifluoromethyl toluene.

1. The crude mixture from up to three separate reactions is mixed with enough powdered NaF to react with the theoretical amount of HF generated during the reactions.

2. This mixture is allowed to react for approximately one hour and is then filtered to remove the NaF·HF.

3. The solution is distilled at atmospheric pressure in a one inch diameter, 2 feet long glass distillation column packed with stainless steel "Canon" packing (size 0.16 x 0.16). A one to one reflux ratio was used and the p-trifluoromethyl toluene cut was taken between 130 and 132°C.

4. The p-trifluoromethyl toluene cut is analyzed on the gas chromatograph to determine purity.

IV. Discussion and Results

A. P-Toluic Acid Reactions - 300 ml Autoclave

A series of fifteen reactions were performed in the 300 ml autoclave to study the parameters which affect the conversion of p-toluic acid and SF_4 to p-trifluoromethyl toluene. The purpose of these runs were to determine the conditions which optimize the yield of p-trifluoromethyl toluene and to obtain data which would permit scale up of this reaction and the subsequent reactions of 3,6-phenanthrene dicarboxylic acid with SF_4. The operating data and results for these runs are presented in Table I.

Runs 1 through 5 were used to obtain analytical samples and to determine a suitable workup technique to purified product. No quantitative yield data was obtained on these runs except that through workup of Run No. 5 it was found that the yield of p-trifluoromethyl toluene was very low since over 50% of the acid charged to the reactor was recovered. This was done by reacting the crude with a 10% NaOH solution and acidifying the solution to recover the acid. This SF_4 reaction was performed at 120°C for 20 hours and indicated that the reaction does not proceed to the trifluoromethyl group in significant yield at this temperature.

Runs #6 and #9 were essentially duplicate runs performed at nominal conditions of 150°C, 1100 psig and a reaction period of 8 hours. Yields of p-trifluoromethyl toluene were 38% and 33% for these two runs. Run #10 was performed at essentially the same temperature and pressure with the reaction time increased to 18 hours. In this case the yield was improved to 53%. For Run #11, the reaction time was restored to eight hours and the temperature increased to 190°C with a corresponding increase in pressure to 1350 psig. The yield of p-trifluoromethyl toluene was 49% for this run. Run #14 was performed using the elevated temperature and pressure of #11 and the prolonged time period of #10. In this case the yield of p-trifluoromethyl toluene was increased to 68%. Run #15 was made to evaluate the effect of pressure on the reaction. The charge of p-toluic acid was increased by 50% and the same molar ratio of SF_4 was used. This resulted in a larger charge to the reactor and a corresponding increase in total pressure. For this run, the reaction temperature was 160°C, the reaction pressure was 2000 psig, and the reaction time was 18 hours. The yield of p-trifluoromethyl toluene was 78% for this run. This represents the highest yield of any of the runs and established the conditions under which yields of 75-80% could be achieved.

Figure II is a plot of the yield data discussed above at constant pressure, temperature and reactant concentrations. In general, increasing the reaction time, temperature, and pressure all tended to increase the yield with the increased pressure being particularly significant. Contrasting Run #15 to Run #11, the yield of p-trifluoromethyl toluene was increased from 53% to 78% by increasing the pressure from 1100 psig to 2000 psig while keeping the temperature constant at 150°C and the reaction time at 18 hours. Also, plotted on Figure II is the yield of p-trifluoromethyl toluene plus p-toluic acid fluoride at the various reaction conditions. This yield represents the yield which could be expected if the acid fluoride is recycled as would be done on a commercial scale. For Run #15, this yield was 97.4%. In none of the runs was any attempt made to recycle the acid fluoride. In general, this yield dropped with increasing temperature and longer reaction times. Therefore, it is expected that increasing the reaction time (>18 hours) and going to higher temperature (>190°C) would not improve yields but rather increase the amount of undesired products.

In addition to the runs already discussed, four other runs were performed. Runs #7 and #8 produced black solids (the appearance of coal) and no desired products. These runs were performed with a new supply of SF_4 which was subsequently found to contain >10% S_2F_2. All previous runs used material containing less than 2% S_2F_2 and gave a liquid product. Use of this material was discontinued and all subsequent runs used SF_4 containing less than 2% S_2F_2.

Two runs were made using the p-toluic acid fluoride as the starting material. This material was prepared by converting the acid to the acid chloride and reacting the acid chloride with HF to obtain the acid fluoride. Run #12 was conducted using the acid fluoride prepared in this manner with a 50% excess SF_4 at 150°C for 18 hours. This reaction failed to produce any p-trifluoromethyl toluene and the acid fluoride was recovered intact. This material was recharged to the reactor along with an equal molar quantity of HF and a 50% excess of SF_4. In this case a high yield (76%) of p-trifluoromethyl toluene was obtained indicating the need for HF to catalyze the reaction. For reactions using the acid as the charge, HF is generated on an equal molar basis in the conversion of the acid to the acid fluoride as the initial step of the reaction.

Attached in Figure III is the pressure-temperature relationship for Runs No. 13 and 15. Run No. 13 was an acid fluoride run while Run No. 15 was an acid run. The relative quantities of HF, SF_4 and organic material were the same for both runs but the resultant gaseous products are slightly different since more SOF_2 is generated in the acid run.

Workup of the crude material was performed by distillation in a manner similar to that indicated in the procedure section of the report. However, in these workups the crude reaction product was initially diluted with an equal volume of pentane and the distillation was performed using a shorter column with no reflux. The workup was performed in two separate batches with Runs #9 and #10 constituting the initial batch and Runs #6, 11, 14 and 15 constituting the second batch. Overall a total of 86.5% of the p-trifluoromethyl toluene and 94.5% of the p-toluic acid fluoride were recovered based on the analysis of the crude. The total recovery of p-trifluoromethyl toluene as pure material (>99%) was 76.5% of the analytical results, with the remaining material contained in the high boiling cuts.

A total of 161.3 grams of >99% purity p-trifluoromethyl toluene was recovered from these runs. One hundred thirty grams of this material was shipped to Starks Associates Inc., 1280 Niagara Street, Buffalo, New York on August 27, 1969. The analytical data for this sample is contained in section VI of the report. The remaining material was retained by Air Products and Chemicals, Inc., for analytical samples and future references.

B. P-Toluic Acid Reactions - 1750 ml Autoclave

Ten runs were made in the 1750 ml stainless steel autoclave to produce a total of 3297 grams of p-trifluoromethyl toluene. The operating conditions and results of these runs are contained in Table II.

The molar yield of p-trifluoromethyl toluene (based on GLC analysis) averaged 72% for all ten runs and ranged from 57 to 85%. The molar yield of p-trifluoromethyl toluene and p-toluic acid fluoride (based on GLC analysis) averaged 87% for all runs and ranged from 77 to 100%. The recovery of >99% purity p-trifluoromethyl toluene through workup and distillation was 90-91% of the analytical data. The average molar yield of recovered p-trifluoromethyl toluene (>99% purity) based on the starting p-toluic acid was 62% - 65% based on data obtained for the combination of Runs 32, 33, and 34 and Runs 38, 39, and 40. This data is detailed in Table II. No attempt was made during these runs to recover p-toluic acid fluoride and, therefore, no recovered yield of p-trifluoromethyl toluene plus p-toluic acid fluoride was obtained.

Table III is a summary of the samples of p-trifluoromethyl toluene which were produced and delivered under this contract.

C. Corrosion Data - P-Toluic Acid Reactions

The hastelloy reaction vessel showed no visible corrosion during this series of reactions but no quantitative data was obtained on corrosion rate. A corrosion rate of 0.002 inches/year on 316 stainless steel was determined during the series of reactions in the 1750 ml stainless steel reactor. This data was obtained by measuring the weight loss of the reactor's stainless steel (type 316) turbine agitator for the last eight reaction runs in the reactor. The rate was calculated by assuming corrosion occurred only at the elevated temperatures of the reaction, which amounted to a total of 135 hours for these tests. Therefore, the calculated data would represent a maximum corrosion rate since it ignores the time in which the solution was in contact with the agitator at lower temperatures. This data represents an average corrosion rate and does not consider any pitting or stress corrosion. However, the data does indicate that 316 stainless steel is a suitable material of construction for use in running this type of reaction.

D. 3,6-Phenanthrene Dicarboxylic Acid - 300 ml Autoclave

A total of twenty individual reactions of SF_4 with 3,6-phenanthrene dicarboxylic acid or its derivative 3,6-phenanthrene dicarbonyl fluoride were performed in the 300 ml hastelloy autoclave. In three of these runs (19, 27 and 36), 3,6-phenanthrene dicarbonyl fluoride prepared in a previous run was used while two other runs (42 and 45) used a mixture of 3,6-phenanthrene dicarboxylic acid and 3,6-phenanthrene dicarbonyl fluoride. The operating conditions and results of these runs are summarized in Table IV. A summary of the IR observation for these runs are given in Table VI and the GLC quantitative analysis for the runs are summarized in Table VII.

The parameters studied in these reactions were temperature over the range 20 to 225°C, pressure over the range of 110 to 2400 psi, SF_4 ratio of 50 to 4500% excess, reaction times of 1 to 18 hours and the effect of HF as a catalyst and the use of inert type solvents. Because of the limited availability of 3,6-phenanthrene dicarboxylic acid, the charge of 3,6-phenanthrene dicarboxylic acid was generally limited to 10 grams per run and in most cases large excesses of SF_4 were used to obtain the desired pressure. In several runs where SF_4 was used in only a moderate excess, the higher pressures were obtained by adding N_2 to the reactor.

The initial run of this series (#17) produced relatively pure (>95%) 3,6-phenanthrene dicarbonyl fluoride in a quantitative yield. This reaction was run at 112°C using a large excess of SF_4 to produce an autogeneous pressure of 2400 psig. The purity was estimated based on a comparison to the IR spectrum (Figure IX) of a sample of 3,6-phenanthrene dicarbonyl fluoride synthesized as indicated in Section V of the report. Run #18 was performed in a similar manner at a temperature of 164°C and again produced primarily 3,6-phenanthrene dicarbonyl fluoride and no significant amount of 3,6-bis(trifluoromethyl)phenanthrene. Run #28 was subsequently performed at the same conditions as #17 to produce 3,6-phenanthrene dicarbonyl fluoride for use in other reactions.

Runs #19, 20 and 21 were made using anhydrous hydrogen fluoride as a catalyst in an attempt to promote conversion to 3,6-bis(trifluoromethyl)phenanthrene. Exhaustive analysis of this material by extraction, mass spectrograph and TLC indicated substitution at the 9 and 10 position and a multitude of compounds, including some compounds in which the phenanthrene ring had been split. This data was obtained by a combination of column chromatography and UV analysis as presented in Section VII-H and Table XII and NMR analysis as presented in Section VII-D and Figure XXV. GLC analysis of #21 (Table VII) showed 1% 3,6-bis(trifluoromethyl)phenanthrene with a number of other unidentified compounds totaling ∿7% of the sample. Additional work was done with HF as a catalyst and using 3,6-phenanthrene dicarbonyl fluoride as the starting material. These experiments were conducted in Runs #27 and #36 at temperatures of approximately 100°C. In both cases, GLC analysis (Table VII) indicated less than 0.1% 3,6-bis(trifluoromethyl)phenanthrene and a variety of other compounds. Soxhlet extraction (Figure 27) of #27 using heptane showed that only 24% of the material could be extracted. Run #31 was performed with 3,6-phenanthrene dicarboxylic acid as the starting material (in methylene chloride solvent) and using HF as a catalyst at a low temperature (20°C) and produced >95% 3,6-phenanthrene dicarbonyl fluoride and <0.1% 3,6-bis(trifluoromethyl)phenanthrene.

Since the above data indicated that HF had a determental effect on the reaction at elevated temperatures, its use was discontinued and further work was done without HF at temperature above 180°C in an attempt to promote conversion to 3,6-bis(trifluoromethyl)phenanthrene. Four runs (#22, 23, 25 and 26) were made over the temperature range of 180 to 220°C. By GLC analysis these runs showed an improvement in the conversion to 3,6-bis (trifluoromethyl)phenanthrene, with run #26 containing 4.1% of the desired product. Run #26 was performed at 220°C, 2500 psig and with a large excess of SF_4. Mass spectral analysis (Table VIII) of #26 showed the presence of significant quantities of compounds corresponding to the molecular weights of 3,6-bis (trifluoromethyl)phenanthrene and 3-trifluoromethyl phenanthrene -6-carbonyl fluoride and 3,6-phenanthrene dicarbonyl fluoride.

Based on these results which showed that a limited conversion to 3,6-bis(trifluoromethyl)phenanthrene could be obtained at elevated temperatures, a run was made at a high temperature while using an inert solvent to suspend the material during the reaction. Run #30 was made at 185°C and 1900 psig using benzotrifluoride as a solvent. GLC analysis (Table VII) of this material showed 8.2% 3,6-bis(trifluoromethyl)phenanthrene in the crude product. Quantitative analysis (Table X and Figure

XXXII) of this run by TLC gave 7.5% 3,6-bis(trifluoromethyl) phenanthrene, 26% 3,6-phenanthrene dicarbonyl fluoride, and 48% 3-trifluoromethyl phenanthrene-6-carbonyl fluoride, which amounts to a yield of 80% for product material or intermediates. This analysis was performed on the methoxylated reaction product as indicated in Section VII-F. NMR data (Figure XXVI) confirmed the presence of the three major components in the sample and an improved GLC analysis (Section VII-E and Figure XXX) on the methoxylated product further confirmed the results obtained by TLC.

Run No. 35 was made using a more dilute concentration of 3,6-phenanthrene dicarboxylic acid to benzotrifluoride (20 gms. to 100 gms.) with a corresponding reduction in SF_4 concentrations to a three fold excess. In this case, GLC analysis (Table VII) showed 2.5% 3,6-bis(trifluoromethyl)phenanthrene and only a trace of 3,6-phenanthrene dicarbonyl fluoride and 3-trifluoromethyl phenanthrene-6-carbonyl fluoride by TLC analysis.

Run No. 37 was then performed as an exact duplicate to #30 with the exception that it was necessary to use a new batch of (AGC-W 71.4) of 3,6-phenanthrene dicarboxylic acid since all the previous batch (AGC-W 71.3) had been consumed. In this case, GLC analysis (Table VII) showed 5.5% 3,6-bis(trifluoromethyl)phenanthrene and quantitative TLC analysis (Table X) showed a yield of 4.6% 3,6-bis(trifluoromethyl)phenanthrene, 27% 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 26% 3,6-phenanthrene dicarbonyl fluoride. This amounts to a total yield of 57.6% for products and intermediates as opposed to the 80% figure obtained in #30.

Run No. 41 used the same concentration of 3,6-phenanthrene dicarboxylic acid, benzotrifluoride and SF_4 as #30 and was performed at a higher reaction temperature (210 to 220°C). This run produced the highest yield of 3,6-bis(trifluoromethyl)phenanthrene of any of the runs. GLC analysis (Table VII) showed 17.5% 3,6-bis(trifluoromethyl)phenanthrene in the crude solid corresponding to a 19.0% yield. TLC analysis (Table X) showed 6.7% 3,6-bis(trifluoromethyl)phenanthrene in the crude reaction mixture (containing benzotrifluoride) which corresponded to a 22.4% yield. TLC analysis also showed a 2.4% yield of 3,6-phenanthrene dicarbonyl fluoride and 17.5% yield of 3-trifluoromethyl phenanthrene-6-carbonyl fluoride, giving a total yield of 42% for product and intermediates. This run proved to be the most successful in terms of product conversion while #30 was the most successful in terms of yield of product plus intermediates.

Runs #42 and 43 were made using a mixture of 3,6-phenanthrene dicarboxylic acid and 3,6-phenanthrene dicarbonyl fluoride in the benzotrifluoride solvent. These runs were performed to evaluate conditions in which HF was present in less than the molar quantities present in a reactor starting with pure 3,6-phenanthrene dicarboxylic acid. Run #42 contains a ratio of 6.4 parts 3,6-phenanthrene dicarbonyl fluoride to 3.6 parts 3,6-phenanthrene dicarboxylic acid and was reacted at 180°C. GLC analysis showed a 5.5% yield of 3,6-bis(trifluoromethyl) phenanthrene. TLC data on 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 3,6-phenanthrene dicarbonyl fluoride were not obtained at this point. This reaction product was returned to the reaction with an additional 20% of acid and reacted at a higher temperature (220°C). In this case, GLC showed <1% product and TLC analysis (Table X) showed very little of 3,6-bis(trifluoromethyl)phenanthrene, 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 3,6-phenanthrene dicarbonyl fluoride and an unidentified compound running beyond 3,6-bis(trifluoromethyl)phenanthrene on the TLC plate.

Run No. 46 was made using the temperature conditions of #40 with an increase in the amount of benzotrifluoride. The benzotrifluoride concentration was increased to bring its liquid concentration to a comparable state to that used in #30; that is, to compensate for the amount of vaporization between 180 and 220°C. This reaction was not successful in producing 3,6-bis(trifluoromethyl)phenanthrene (<1% as indicated by GLC and TLC analysis. However, TLC analysis (Table X) did show a 33% yield of 3,6-phenanthrene dicarbonyl fluoride and 8% yield of 3-trifluoromethyl phenanthrene-6-carbonyl fluoride with the remaining material staying at the origin.

A limited amount of work was done on attempting to isolate pure compounds from the crude reaction mixture. The most promising technique for concentrating the 3,6-bis(trifluoromethyl)phenanthrene was obtained in the soxhlet extraction with heptane as reported in Section VII-G. These studies showed that a 5 to 14 fold increase in 3,6-bis(trifluoromethyl)phenanthrene concentration could be obtained. For crude reaction mixture #26, the 3,6-bis(trifluoromethyl) phenanthrene was concentrated from 4.1% to 19.1% by overnite extraction with heptane (Figure XXXIII). This was the highest concentration of 3,6-bis(trifluoromethyl)phenanthrene obtained in any of the fractions obtained by the soxhlet extraction. Since major emphasis in the program was to determine the optimum reaction conditions and use analytical tools to analyze the results, the work in this area was limited. No attempts were made to concentrate the reaction product from Run No. 41 which originally showed 17.5% product in the crude reaction mixture.

E. Economic Evaluation - 3,6-Phenanthrene Dicarboxylic Acid Process

An economic evaluation of the production of 3,6-bis(trifluoro methyl)phenanthrene on a semi-commercial scale was made based on the information gathered in this study. Figure XXXXI is a flowsheet of a production process based on a 3,6-phenanthrene dicarboxylic acid conversion of 20% to 3,6-bis(trifluoromethyl) phenanthrene, 20% to 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 10% to 3,6-phenanthrene dicarbonyl fluoride with an 80% recycle recovery of the intermediate products. Since SF_4 requirement per pound of 3,6-bis(trifluoromethyl)phenanthrene are large (3.5 lb. SF_4/lb 3,6-bis(trifluoromethyl)phenanthrene), the cost of SF_4 is the most significant cost item in the process. At 3,6-bis(trifluoromethyl)phenanthrene production rates of 3,000 lbs/yr, SF_4 requirements would amount to approximately 10,000 lbs/yr at which SF_4 is expected to be priced in the $5-$10/lb. range. At the higher cost, this would amount to an SF_4 cost of $35 per pound of 3,6-bis(trifluoromethyl)phenanthrene. In addition, the cost of labor, depreciation, and return on investment would amount to approximately $5/lb. The selling price at 3,000 lb/yr 3,6-bis (trifluoromethyl)phenanthrene would then be estimated at $40/lb plus 1.9 times the per pound cost of the 3,6-phenanthrene dicarboxylic acid.

At higher production level of 30,000 to 50,000 #/yr 3,6-bis (trifluoromethyl)phenanthrene, where SF_4 requirements would excess 100,000 #l yr, the cost of SF_4 is expected to be in the range of $3/lb. At this SF_4 cost, the selling price would be expected to be in the vicinity of $15/lb plus the additional per pound cost of the 3,6-phenanthrene dicarboxylic acid.

V. Synthesis and Identification of Pure Compounds

A. 3,6-Bis(trifluoromethyl)phenanthrene (b-TFMP)

To 0.1 g of copper sulfate in 16 ml of quinoline was added 0.5 g of 3,6-bis(trifluoromethyl)phenanthrene - 9 - carboxylic acid. The mixture was heated at 215°C for 3 hours. After the mixture was cooled, 120 ml of benzene was added. The solution was filtered, and the filtrate was washed thoroughly with 1N hydrochloric acid, 1N potassium carbonate, water and then dried over calcium chloride. Filtering off the calcium chloride and evaporation of the benzene produced tan colored crystals. Recrystallization of these crystals from absolute ethanol yielded 0.1189 g of slightly grey, needle-like crystals with m.p. 140.5 - 141.5°C.

Anal. Calcd. for $C_{16}H_8F_6$: C, 61.16; H, 2.57; F, 36.27

Found: C, 60.99; H, 2.63; F, 36.12

NMR: All ring protons are in place except for those in the 3 and 6 positions.

Mass Spect: Calc. Molecular Weight, 314.23

Found, 314

Infrared: The strong absorbance at 7.55μ and 8.95μ indicates the presence of trifluoromethyl groups. No absorbance at 5.5μ to 6.0μ indicates the absence of a carboxylic acid group. (Figure VI)

Ultraviolet: Comparison of the extinction coefficient (k) below with those of phenanthrene and 3,6 - bis(trifluoromethyl)phenanthrene - 9 - carboxylic acid indicates the phenanthrene ring is intact. (Figure VII)

	λ252	λ301	λ334
Phenanthrene	k=50,000	k=13,000	k-250
3,6-Bis(trifluoromethyl) phenanthrene	k-64,200	k=12,600	k=291
3,6-Bis(trifluoromethyl) phenanthrene-9-carboxylic acid	k=52,200	k=11,000	k=435

Gas Chromatography: Dissolving a sample of 3,6-bis(trifluoromethyl)phenanthrene in acetone and then chromatographing the sample showed (other than the solvent peak) one major product peak at 11.9 minutes.

Directions for this type of decarboxylation were found in the following references:

1. Rapoport, H., Williams, A. R., and Cisney, M. E., J. Am. Chem. Soc., 73, 1418 (1951).
2. Nodiff, E. A., private communication from Bing T. Poon to James F. Tompkins, dated 11/4/69.

B. 3,6-Phenanthrene Dicarbonyl Fluoride (PDCF)

A 2:1 ratio of benzoic acid to 3,6-phenanthrene dicarboxylic acid was heated to 135°C. Thionyl chloride was added slowly until it was in excess. After cooling and setting for 24 hours the excess thionyl chloride was distilled. The remaining solids were washed with ether to remove the benzoyl chloride. Recrystallation of the remaining material from a tetrahydrofuran benzene mixture gave white, needle-like crystals melting from 178-181°C. This material was identified as being 3,6-phenanthrene dicarbonyl chloride. An infrared spectrum of this material is shown in Figure VIII.

The 3,6-phenanthrene dicarbonyl chloride was then stirred for 16 hours with excess hydrogen fluoride. Distillation of the excess hydrogen fluoride, and recrystallation of the solids from a tetrahydrofuran-benzene mixture gave white, needle-like crystals melting from 234-236°C.

Anal. Calcd. for $C_{16}H_8O_2F_2$: C, 71.11; H, 2.98.

Found: C, 71.0; H, 3.18.

Mass Spect: Calcd. Molecular Weight, 270.24.

Found, 270.

Infrared: The strong absorbance at 5.55 indicates the presence of carbonyl fluoride groups. No absorbance at 5.9 indicates the absence of the carboxylic acid group. (Figure IX).

C. 3,6-Bis(carbomethoxy)phenanthrene

The diester was prepared by adding excess ethereal diazomethane to a slurry of the diacid (as received from Aerojet General) in ether. The ether was removed and the ester was recrystallized from ethanol, m.p. 203-206°C.

D. 3-Carbomethoxy-6-trifluoromethyl Phenanthrene

Approximately 1 mg of the material giving the largest spot upon TLC of methanol treated run #30 was isolated by preparative TLC (Mallinkrodt Chromar 1000, developed in 3:1 benzene Chloroform). The infra-red spectrum (KBr pellet) showed a carbonyl band at 1715 cm^{-1} and CF_3 bands at 1320 and 1110 (or 1125) cm^{-1}. The mass spectrum of the same sample showed a strong parent ion at the expected value (m/e 304).

E. Elemental Analysis - 3,6-phenanthrene Dicarboxylic Acid

Table V gives the data for the elemental analysis of two batches (AGC W71.3 and AGC W71.4) of 3,6-phenanthrene dicarboxylic acid along with data furnished by Aerojet General Corporation.

VI. Analytical Procedure and Results - P-trifluoromethyl Toluene

A sample of p-trifluoromethyl toluene was isolated by distillation and characterized to be the pure compound by the following data:

Boiling Point - °C	130.5 - 131.5 (Lit.(1) 129-130)
Refractive Index @ 24.5°C	1.4241 (Lit.(1) 1.4276)
Infrared	Attached as Figure IV

This sample was used as an analytical standard for Gas Chromatographic analysis. Attached as Figure V is the Gas Chromatogram of the sample of p-trifluoromethyl toluene which was furnished to Starks Associates as part of this program. Figure V includes the pertinent data as to type of column, temperature program, retention time and other parameters used to perform this analysis. The purity of samples 5043.26 and 5043.32, which were delivered to Walter Reed, were determined on the Gas chromatograph in a similar manner.

In addition to analyzing the purified product, the Gas Chromatographic analysis was extended for use on the crude reactor product. The relative response factor of p-trifluoromethyl toluene and p-toluic acid fluoride to diethyl succinate was determined by using pure samples. The diethyl succinate was then used as an internal standard by adding a known amount to a sample of crude and analyzing on the Gas Chromatograph in the same manner as detailed in Figure V. For analyzing the crude reaction product, the analytical system had to be compatible with HF. A stainless steel syringe was used for injecting the sample and the column was originally chosen based on a knowledge that it was compatible with HF.

(1) Chemical Abstracts, Vol. 65, 18542, 1966.

VII. Analytical Procedures and Results (3,6-bis(trifluoromethyl)phenanthrene)

A. Infrared Spectroscopy

All the infrared spectra were obtained by mixing the compound in question with potassium bromide. The mixture was pressed into a pellet form with a mini-press, and scanned with a Beckman IR-5 Spectrophotometer. The spectra were examined for the presence or absence of the following strong and sharp identifiable bands.

5.50	-	5.60	-COF
5.75	-	5.85	-COCl
5.90	-	6.00	-COOH
7.50	-	7.60	$-CF_3$
8.90	-	9.00	$-CF_3$

The following list itemizes the infrared spectra appearing in this report:

3,6-Bis(trifluoromethyl)phenanthrene	Figure VI
3,6-Phenanthrene Dicarbonyl Chloride	Figure VIII
3,6-Phenanthrene Dicarbonyl Fluoride	Figure IX
3,6-Phenanthrene Dicarboxylic Acid	Figure X
3,6-Bis(trifluoromethyl)phenanthrene-9-carboxylic Acid	Figure XI
Phenanthrene	Figure XII
Phenanthrenequinone	Figure XIII
Crude 30	Figure XIV

An interpretation of the infrared spectra of crude samples 21-23, 25-27, 30, 31, 35-37, 41 and 42 is shown in Table VI. The last column on Table VI is an attempt to judge by appearance or absence of certain infrared bands which spectra are closest to the spectrum of pure 3,6-phenanthrene dicarbonyl fluoride. The spectrum that was the closest to 3,6-phenanthrene dicarbonyl fluoride

(Run #17) was arbitrarily assigned the number 1 while the spectrum that was the furtherest away (Run #20 - which showed no carbonyl fluoride bands and strong trifluoromethyl bands) was arbitrarily assigned the number 14. The spectra assigned the numbers between 6 and 9 are the spectra of the crude samples having the most product. Spectra assigned numbers 1 to 5 appear to be from crude samples that were not fluorinated enough, while spectra that were assigned numbers 10 to 14 appear to be from crude samples that were fluorinated too strongly.

B. Ultraviolet Spectroscopy

The ultraviolet spectra were obtained by dissolving a weighed amount of the compound in question with ethanol or chloroform. The solution was scanned with a Perkin-Elmer Model 202 U.V. - Visible Recording Spectrophotometer. The ultraviolet scans were used to determine the extinction coefficients ($k = \frac{A}{bc}$ of the various compounds in question. In "Organic Chemistry" by Cram and Hammond, published by McGraw-Hill, page 620 (1959), the absorption spectra of aromatic hydrocarbons are listed. The following table gives some of the extinction coefficients taken from the above reference.

	λ_{max} A°	κ_{max} Ab / mol-cm	λ_{max} A°	κ_{max} Ab / mol-cm	λ_{max} A°	κ_{max} Ab / mol-cm
Benzene	2,550	220	2,202	6,900	1,840	83,000
Naphthalene	3,120	250	2,750	5,600	2,200	110,000
Anthracene			3,750	7,900	2,520	200,000
Phenanthrene	3,300	250	2,950	13,000	2,520	50,000
Naphthacene			4,730	11,000	2,780	130,000
Pyrene	3,520	630	3,340	50,000	2,400	89,000
Chrysene	3,600	630	3,200	13,000	2,680	141,000
Azulene	6,070	263	3,410	3,410	4,360	55,000

Thus by comparing these extinction coefficients at the prescribed wavelengths one is able to determine if the aromatic ring in the compounds in question has opened up or if it has rearranged to some other aromatic structure.

The following list itemizes the ultraviolet spectra appearing in this report.

0.00000592 M	3,6-bis(trifluoromethyl)phenanthrene	Figure VII
0.0000592 M	3,6-bis(trifluoromethyl)phenanthrene	Figure XV
0.000652 M	3,6-bis(trifluoromethyl)phenanthrene	Figure XVI
0.00000575 M	3,6-bis(trifluoromethyl)phenanthrene-9-carboxylic acid	Figure XVII
0.0000176 M and 0.0000439 M	Crude 23	Figure XVIII
0.0000286 M	5022-19B (fraction from column chromatography studies)	Figure XIX

By studying the ultraviolet spectrum of Crude 23 one can observe that the extinction coefficients are not what they are supposed to be for phenanthrene type compounds. Thus one can conclude that there must be a large quantity of ring rearrangement or polymerization in this sample.

C. Gas Chromatography

Instrument: Loenco 160 Series

Carrier Gas: Helium

Column: 20' x 1/4" copper tubing packed with 30% SE-30 silicon oil on 60/80 mesh Chromosorb W.

Temperature: 300°C Isothermal

Injection Port Temperature: 300°C

Detector Temperature: 300°C

Filament Current: 50 milliamps

Sample Size: 8μ 1

Recorder: Beckman 10-inch recorder with Disk Integrator

With the above chromatography system various samples were analyzed for product content. The product under these conditions eluted from the column after 11.9 minutes. A peak appearing at 5.9 minutes was identified as being a compound having a phenanthrene-like structure with a CF_3 group at both the 3 and 6 ring positions. Further studies of this compound showed that the ring protons in the 9 and 10 positions were also substituted. With this chromatograph system various other chromatographic peaks appeared out to twenty minutes, but these peaks were never identified. Figure XX shows a gas chromatogram of a typical reaction run.

The samples were analyzed by gas chromatography by using an internal standard technique. The internal standard used was p-trifluoromethyl toluene (p-TFMT). This technique was developed by the following method. A standard was prepared containing acetone and weighed amounts of p-trifluoromethyl toluene and 3,6-bis(trifluoromethyl)phenanthrene. When chromatographing this standard with the present chromatographic conditions, p-trifluoromethyl toluene eluted from the column after 3 minutes. By knowing the ratio of the weights of the p-trifluoromethyl toluene and the 3,6-bis(trifluoromethyl)phenanthrene in the standard, and measuring the area of the chromatograph peaks of each of these components in the standard, one is able to calculate the responce of the one component relative to the other on an equal weight basis. For example if the standard had been prepared with 1.50 grams of p-trifluoromethyl toluene and 1.00 gram of 3,6-bis(trifluoromethyl)phenanthrene and upon chromatographing this sample the p-trifluoromethyl toluene produced 150,000 counts while the 3,6-bis(trifluoromethyl)phenanthrene produced 71,000 counts, one could reason that since 1.50 grams of p-trifluoromethyl toluene produced 150,000 counts then 1.00 gram of the same material should yield 100,000 counts. Thus by comparing 1.00 gram of p-trifluoromethyl toluene which gives 100,000 counts to 1.00 gram of 3,6-bis(trifluoromethyl)phenanthrene which gives 71,000 counts, one can say that the 3,6-bis(trifluoromethyl)phenanthrene gives 0.71 times as many counts as an equal weight of p-trifluoromethyl toluene. Experiments have shown 0.71 to be the actual number for these studies. Figure XXI shows a chromatogram of the standard prepared by dissolving a weighed amount of p-trifluoromethyl toluene and 3,6-bis(trifluoromethyl)phenanthrene in acetone. When a crude sample is received for analysis it is weighed into acetone along with a weighed amount of p-trifluoromethyl toluene. This mixture is then chromatographed. Again by knowing the ratio of the weights of the crude sample and the p-trifluoromethyl toluene in the mixture, and measuring the area of the chromatograph peaks of each of these components in the mixture, and also knowing that 3,6-bis(trifluoromethyl)phenanthrene responds 0.71 times as much as p-trifluoromethyl toluene, one is able to calculate the quantity of 3,6-bis(trifluoromethyl)phenanthrene in the crude sample. For example if the mixture had been prepared with 1.00 gram of crude sample to be analyzed and 2.00 grams of p-trifluoromethyl toluene, and upon chromatographing the p-trifluoromethyl toluene produced 200,000 counts and the peak corresponding to 3,6-bis(trifluoromethyl) phenanthrene produced 14,200 counts, one could reason that since 2.00 grams of p-trifluoromethyl toluene produces 200,000 counts then 1.00 grams of p-trifluoromethyl toluene should yield 100,000 counts. Therefore, if the crude sample to be analyzed was 100% 3,6-bis(trifluoromethyl) phenanthrene product, the peak corresponding to the 3,6-bis(trifluoromethyl)phenanthrene should give 71,000 counts. (Previously it was shown that 1.00 gram of 3,6-bis(trifluoromethyl)phenanthrene gives only 0.71 times as many counts as 1.00 gram of p-trifluoromethyl toluene). Since the 3,6-bis(trifluoromethyl) phenanthrene gave only 14,200 counts, by ratioing this with 71,000 counts, one can calculate that there is 20% 3,6-bis (trifluoromethyl)phenanthrene in the crude sample. Figure XXII shows a chromatogram of a weighed amount of p-trifluoromethyl toluene and solvent extraction sample 26-4 dissolved in acetone. This chromatogram illustrates some of the typical peaks which usually appear from various samples. The unknown peaks are given a response of half as much and twice as much as that of 3,6-bis(trifluoromethyl)phenanthrene. This gives an upper and lower concentration range for the unknown compounds. The upper and lower concentration ranges are then averaged, and this average number is the number which appears in the reports for concentrations of unknown peaks.

This internal standard technique was used because it does not require the gas chromatographer to repetively reproduce sample injection sizes.

Table VII is a summary of the gas chromatographic analysis of the crude reaction products for all the runs after Run No. 20.

D. Nuclear Magnetic Resonance Spectral Analysis

The NMR spectra were obtained on a Varian Model A-60A spectrometer. The samples were analyzed at room temperature in standard 5 mm. O.D. sample tubes using tetramethylsilane as an internal standard. The sweep width was 1000 cps and the sweep time was 250 sec. Chemical shift values were obtained from the precalibrated scale on the chart paper.

The NMR spectra proved very useful for identifications of pure or semi-pure materials. However, the crude reaction products contained a wide range of materials giving such similar NMR spectra that, in general, specific assignments were not possible.

The NMR spectrum of 3,6-phenanthrene-di-carboxylic acid (sample number 5022-8A) is shown in Figure XXIII. The broad peak at -5.0 ppm, which on addition of D_2O sharpens and shifts to -4.0 ppm, is assigned to the two acidic protons. The chemical shifts of the 1,2 and 7,8 protons must be nearly the same since the spin-spin splitting, due to J_{12} and J_{78}, is not observed in the spectrum. Hence, the peak at -8.2 ppm is assigned to the 1,2 and 7,8 protons. The 9,10 protons are assigned to the singlet peak at -8.0 ppm. This leaves the singlet at -9.5 ppm to be assigned to the 4,5 protons. The above assignments are consistant with the expected chemical shifts due to the anisotropic ring current effect in the aromatic phenanthrene rings.

The NMR spectra of the 3,6-phenanthrene-di-carboxylic acid fluoride are shown in Figure XXIV. The spectral assignments are similar to those for 3,6-phenanthrene-di-carboxylic acid except for the absence of the acidic protons. The assignment is as follows: the 4,5 protons are at -9.2 ppm, the 1,2 and 7,8 protons are at -8.2 ppm, and the 9,10 protons are at -8.0 ppm.

The NMR spectrum of Crude 21 is shown in Figure XXV. The broad peaks are apparently due to a wide range of products in the crude. The NMR spectrum of Crude 30, which was a much higher yield reaction, is shown in Figure XXVI. The qualitative differences in the two spectra are quite apparent. The chemical shifts for the 4,5 protons suggested that Crude 30 contained three main components. This was later confirmed by G.C.-M.S. analysis.

E. Gas Chromatographic and Mass Spectral Analysis

The mass spectral (M.S.) analyses and gas chromatographic-mass spectral analyses (G.C.-M.S.) were performed using a Perkin Elmer Model-270 G.C.-M.S. spectrometer. A 6 ft. x 1/8 in., stainless steel column, containing 5% SE-30 on Chromosorb W, was used in the gas chromatographic section of the instrument. The G.C.-M.S. gas chromatograms were obtained by recording the total ion current of the mass spectrometer. The mass spectra were scanned in real time as the peaks eluted from the gas chromatographic column.

The crude reaction products and starting materials were also analyzed in the mass spectrometer using a solids probe technique. This was necessary since the carboxylic acid fluoride derivatives would not elute from the gas chromatographic columns because, we believe, of their reactivity with the G.C. column packing. Also, we wanted to look for possible high molecular weight materials of low volatility. The solids probe was initially inserted at room temperature and then slowly heated to 200°C. Several mass spectral scans were taken as the temperature was increased. This allowed a partial separation of materials due to the differences in volatility of the various components in the crude samples.

In an attempt to obtain better quantitative data on the components in the crudes, the carboxylic acid fluoride components were converted into their methyl esters by reaction with methanol. The methyl esters were eluted and resolved without difficulty. The crudes were examined by regular gas chromatography using flame ion detection (Beckman GC-5). The column was 6 ft. x 1/8 in., stainless steel, and packed with 5% SE-30 on Chromosorb W.

The mass spectral data (solids probe) of a crude product are shown in Table VIII. The table lists only the more intense m/e peaks. The numbers in parentheses are relative intensities with the base peak assigned an intensity value of ten.

A G.C.-M.S. analysis was performed on Crude 26 for further elucidation of the reaction products. The total ion current chromatogram is shown in Figure XXVII. The mass spectra were obtained for each of these components as they eluted from the gas chromatographic column. The m/e data for the more intense spectral peaks are shown in Table IX.

The gas chromatograms of Crudes 26 and 30 are shown in Figures XXVIII and XXIX. respectively. These were obtained using the Beckman GC-5 chromatograph with flame ion detection. As can be seen, the two chromatograms are similar. The main difference is the much higher yield of 3,6-bis(trifluoromethyl)phenanthrene in Crude 30.

The crude materials were treated with methanol in an attempt to obtain quantitative data on the reaction product by gas chromatography. The gas chromatogram for the methoxylated Crude 30 is shown in Figure XXX. The two new peaks have been shown by G.C.-M.S. to be the methyl esters of 3,6-phenanthrene dicarbonyl fluoride and 3-(trifluoromethyl)phenanthrene-6-carbonyl fluoride. An estimate of component concentrations based on peak heights in crude 30, gave 13% 3,6-bis(trifluoromethyl)phenanthrene, 40% 3-trifluoromethyl phenanthrene-6-carbonyl fluoride, 23% 3,6-phenanthrene dicarbonyl fluoride, and 24% other materials. The percentages were calculated assuming equal detector sensitivity for all sample components.

F. Thin Layer Chromatographic Analysis

A survey of thin layer chromatographic systems showed that the product, 3,6-bis(trifluoromethyl)phenanthrene could be resolved from other materials formed in the runs under the following conditions:

Plates: E. Merck 4GF, 250 micron

Activation: none

Solvent: Cyclohexane-carbon tetrachloride 1:1 by volume

Development: 15 cm

Visualization: Fluoresence quenching

Sample size: Sufficient to contain 1/4 to 1 microgram of product.

Improved resolution for quantitative work (v.i.) was obtained by employing 4:3 cyclohexane-carbon tetrachloride and developing plates twice. Figure XXXI shows the TLC plate for a known sample of 3,6-bis(trifluoromethyl)phenanthrene and several crude reaction products.

Samples of the intermediate product, 3,6-phenanthrene dicarbonyl fluoride (product from run 17) could not be moved from the origin regardless of solvent polarity up through acetonitrile. This behavior indicated acylation of the plate, and the acid fluoride groups were converted to methyl ester groups by reaction with methanol using pryidine catalyst. A 5 to 30 mg sample was accurately weighed and added to 3.00 ml methanol along with an amount of pyridine approximately equal in weight to the sample. The solution was warmed in a closed container for two hours and thence used directly. The conditions used for chromatography were as follows:

Plates: E. Merck 4GF, 250 micron

Activation: none

Solvent: Benzene-chloroform 3:1 by volume

Development: 15 cm

Visualization: Fluorescence quenching

Sample size: Sufficient to yield 0.2 to 2 microgram substance.

The bis-trifluoromethyl product was unresolved from unidentified materials in the latter solvent system, but 3,6-bis(carbomethoxy) and 3-carbomethoxy-6-trifluoromethyl phenanthrenes were well separated from each other and from extraneous materials. Twofold development was utilized on quantitative runs. Figure XXXII and XXXIII show the TLC plates for a known sample of 3,6-bis-(carbomethoxy)phenanthrene compared to the methoxylated reaction product for several reaction runs.

No attempt was made to achieve complete and reproducible saturation of developing chambers. Because R_f values are not exactly reproducible under these conditions, known standards were run on every plate.

Quantitative measurements were made with a Farrand Optical Co. Chromatogram Scanner. A peak area vs. quantity curve was generated for each plate by including 3 or 4 standard samples straddling the unknown. Measurement was by UV absorption and was made at the following wavelengths:

3,6-bis(trifluoromethyl)phenanthrene	250 nm
3,6-bis(carbomethoxy)phenanthrene	315 nm
3-carbomethoxy-6-trifluoromethyl phenanthrene	315 nm

Since a standard sample of the last compound was not available, approximate assay was made by using the peak area vs. amount curve for the diester. Because the diester λ_{max} (315 nm) is longer than that of the monoester (295 nm), this assumption probably led to low results. Attached in Table X is a summary of the quantitative results obtained for Runs 30, 37, 41 and 46. Table XI summarizes the qualitative observations for a number of other runs.

G. Solvent Extraction Studies

In an attempt to separate components by their solubility differences in various solvents the following extractions were carried out in soxhlet extraction apparatuses.

1. A 4.00 gram sample of 3,6-phenanthrene dicarboxylic acid was extracted with 300 ml of acetone for 18 hours. Reweighing the material in the Soxhlet extraction thimble showed that 3.20 grams still remained unextracted.

2. A 4.00 gram sample of crude material from Run #17 (which was later shown to be essentially pure 3,6-phenanthrene dicarbonyl fluoride) was extracted with 300 ml of acetone for 6 hours. Reweighing the material in the Soxhlet extraction thimble showed that 1.30 grams still remained unextracted.

3. A 4.02541 gram sample of crude 23 was extracted successively with heptane, benzene, diethyl ether, and acetone. Figure XXXIV shows a flow sheet of this extraction. After each extraction fraction was collected and dried, it was weighed, gas chromatographed, scanned on an infrared spectrophotometer, and melting points were determined on some of the fractions. The heptane extraction recovered 44.9% of the product material known to be in the starting sample of Crude 23, while the benzene extraction recovered 39.5% of the product material (3,6-bis(trifluoromethyl)phenanthrene) known to be in the starting sample of Crude 23.

4. A 4.73280 gram sample of Crude 25 was extracted under the same conditions as was Crude 23. Figure XXXV shows a flow sheet of this extraction. The heptane extraction recovered 57.1% of the product material known to be in the starting sample of Crude 25, while the benzene extraction recovered 21.0% of the product material (3,6-bis(trifluoromethyl)phenanthrene) known to be in the starting sample of Crude 25.

5. A 3.49667 gram sample of Crude 26 was extracted under the same conditions as was Crude 23. Figure XXXVI shows a flow sheet of this extraction. The heptane extraction recovered 59.7% of the product material known to be in the starting sample of Crude 26, while the benzene extraction recovered 23.7% of the product material (3,6-bis(trifluoromethyl)phenanthrene) known to be in the starting sample of Crude 26.

6. A 1.10127 gram sample of Crude 27 was extracted under the same conditions as was Crude 23. Figure XXXVII shows a flow sheet of this extraction.

7. A 3.42999 gram sample of Crude 30 was extracted under the same conditions as was Crude 23. Figure XXXVIII shows a flow sheet of this extraction. The heptane extraction recovered 84.0% of the product material known to be in the starting sample of Crude 30, while the benzene extraction recovered 1.7% of the product material (3,6-bis(trifluoromethyl)phenanthrene) known to be in the starting sample of Crude 30.

8. A 1.9636 gram sample of Crude 31 was extracted under the same conditions as was Crude 23. Figure XXXIV shows a flow sheet of this extraction.

Summarizing these extractions shows that by extracting with heptane or benzene most of the 3,6-bis(trifluoromethyl)phenanthrene can be extracted from a crude mixture. Also from studying the infrared spectra of the heptane and benzene extract fractions it appears that some of the 3-trifluoromethyl phenanthrene-6-carbonyl fluoride 3-trifluoromethyl phenanthrene-6-carbonyl fluoride also appears in these extract fractions.

H. Column Chromatography

Column chromatography was also used in an attempt to separate the various components in each sample.

In this experiment 4.00 grams of Crude 21 was extracted with 300 ml of acetone in a Soxhlet Extractor for 18 hours. The acetone extract was cooled, and then evaporated leaving 3.60 grams of a shiny brown residue. A slurry containing 2.20 grams of this residue mixed with 20 ml of heptane was placed on the top of a chromatograph column. The 16" x 3/4" column had been previously packed with Silica Gel which had been activated at 107°C for 2 hours. After the sample was placed on the column, the column was successively washed with heptane, various heptane-chloroform mixes, chloroform, various chloroform-acetone mixes and acetone. The samples eluting from the column were collected in 200 ml fractions and evaporated. They were then weighed, and the larger samples were scanned in the ultraviolet and infrared regions as well as gas chromatographed. Figure XXXX shows the chromatogram obtained by plotting weight of each fraction collected versus the order of elution of the fraction. At the top of the chromatogram is listed the solvent used to elute each fraction. Of the total of 2.20 grams placed on the column, 2.1137 grams was eluted and collected off the column giving an accountability of 96.1%. Table XII lists some of the characteristics of the larger samples collected from the chromatograph column. Sample 5022-19B contains the largest percentage by weight of product, while samples 5022-19G, -19K and -19M probably contain a large quantity of 3-trifluoromethyl phenanthrene-6-carbonyl fluoride. The ultraviolet studies show that sample 5022-19B contains the most phenanthrene ring character while samples coming off the column later show loss of the phenanthrene ring character.

VIII. Conclusions and Recommendations

P-Trifluoromethyl Toluene Studies

1. Reactions studies in the 300 ml and 1750 ml autoclave showed that a 75-80% yield of p-trifluoromethyl toluene in the crude reaction mix can be obtained by reacting p-toluic acid with SF_4 under the following set of reaction conditions:

   SF_4 concentration - 50% molar excess

   Temperature - 160-170°C

   Time - 16-18 Hrs.

   Pressure - 2,000-2,500 psig (autogeneous pressure developed by adjusting quantity of reactants to reactor size)

2. A yield of >95% for crude p-trifluoromethyl toluene can be obtained under the above conditons of p-toluic acid fluoride is recycled. Studies to determine the feasibility of recycling this material should be made to determine the optimum yield.

3. Recovery of >99% purity p-trifluoromethyl toluene from the crude reaction mixture by distillation was 90% of that indicated by the analytical data.

4. The average overall recovered yield of >99% purity p-trifluoromethyl toluene based on the p-toluic acid charged was 63.5% as determined by the combination of six runs in the 1750 ml reactor.

5. A minimum temperature of 140°C was required to make the reaction proceed beyond the acid fluoride to the trifluoromethyl function in any significant yield. This situation relates to using SF_4 without any catalyst.

6. HF was shown to have a significant catalytic effect upon the reaction of SF_4 with the p-toluic acid fluoride. At 140°C, no reaction to the trifluoromethyl function was observed without HF while a 76% conversion was obtained at the same temperature with HF (equal molar quantity to that of p-toluic acid). However, HF was not shown to be a beneficial catalyst when working with 3,6-phenanthrene dicarboxylic acid as it promoted undesirable side reactions.

7. The presence of large amounts of S_2F_2 (>10%) in the SF_4 produces decomposition products and none of the desired product. An S_2F_2 level of <2% in the SF_4 was acceptable. This data was developed with the p-toluic acid reactions and it is expected that similar results would be obtained in the 3,6-phenanthrene dicarboxylic acid reactions.

8. A corrosion rate of <0.002 inches/year for 316 stainless steel was determined under reaction conditions, indicating that 316 stainless steel is a suitable material of construction for use in these reactions.

3,6-Phenanthrene Dicarboxylic Acid Studies

1. Reaction studies in the 300 ml autoclave showed that a 22% conversion to 3,6-bis(trifluoromethyl)phenanthrene could be obtained by reaction of SF_4 with 3,6-phenanthrene dicarboxylic acid in the presence of an inert solvent. An additional yield of 2.4% 3,6-phenanthrene dicarbonyl fluoride and 17.5% 3-trifluoromethyl phenanthrene-6-carbonyl fluoride (intermediate compounds) was also obtained with the remaining material unidentified. These results were obtained using the following reaction conditions:

   Temperature - 210 to 220°C

   Pressure - 1950 to 2150 psig

   Reaction Time - 16 hours

   SF_4 Concentration - 1100% excess

   Solvent - Benzotrifluoride (3 parts [by weight] to 1 part 3,6-phenanthrene dicarboxylic acid)

   A similar reaction performed at a lower temperature (180°C) gave a lower conversion (8.1%) to 3,6-bis(trifluoromethyl)phenanthrene but a higher yield of the intermediates (48% 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 26% 3,6-phenanthrene dicarbonyl fluoride).

2. Further reaction studies should be conducted to study the effect of temperature between 180 and 220°C and also the type and concentration of solvent in order to optimize the yield of 3,6-bis(trifluoromethyl)phenanthrene while keeping the yield of intermediate compounds as high as possible.

3. Studies to determine techniques for isolating and purifying the desired compounds from the reaction mixture should be made to substantiate the analytical yields presented above.

4. Relatively pure (>95%) 3,6-phenanthrene dicarbonyl fluoride could be produced in quantitative yields from the 3,6-phenanthrene dicarboxylic acid by reaction with SF_4 at temperatures of 110 to 160°C.

5. Studies on optimizing the SF_4 used in these reactions should be made, since the excess quantities used in these reactions would make the process commercially uneconomical.

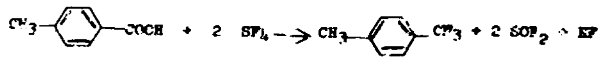
6. The use of HF as a catalyst was shown to be detrimental when used at elevated temperatures in molar quantities greater than that generated during the conversion of 3,6-phenanthrene dicarboxylic acid to 3,6-phenanthrene dicarbonyl fluoride. Further reactions using smaller quantities of HF or reactions using a combination of 3,6-phenanthrene dicarboxylic acid and 3,6-phenanthrene dicarbonyl fluoride should be investigated.

7. The sensitivity of the 9 and 10 hydrogen to reaction was shown as substitution will occur at these positions under certain reaction conditions, particularly in the presence of HF at elevated temperatures.

8. Economic evaluation of this process based on a 20% conversion to 3,6-bis(trifluoromethyl)phenanthrene and an overall 50% yield of 3,6-bis(trifluoromethyl)phenanthrene plus intermediates showed that a selling price of ~$15 per pound could be achieved at production rates of 30,000 to 50,000 lb/yr. For smaller requirements, such as 3,000 lb/yr 3,6-bis(trifluoromethyl)phenanthrene, the selling price would be $40/lb. These figures do not include the cost of 3,6-phenanthrene dicarboxylic acid, which should be added at 1.9 times the per pound cost of 3,6-phenanthrene dicarboxylic acid.

Table I
Reaction Conditions

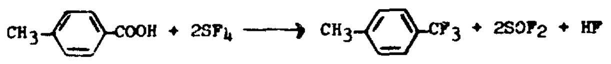
300 ml Reaction Vessel



Run No.	Date	SF_4 Charge GMS	SF_4 Charge Moles	P-Toluic Acid Charge GMS	P-Toluic Acid Charge Moles	Heating Cycle Temp. °C	Heating Cycle Max. psig	Heating Cycle Time Hrs.	Reaction Conditions Temp. °C	Reaction Conditions Max. psig	Reaction Conditions Time Hrs.	Crude Recovery GMS	Crude Analysis	Crude Yields -%- CF_3	Crude Yields -%- CF_3 & COF	Crude Yields -%- CF_3/COOH-COF	Remarks
1	7-11-69	135	1.25	57	0.42	25-100 100-150	580 925	1 1	98-100 142-150	580 925	1 5	33.6 (Some Spill)	None	-	-	-	Crude Product Added to Pentane + NaF
2	7-14-69	135	1.25	57	0.42	25-95	600	3	95-100	625	7	68.7	None	-	-	-	Crude Product Added to Pentane + NaF
3	7-16-69	135	1.25	57	0.42	20-135	900	4	145-150	1060	5 1/2	63.5	None	-	-	-	Removed excess lines to Pressure Gauge
4	7-18-69	155	1.43	57	0.42	20-150	1120	3	145-150	1125	7 1/2	50.0 (Some Spill)	None	-	-	-	Added 20 GMS SF_4 to Compensate for Gauge Volume (10 ml) - Analytical.
5	7-23-69	155	1.43	57	0.42	20-120	800	4	120 (TC Failed)	800	20	No Weight	None	-	-	-	Crude to Caustic; 2.2 GMS CF_3 Recovered: 30.8 GMS P-toluic acid recovered from Caustic.
6	7-28-69	155	1.43	57	0.42	25-150	1050	2 1/2	150-152	1050	7 1/2	70.1	CF_3 - 36.7 COF-45.3 Unknown-1.0 HF + Res.-17	38.2	93.0	84.0	New analytical Procedure Crude Retained for Distillation.
7	7-30-69	155	1.43	57	0.42	25-190	1675	1	190-193	1950	8	76 (Black Solids)	None	-	-	-	Coal Type Solids. SF_4 Contained ~15% S_2F_2.
8	8-1-69	155	1.43	57	0.42	25-150	1150	1	137-146	1300	14	19 - Liq. 57 - Solids	None	-	-	-	Coal Type Solids Same SF_4 as No. 7
9	8-6-69	155	1.43	57	0.42	20-150	1025	3 1/2	146-151	1125	7 1/4	70	CF_3 - 32.1 COF-53.2 UNK.-0.1 HF + Res.-14.6	33.4	100	100	New SF_4 - 2.0% S_2F_2 used on all future runs. Crude retained for Distillation.
10	8-7-69	155	1.43	57	0.42	20-146	960	2	143-153	1030	18	72.3	CF_3 - 49.4 COF-31.4 Unk.-0.3 HF + 18.9	53.4	92.5	88.0	Retained for Distillation.
11	8-11-69	155	1.43	57	0.42	25-178	1360	2 1/2	190-193	1360	7 1/2	72.0	CF_3 - 45.7 COF - 39.3 Unk. - 0.2 HF + Res. -14.7	48.9	98	95.5	Retained for Distillation.
12	8-12-69	160	1.48	118 (COF)	0.86	25-152	860	2	148-152	910	18	123.5	CF_3 -<1.0	<1.0	-	-	Acid Fluoride Prepared separately. No reaction. Recharged in Run #13.
13	8-13-69	160	1.48	110 (#12) 16HF	0.80 0.80	25-150	1760	2	148-152	910	18	147	CF_3 - 66.5 COF - 5.4 Unk.- 4.4 HF + Res-23.8	76.5	84.0	84.0	Material Retained - Not included in Distillation of pure sample.
14	8-14-69	155	1.43	57	0.42	25-180	1360	1 1/2	180-185	1450	18	74.0	CF_3 - 62.4 COF - 17.5 Unk. - 3.0 HF + Res. -18.6	68.6	91.4	89.0	Retained for Distillation.
15	8-18-69	231	2.14	81	0.60	20-165	2000	2	155-165	2000	18	106.4	CF_3 - 70.3 COF - 14.9 Unk. - 1.8 HF + Res. -13.9	78.5	98.0	97.4	Retained for Distillation

Table II

P-Toluic Acid Reaction Conditions
1750 ml Autoclave



Run No.	Date	SF_4 Charge GMS	SF_4 Charge Moles	P-Toluic Acid Charge GMS	P-Toluic Acid Charge Moles	Heating Cycle Temp. °C	Heating Cycle Max. psig	Heating Cycle Time Hrs.	Reaction Conditions Temp. °C	Reaction Conditions Max. psig	Reaction Conditions Time Hrs.	Crude Recovery GMS	Crude Analysis -%-	Crude Yields % CF_3	Crude Yields % CF_3 + COF	Crude Yields % $\frac{CF_3}{COOH-COF}$	Remarks
[illegible]	11-18-69	1250	11.2	472	3.46	20-156	1350	2	160-162	1500	8	578	CF_3 82 COF 13 UNK 0.6 Res.+HF 4.4	85	100	100	Scale-up run 165.Gms, p-trifluoromethyl toluene recovered in distillation
[illegible]	12-11-69	1380	12.8	520	3.82	20-160	1790	3 1/2	167	2980	15 1/2	576	CF_3 81.9 COF 4.8 UNK 3.0 Res.+HF 10.3	77.2	82.3	81.4	Agitator stopped overnite Pressure increased overnite - 392 gms. p-trifluoromethyl toluene recovered in distillation (54%)
32	12-17-69	1380	12.8	520	3.82	20-160	1150	2	160	1140	15 1/2	546	CF_3 63.1 COF 24.6 UNK 2.0 Res.+HF 10.3	56.5	82.4	81.5	Distilled as one batch. 1104 gms p-trifluoromethyl toluene recovered in distillation. 1232 gms p-trifluoromethyl toluene by analysis. Recovered 90% of theoretical. Overall yield for 3 runs based on recovered distilled p-trifluoromethyl - 62.1%.
33	12-18-69	1380	12.8	520	3.82	20-162	2080	2 1/2	170	3000	16 1/2	592	CF_3 79.1 COF 6.2 UNK 1.8 Res.+HF 13.0	77.0	83.7	82.5	
34	12-19-69	1250	11.2	472	3.46	20-160	1400	3	170	2380	16	561	CF_3 73.8 COF 9.7 UNK 2.4 Res.+HF 14.1	75.0	86.2	85.6	
35	1-8-70	1250	11.2	472	3.46	20-165	1500	2 1/2	160	1720	15 1/2	513	CF_3 62.7 COF 17.1 UNK 2.9 Res.+HF 17.3	58.2	76.7	71.3	Distilled as one batch. 1058 gms p-trifluoromethyl toluene recovered in distillation. 1156 gms p-trifluoromethyl toluene by analysis - Recovered 91% of theoretical. Overall yield for 3 runs based on recovered distillation - 64.7%
39	1-9-70	1250	11.2	472	3.46	20-160	1500	2 1/8	172	2450	17 1/2	540	CF_3 78.0 COF 8.9 UNK 4.2 Res.+HF 9.0	76.2	86.3	85.0	
40	1-12-70	1250	11.2	472	3.46	20-161	1300	2 1/4	160	1710	21 1/2	563	CF_3 75.8 COF 13.1 UNK 3.5 Res.+HF 7.5	77.4	93.0	91.5	
43	1-19-70	1250	11.2	472	3.46	20-163	1460	3	163-154	1460-1510	15 1/2	560	CF_3 62.3 COF 22.1 UNK 0.3 Res.+HF 15.3	63.0	89.0	85.1	Distilled as one batch. 578 gms. p-trifluoromethyl toluene recovered in distillation. No yield data since distillation not carried to completion.
44	1-20-70	1250	11.2	472	3.46	20-163	1350	2 1/2	163	1650	16 1/4	565	CF_3 70.2 COF 16.9 UNK 2.0 Res.+HF 10.8	71.1	91.2	89.0	

Table III

P-Trifluoromethyl Toluene Samples Delivered To Contractors

APCI Sample No.	Delivered To	Date Shipped	Quantity GMS	Purity(1) - %	Refractive Index
5007-27A	Starks Associates, Inc. 1280 Niagara St. Buffalo, N. Y.	Aug. 27, 1969	130	99.4	1.4241 @ 24.5°C
5043.26	Dept. of Organic Chemistry Division of Medical Chemistry Walter Reed Army Institute of Research Walter Reed Medical Center Washington, D. C.	Dec. 30, 1969	1500	99.6	1.4237 @ 24°C
5043.32	Dept. of Organic Chemistry Division of Medical Chemistry Walter Reed Army Institute of Research Walter Reed Medical Center Washington, D. C.	Jan. 30, 1970	1503	99.1	1.4201 @ 30°C

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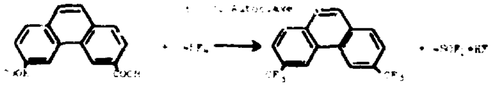
(1) Area % GLC

[illegible]-Phenanthrene Dicarboxylic Acid Reaction Conditions
[illegible] Autoclave



		Charge															
Run No.	Date	PDCA(1) Acid GMS	Moles	Sample No.	SF4 GMS	Moles	HF GMS	HF Moles	Solvent GMS	N2 PSI	Reaction Conditions Temp. °C	Press. psig	Time Hrs.	Crude Recovery GMS	Crude Analysis IR	GLC	Remarks
[illegible]	[illegible]	[illegible]	[illegible]	AGC-W71.[illegible]	[illegible]	[illegible]	[illegible]	-	-	0	112	2400	7 1/2	12.70 (9.9 Dry)	Strong COF No COOH Little CF3	None	Tan Powder - M. Pt. 218-224°C. Practically pure Di Acid Fluoride
[illegible]	[illegible]	[illegible]	[illegible]	AGC-W71.[illegible]	[illegible]	[illegible]	[illegible]	-	-	0	164	1840	7 1/2	11.6 (s) (10.2 Dry)	Same as No. 17	None	Dark Brown Powder - M. Pt. 198-214. Re-charged in Run #19
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	18	0.9	-	0	180	2040	7 1/2	12.7 (l+s) (10.2 Dry)	CF3 Strong Little COOH and COF	None	Dark Liquid and Solid - Dried to remove HF (Rm. Temp.) Washed with NaOH - 56% recovered as brown powder.
[illegible]	[illegible]	[illegible]	[illegible]	AGC-W71.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	0	100	1760	6	23.5 (l+s) (12.0 Dry)	Same as No. 19	None	Dark liquid and solid - Dried to remove HF(~50%) Washed with NaOH - ~50% recovered as brown powder.
[illegible]	[illegible]	[illegible]	[illegible]	AGC-W71.[illegible]	24	[illegible]	[illegible]	0.1	-	1100	110	1780	8	12 (s)	COF Present CF3 Present COOH Little	1.0% TFMP(5)	Crude very soluble in Acetone
[illegible]	[illegible]	[illegible]	[illegible]	AGC-W71.[illegible]	24	[illegible]	0	-	-	1060	140	2090	8	8.8 (s)	CF3 Little COF Strong	0.4% TFMP	Crude - Dark gray solid-Acetone Ins.
[illegible]	[illegible]	[illegible]	[illegible]	AGC-W71.3	24	0.22	5	-	-	[illegible]60	220	[illegible]	9	9.4 (s)	Similar to No. 21	1.0% TFMP	Crude - Hard black Solid - Acetone Soluble
[illegible]	12-1-69	10	0.047	AGC-W71.3	24	0.22	0	-	-	860	220	2040	1	8.6 (s)	Similar to No. 22	0.5% TFMP	Gummy Solid
[illegible]	12-4-69	10	0.037	AGC-W71.4	200	1.85	0	-	-	0	220	2500	8	[illegible]	Similar to No. 22	4.0% TFMP	Heavy Liquid - Tarry and Black
[illegible]	[illegible]	4	0.015	PDCF #17	32	0.296	25	-	-	1100	100	1660	1	14 (Fuming Black Liquid) 2.1 GMS Solid	Strong CF3 Several Additional Peaks	0.02% TFMP	Fuming Liquid - Brown Solid
[illegible]	12-10-69	20	0.074	AGC-W71.3	300	2.68	0	-	-	0	115	1650	12	23.9 Brown Powder	Strong COF Little CF3 >90% D.A.F.	-	Brown Powder
[illegible]	[illegible]	10	0.037	AGC-W71.3	180	1.67	0	-	BTF(4) 30	0	110 170-185	160 1630-1910	1 14	25.4 Black Liq. and Solid	Similar to No. 23	3.2% TFMP	6.1 grams solid - 8.2% b-TFMP TLC - 26% PDCF(2) and 48% TFMP-CF(3)
[illegible]	12-17-69	1.5	[illegible]	AGC-W71.3	120	1.11	24	1.20	CH_2Cl_2 60	0	20	110	17 1/2	21.5 GMS Liq.	Di Acid Fluoride	0.05% TFMP	After Evap. - Brown Powder
35	12-18-69	20	0.074	AGC-W71.4	110	1.02	0	-	BTF 100	0	110 170	No Rdg. Plugged Lines	1 12 1/2	105.7 GMS Liq. (22.5 GMS Solid)	Similar to No. 21 & 26	2.5% TFMP	TLC shows little PDCF and TFMP-CF
[illegible]	12-23-69	10	0.037	PDCF #28	110	1.02	4	0.2	BTF 91.5	0	103	360	17 1/2	110.6 GMS Black Liq. (20.6 GMS Solid)	Between No. 19 & 21	40.1% TFMP	TLC shows little PDCF and TFMP-CF
37	1-6-[illegible]	10	0.037	AGC-W71.4	180	1.67	0	-	BTF 30	0	110 180 to 160	660 1660 to 1260	1 16 1/2	30.5 GMS Black Liq. (8.1 GM Solid)	Similar to No. 30	5.5% TFMP	TLC (on Liquid) Yield 6.5% PDCF 26% 6.8% TFMP-CF 27% 1.3% TFMP 4.6%
41	1-12-70	10	0.037	AGC-W71.4	180	1.67	0	-	BTF 30	0	220 to 210	2150 to 1950	16	39.5 GMS Black Liq. (12.0 GM Solid)	Similar to No. 35	17.5%	TLC (on Liquid) Yield 0.6% PDCF 2.4% 4.8% TFMP-CF 17.5% 6.7% TFMP 22.5%
43	[illegible]	3.4 plus 6.6	0.0[illegible]35 0.0239	AGC-W71.4 PDCF #28	180	1.67	0	-	BTF 30	0	182	1560	18	43 GMS (Black Liq.)	Similar to No. 23, 30 and 37	5.5%	Liquid Analyzed 1.5% b-TFMP which is ~5.5% based on solids.
[illegible]	1-20-70	9.4 2.0	0.035 0.0075	#42 AGC-W71.4	180	1.67	0	-	BTF 35	0	160 218	1300 1920	1 17	42.1 GMS (Black Liq.)	-	41.0%	Liquid Analysis showed essentially no b-TFMP — only peaks beyond b-TFMP
[illegible]	1-21-70	10	0.037	AGC-W71.4	180	1.67	0	-	BTF 50	0	110 225	525 2340	1 1	65 GMS (l) 13.1 GMS (s)	-	41.0%	Solid analysis - 41% b-TFMP. TLC (on Solid) 33% PDCF 8% TFMP-CF 41.07 TFMP

(1) PDCA - 3,6-phenanthrene dicarboxylic acid

(2) PDCF - 3,6-phenanthrene dicarbonyl fluoride

(3) TFMP-CF - 3-trifluoromethyl phenanthrene-6-carbonyl fluoride

(4) BTF - benzotrifluoride

(5) TFMP - 3,6-bis trifluoromethyl phenanthrene

Table V

Elemental Analysis of 3,6-Phenanthrene-di-Carboxylic Acid Starting Material

	Batch AGC-W71.3	Batch AGC-W71.4	Batch AGC-W71.4(2)
% Carbon	69.88	70.61	71.41
% Hydrogen	4.28	3.77	3.94
% Nitrogen	Trace (0.1-0.3)	Trace (~0.3%)	0.61
% Chlorine	0.88	0.08	-
% Ash	1.46	0.32	-
Major Metals(1) (>0.01%)	Fe, Cu, Na	Fe, Si, Na	Na <0.1%
Minor Metals (<0.01% & >0.0001%)	Mg, Si	Mg	Cu <5 ppm
Trace Metals (<0.0001%)	Mn, Ag, B, Ti, Ni, Al, Ca, Cr	Sn, Cu, Ag, Mn, Ti, Ni, Al, Ca	Fe, Mg, Al <1 ppm

(1) Arc emission spectrographic analysis of the ash.

(2) Data supplied by Aerojet-General.

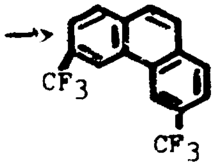
Table VI

Infrared Observations
3,6-Phenanthrene Dicarboxylic Acid Reactions

	$\overset{\overset{O}{\|}}{C}$-F	CF_3				
	5.6	7.55μ	8.95μ	Di-COF	Comments	Closest to Pure Di-COF
Run #17	Yes	No	No	Yes	Almost pure Di-COF	1
Run #18	Yes	Trace	Trace	Yes	Almost the same as #17	2
Run #19	Trace	Yes	Yes @ 8.85	No	Strong C-F	12
Run #20	No	Yes	Yes @ 8.78	No	Strong C-F (Similar to 19)	14
Run #21	Yes	Yes	Yes	Minor	Strong C-F (Different from 19 or 20)	10
Run #22	Yes	Yes Minor	Yes Minor	Yes Major	Similar to #18, but with a little more CF_3	3
Run #23	Yes	Yes	Yes	Some	Strong C-F, but also some Di-COF	5
Run #25	Yes	Yes	Yes	Yes Major	Similar to #22	3
Run #26	Yes	Yes	Yes	No Trace	Sharp I. R.	8
Run #27	Yes	Yes	Yes	No	Strong C-F	13
Run #30	Yes	Yes	Yes	Some	Similar to #23, but with a little more CF_3	7
Run #31	Yes	Yes	Yes Minor	Yes Minor	Similar to #22, but with a little more CF_3	4
Run #35	Yes	Yes	Yes	No	Similar to #21 and #26	9
Run #36	Yes Minor	Yes Major	Yes Major	No	Between 21 and 19	11
Run #37	Yes	Yes	Yes	Some	Similar to #30	7
Run #41	Yes	Yes	Yes	No	Similar to #35	9
Run #42	Yes	Yes	Yes	Yes	Similar to #23, #30 and #37	6
Run #45					Not Run	
Run #46					Not Run	

Table VII

Gas Chromatographic Analysis
3,6-Phenanthrene Dicarboxylic Acid Reactions
Percent in the Following Crude Materials

Peak in Minutes	Compound	21	22	23	25	26	27	30	31	35	36	37	41	42*	45*	46*
5.05	(1)	0.92		0.22		0.93	0.63			1.25	5.66		0.80			
7.0		0.15						1.04	2.13		0.26					
9.1		3.06	0.82	1.99	0.31	1.12	0.11		0.26	06	1.38		3.11			
9.6		0.33		0.22		0.43	0.24	0.43	0.09	0.81	0.18	1.05	3.71			
10.4		0.37		0.09		0.28	0.20		0.09	0.14			0.96			
11.9 →		0.99	0.39	1.03	0.48	4.11	0.03	8.19	0.05	2.55	0.1	5.53	17.5	5.5	<1.0	<1.0
14.3		1.07	1.34	0.53		0.28	1.32		0.35		0.23		0.43			
15.6		1.01		1.06		3.97	0.58				4.06		3.97			
17.3		0.13	—	0.13	—	—	—	—	—	—	—	—	0.24			
Total		8.03	2.55	5.27	0.79	11.12	3.11	9.66	2.97	6.81	11.87	6.58	29.75			

*Analysis was performed on the liquid sample only for product material. The other peaks were not calculated.

(1)

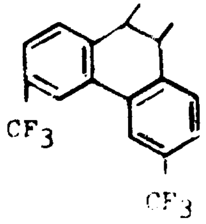
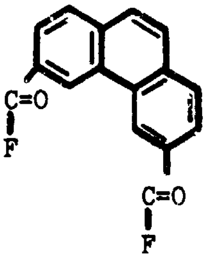


Table VIII

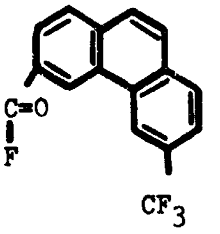
Solids Probe Mass Spectral Data for Crude 26

Scan	Probe Temp.	Major m/e Peaks
1	75°C	270(6), 292(8), 314(10), 348(8), 350(6), 382(5), 388(4)
2	120°C	292(10), 314(10)
3	150°C	292(10), 314(9), 348(6), 382(5), 388(4)
4	175°C	264, 270, 292, 314
5	210°C	243, 251, 345, 518, 586, 614, 633, 634, 635, 636, 655, 656, 657, 658, 666, 688

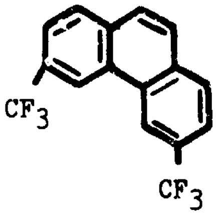
Expected Intermediates and Product



Mol. Wt. 270

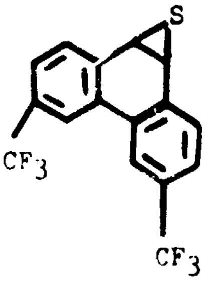


292

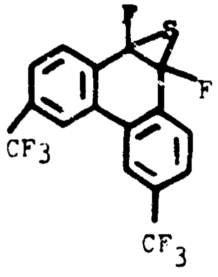


314

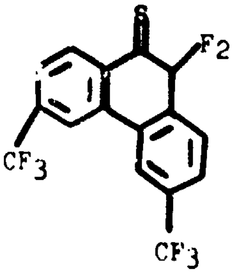
Possible Substitution Products



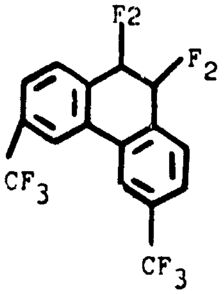
346



362



382



388

Table IX

G.C.-M.S. Analysis of Crude 26

G.C. Peak	Major Mass Peaks
8	339, 348, 350, 369, 388
10	350, 363, 382
12	314
14	296, 311, 327, 346, 348

Table X

Thin Layer Chromatography Analysis Quantitative Results

Run No.	3,6-Bis(trifluoromethyl) Phenanthrene - %	3,6-Bis(carbomethoxy) Phenanthrene - %	3-Carbomethoxy-6-trifluoromethyl Phenanthrene(1) - %
30 (Solids)	7.5	26	48
37 (2)	1.3	6.5	6.8
37 (Solids Basis)	4.6	26	27
41(2)	6.7	0.6	4.8
41 (Solids Basis)	2.4	17.5	22.5
46 (Solids)	< 1	33	8

(1) Assay depends upon assumption of calibration curve for 3,6-bis (carbomethoxy)Phenanthrene.

(2) Analysis of reactor effluent including solvent.

Table XI

Thin Layer Chromatography Analysis
Qualitative Observations

Legend

b-TFMP - 3,6-bis(trifluoromethyl)phenanthrene

DME - 3,6-bis(carbomethoxy)phenanthrene

TME - 3-carbomethoxy-6-trifluoromethyl phenanthrene

X - Spot faster than b-TFMP in cyclohexane - carbon tetrachloride

Y - Spot slower than b-TFMP in cyclohexane - carbon tetrachloride

Z - Spot slightly faster than TME in benzene - chloroform

Run 26 - Contains 3,6-bis(trifluoromethyl)phenanthrene and similar amounts of X and Y. Methanolized mixture contains trace DME and small amount TME.

Run 30 - Contains 3,6-bis(trifluoromethyl)phenanthrene, trace X and no Y. Methanolized product contains substantial DME and TME.

Run 31 - Trace 3,6-bis(trifluoromethyl)phenanthrene, small amount X, no Y. Methanolized product contains more DME than 30, less TME.

Run 35 - Methanolized product contains trace DME, trace TME, no observable 3,6-bis(trifluoromethyl)phenanthrene and substantial X and/or Y.

Run 36 - Methanolized product contains less DME and TME than 35 and substantial X and Y.

Run 37 - Contains some 3,6-bis(trifluoromethyl)phenanthrene. Methanolized product contains DME and TME and some Z.

Run 41 - Contains substantial 3,6-bis(trifluoromethyl)phenanthrene and large amount X. Methanolized product contains trace DME and amount of TME similar to 37.

Run 45 - Much X, obscures any 3,6-bis(trifluoromethyl)phenanthrene present. Methanolized product contains no DME or TME but substantial Z.

Run 46 - Contains trace 3,6-bis(trifluoromethyl)phenanthrene and trace X. Methanolized product contains much DME, some TME and some Z.

Table XII

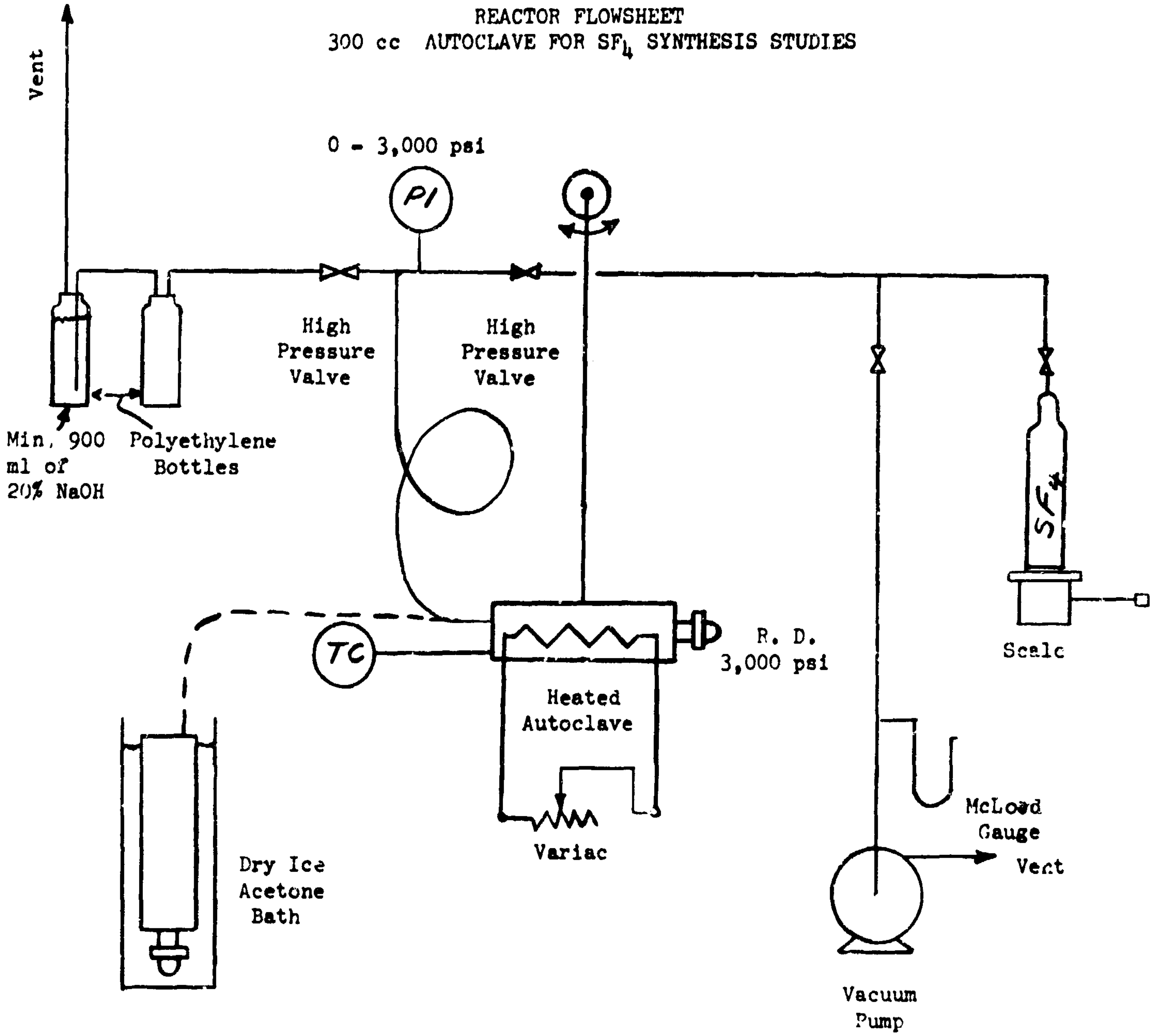
Column Chromatography Results - Run #21

Peak	Weight	Eluting Solvent	Ultraviolet Study			Gas Chromatograph Study					Infrared Study			
			λ252 kx1000	λ301 kx1000	λ334 k	6" pk.	9.1" pk.	11.9" pk. prod.	14.3" pk.	15.6" pk.	COF 5.5μ	COOH 5.9μ	7.55μ	8.95μ
5022-19B	0.0329g	C_7H_{16}	42.7	8.74	1399	w	s	m	m	m	n	n	s	s
5022-19G	0.1741g	5% $CHCl_3$ in C_7H_{16}	31.6	9.37	6076	w	s	m	m	m	s	t	s	s
5022-19K	0.1263g	25% $CHCl_3$ in C_7H_{16}	23.4	9.65	7614	m	s	m	m	m	s	t	s	s
5022-19M	0.3086g	50% $CHCl_3$ in C_7H_{16}	29.4	9.22	5294	m	m	m	m	m	s	w	s	s
5022-19R	0.1198g	75% $CHCl_3$ in C_7H_{16}	16.2	7.52	4902	w	w	w	w	w	m	m	s	s
5022-19V	0.0577g	$CHCl_3$	17.3	8.52	6054	n	t	t	n	n	w	m	s	s
5022-19-4	0.1994g	50% $CHCl_3$ in Acetone	18.2	10.4	8194	7.1" peak m	n	t	n	n	w	s	s	s
5022-19-6	0.0347g	Acetone	11.3	6.44	4897	n	n	n	n	n	t	s	s	s

s = strong m = medium w = weak t = trace n = none

FIGURE I

REACTOR FLOWSHEET
300 cc AUTOCLAVE FOR SF_4 SYNTHESIS STUDIES



NOTE:

1. All piping, valving and connections in high pressure section to be rated at a minimum of 5,000 psi.
2. System to be tested with N_2 @ 2,500 psi and 190°C.

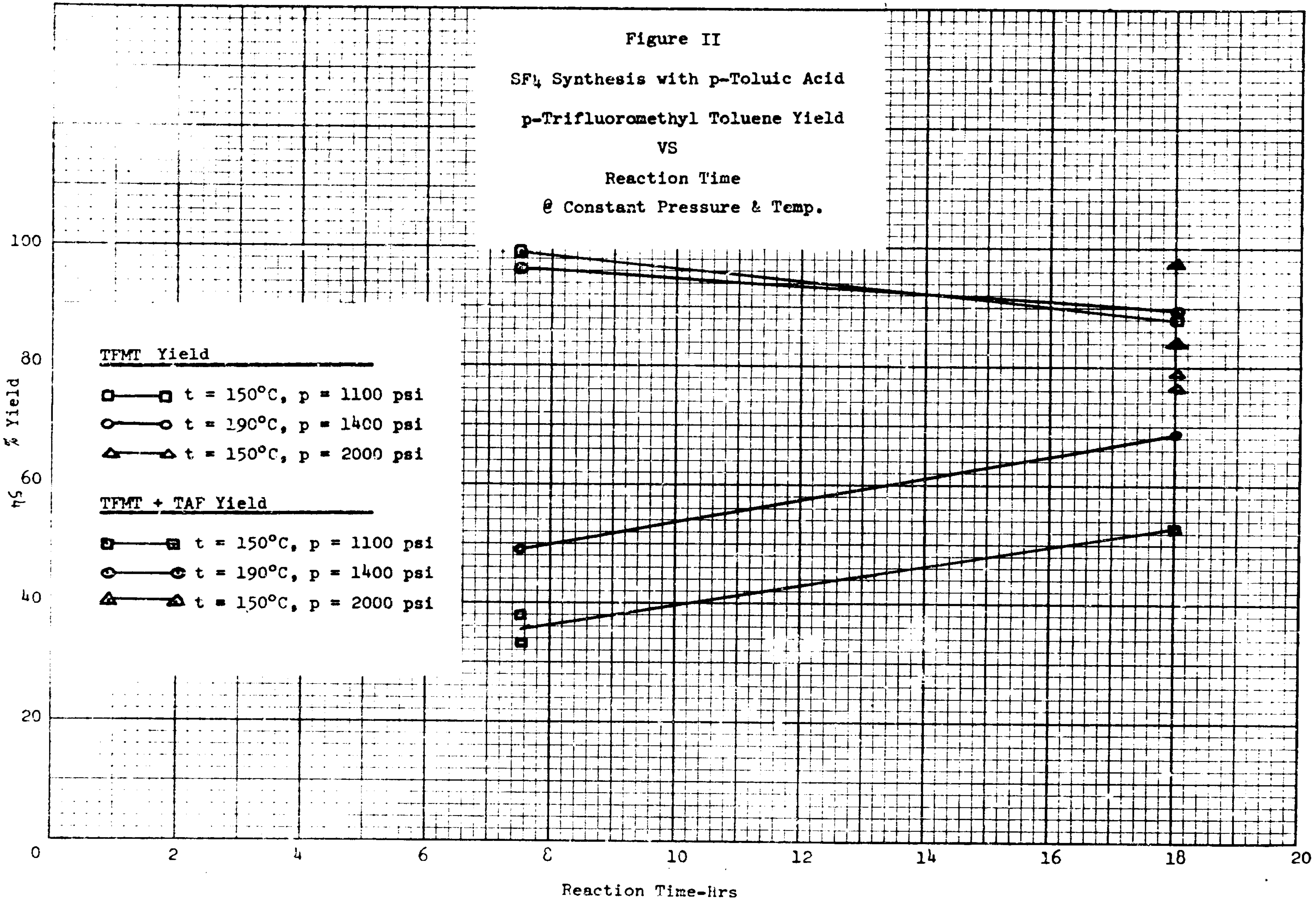


Figure II

SF$_4$ Synthesis with p-Toluic Acid

p-Trifluoromethyl Toluene Yield

VS

Reaction Time

@ Constant Pressure & Temp.

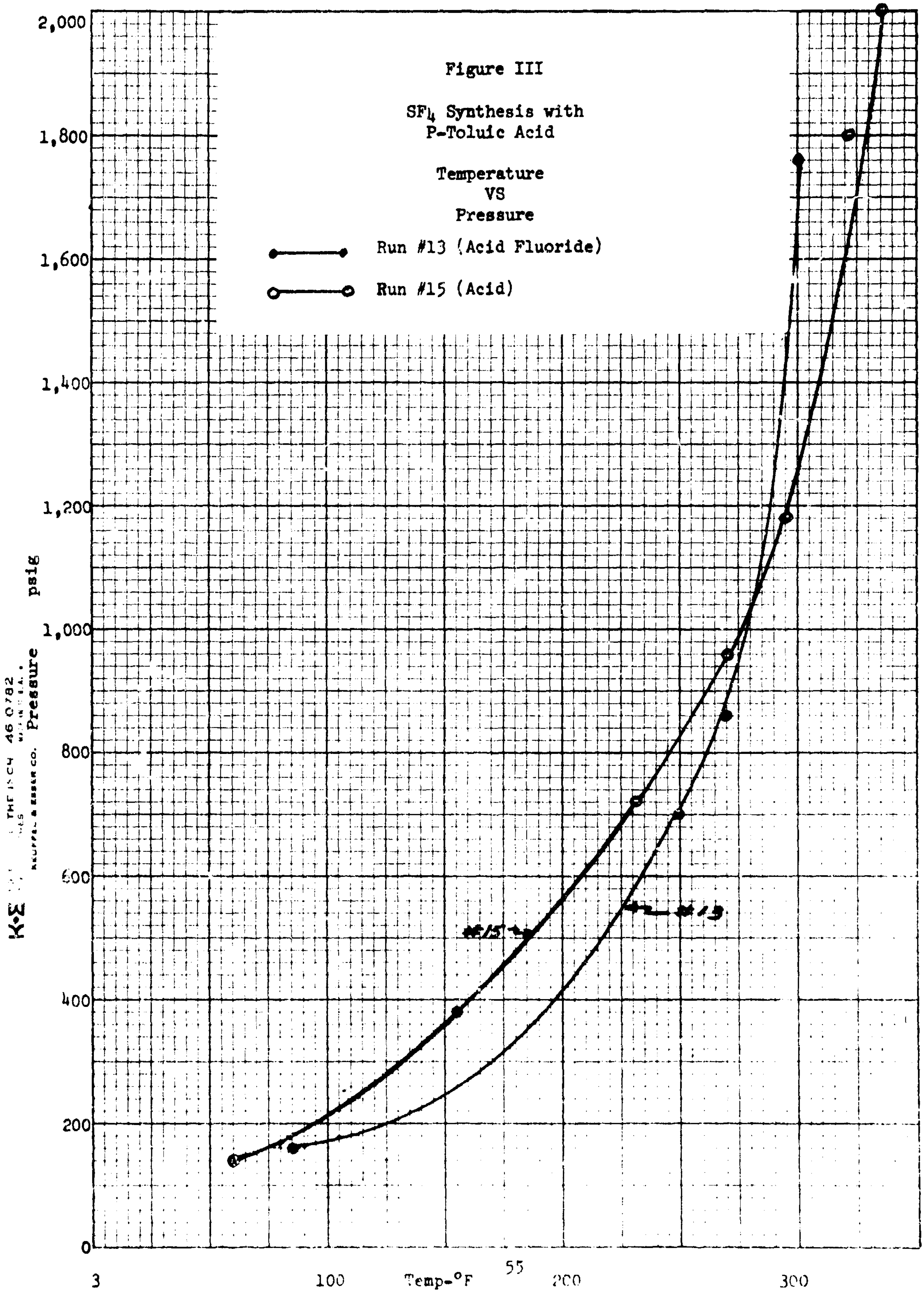
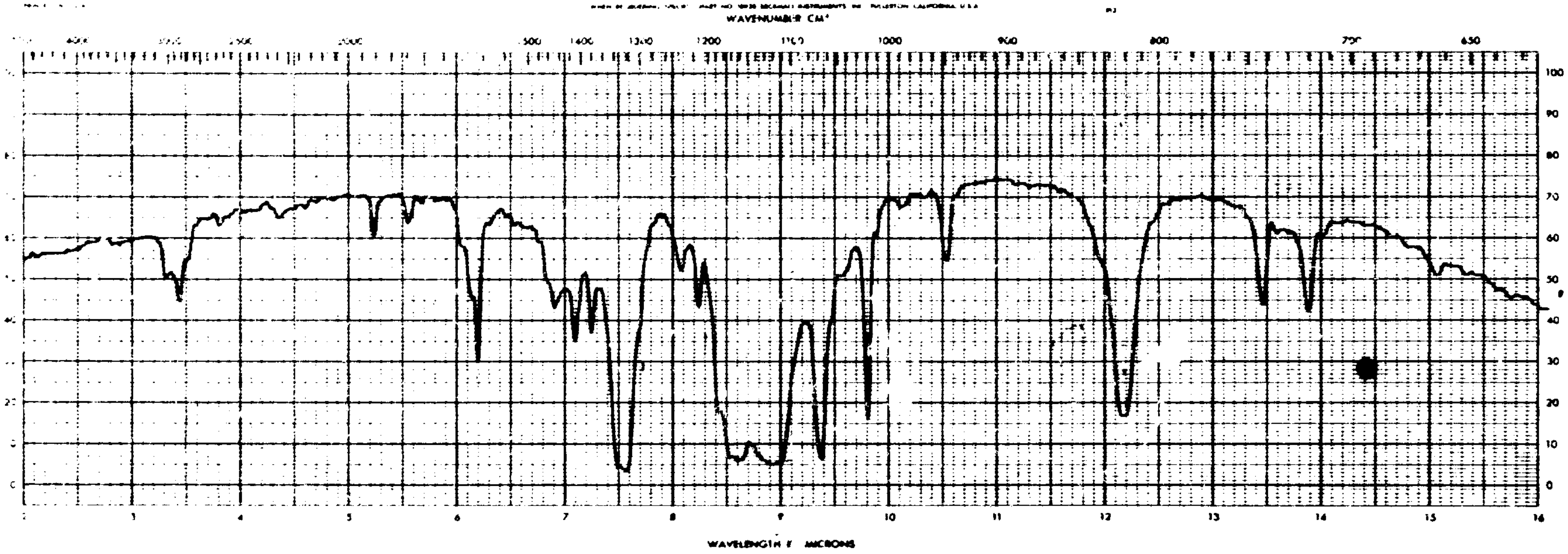


Figure III

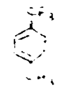
SF_4 Synthesis with P-Toluic Acid

Temperature VS Pressure

FIG. IV



SPECTRUM NO. ____
DATE 6-25-[illegible]
SAMPLE 50[illegible]
SOURCE ____
STRUCTURE



PATH ____
SOLVENT ____
CONCENTRATION ____
PHASE 2- NaCl Flat
COMMENTS ____
ANALYST D K L

Beckman
INFRARED
SPECTROPHOTOMETER

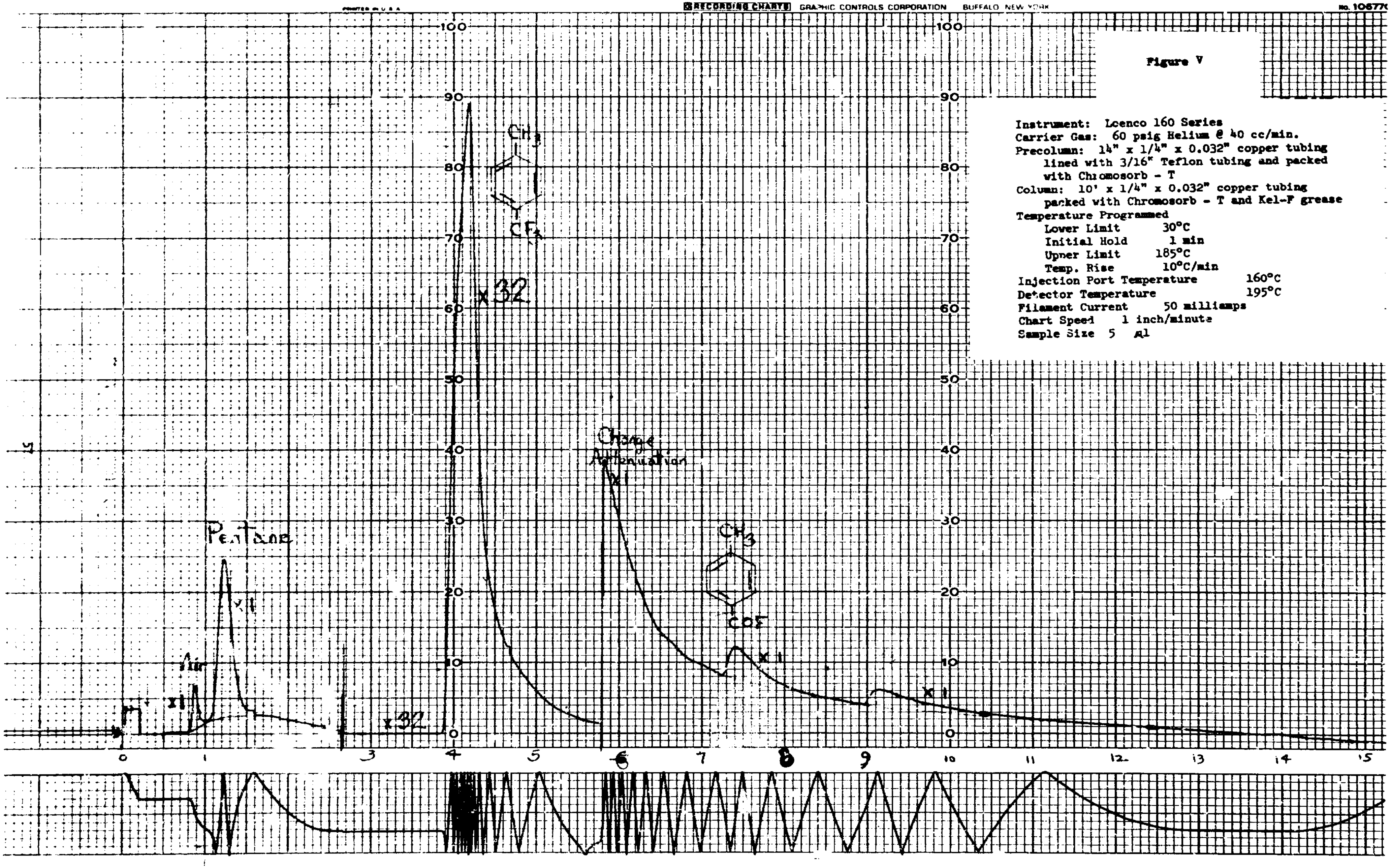
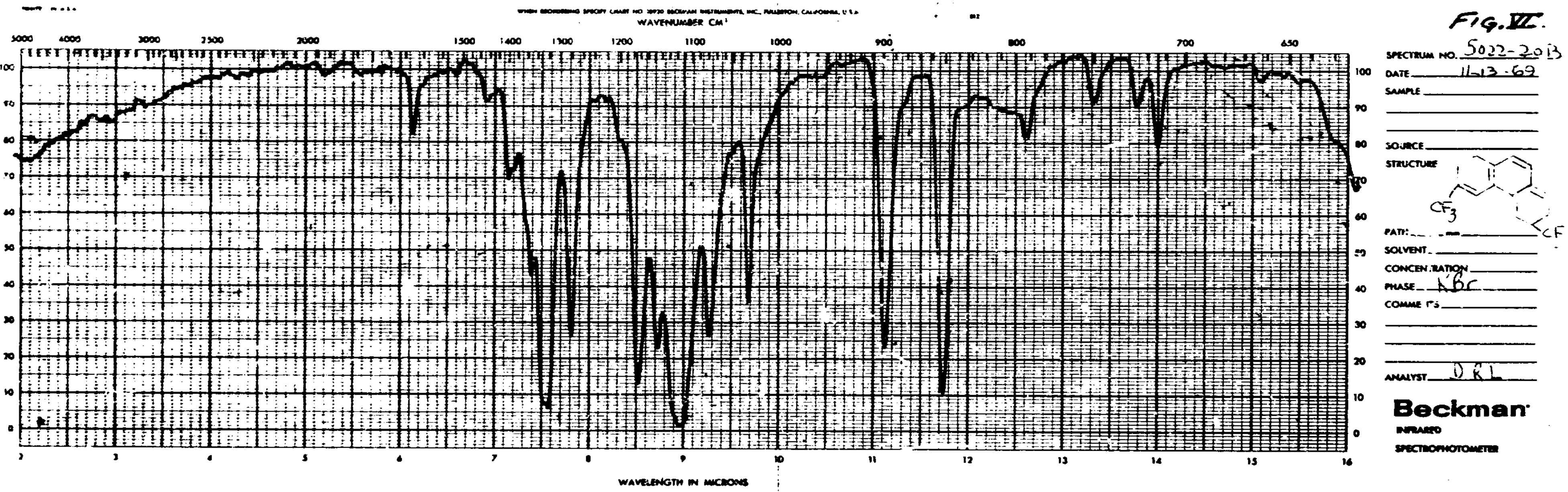


Figure V

Instrument: Loenco 160 Series
Carrier Gas: 60 psig Helium @ 40 cc/min.
Precolumn: 14" x 1/4" x 0.032" copper tubing
lined with 3/16" Teflon tubing and packed
with Chromosorb - T
Column: 10' x 1/4" x 0.032" copper tubing
packed with Chromosorb - T and Kel-F grease
Temperature Programmed
Lower Limit 30°C
Initial Hold 1 min
Upper Limit 185°C
Temp. Rise 10°C/min
Injection Port Temperature 160°C
Detector Temperature 195°C
Filament Current 50 milliamps
Chart Speed 1 inch/minute
Sample Size 5 μl

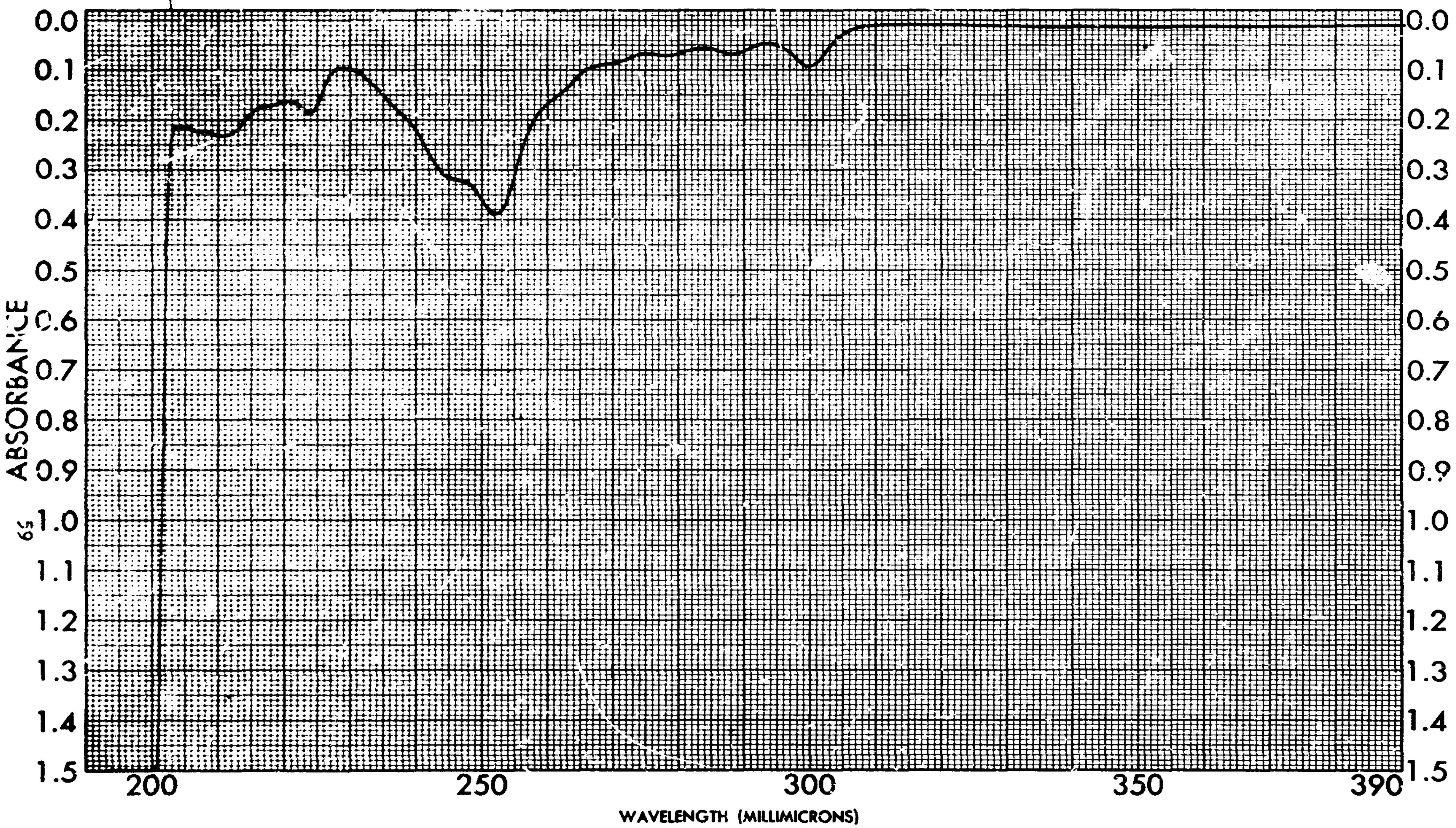
FIG. VII.



SPECTRUM NO. 5022-2013
DATE 11-13-69
SAMPLE
SOURCE
STRUCTURE
PATH
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS
ANALYST DKL

Figure VII

UV



SAMPLE  [illegible]

ORIGIN [illegible]

SOLVENT [illegible]

CURVE NO. 1

CONC. 0.00000592 M

CELL PATH 1 cm

REFERENCE 95 % Ethanol

SCAN SPEED Slow

SLIT

OPERATOR D R L

DATE 11-17-6[illegible]

REMARKS

PART NO 202-1511

PERKIN ELMER

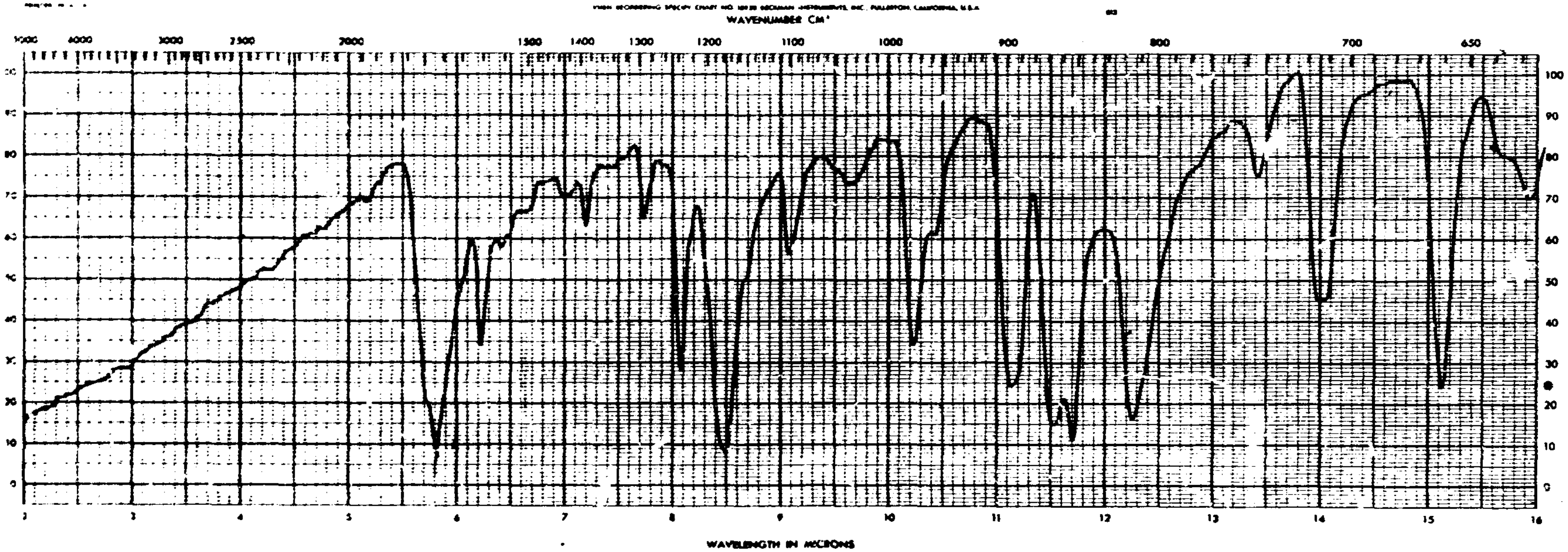


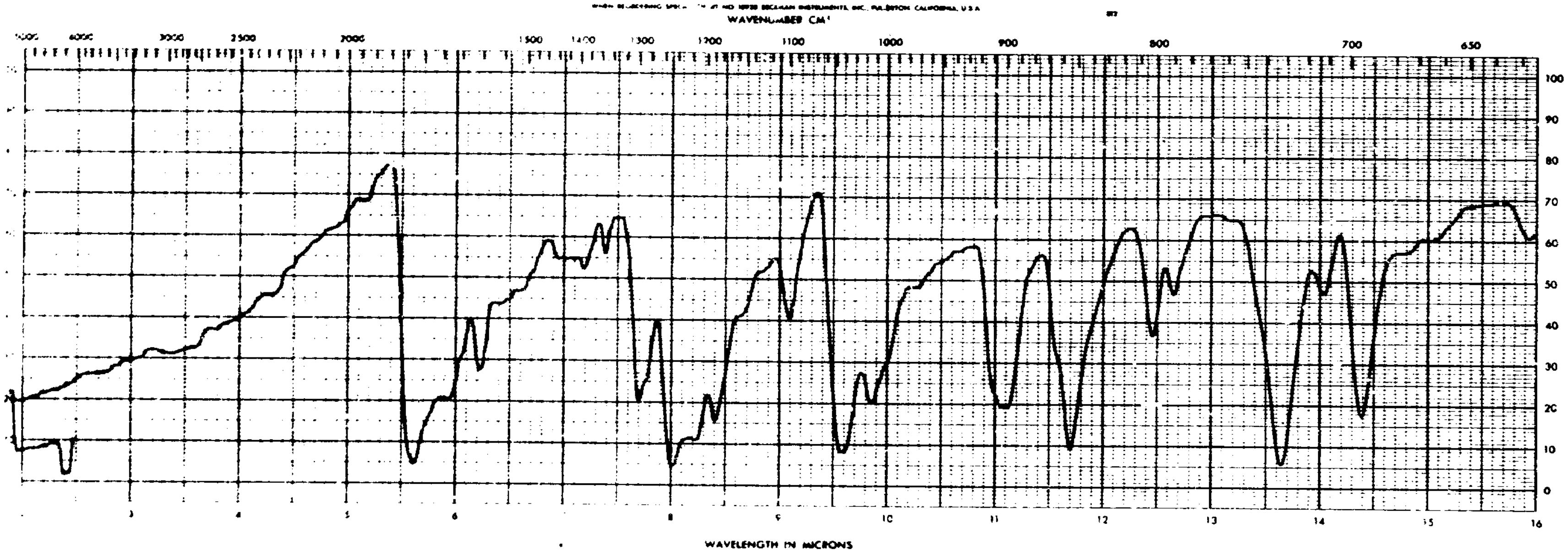
Fig. VIII

SPECTRUM NO. 1
DATE 2-16-69
SAMPLE
SOURCE E. [illegible]
STRUCTURE

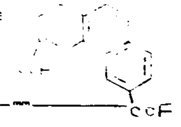
PATH
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS
ANALYST D.F.L.

Beckman
INFRARED
SPECTROPHOTOMETER

Fig IX



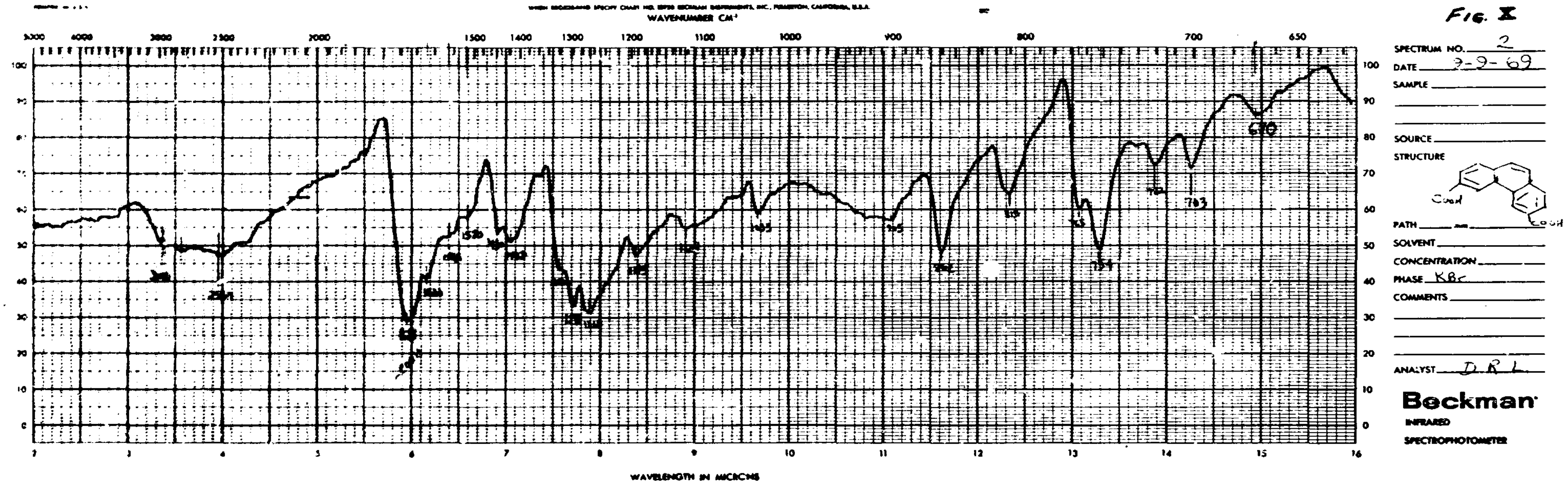
SPECTRUM NO. ______
DATE 3-17-63
SAMPLE ______
SOURCE E Gacis
STRUCTURE



PATH ______ mm ______
SOLVENT ______
CONCENTRATION ______
PHASE Nuj
COMMENTS ______
ANALYST ______

Beckman
INFRARED
SPECTROPHOTOMETER

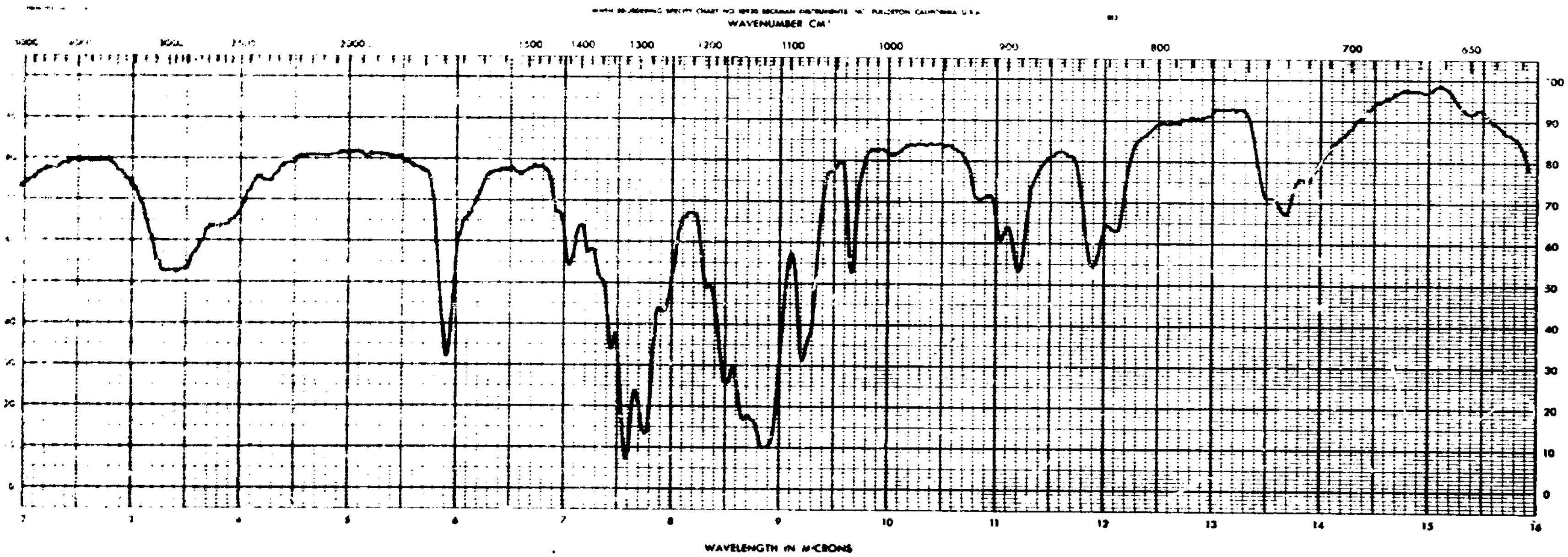
FIG. X



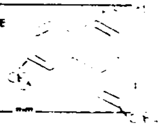
SPECTRUM NO. 2
DATE 3-9-69
SAMPLE
SOURCE
STRUCTURE
PATH
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS
ANALYST D.R.L.

Beckman
INFRARED
SPECTROPHOTOMETER

Fig. XI



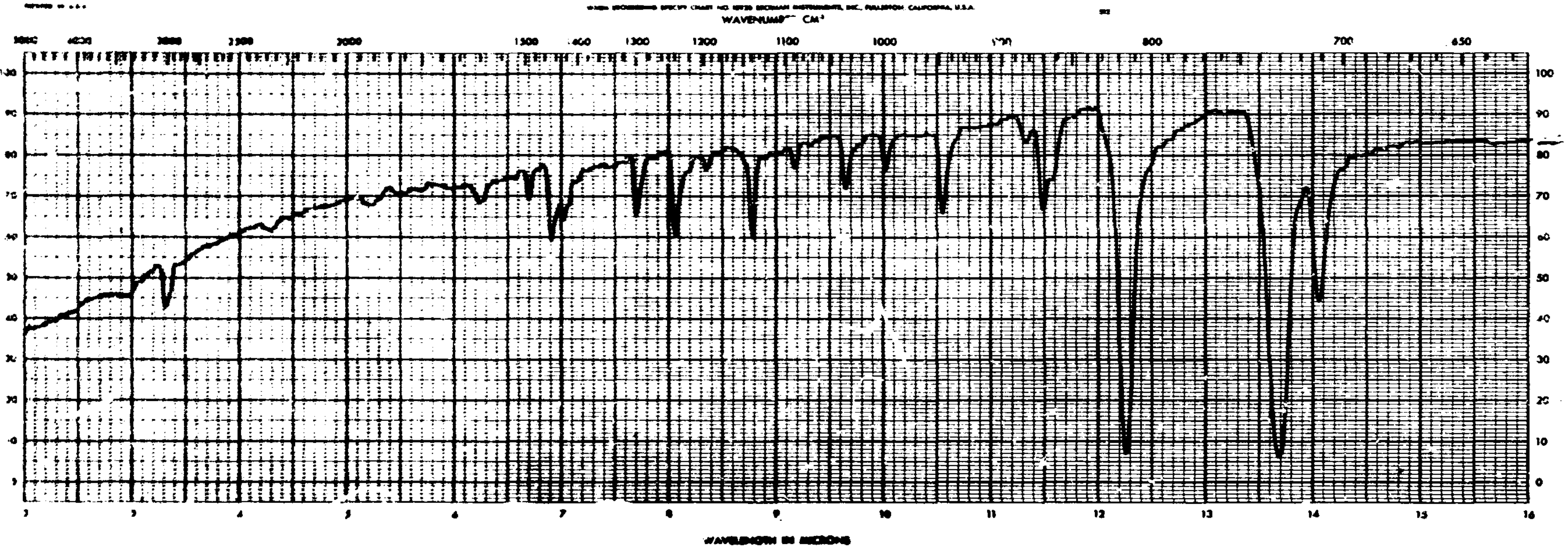
SPECTRUM NO.
DATE [illegible]
SAMPLE
SOURCE
STRUCTURE



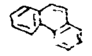
PATH mm
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS
ANALYST D.R.L.

Beckman
INFRARED
SPECTROPHOTOMETER

FIG. XII



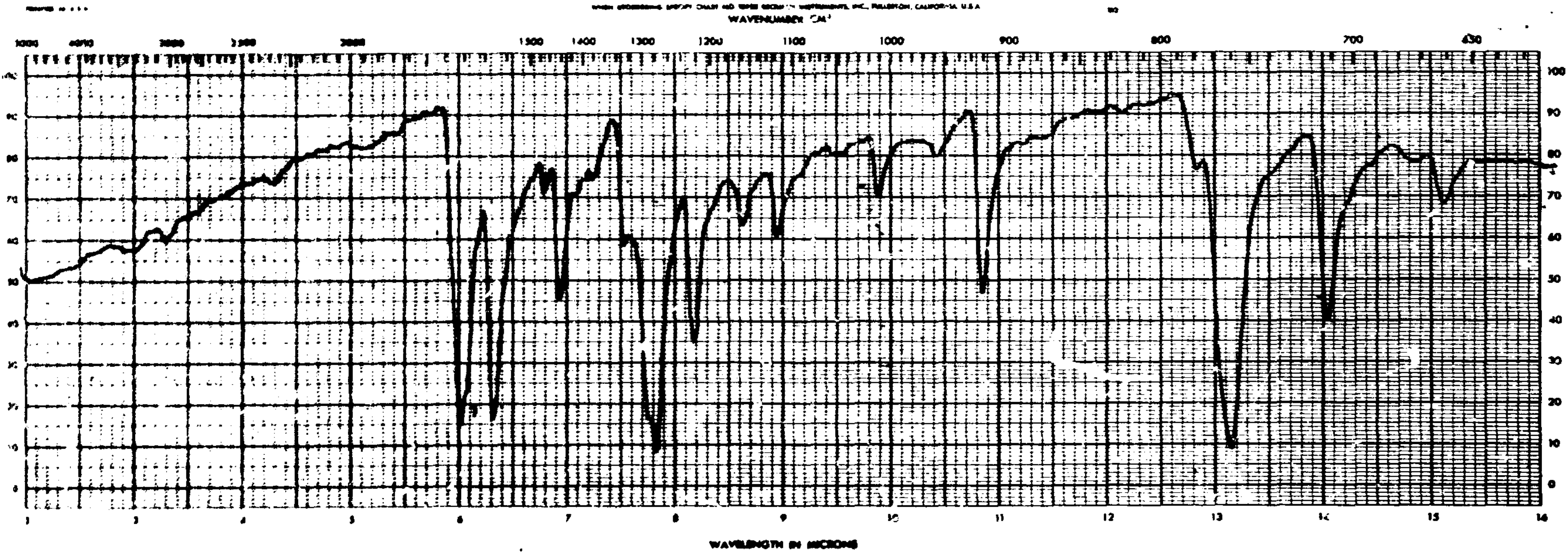
SPECTRUM NO.
DATE 12-8-69
SAMPLE [illegible]
SOURCE
STRUCTURE



PATH mm
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS
ANALYST DLM

Beckman
INFRARED
SPECTROPHOTOMETER

Fig. XIII



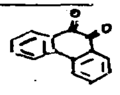
SPECTRUM NO. ______

DATE Phenanth[illegible] ...on

SAMPLE ______

SOURCE ______

STRUCTURE



PATH ____ mm ____

SOLVENT ______

CONCENTRATION ______

PHASE KBr

COMMENTS ______

ANALYST LGF

Beckman
INFRARED
SPECTROPHOTOMETER

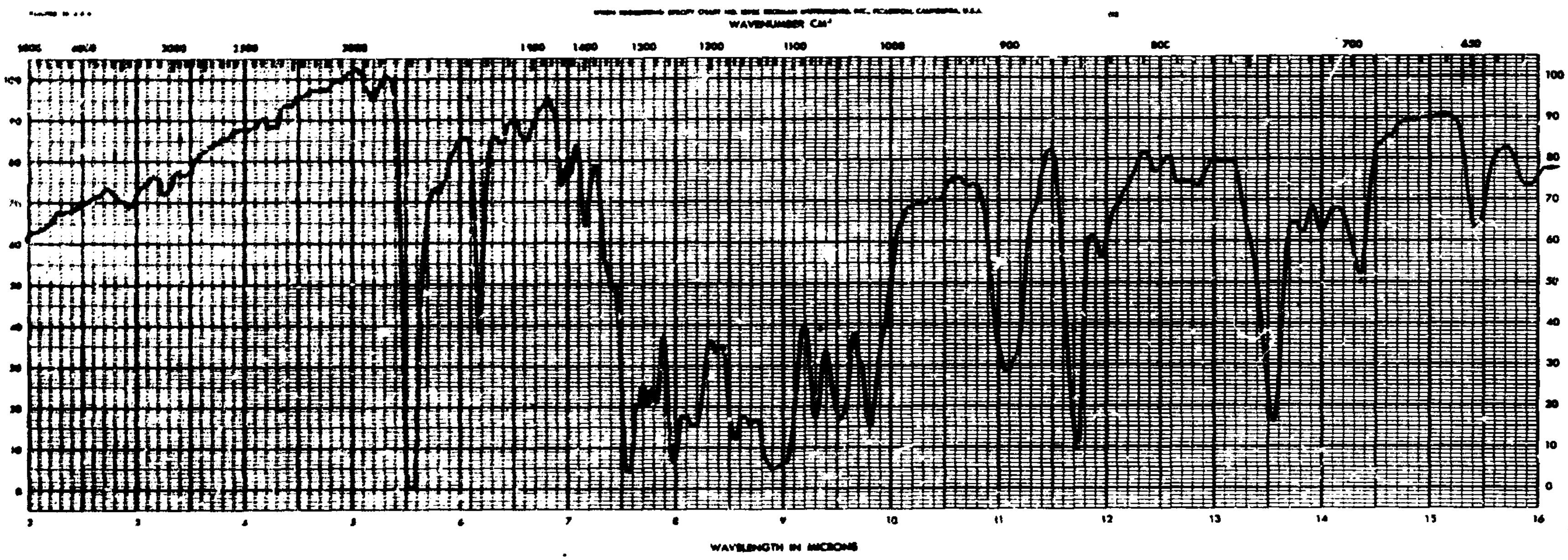


FIG. [illegible]

SPECTRUM NO.

DATE 12/18/69

SAMPLE Crude #30

SOURCE

STRUCTURE

PATH

SOLVENT KBr

CONCENTRATION

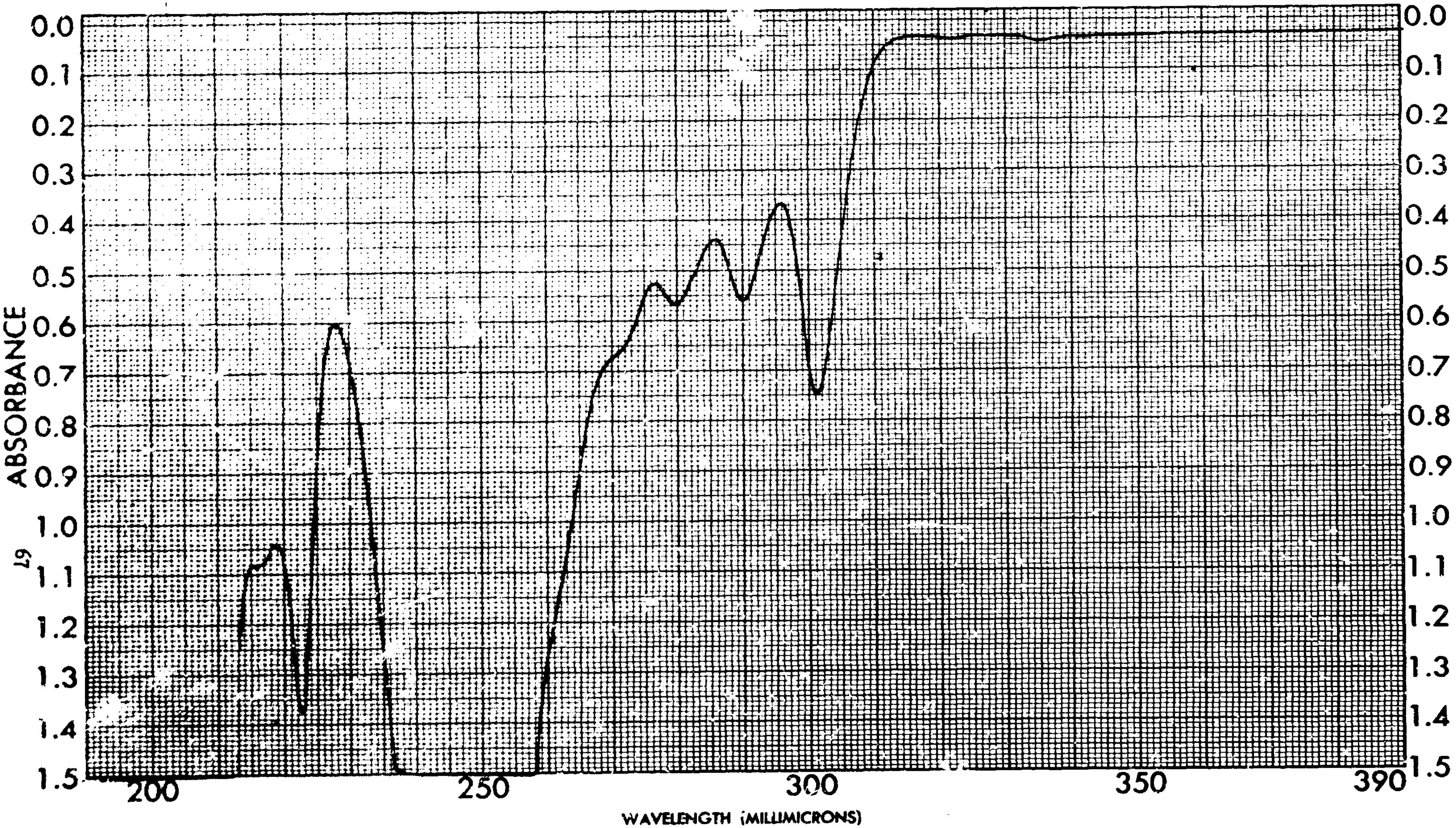
PHASE

COMMENTS

ANALYST D.L.M.

Beckman
INFRARED
SPECTROPHOTOMETER

FIG. XV



SAMPLE 

ORIGIN 5022-28B

SOLVENT 95% Ethanol

CURVE NO. 2

CONC. 0.000592 M

CELL PATH 1 cm

REFERENCE 95% Ethanol

SCAN SPEED Slow

SLIT

OPERATOR D R L

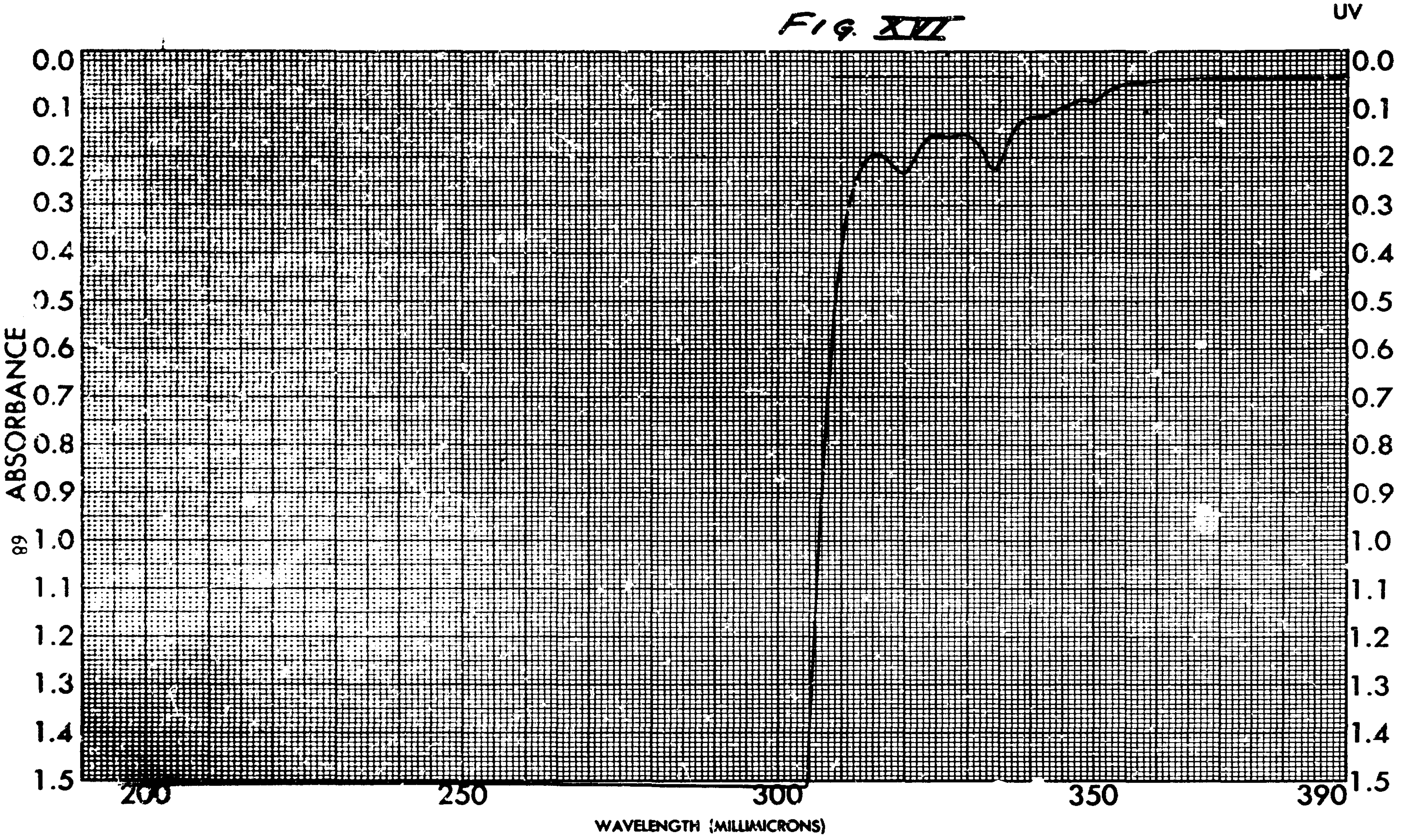
DATE 11-17-69

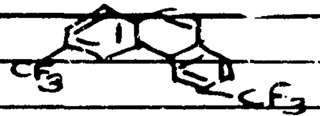
REMARKS

PART NO 202-1511

PERKIN-ELMER

FIG. XVI



SAMPLE


ORIGIN 5022-20B
SOLVENT 95% Ethanol

CURVE NO. 3
CONC. 0.000652 M
CELL PATH 1 cm
REFERENCE 95% Ethanol

SCAN SPEED Slow
SLIT
REMARKS

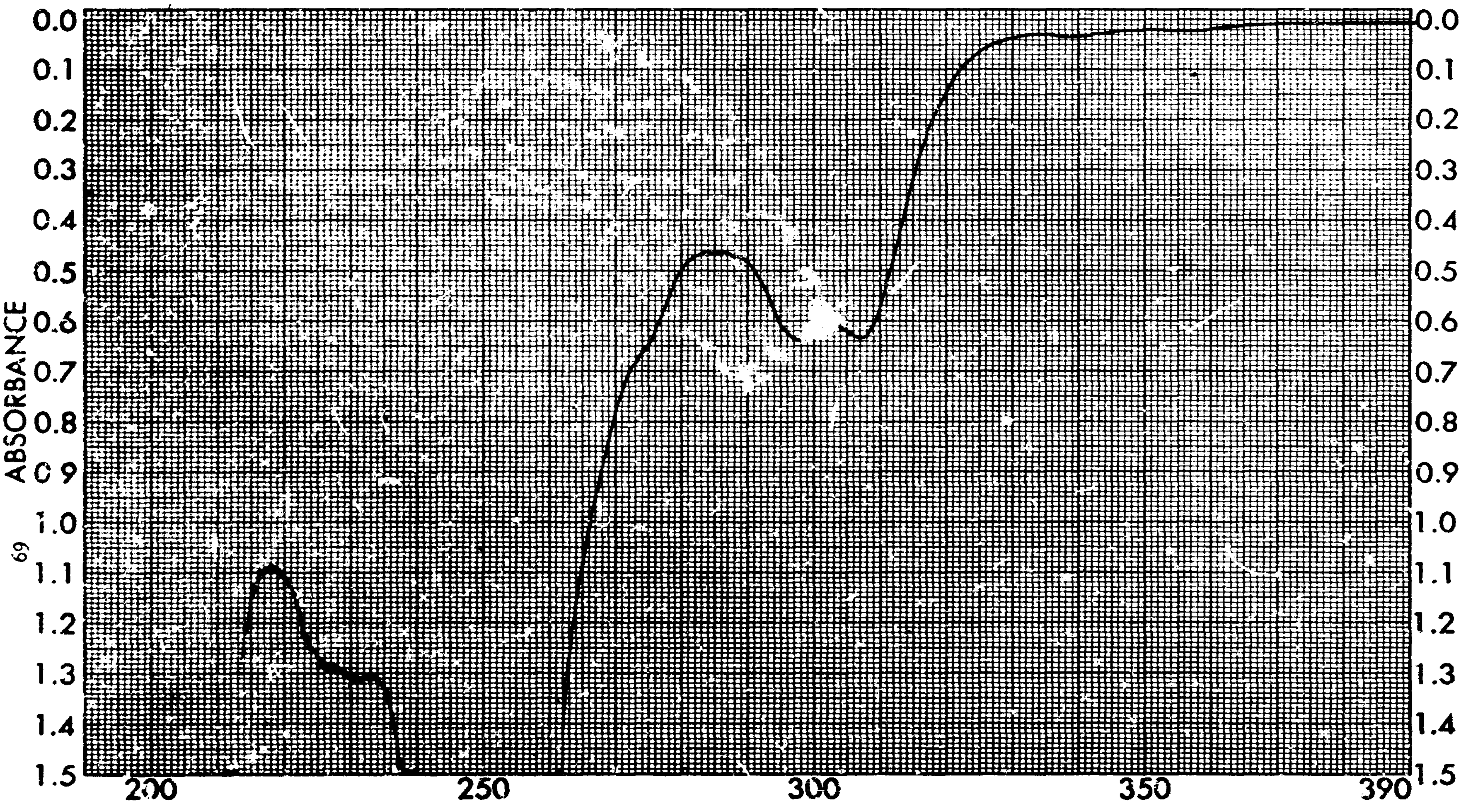
OPERATOR D.R.L.
DATE 11-17-69

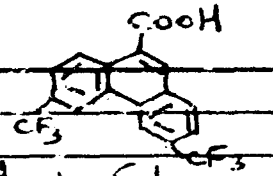
PART NO. 202-1511

PERKIN-ELMER

FIGURE XVIII

UV

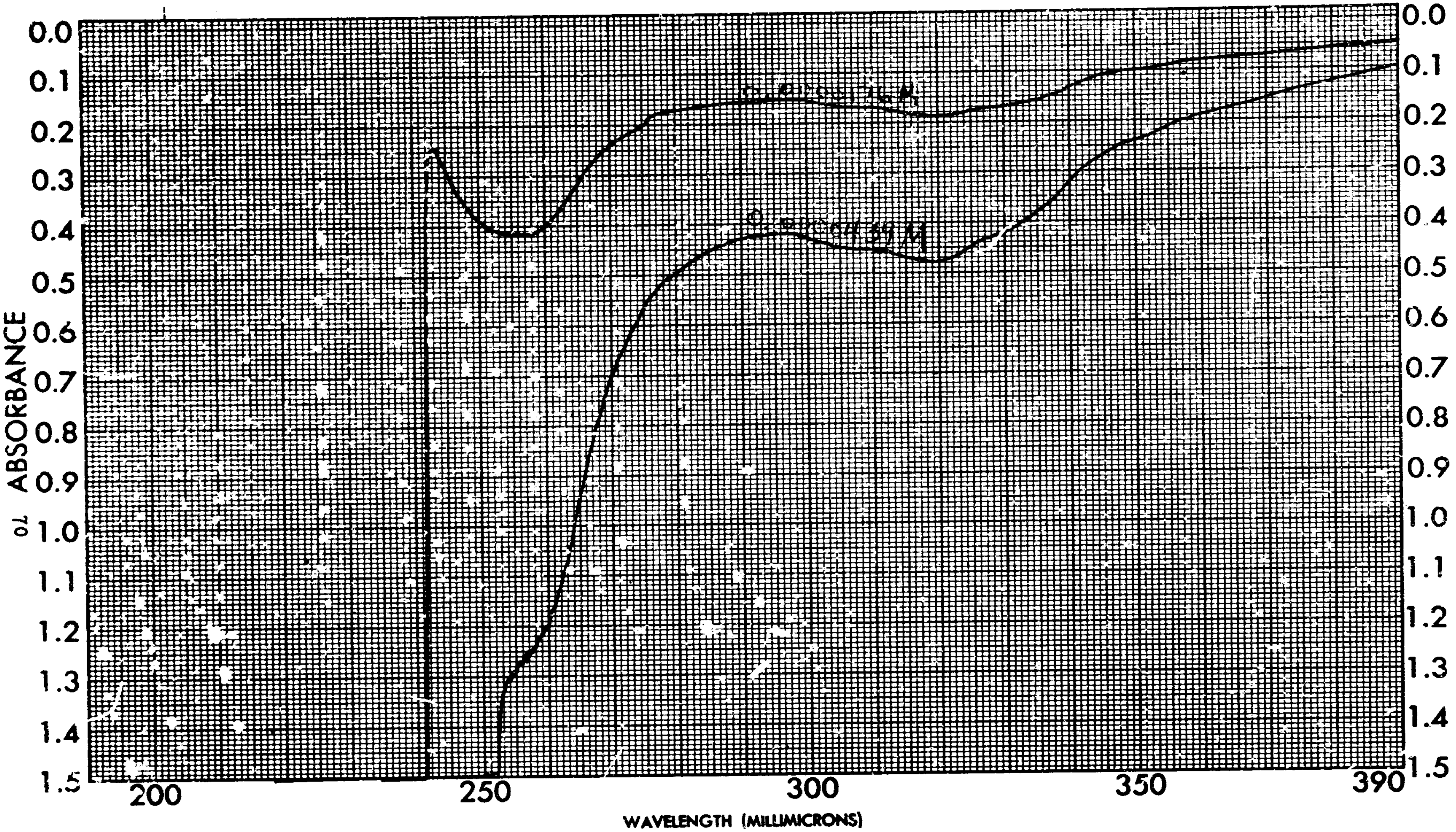


SAMPLE 	CURVE NO. 4	SCAN SPEED Slow	OPERATOR D R L
	CONC. 0.0000575 M	SLIT	DATE 11-17-69
ORIGIN Aldrich Chemical	CELL PATH 1 cm	REMARKS	
SOLVENT 95% Ethanol	REFERENCE 95 % C_2H_5OH		

PART NO. 202-1511

PERKIN-ELMER

FIG. XVIII



SAMPLE Crude 23

ORIGIN

SOLVENT CHCl3

CURVE NO. 5022-31A

CONC. 0.0000176 + 0.0000439

CELL PATH 1 cm

REFERENCE CHCl3

SCAN SPEED Slow

SLIT

OPERATOR D. R. L.

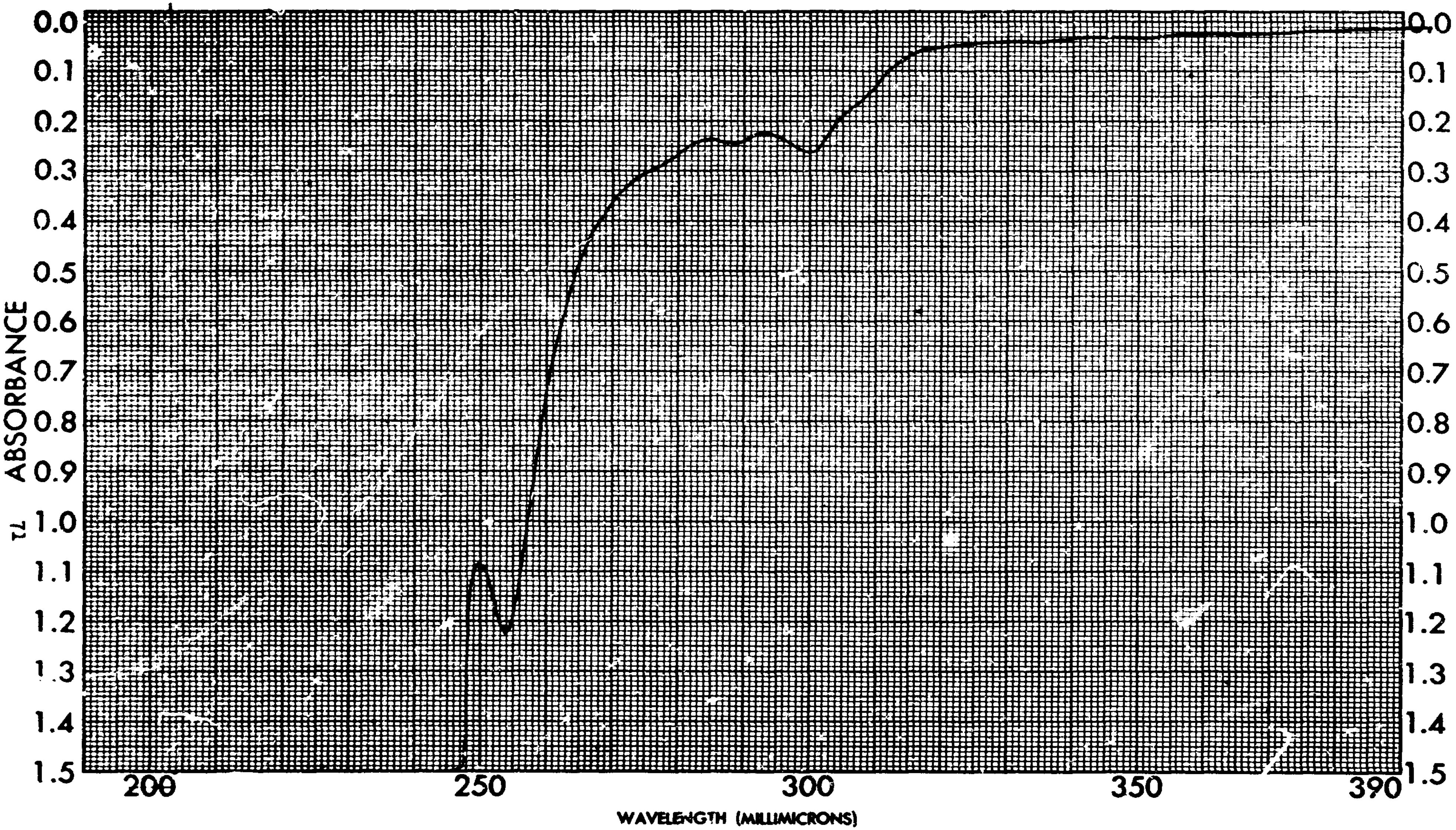
DATE 11-25-69

REMARKS

PERKIN-ELMER

PART NO. 202-1511

Fig. XIX



SAMPLE 5022-19B
ORIGIN
SOLVENT CHCl3

CURVE NO. 5022-28A
CONC. 0.0000286 M
CELL PATH 1 cm
REFERENCE CHCl3

SCAN SPEED Slow
SLIT
REMARKS

OPERATOR D.R.L.
DATE 11-25-64

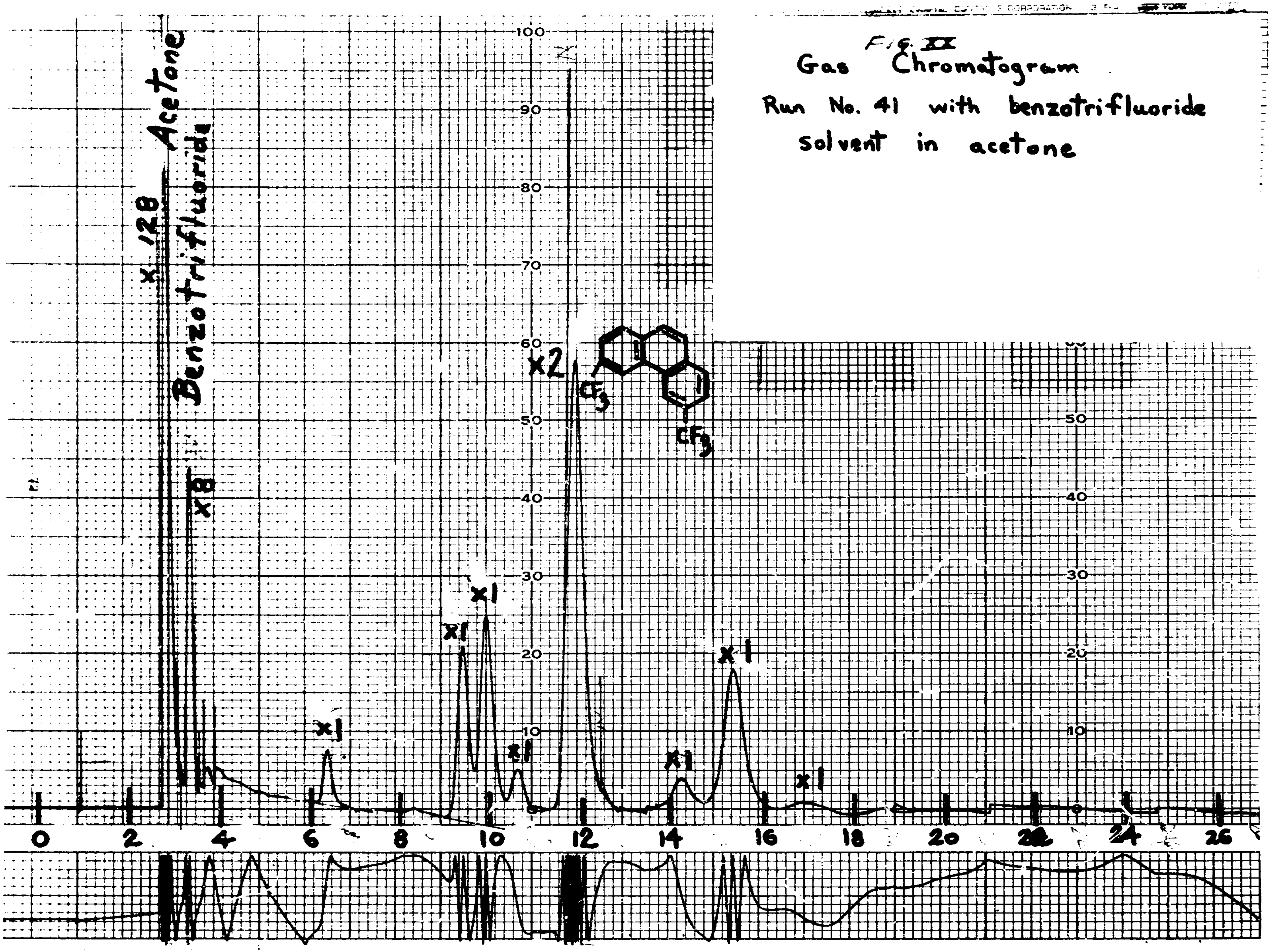
PART NO. 202-1511

PERKIN-ELMER

Fig. XX

Gas Chromatogram

Run No. 41 with benzotrifluoride
solvent in acetone



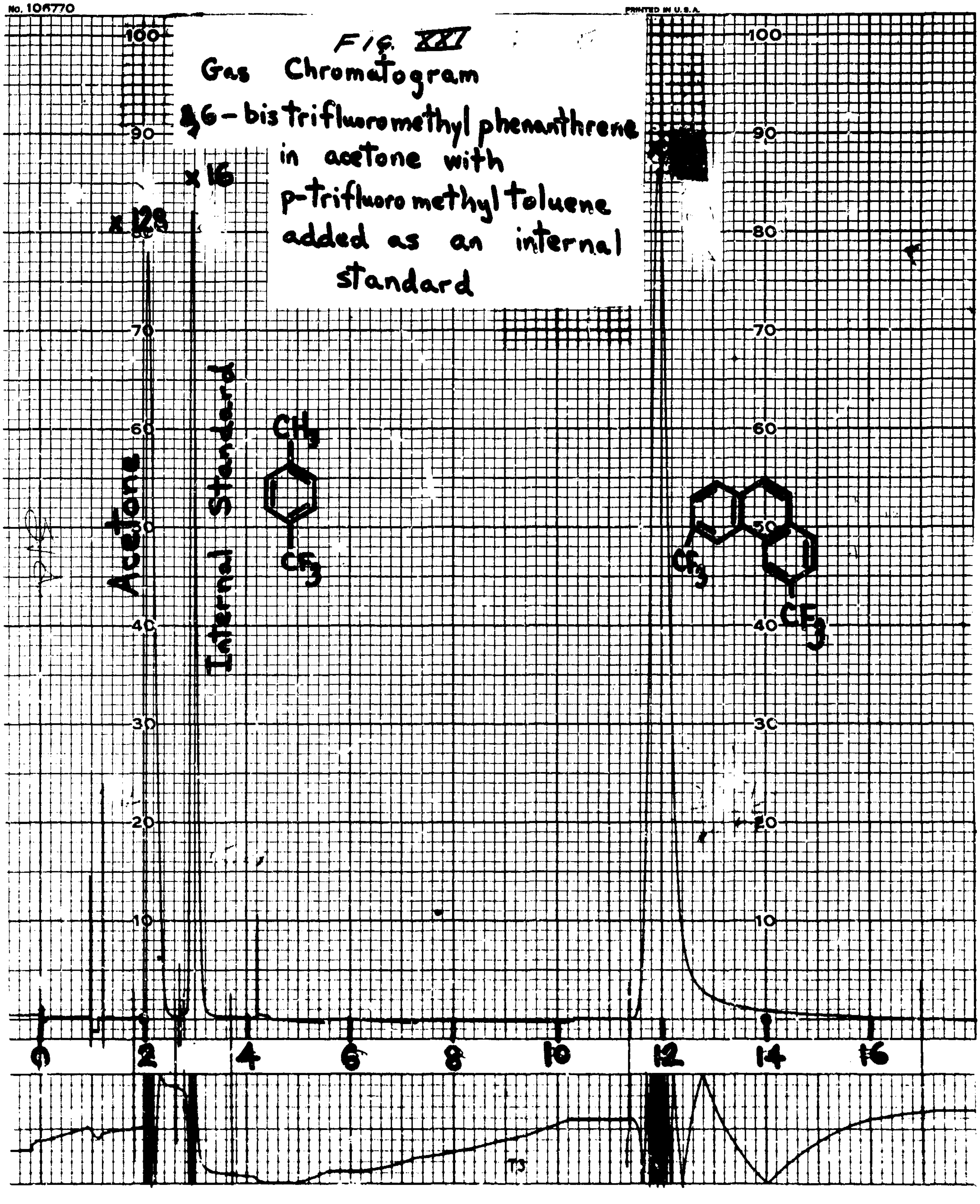


FIG. XXI

Gas Chromatogram 3,6-bistrifluoromethyl phenanthrene in acetone with p-trifluoromethyl toluene added as an internal standard

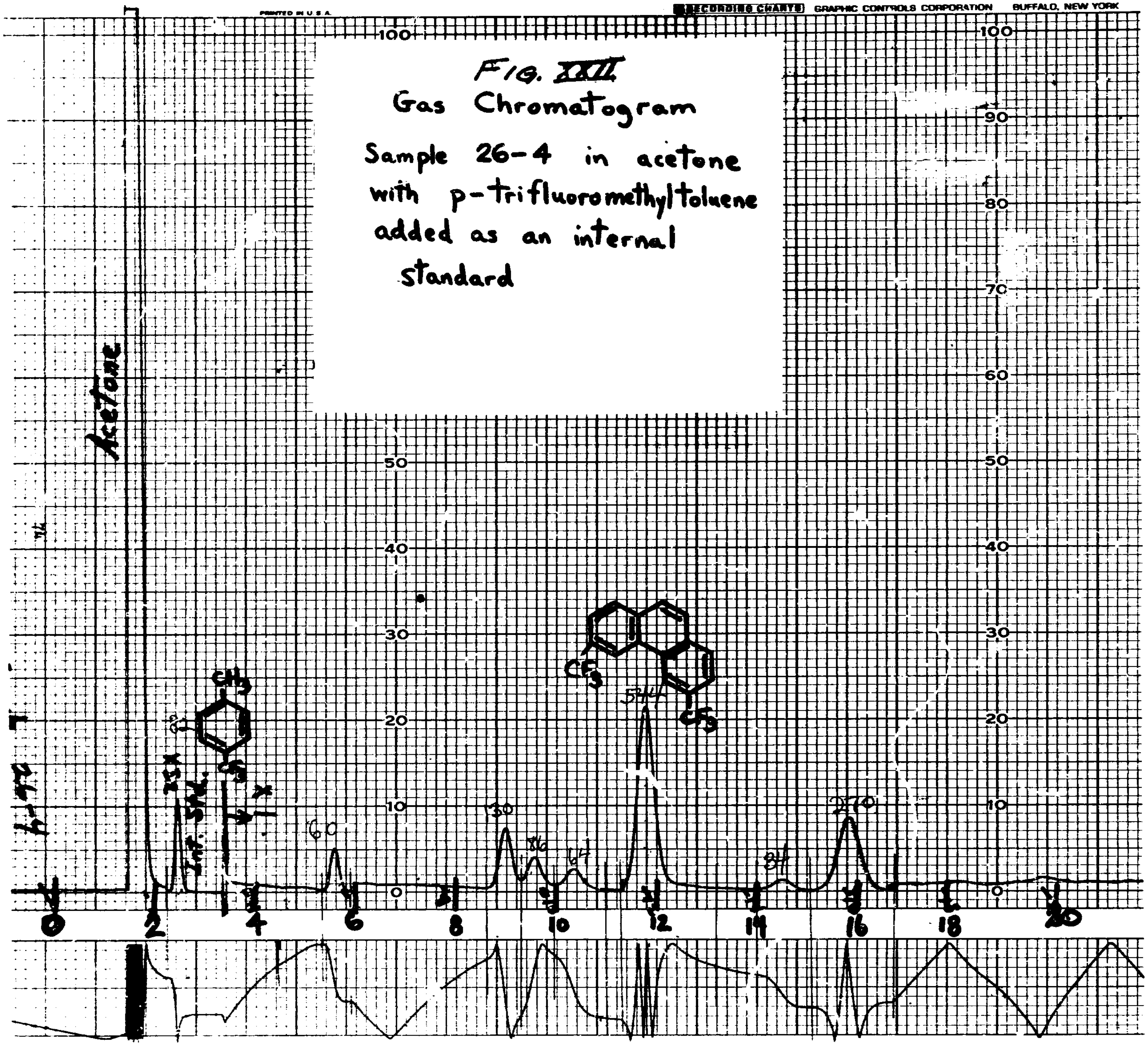
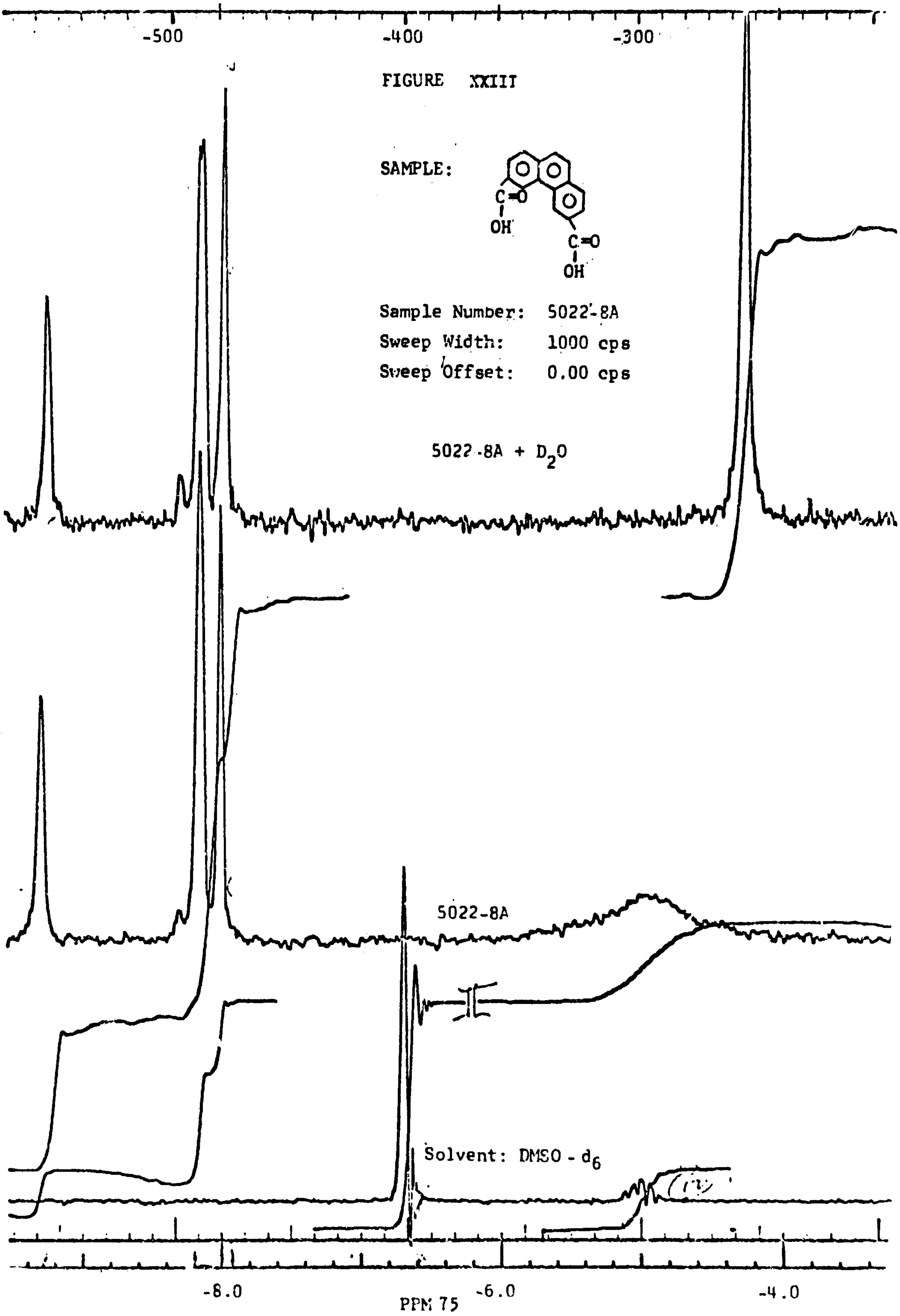


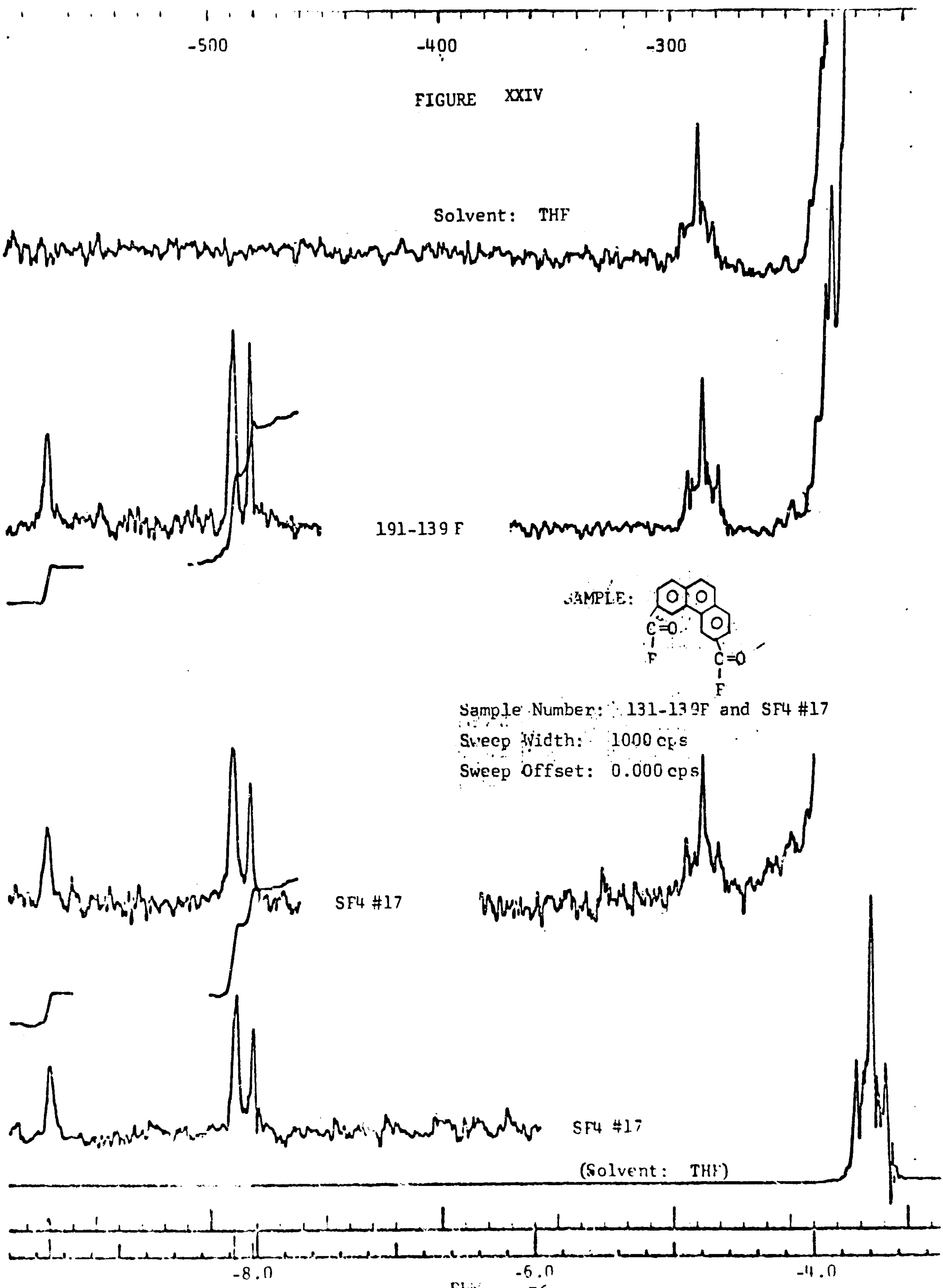
FIG. XXII
Gas Chromatogram
Sample 26-4 in acetone with p-trifluoromethyltoluene added as an internal standard

FIGURE XXIII



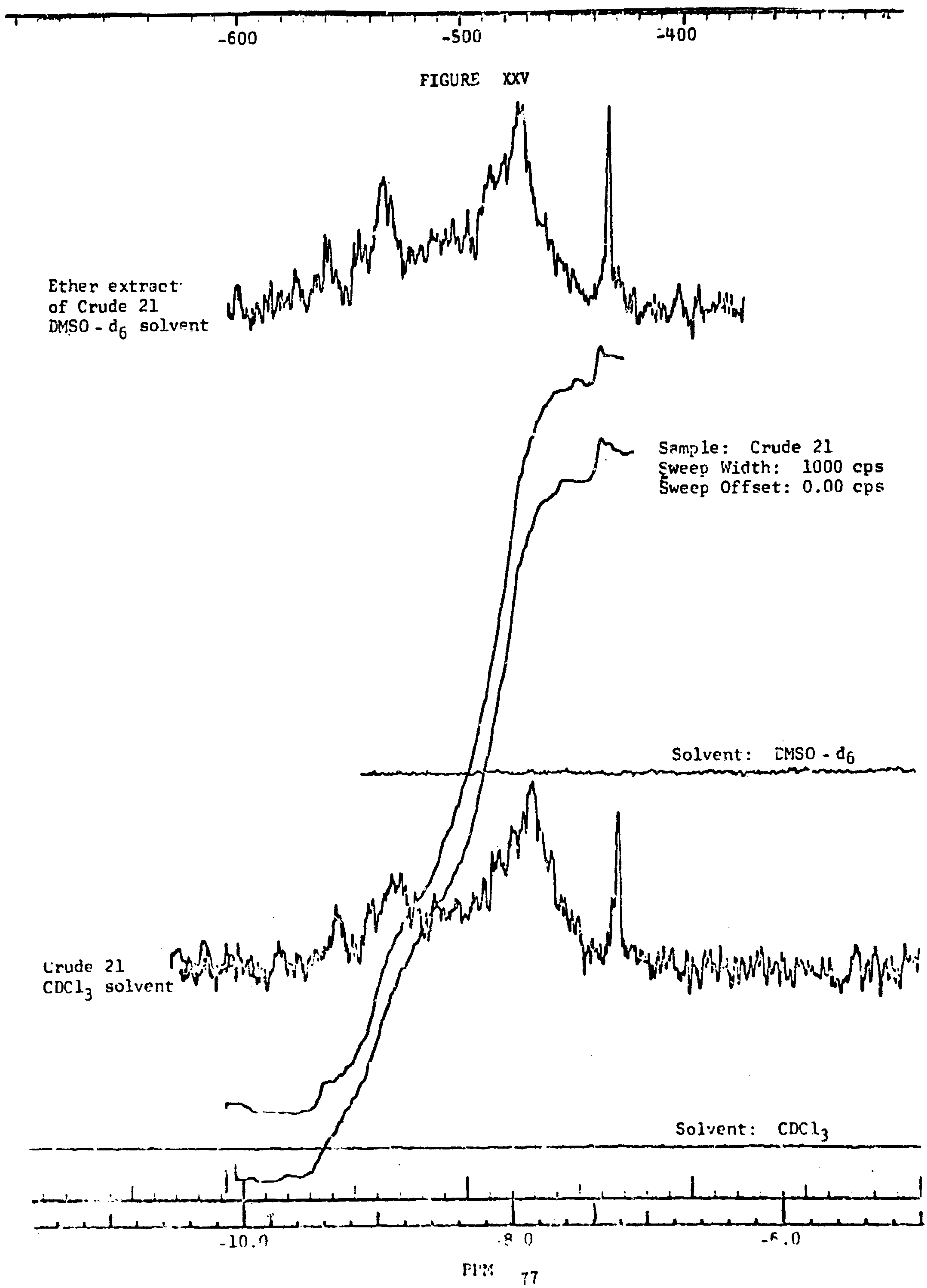
Sample Number: 5022-8A
Sweep Width: 1000 cps
Sweep Offset: 0.00 cps

FIGURE XXIV



Sample Number: 131-139F and SF4 #17
Sweep Width: 1000 cps
Sweep Offset: 0.000 cps

FIGURE XXV



Sample: Crude 21
Sweep Width: 1000 cps
Sweep Offset: 0.00 cps

FIGURE XXVI

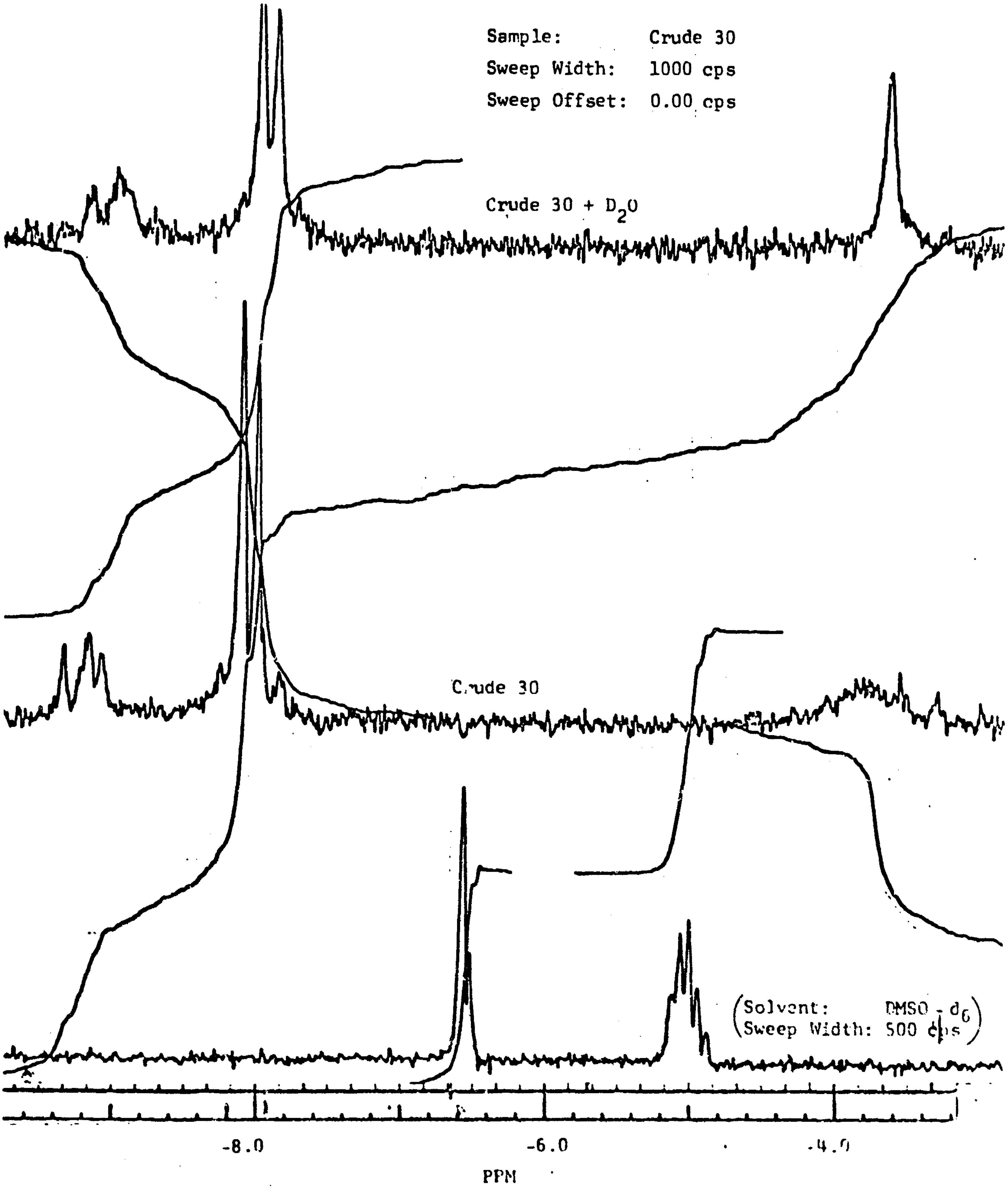
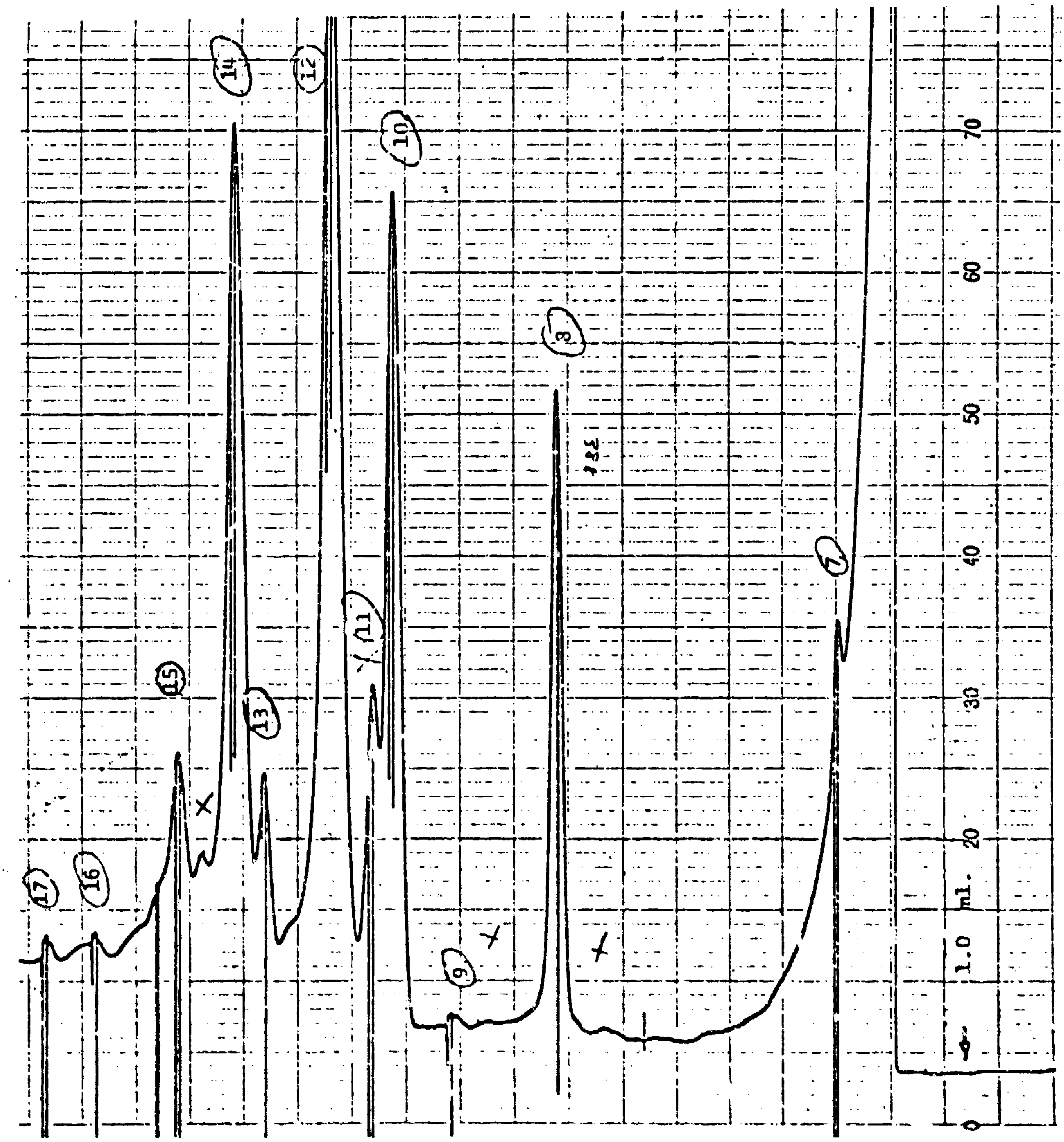

Sample: Crude 30
Sweep Width: 1000 cps
Sweep Offset: 0.00 cps
Crude 30 + D_2O
Crude 30
(Solvent: DMSO - d_6
Sweep Width: 500 cps)
-8.0
-6.0
-4.0
PPM

FIGURE XXVII

Sample: Crude 26

Column: 5% SE-30 on Chromosorb W

Program: 100°C-225°C @ 4°/min.



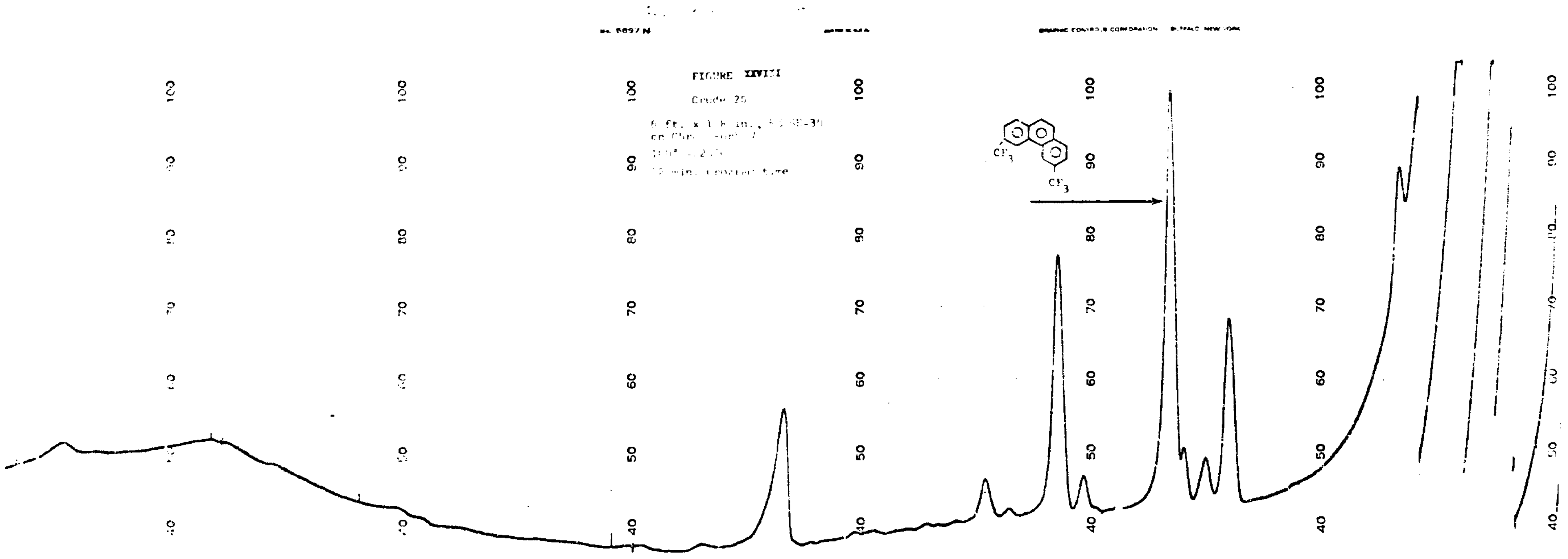


FIGURE XXVIII

Crude 25

6 ft. x 1/8 in., 5% SE-30
on Chrom. [illegible]
[illegible] - 2[illegible]
[illegible] min. retention time

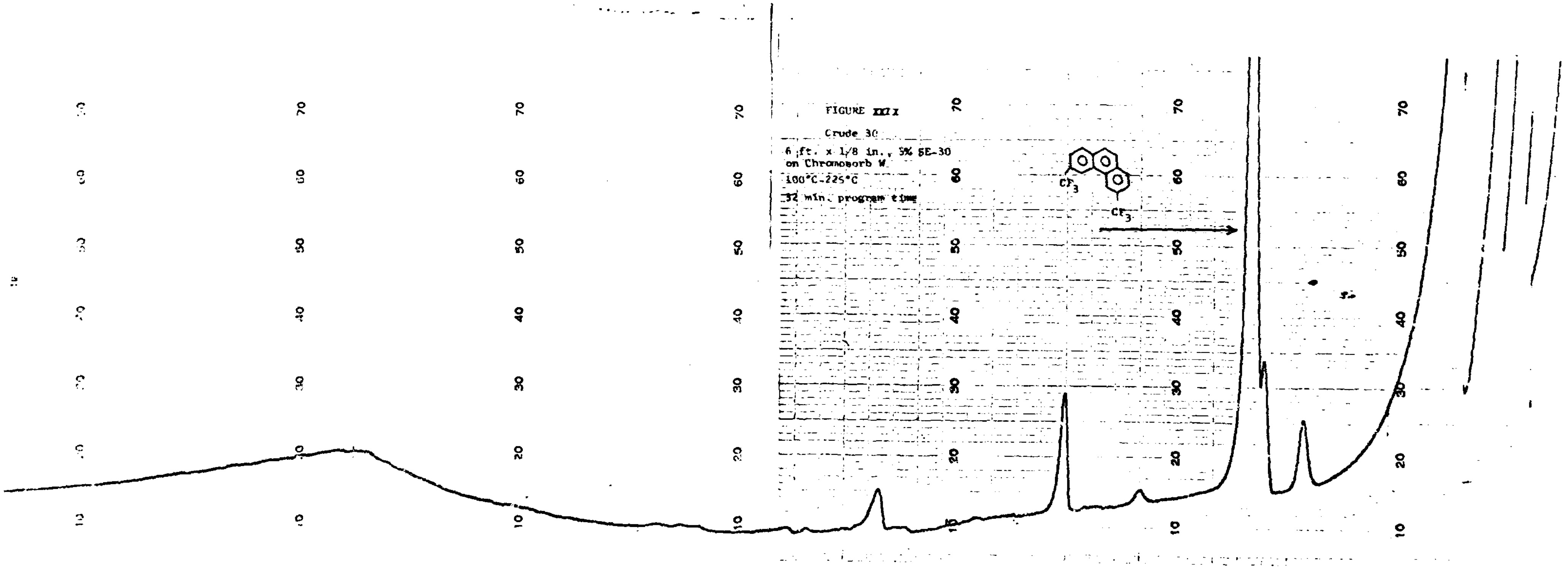


FIGURE XXIX

Crude 30

6 ft. x 1/8 in., 5% SE-30
on Chromosorb W

100°C-225°C

32 min. program time

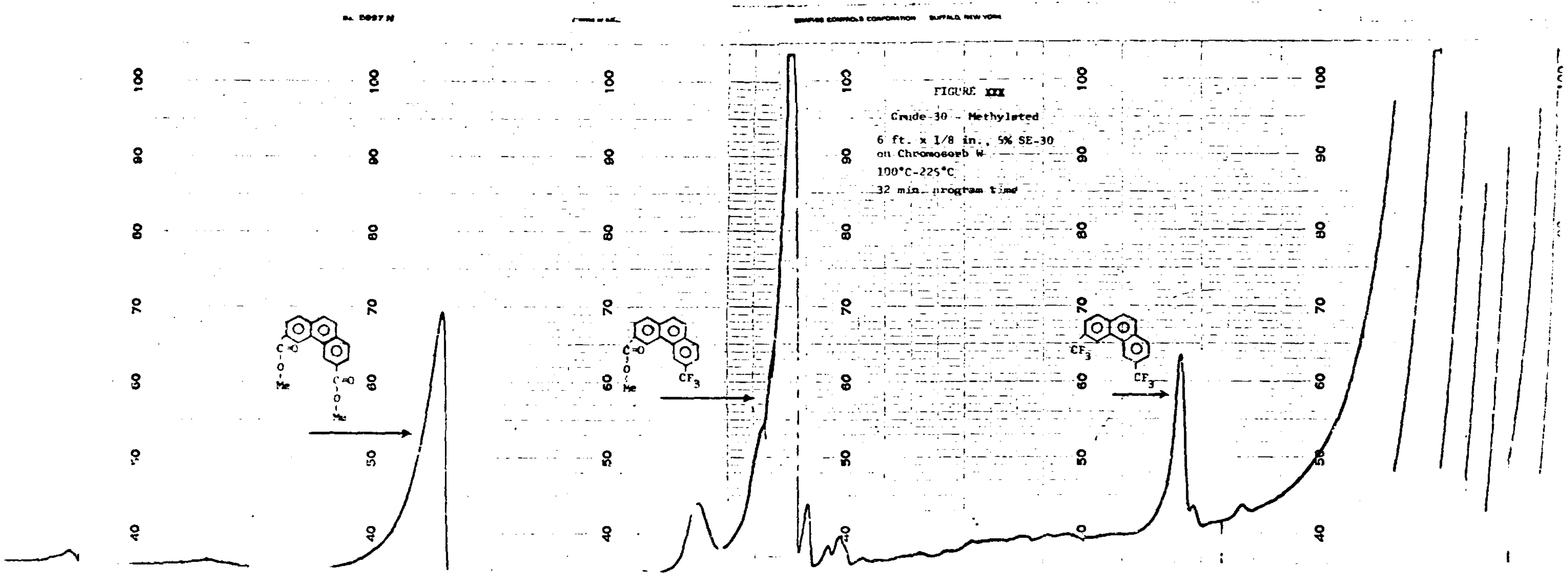


FIGURE XXX

Crude-30 - Methylated

6 ft. x 1/8 in., 5% SE-30
on Chromosorb W
100°C-225°C
32 min. program time

Figure XXXI

TLC Analysis
3,6-Trifluoromethyl Phenanthrene
and Crude Reaction Products #26, 30, 31, 35, 36
Cyclohexane - CCl_4 Solvent

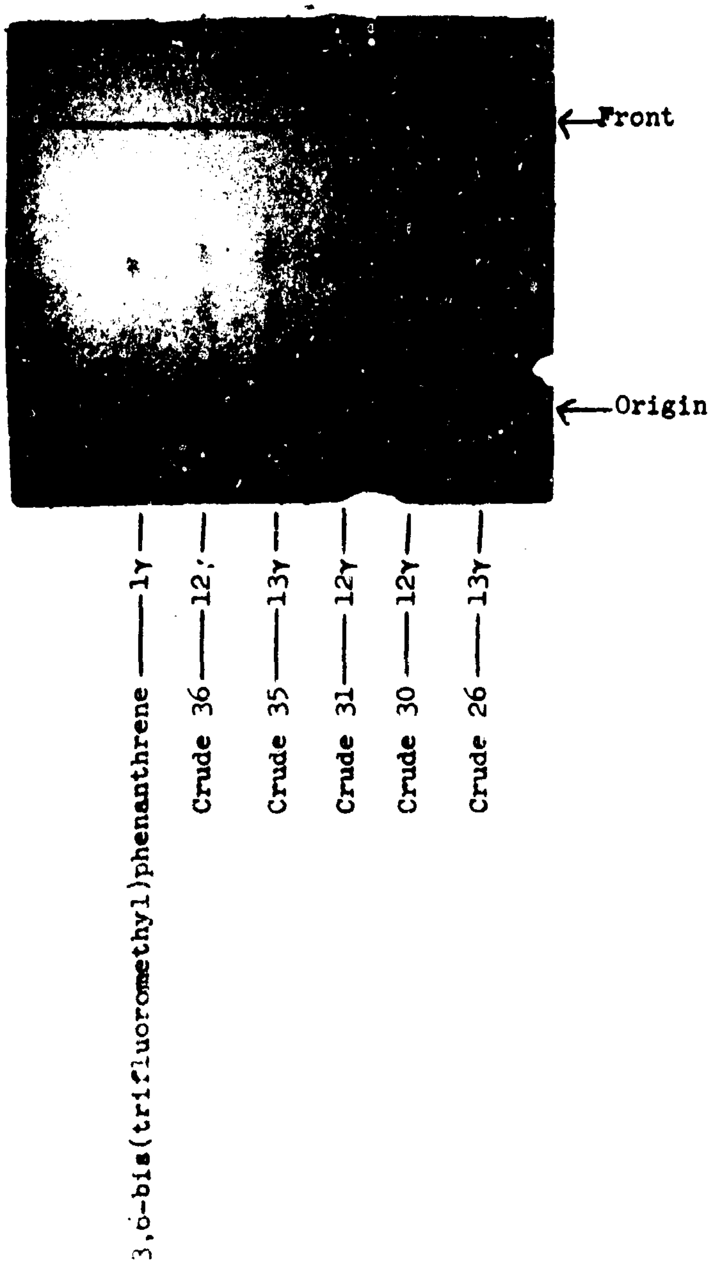


Figure XXXII

TLC Analysis
3,6-bis-Trifluoromethyl Phenanthrene
and 3,6-bis-Carbomethoxy Phenanthrene
and Methoxylated Reaction Products #26, 30, 31
Benzene-$CHCl_3$ Solvent
3:1

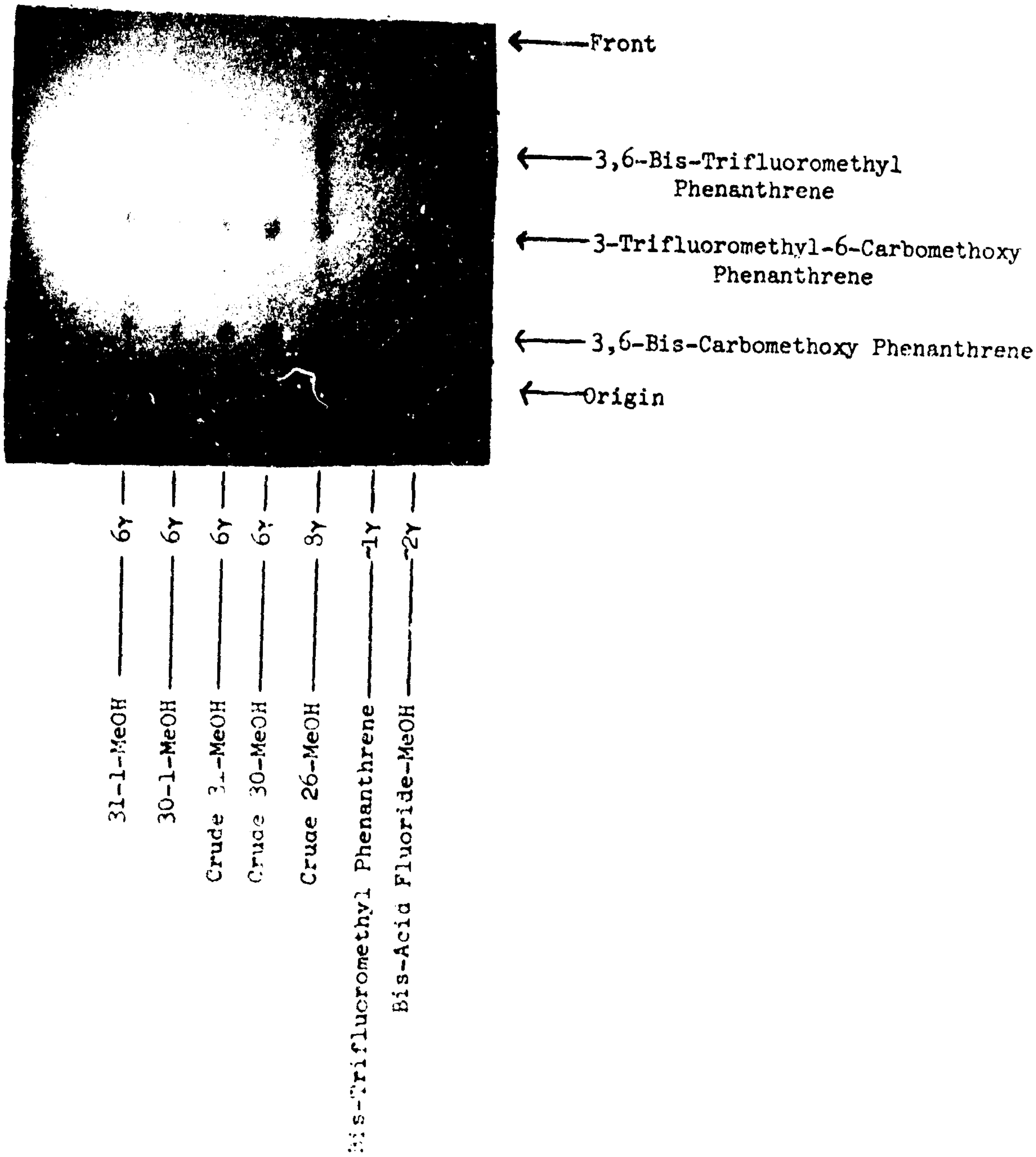
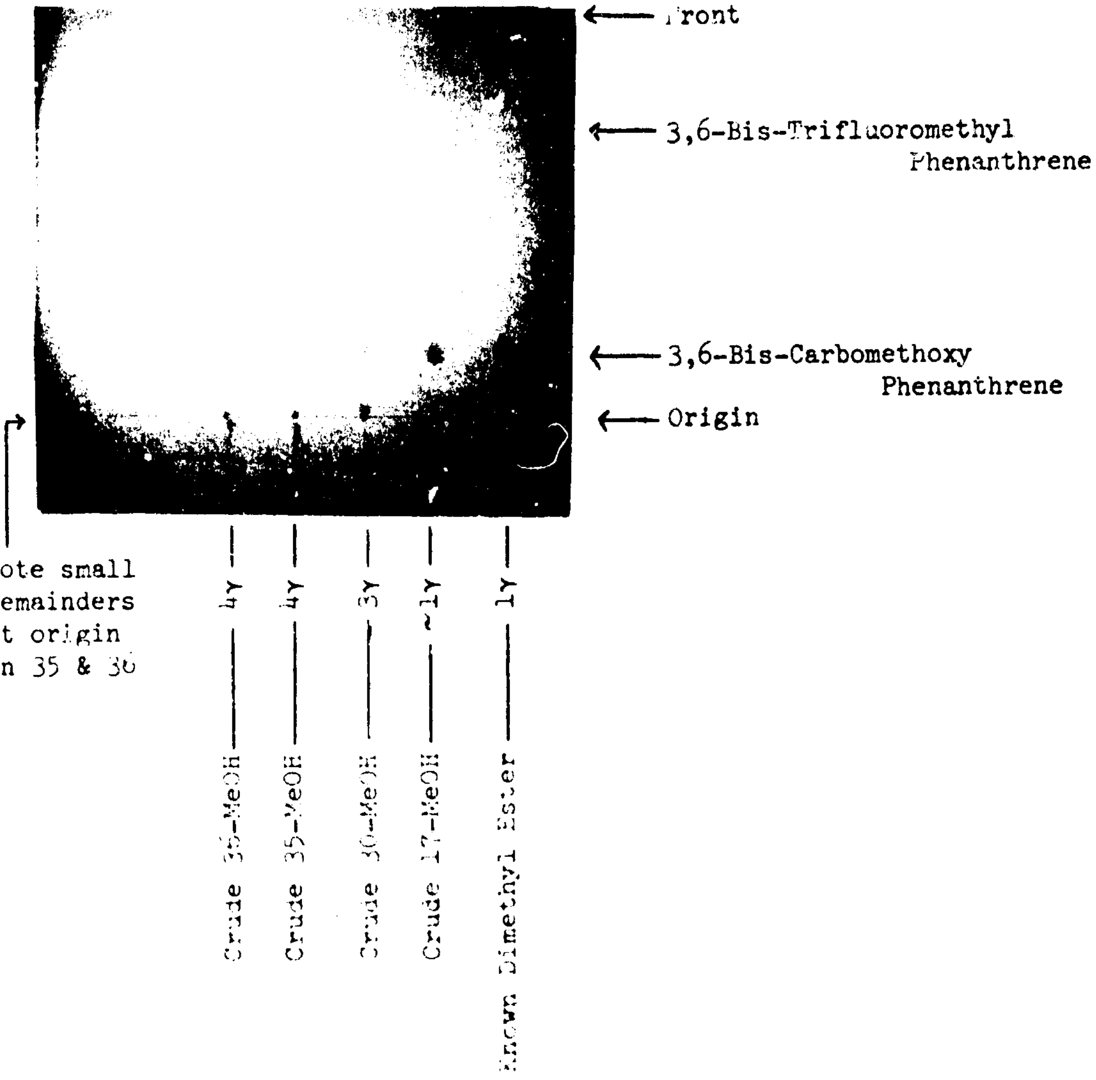


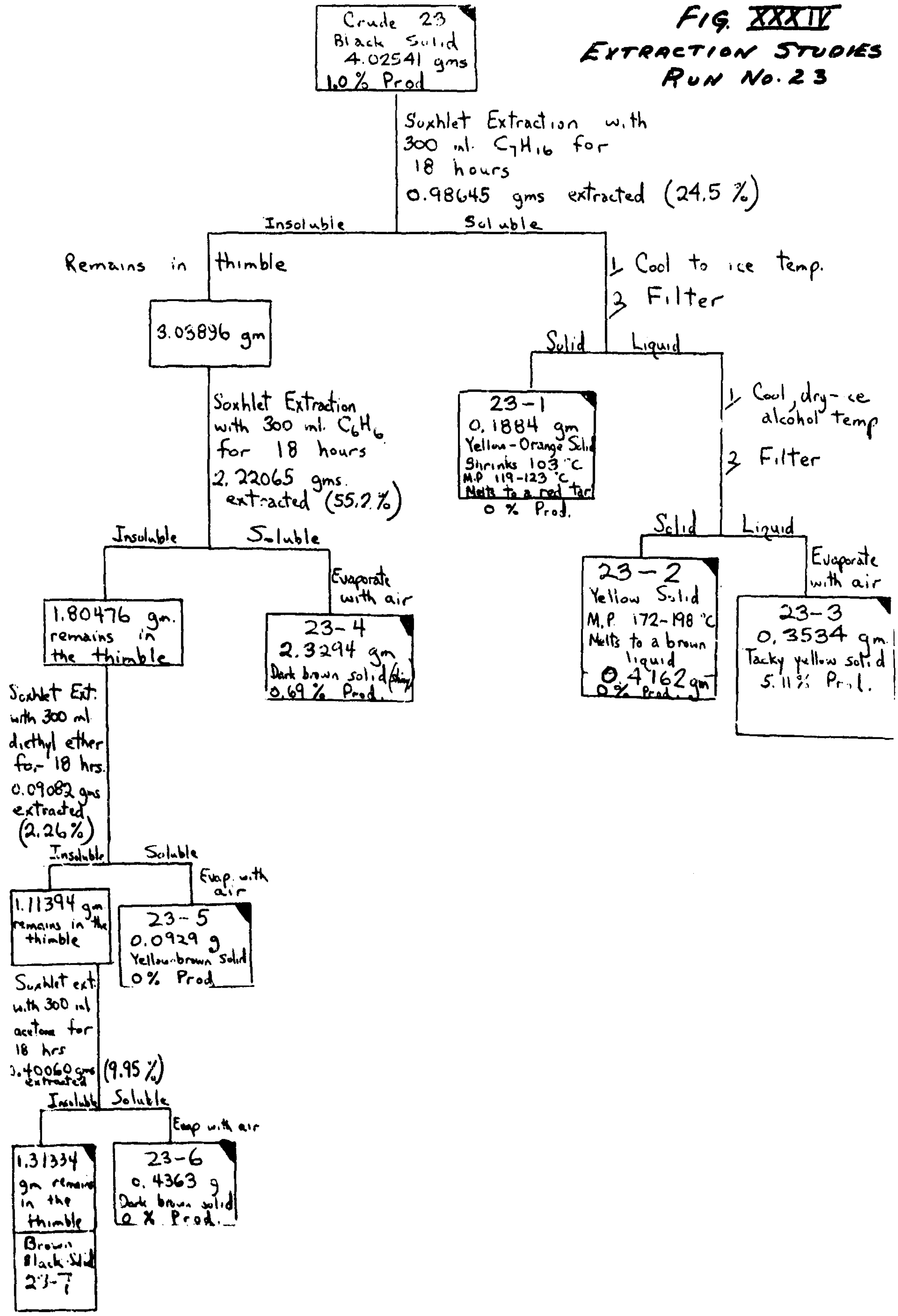
Figure XXXIII

TLC Analysis
Methoxylated Reaction Products #17, 30, 35, 36
Benzene-$CHCl_3$ Solvent
2:1



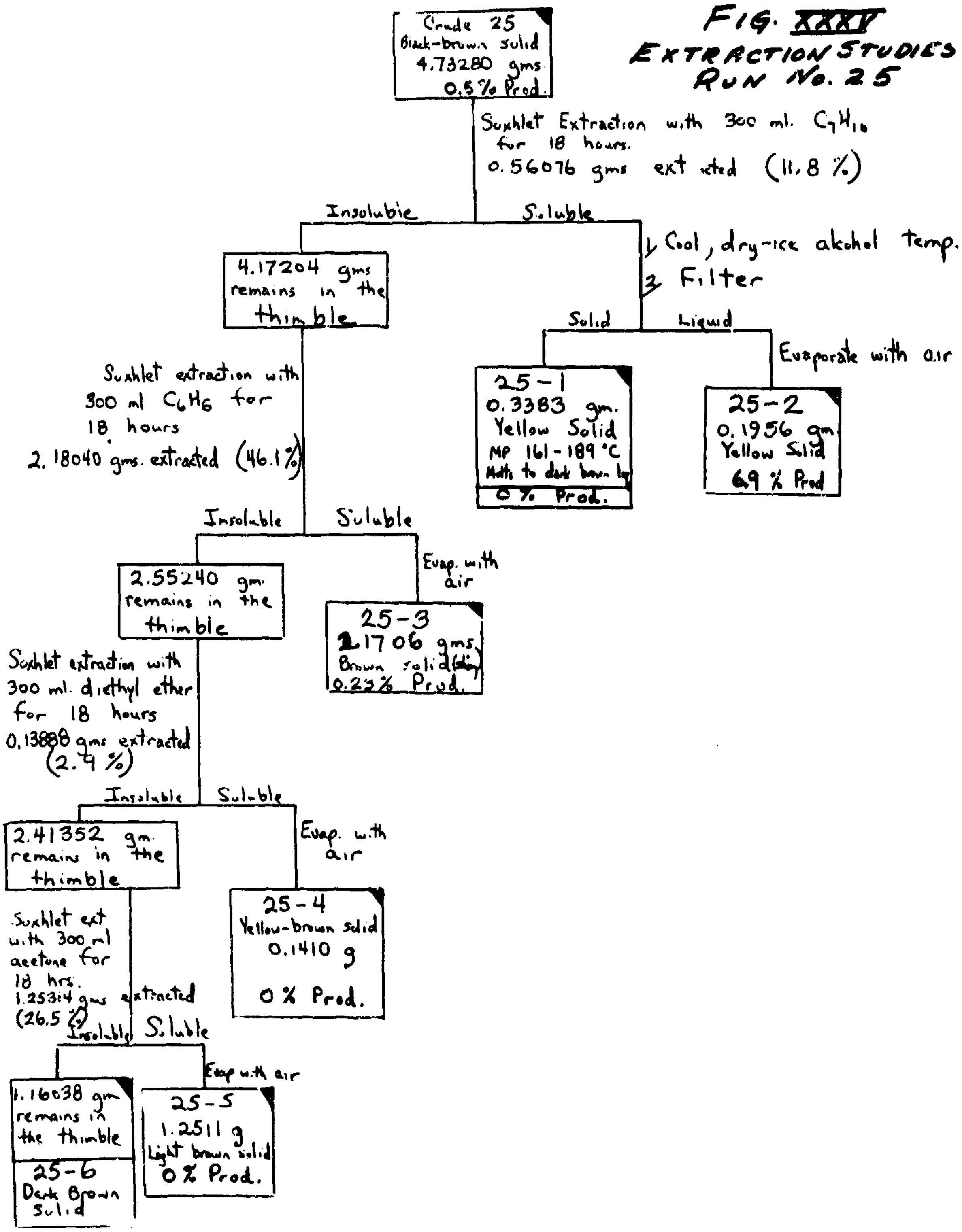
Note small
Remainders
at origin
in 35 & 36

FIG. XXXIV
EXTRACTION STUDIES
RUN NO. 23



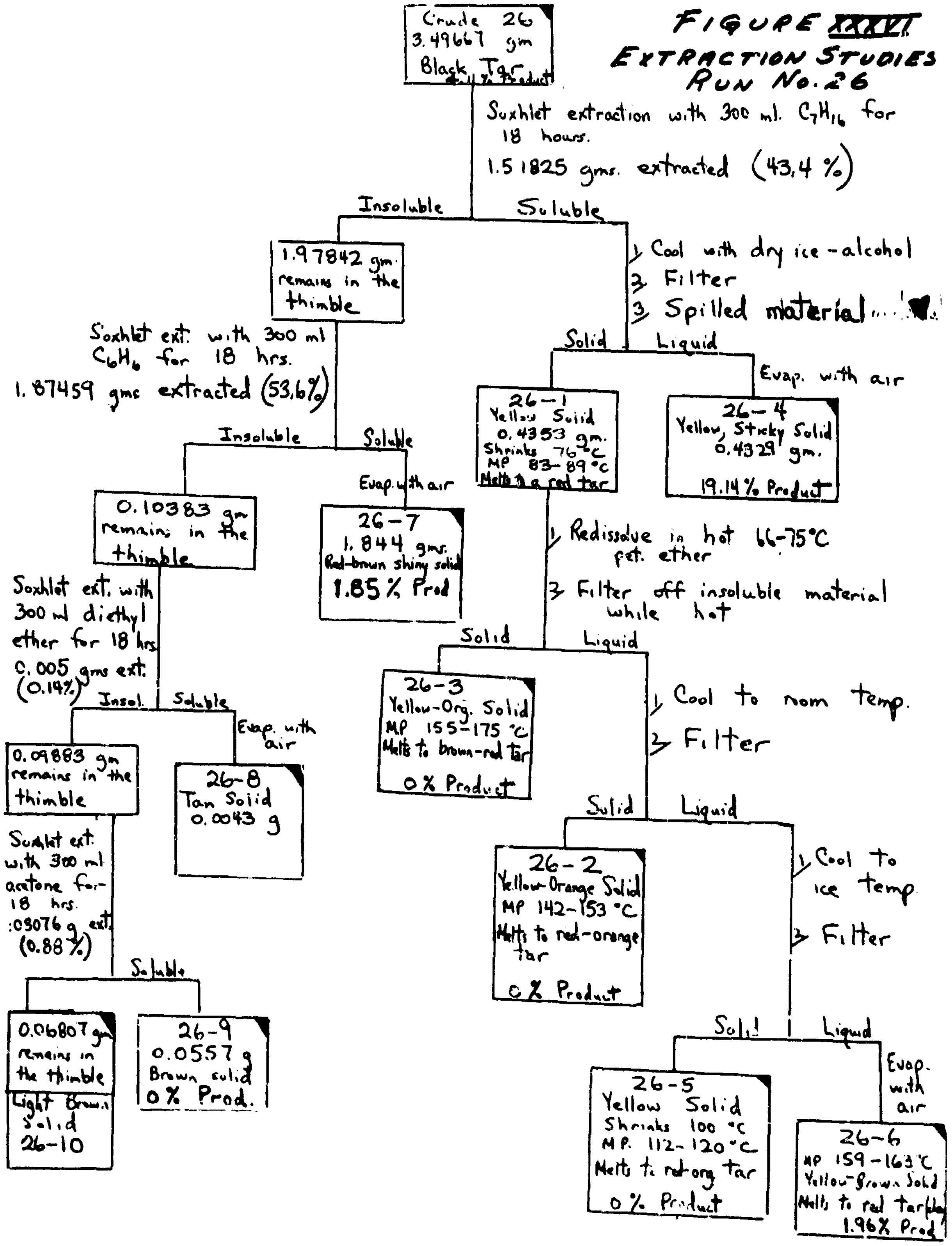
Note: The percent product stated on each sample fraction refers to the percentage of 3,6-bis(trifluoromethyl) phenanthrene found in each individual fraction.

FIG. XXXV
EXTRACTION STUDIES
RUN No. 25



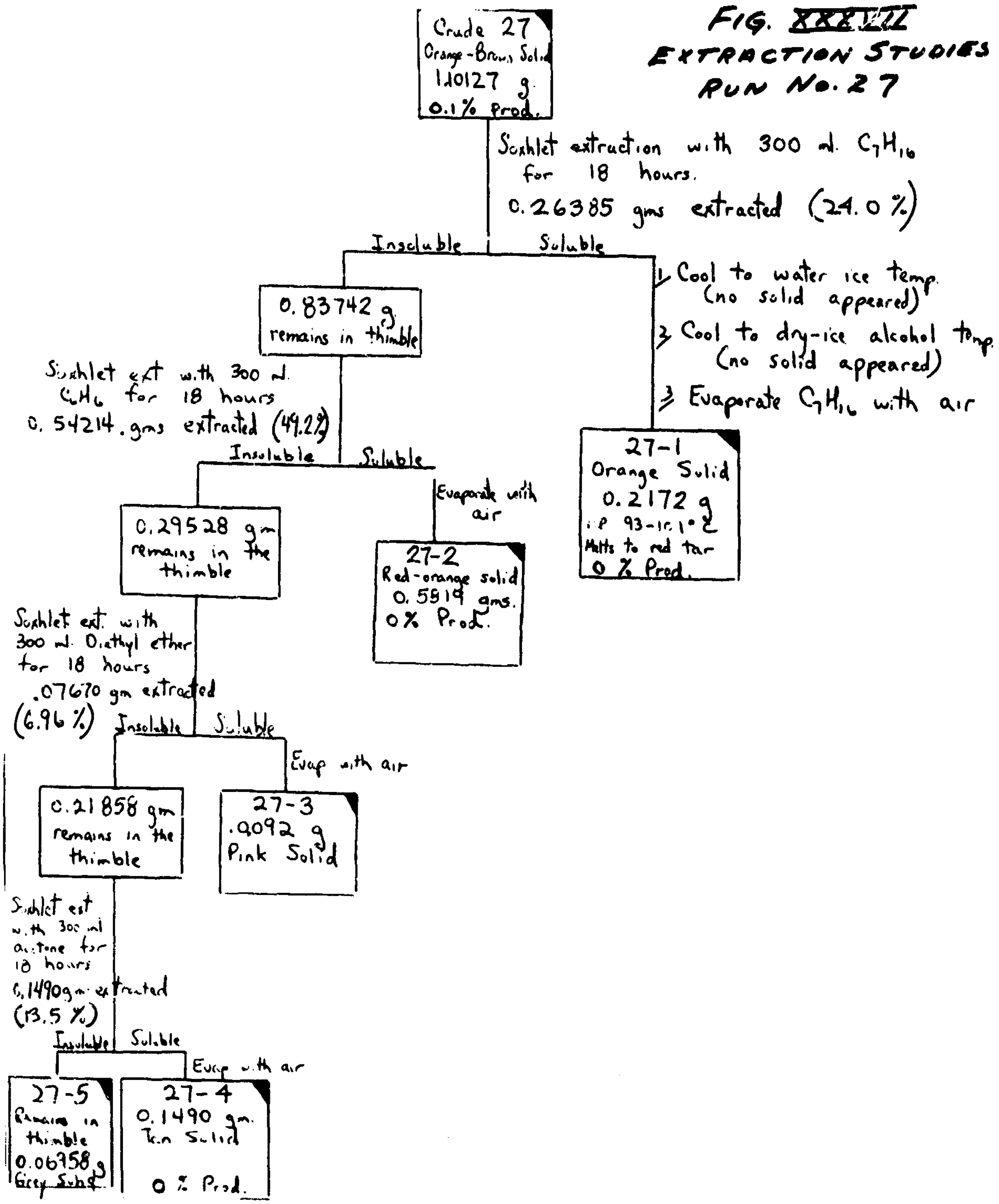
Note: The percent product stated on each sample fraction refers to the percentage of 3,6-bis(trifluoromethyl)phenanthrene found in each individual fraction.

FIGURE XXXVI
EXTRACTION STUDIES
RUN No. 26



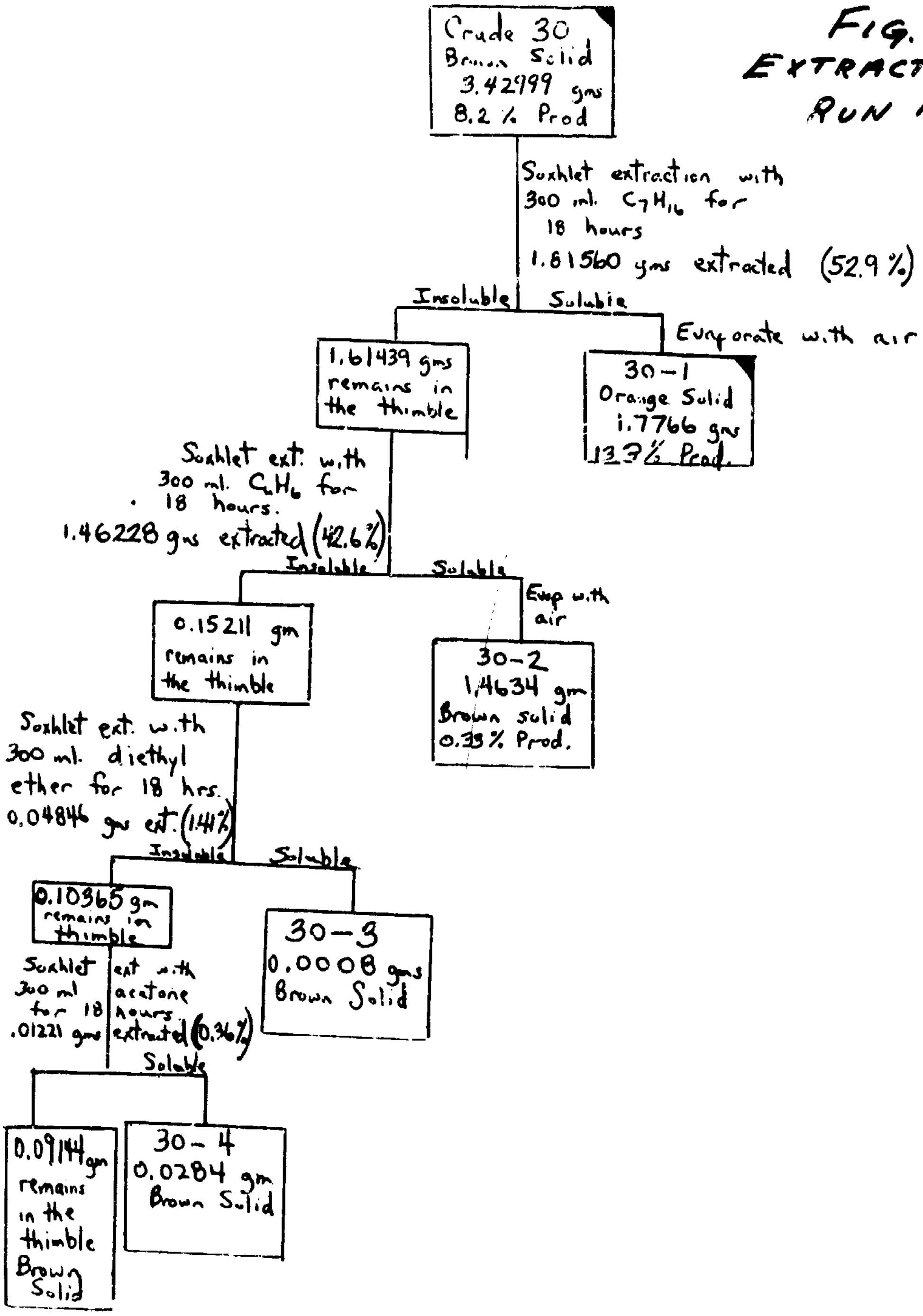
Note: The percent product stated on each sample fraction refers to the percentage of 3,6-bis(trifluoromethyl)phenanthrene found in each individual fraction.

FIG. XXXVIII
EXTRACTION STUDIES
RUN No. 27



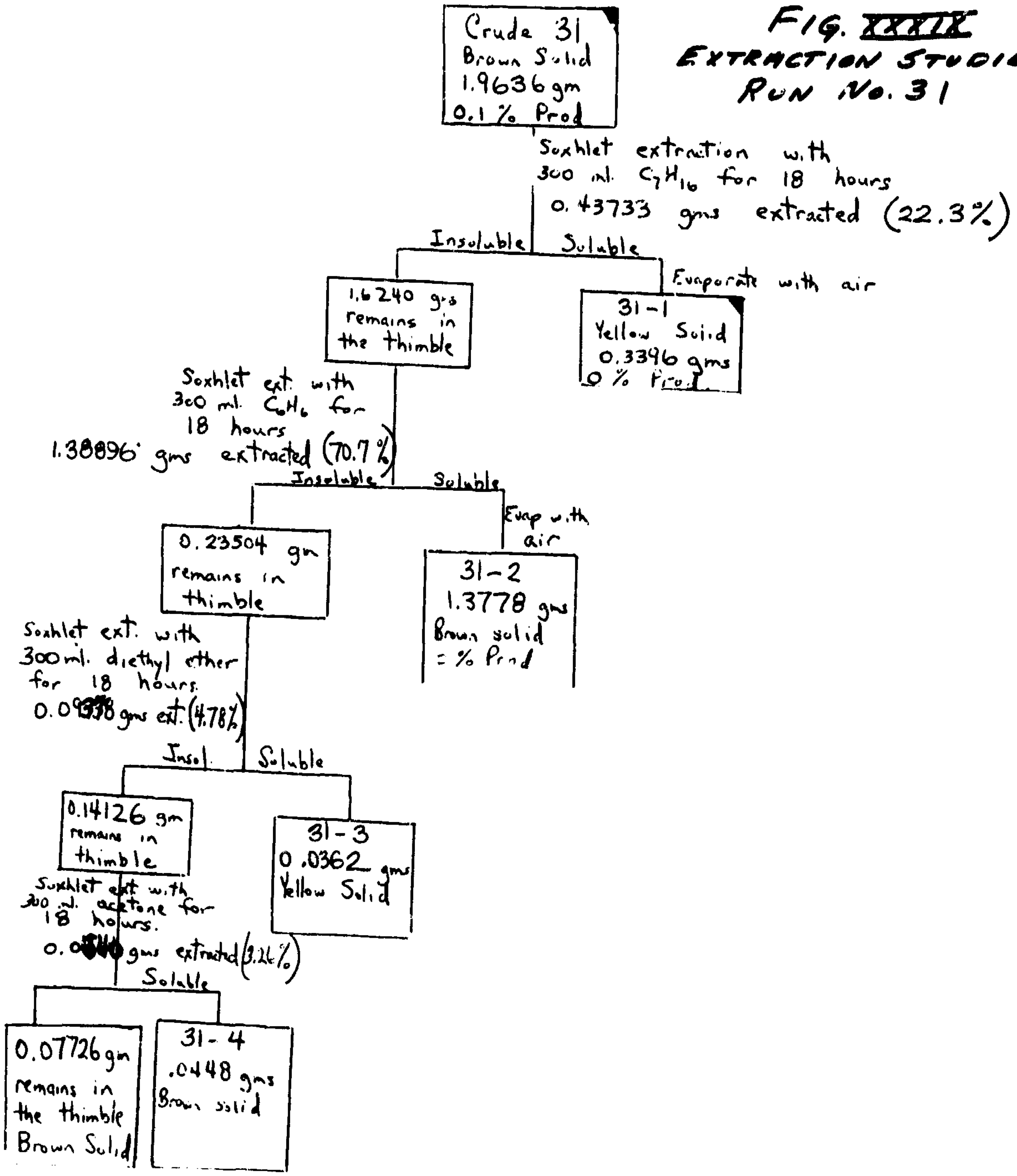
Note: The percent product stated on each sample fraction refers to the percentage of 3,6-bis(trifluoromethyl)phenanthrene found in each individual fraction.

FIG. XXXVIII
EXTRACTION STUDIES
RUN NO. 30



Note: The percent product stated on each sample fraction refers to the percentage of 3,6-bis(trifluoromethyl)phenanthrene found in each individual fraction.

FIG. XXXIX
EXTRACTION STUDIES
RUN NO. 31



Note: The percent product stated on each sample fraction refers to the percentage of 3,6-bis(trifluoromethyl)phenanthrene found in each individual fraction.

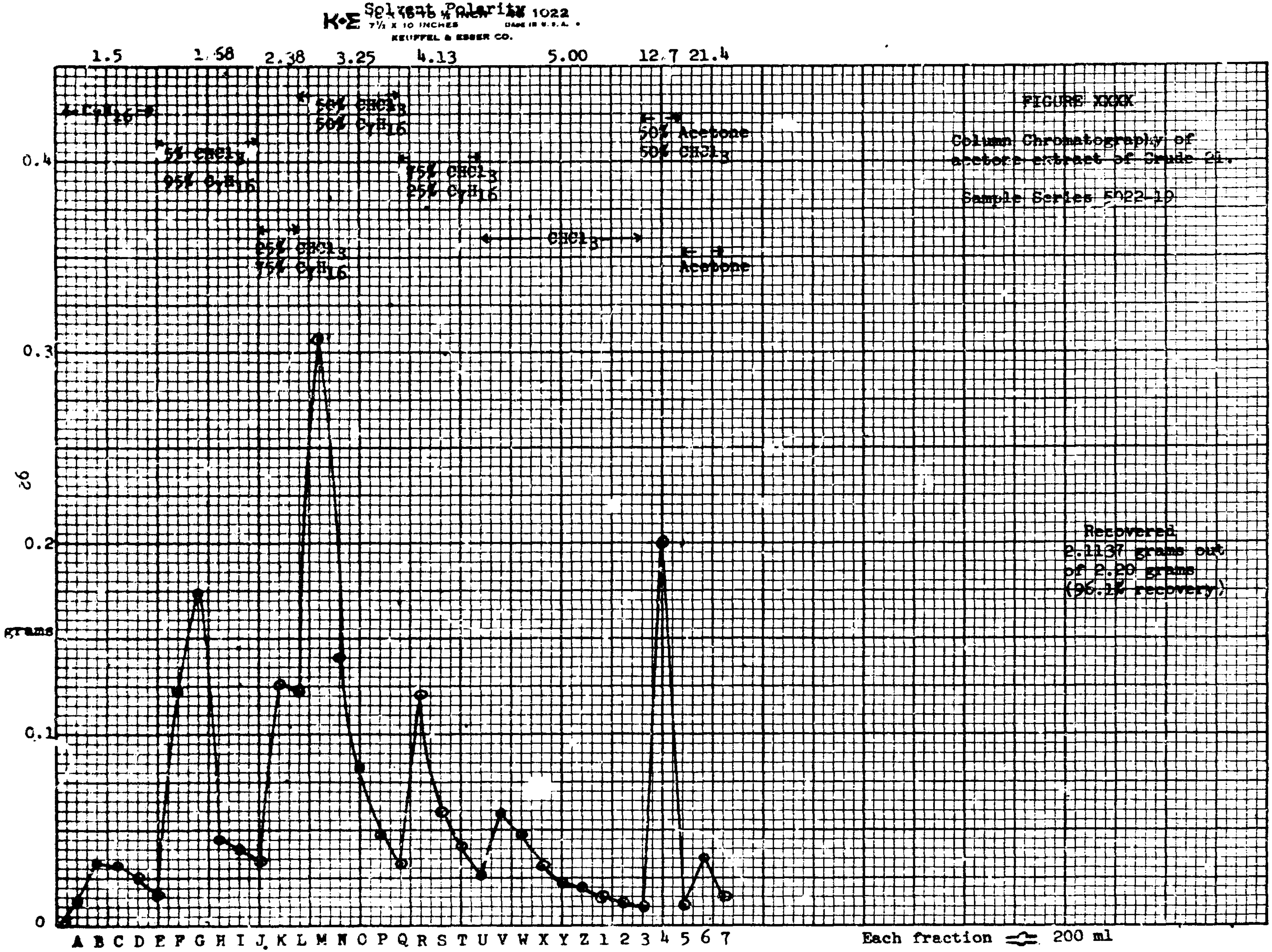


FIGURE XXXX

Column Chromatography of acetone extract of Crude 24.

Sample Series 5022-19

Recovered
2.1137 grams out
of 2.20 grams
(96.1% recovery)

FIGURE XXXXI

Proposed Production Process
SF_4 Reaction with 3,6-phenanthrene dicarboxylic acid (PDCA)

PDCA Conversions

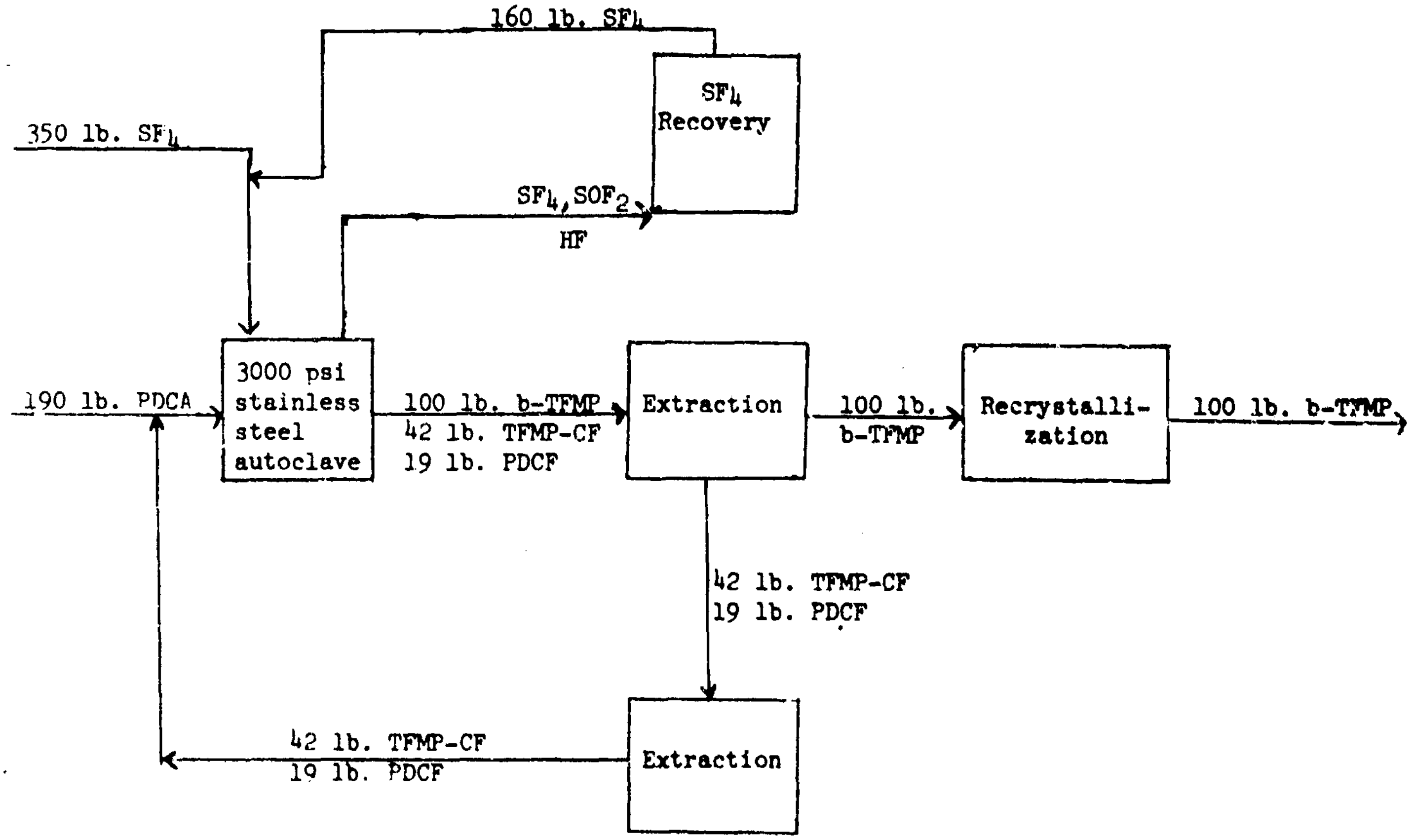
20% to 3,6-bis-(trifluoromethyl)phenanthrene (b-TFMP)
20% to 3-(trifluoromethyl)phenanthrene-6-carbonyl fluoride (TFMP-CF)
10% to 3,6-phenanthrene dicarbonyl fluoride (PDCF)

Recycle Conversions

80% TFMP-CF to b-TFMP
80% PDCF to b-TFMP

SF_4 Conditions

50% excess with 95% recovery



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4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

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James F. Tompkins

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13. ABSTRACT

The object of this work was to investigate, on a laboratory scale, the individual reactions of SF_4 with p-toluic acid to produce p-trifluoromethyl toluene and of 3,6-phenanthrene dicarboxylic acid to produce 3,6-bis(trifluoromethyl) phenanthrene. This laboratory data was to serve as a basis for scaleup of this reactions to a commercial process.

A total of 46 runs were conducted during this investigation with 16 runs performed with p-toluic acid in a 300 ml autoclave, 10 runs with p-toluic acid in a 1750 ml autoclave, and 20 runs with 3,6-phenanthrene dicarboxylic acid in the 300 ml autoclave. The parameters investigated were temperature over the range of 20°C to 225°C, pressure over the range of 140 to 3,000 psig, reaction times from one to 18 hours, SF_4 concentrations at 50% to 4,500% excess, catalysis with hydrogen fluoride and the use of inert solvents for the 3,6-phenanthrene dicarboxylic acid runs.

The p-toluic acid reaction was initially studied in a 300 ml hastelloy autoclave and a 78% p-trifluoromethyl toluene conversion was obtained at reaction conditions of 160°C, 1600 psig, 16 hour reaction time with a 50% molar excess of SF_4. Recycle of the p-toluic acid fluoride generated during this reaction would increase the yield of p-trifluoromethyl toluene to over 95% for these conditions. This reaction was scaled to a 1750 ml stainless steel autoclave

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in which a total of ten runs were made. The conversion to p-trifluoromethyl toluene using similar reaction conditions averaged 72% (57 to 85% range) for these runs and the yield averaged 87% (77 to 100% range) including recycle of the p-toluic acid fluoride. Purification of the crude reaction product by distillation gave a 90% recovery of >99% purity p-trifluoromethyl toluene from the reaction mixture. From this series of reactions, two 1500 grams samples of p-trifluoromethyl toluene was delivered to the Walter Reed Medical Center.

Twenty reactions of 3,6-phenanthrene dicarboxylic acid or its derivative 3,6-phenanthrene dicarbonyl fluoride were performed in the 300 ml autoclave. Relatively pure (>95%) 3,6-phenanthrene dicarbonyl fluoride was produced in quantitative yields from 3,6-phenanthrene dicarboxylic acid by reaction with SF_4 at temperatures of 110 to 160°C. The highest conversion (22.5%) of 3,6-bis(trifluoromethyl)phenanthrene was obtained by suspending the 3,6-phenanthrene dicarboxylic acid in benzotrifluoride and reacting at a temperature of 210 to 220°C, pressure of 1950-2150 psig, reaction time of 16 hours with a 1100% excess of SF_4. In addition, a 17.5% yield of 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 2.4% yield of 3,6-phenanthrene dicarbonyl fluoride was obtained. A similar reaction performed at a lower temperature gave a lower conversion (8.1%) to 3,6-bis(trifluoromethyl)phenanthrene but a higher yield of the intermediates (48% 3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 26% 3,6-phenanthrene dicarbonyl fluoride). This yield data is based on an analysis of the crude reaction mixture by quantitative GLC and TLC analysis. These analytical tools were developed during the course of this study and can be now routinely used for analysis of 3,6-bis(trifluoromethyl)phenanthrene directly. The major intermediates (3-trifluoromethyl phenanthrene-6-carbonyl fluoride and 3,6-phenanthrene dicarbonyl fluoride) can be quantitatively determined by reacting the crude reaction mixture with methanol and determining their concentrations based on the response of the corresponding methyl esters. A purified sample of 3,6-bis(trifluoromethyl)phenanthrene was not obtained from these reactions but studies on the soxhlet extractors showed promise that separation and isolation is possible.

A sample of purified 3,6-bis(trifluoromethyl)phenanthrene was obtained by decarboxylating the 3,6-bis(trifluoromethyl)phenanthrene-9-carboxylic acid. Identification of this compound (section V-A) was confirmed by IR, melting point, NMR, UV and elemental analysis. This sample served as a standard for GLC and TLC analysis of the crude reaction product.

Corrosion data gathered during the course of the p-toluic acid reactions showed a corrosion rate of <0.002 inches per year on 316 stainless steel under reaction conditions.

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(Second Page)

An economic evaluation of the production of 3,6-bis(trifluoromethyl) phenanthrene based on a 20% conversion to 3,6-bis(trifluoromethyl) phenanthrene plus an additional 30% yield of recycleable intermediates showed that a selling price (excluding 3,6-phenanthrene dicarboxylic acid costs) of ~$15/pound could be achieved at 30,000 to 50,000 lbs per year 3,6-bis(trifluoromethyl)phenanthrene. For smaller requirements, (~3,000 lbs/yr), the selling price (excluding 3,6-phenanthrene dicarboxylic acid costs) would be ~$40/lb. These figures reflect an expected SF_4 selling price of $10 per pound at the lower production rate and $3 per pound at the higher production rate.