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The reconversion of ethylene thioketals to ketones

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THE RECONVERSION OF ETHYLENE THIOKETALS
TO KETONES

by

Jeffrey Paul Ginther, *U.C. 1974*
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Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE

March, 1974

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ABSTRACT

GINTHER, JEFFREY PAUL The Reconversion of Ethylene Thioketals to Ketones. Department of Chemistry March, 1974.

Many aldehydes, ketones and other carbonyl-containing compounds react with 1,2-ethanedithiol to give the highly stable cyclic thioacetals or thioketals. The problem lies in reconverting the substituted 1,3-dithiolanes to the carbonyl compound without altering the other substituents of the molecule. We propose a new, direct method of exchange with formaldehyde to reconvert the 1,3-dithiolane to the carbonyl compound. This was accomplished with 2,2-diethyl-1,3-dithiolane. Also, a mechanism is proposed, involving the formation of a sulfonium ion intermediate. In preparation for the exchange study seven 1,3-dithiolanes were synthesized.

This Thesis

Submitted by

Jeffrey Paul Ginter

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

Howard E. Sheffer

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I would like to express my gratitude to Dr. Howard E. Sheffer, without whose help and guidance this work would not have been possible.

I would also like to thank the following people, who were of invaluable help: Dr. W. H. Thielking of Sterling Research Institute for his suggestions, Wm. McIver and Beverly Adams of Schenectady Chemicals, Inc., for the carbon-hydrogen analyses, Howard Goodman for the NMR spectra and Fabian Michel for his translation.

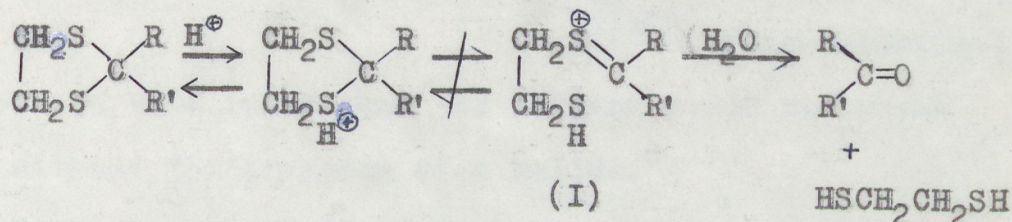
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INTRODUCTION AND HISTORICAL BACKGROUND

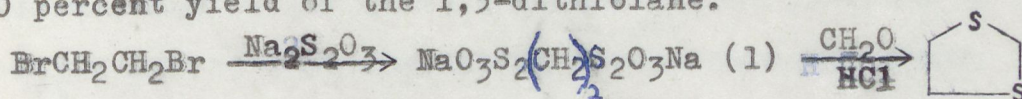
Often one desires to carry out a reaction on a molecule containing both a carbonyl group and some other functional group in which case it may be necessary to protect the carbonyl group. One simple method is to treat the carbonyl compound with ethylene glycol to generate an ethylene ketal. These are stable derivatives which can be converted back to the original carbonyl compound under acidic conditions. It is known that ethylene thioketals are much more stable to acid than ethylene ketals due to the weak electron releasing nature of sulfur.



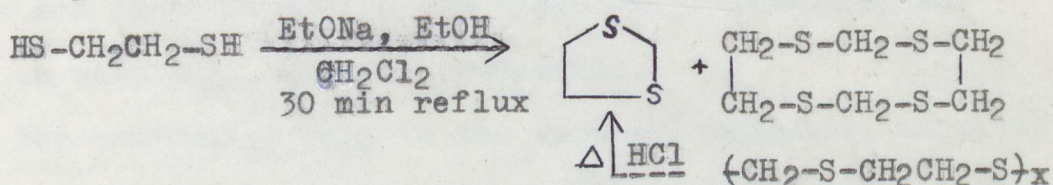
The intermediate (I) has a very small probability of forming since there is very poor overlap between the 3p orbitals of sulfur and the empty 2p orbital of carbon. This tendency of sulfur not to form carbon-sulfur double bonds also is observed in the difficulties in preparing thioketone monomers.¹

Preparation of cyclic thioketals was first studied by Fasbender^{2,3} in 1887. The parent compound, the thioacetal of formaldehyde, was first isolated by Gibson⁴ in 1930 by reacting 1,2-ethanedithiol with formalin with hydrochloric acid as the catalyst. This method, however, gives only a 30 percent yield, according to Challenger⁵, accompanied by

a large amount of polymer. The Bunte salt (1) can be reacted with formalin and hydrochloric acid to give a 50 to 60 percent yield of the 1,3-dithiolane.⁶



Methylene chloride and 1,2-ethanedithiol in the presence of base gave a 26 percent yield of 1,3-dithiolane with a ten-membered ring and polymer. This polymer later gave a 30 percent yield of 1,3-dithiolane upon heating, according to Tucker and Reid.⁷



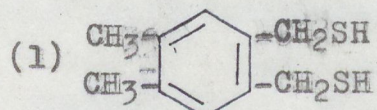
Meadow and Reid found that the polymer would not break down without the presence of a halide.⁸

Dithiolanes substituted on the 2- position were first studied by Fasbender^{3,4} when he treated an aldehyde or a ketone with 1,2-dimercaptans in hydrogen chloride gas. This is still the accepted procedure with a few minor modifications, such as using p-toluene sulfonic acid and azeotroping off the water with benzene⁹, or using boron trifluoride etherate.¹⁰ Hauptmann¹¹ has used zinc chloride, another Lewis acid.

The masking has been applied to sugars, first by Lawrence¹² in 1896, using 1,2-ethanedithiol with aqueous hydrochloric acid as the catalyst. Zinner¹³ proposed in 1953 to use ion-exchange resins to remove the catalyst in the sugar reactions. Fieser used this masking of carbonyls

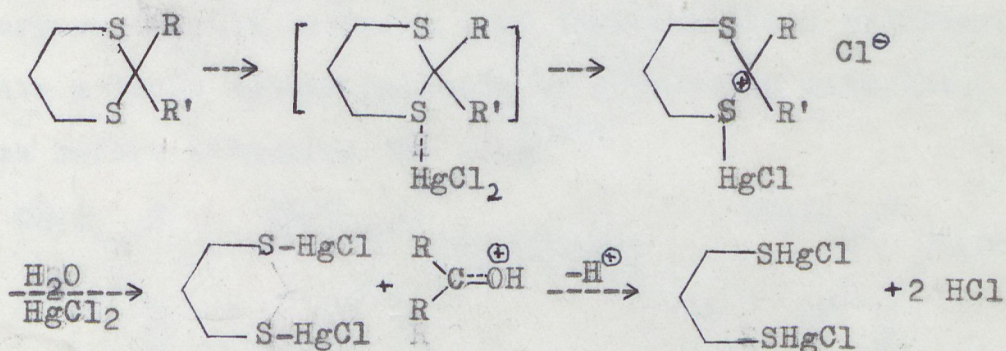
on some of the steroid series using boron trifluoride etherate as a catalyst.¹⁰

Israel Shahak and Ernst Bergmann¹⁴ were prompted to look for a method less irritating to the nose and neater to work with, so instead of using 1,2-ethanedithiol, 1,2-dimethyl-4,5-bis(mercaptomethyl)benzene (1), was employed to



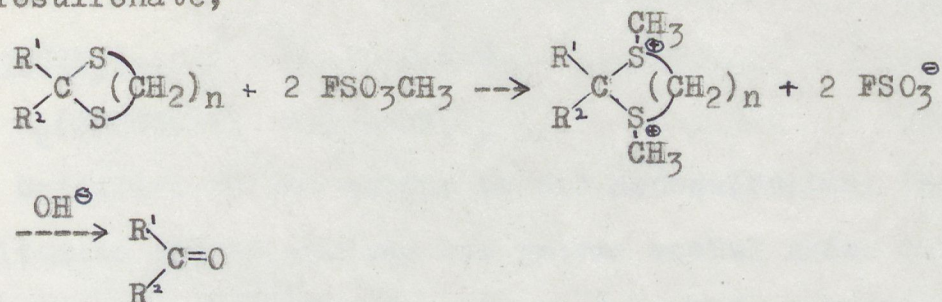
give crystalline, odorless thioketals which are stable to acids and bases as well as to organo-magnesium, organo-lithium compounds, and to borohydride.

The conversion back to the carbonyl compound, as noted above, is the most troublesome problem. There are a number of methods available for this, the earliest being the use of mercury salts.^{15,16,17,17a} Seebach¹⁷ envisions the mechanism as the mercury acting as a Lewis acid:

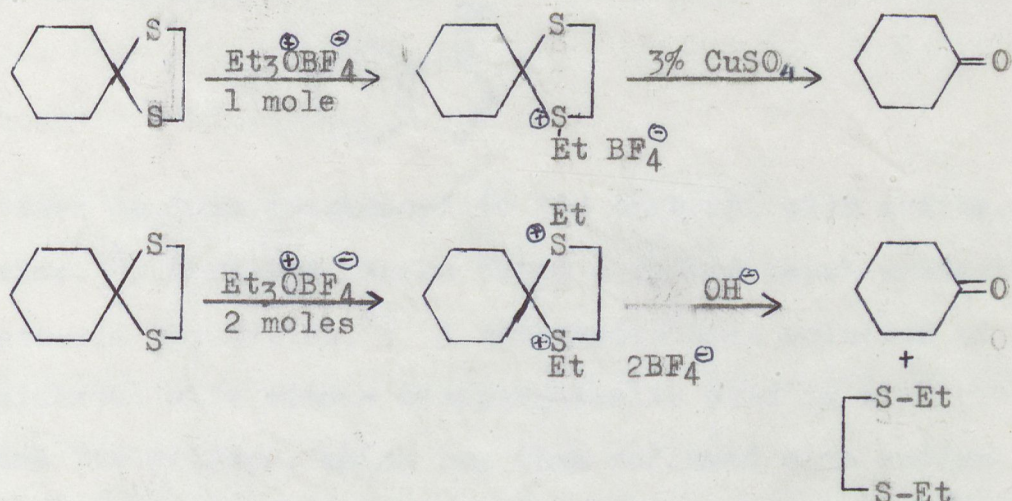


Some found the acetate salts of mercury to be better¹⁶, and Fischer^{17a} was able to use silver nitrate in the same manner. Various agents were used to remove the acid, including cadmium carbonate²⁶, calcium carbonate, and mercury (II) oxide.¹⁶ Other electrophilic reagents have proven very successful, for example, the use of methyl

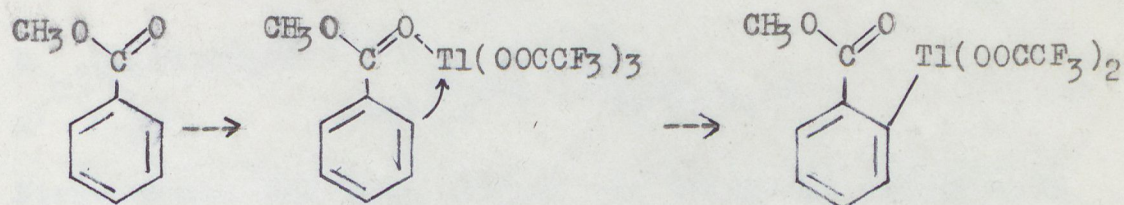
fluorosulfonate,¹⁸



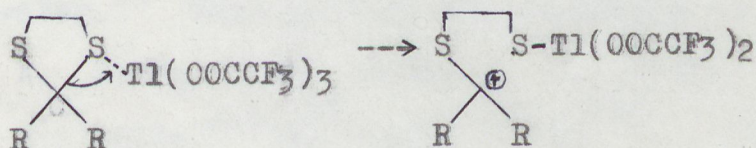
and triethyloxonium tetrafluoroborate¹⁹.

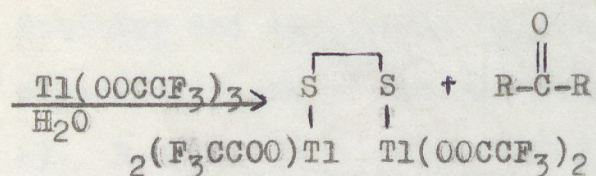


Thallium (III) trifluoroacetate²⁰ may act as do the mercury salts. It is known that thallium (III) trifluoroacetate attacks methyl benzoate by complexing with the oxygen before attacking the ring.^{20a}

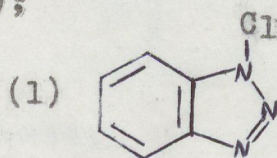


Perhaps the following happens then:

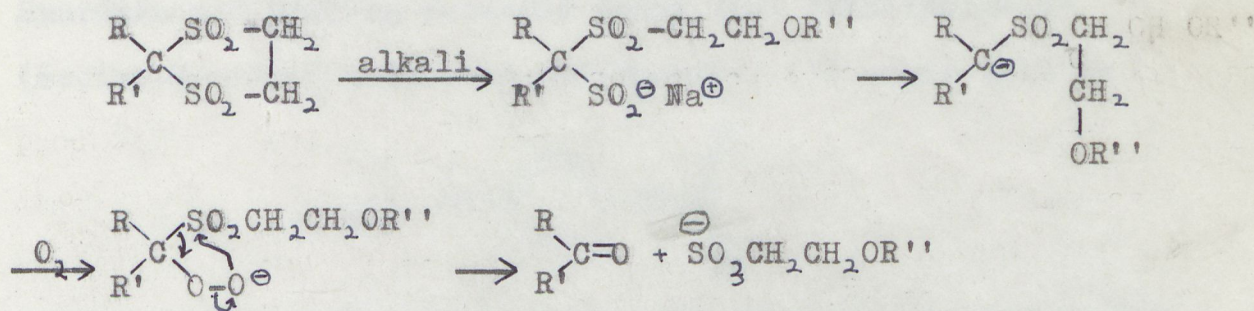




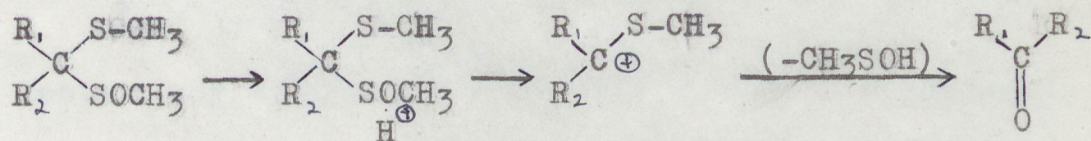
Oxidation of the sulfur to the monosulfoxide, the disulfoxide or the sulfone has proven useful under certain circumstances. The disulfoxide is formed from 1-chloro-benzotriazole (1);



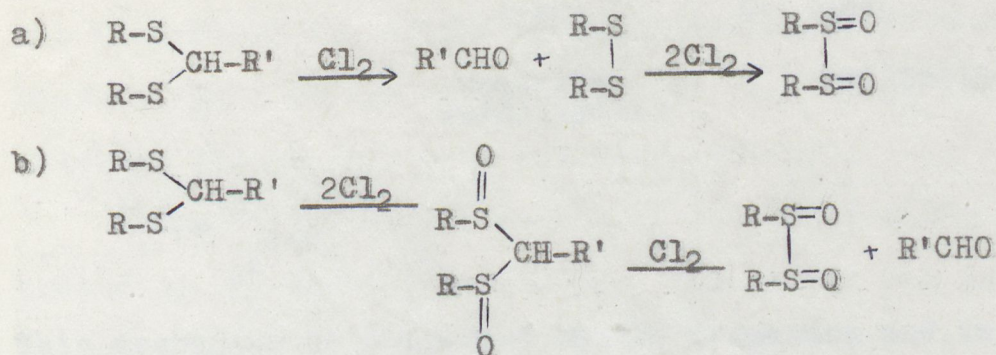
the former is then decomposed to the carbonyl with sodium hydroxide.²¹ Daum and Clarke tried a rather harsh oxidation on a steroid derivative.²² A tetrahydrofuran solution of the thioketal with excess monoperphthalic acid in ether produced the sulfone, which was then refluxed with sodium ethoxide in a nitrogen atmosphere. Oxygen was then bubbled through the solution to produce the ketone.



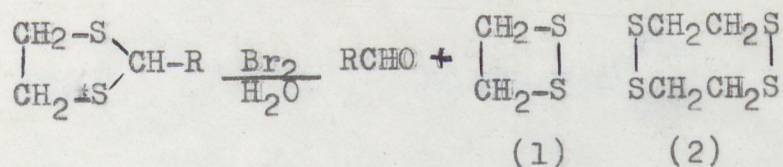
Nieuwenhuys and Louw oxidize the thioketal either with hydrogen peroxide in acetone and water, or by sodium periodate and water.²³ They picture the following as taking place:



Gauthier and Vaniscotte oxidize with bromine²⁴, or chlorine, postulating one of the following mechanisms:

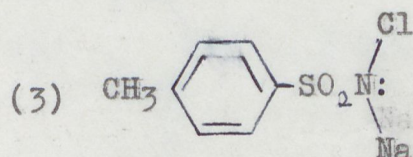


When bromine was used,

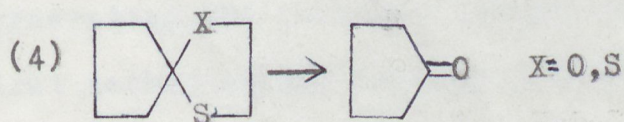


both (1) and (2) were obtained, so mechanism a) may be the correct one.

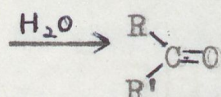
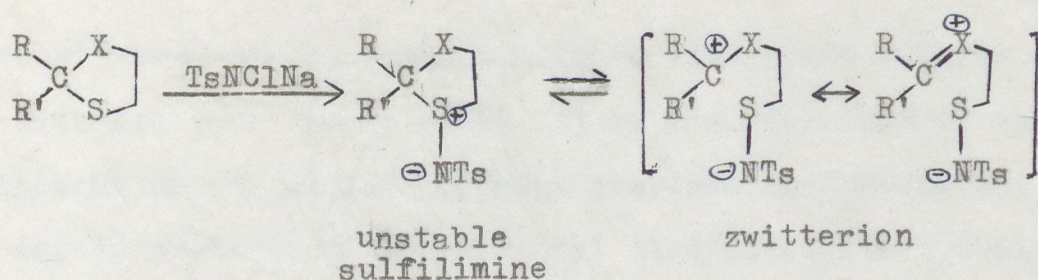
Both Seebach²⁵ and Corey and Crouse²⁶ have found N-bromosuccinimide and N-chlorosuccinimide successful. Huurdman and Wynberg recently found that "Chloramine-T" (sodium-N-chloro-p-toluene sulfonamide) (3) works well in



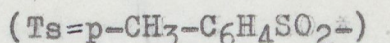
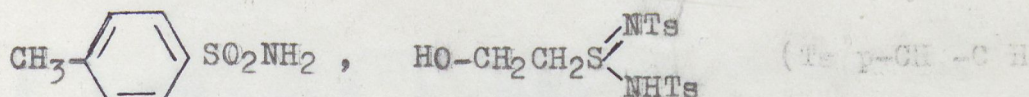
aqueous methanol-ethanol solution.²⁹ Emerson and Wynberg^{27a} worked with both dithiolanes and oxathiolanes (4).



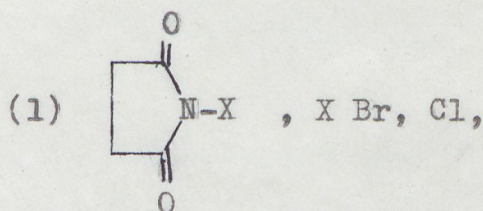
They tentatively believe that the sulfur acts as a nucleophile towards the nitrogen and the following takes place:



This mechanism is supported by the formation and isolation of the following:



A second mechanism may be suggested considering that the halogen (chlorine), as the cation, may attack the sulfur, forming a sulfonium ion. This second mechanism may explain the action of N-chloro- and N-bromosuccinimide.(1),



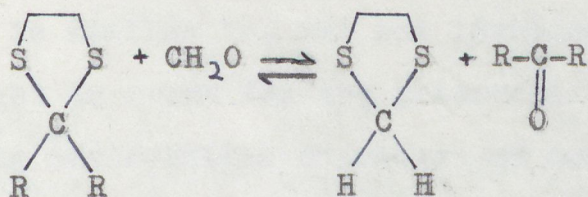
on the dithiolanes. It is known that NBS reacts with hydrogen bromide to form bromine and succinimide, probably generating the positive halogen ion in the process. The first mechanism may be only a minor pathway, but then, the action of benzotriazole on 1,3-dithiolanes might be explained with it.

Finally, to complete this list of potpourri, Ho, Ho,

and Wong²⁸ used ceric ammonium nitrate with great success.

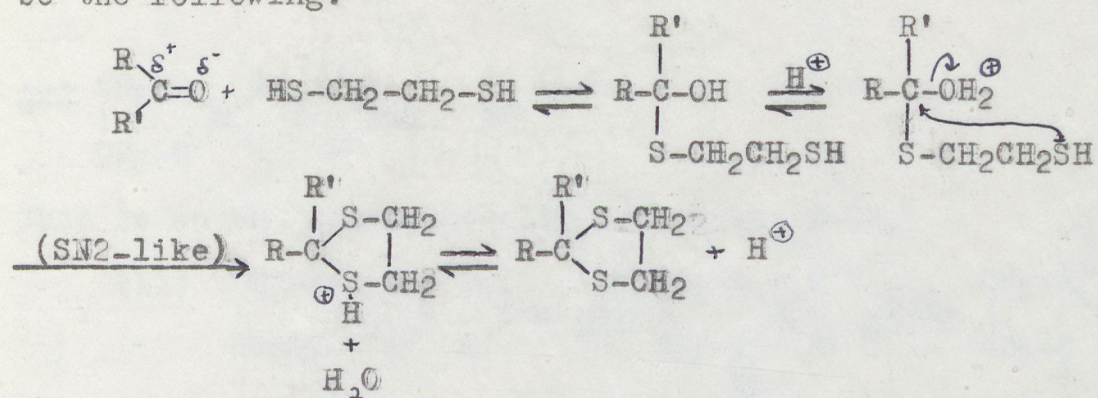
With all this recent study, it is a wonder that no one has thought of the simple exchange proposed in this paper, that is, an exchange of one carbonyl tied up as its 1,3-dithiolane for another more reactive carbonyl.

We first prepared a series of seven 1,3-dithiolanes, including 1,3-dithiolane itself. The latter was prepared so as to be able to identify it as a byproduct in the exchange:

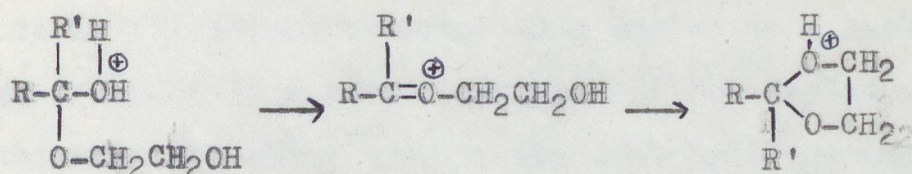


THEORY

The method of formation of thioketals is assumed to be the following:

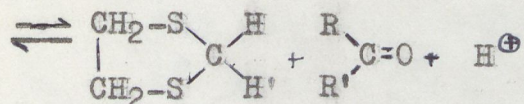
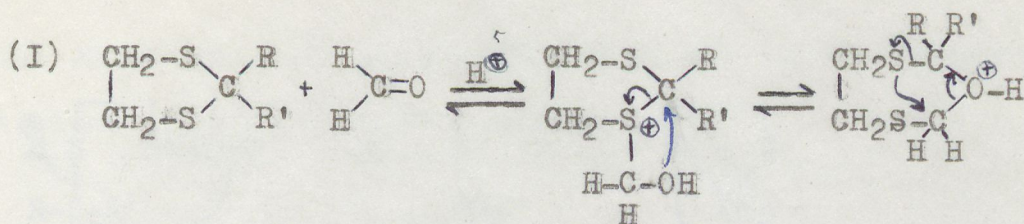


This is similar to, but not identical to, the mechanism thought to occur for the preparation of ketals, *but* the strong nucleophilic character of sulfur brings about an easy displacement of water. The mechanism for ethylene ketal formation would differ in that the step labelled "SN2-like" would be SN1, involving the oxycarbonium ion:

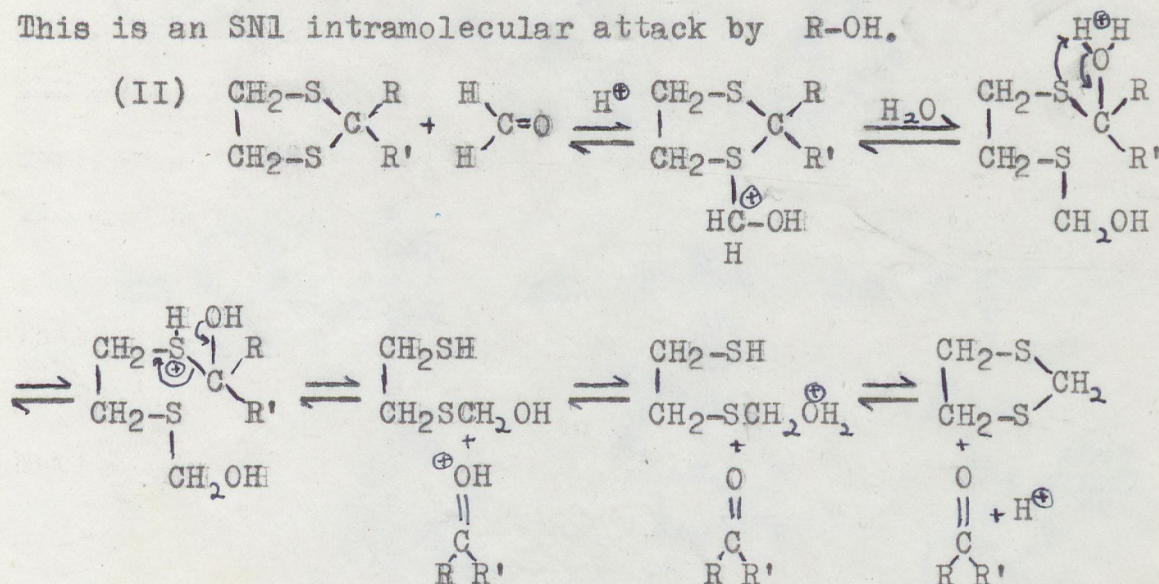


Here one sees a pi bond between the carbon and oxygen which is less likely with sulfur. By the same reasoning the reverse reaction with thioketals is very slow, unless an electrophile becomes attached to the sulfur to make it a good leaving group.

The following exchange mechanisms are therefore suggested.

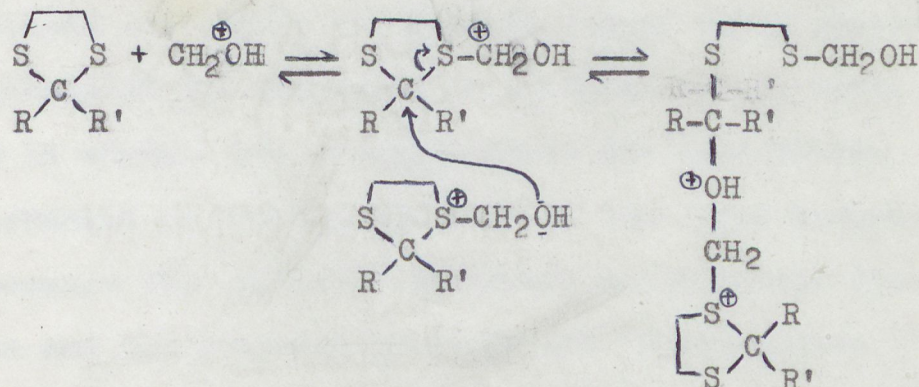


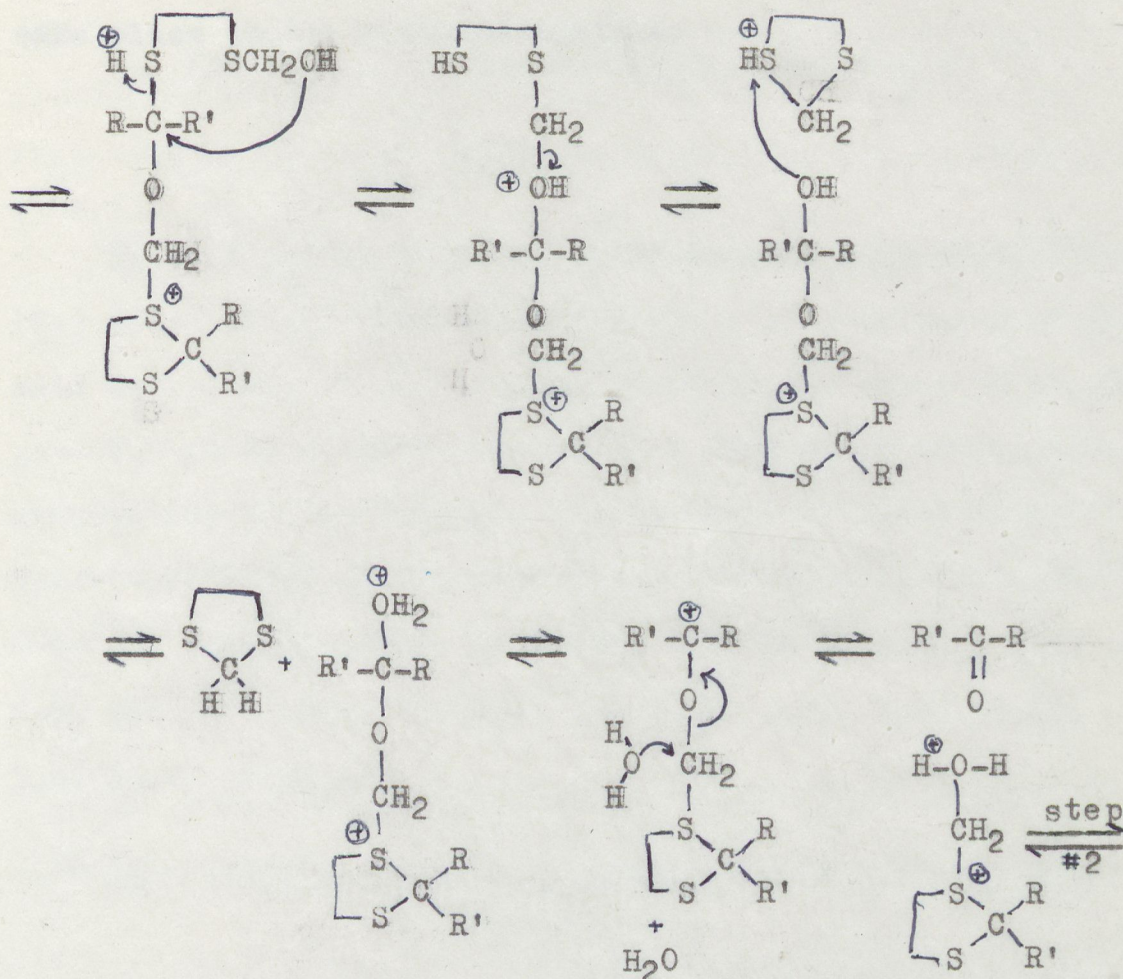
This is an SN1 intramolecular attack by R-OH.



This is an SN2 attack by water with sulfur as a leaving group, followed by a proton exchange to the sulfur with the hemithioketal breaking down to the carbonyl compound.

(III)

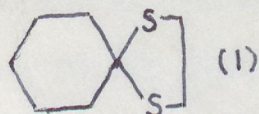




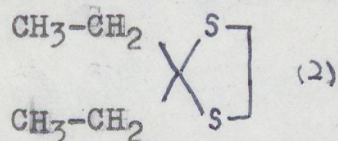
This is an $\text{S}_{\text{N}}2$ intermolecular attack by $\text{R}-\text{OH}$.

The first mechanism involves no water, but does involve a sulfo-carbonium ion which is not too stable. The second mechanism sounds reasonable if there is indeed water present, but the backbone of the mechanism is centered on the water, and if that is absent, the reaction would not take place. The last mechanism is perhaps the best of the three mechanisms suggested because all the water necessary is generated from the reaction and the reaction products are in themselves reaction initiators. All make use of the ability of sulfur to form an intermediate sulfonium ion with strong electro-

philic character. It is possible that all three processes take place in the reaction mixture.

EXPERIMENTALI. Preparation of 1,4-Dithiaspiro(4,5)decane (1):

To 49.1 g (0.5 mole) of cyclohexanone were added 47.1 g (0.5 mole) of 1,2-ethanedithiol, one g of p-toluenesulfonic acid and eleven ml of benzene. Heating for about 30 minutes gave 7.9 ml of water collected in a Dean-Stark trap. After evaporation of the benzene, 74.1 g (85%) of 1,4-dithiaspiro(4,5)decane were collected at 132°/24 mm, (lit. 107°/5 mm²⁹), (sample 5-1): ir S-CH₂, 2675 cm⁻¹; S-CH₂, 1450 cm⁻¹; C-S, 680 cm⁻¹ (Fig. 1); nmr, ppm 3.06 (4,s), 1.82 (4,m), 1.41 (6,m) (Fig. 2).

II. Preparation of 2,2-Diethyl-1,3-dithiolane, (A) (2):

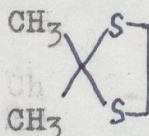
This was prepared by a similar procedure in 65 percent yield, bp 102°/18 mm (sample 101-18-1): nmr, ppm 3.6 (4,s), 2.18 (4,q), 1.16 (6,t), (Fig. 3).

III. Preparation of 2,2-Diethyl-1,3-dithiolane, B:

To 23.6 g (0.25 mole) of 1,2-ethanedithiol were added 21.5 g (0.25 mole) of 3-pentanone, the mixture was shaken well and added slowly to five ml of ice-cooled boron-trifluoride etherate. After stirring and then storing overnight at 0°, the product was then dissolved in ether and washed with one M sodium hydroxide solution and then with

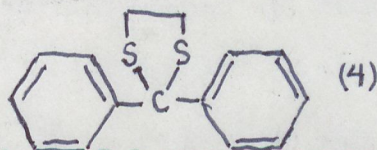
water. After evaporation of the ether, 2,2-diethyl-1,3-dithiolane was collected at 105°/22 mm in a 76 percent yield, (sample 29-2): ir S-CH₂, 1425 cm⁻¹; C-S, 690 cm⁻¹ (Fig. 4); nmr, ppm 3.6 (4,s), 2.18 (4,q), 1.16 (6,t) (Fig.3).

IV. Preparation of 2,2-Dimethyl-1,3-dithiolane (3):



A similar procedure as in III. was used to obtain the 2,2-dimethyl-1,3-dithiolane, boiling at 66-70°/18 mm, (lit. 89°/14 mm³⁰) in a 66 percent yield (sample 39-1): ir S-CH₂, 2700 cm⁻¹; S-CH, 1420 cm⁻¹; C-S, 680 cm⁻¹ (Fig. 5); nmr, ppm 3.21 (4,s), 1.7 (6,s), (Fig. 6).

V. First Attempt at Preparation of 2,2-Diphenyl-1,3-dithiolane (4):



To a solution of benzophenone (0.25 mole) in 100 ml of benzene were added 1,2-ethanedithiol (0.25 mole) and then three ml of boron trifluoride etherate dropwise. After all the catalyst was added, the mixture was stirred well and stored overnight at 0°. The product was then washed with one M sodium hydroxide and water, then distilled at 172-177°/15 mm in a 24 percent yield. This product was deep blue in color and solidified; it was recrystallized twice from 95 percent undenatured ethanol. Initially a melting point of 30-32° was recorded (sample 47-2), but an nmr scan showed excess ethanol. The sample was dried over a Buechner funnel; the mp was then 40-41°. An ir spectrum showed practically

an identical benzophenone spectrum. (Figs. 7,8). It has been noted that impure benzophenone may have a bluish tinge and that it melts at 49° .³¹

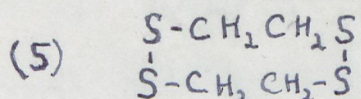
When sample 47-2 was recrystallized in the ethanol a white floc did not dissolve. The floc was dried and melts at $146-148^{\circ}$ (sample 47-1). Note that 2,2-diphenyl-1,3-dithiolane melts at 106° ³²; ir $C=O$, 1660 cm^{-1} ; $S-CH$, 1420 cm^{-1} ; $C-S$, 695 cm^{-1} (Fig. 9). No solvent could be found, including benzene, DMSO, dioxane, carbon tetrachloride, ethanol, water, and chloroform, so that an nmr spectrum could not be taken. A carbon-hydrogen analysis showed: 41.7% C, 4.4% H.

VI. Preparation of 2,2-Diphenyl-1,3-dithiolane:

To 22.8 g (0.125 mole) of benzophenone were added 11.8 g (0.125 mole) of 1,2-ethanedithiol, one g of p-toluene sulfonic acid and ten ml of benzene for use in azeotroping off the water into a Dean-Stark trap. Heating for about 30 minutes gave 2.2 ml of water collected in the trap. Upon cooling, the solution turned brownish and appeared to solidify in part. After this was cooled to room temperature ten ml of one M sodium hydroxide were added, whereupon a violent reaction took place. Much of the volume appeared to solidify into a yellowish substance, with some clear liquid remaining. Ten ml of benzene were added and the mixture shaken. The clear liquid turned greenish at this point. Upon heating this mixture two layers formed again, a dark brown bottom layer and a cloudy, whitish upper layer. This

mixture was then cooled to room temperature.

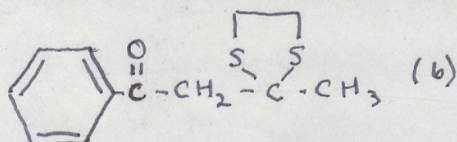
The layers were then separated with a separatory funnel, whereby it was noticed that there were two liquid layers with some crystals not soluble in either. The crystals were dried over a Hirsch funnel. These melted at 104° . Since they were brownish it was thought that they might be impure. They were boiled several times in acetone, which would dissolve any dithiolane or ketone, and when no more of the crystals dissolved, the remaining powder was dried over a Hirsch funnel, and washed with acetone several times. The remaining powder was light brown in color; at 133° the powder changes composition but still has not melted at 207° . (sample 89-1): ir S-CH₂, 1420 cm^{-1} ; C-S, 680 cm^{-1} ; aromatic, 740 cm^{-1} , (Fig. 10). An nmr spectrum could not be taken for lack of a solvent. A carbon hydrogen analysis showed the following: 25.8% C, 4.5% H. With this information it might be possible that sample 89-1 is an eight membered disulfide ring (5) with 26.06% C, 4.37% H, or some polymer of the same composition.



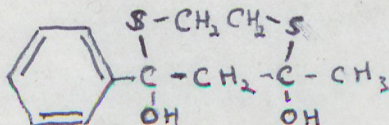
The benzene layer, described above, was dried over anhydrous calcium chloride and filtered. Several crystals formed on the filter paper, melting at $103-105^{\circ}$. When the dry benzene solution was being evaporated the solution turned a green color. When the benzene was completely evaporated the remaining substance cooled to a light green solid, melting at $102-103^{\circ}$. It was not soluble in cold ethanol, but recrystallized white in hot ethanol. The

white solid was dried over a Buechner funnel and melted at $103-104^{\circ}$ (lit. 106^{032}). This was the 2,2-diphenyl-1,3-dithiolane in 64.5 percent yield (sample 85-2): ir S-CH₂, 1420 cm^{-1} ; C-S, 697 cm^{-1} ; aromatic, 3050 cm^{-1} , 1600 cm^{-1} , 1480 cm^{-1} , 740 cm^{-1} (Fig. 11); nmr, ppm 3.25 (4,s), 7.15 (10,m) (Fig. 12).

VII. Preparation of the Cyclic Thioketal of Benzoylacetone (6):

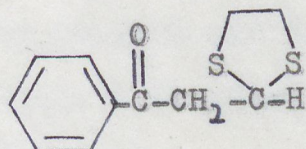


To 8.1 g (0.05 mole) of benzoylacetone were added 4.7 g (0.05 mole) of 1,2-ethanedithiol and 15 ml of benzene. The mixture was shaken well and to it was added two ml of boron trifluoride etherate. There was no immediate change, but it slowly turned cloudy with a slight evolution of heat. This was then stored at 0° for several days. A few crystals, formed at the bottom of the flask, melt at 155° (sample 63-1): ir C-S, 680 cm^{-1} ; S-CH₂, 1440 cm^{-1} ; -OH, 3450 cm^{-1} ; aromatic, 2920 cm^{-1} , 1600 cm^{-1} , 1550 cm^{-1} , 1500 cm^{-1} , 705 cm^{-1} (Figs. 13, 13a); nmr, ppm 7.45(m), 3.29 (2,s), 2.31 (4,s), 1.89 (5,s) (Fig. 14). Note, the solvent used, DMSO-6d, seemed to react with the compound, as the solution turned from clear to brownish upon standing. Consequently the nmr spectrum may not be accurate. A possibility for the structure of sample 63-1 might be:



but this is difficult to tell without an integration on the nmr and a C-H analysis.

Upon washing the rest of the solution with sodium hydroxide and water, an orange color pervaded both aqueous and benzene layers. Upon drying the benzene layer with calcium chloride, most of the color disappeared. The crystals dropped out of solution upon standing at 0°. They were dried over a Buechner funnel and recrystallized with ethanol. A ten percent yield of the dithiolane was collected, melting at 70-71° (sample 63-2). No literature value was available, but a similar compound, (7), is reported to melt



C-H anal. of 63-2
(7) found calc.

| | | |
|---|-------|-------|
| C | 62.2% | 60.5% |
| H | 7.0% | 5.8% |

somewhere in the area of 74.5-80°.33,34

ir c-s, 685 cm^{-1} ; S-CH, 1405 cm^{-1} ; C O, 1700 cm^{-1} ; aromatic, 3000 cm^{-1} , 1600 cm^{-1} , 740 cm^{-1} (Fig. 15); nmr, ppm 1.88 (3,s), 3.15 (,s), 3.61 (2,s), 7.42 (5,m) (Fig. 16). A comparison to the ir spectrum of benzoylacetone indicates a loss of the carbonyl absorption at 1730 cm^{-1} (Fig. 15a).

VIII. First Attempt to Prepare 2-Methyl-1,3-dithiolane:

To 47.1 g (0.5 mole) of 1,2-ethanedithiol were added 44.0 g (1.0 mole) of what was labelled acetaldehyde. It was later found that the acetaldehyde had a boiling range of 71-175°. The reaction flask became slightly warm before the catalyst was added. When one ml of boron trifluoride etherate was added, the flask became hot and the mixture started to reflux. After thirty minutes had elapsed the solution was washed with 0.1 M sodium hydroxide, and dried over anhydrous calcium chloride. The product was then dis-

tilled, whereby four main products were obtained. A yield of 17 percent of the 2-methyl-1,3-dithiolane resulted, bp 68-80°/20 mm (lit. 77°/14 mm ³⁵) (sample 41-1): ir S-CH₂, 2700 cm⁻¹; S-CH₂, 1430 cm⁻¹; C-S, 680 cm⁻¹; significant absorption at 1730 and 3460 cm⁻¹ (Fig. 17); nmr, ppm 4.5 (1,q), 3.15 (4,s), 1.55 (3,d) (Fig. 18).

The other fractions are as follows:

Sample 41-3: bp 142-165°/15 mm
ir S-CH₂, 2700 cm⁻¹; S-CH₂, 1420 cm⁻¹; C-S, 680 cm⁻¹; significant absorption at 1720 and 3400 cm⁻¹ (Fig. 19).
nmr, ppm 4.58 (1,q), 3.67 (2,s), 3.16 (4,s), 2.8 (m), 1.72, (m), 1.17 (d) (Fig. 20).

Sample 41-4: bp 148-174°/15 mm
ir S-CH₂, 2700 cm⁻¹; S-CH₂, 1430 cm⁻¹; C-S, 680 cm⁻¹; significant absorption at 1730, 2550, and 3440 cm⁻¹ (Fig. 21).
nmr, ppm 4.62 (1,q), 3.77 (2,s), 3.20 (4,s), 2.79 (2,m), 1.82 (m), 1.18 (3,d) (Fig. 22).

Sample 41-5: bp 174-177°/15 mm
ir S-CH₂, 2700 cm⁻¹; S-CH₂, 1440 cm⁻¹; C-S, 680 cm⁻¹; significant absorbance at 1720, 2550, and 3420 cm⁻¹ (Fig. 23).
nmr, ppm 4.58 (1,q), 3.80 (1,m), 3.40 (1,s), 3.14 (4,s), 2.78 (6,m), 1.72 (m), 1.10 (3,d) (Fig. 24).

There is also the possibility in all these compounds of C-O absorption at 1150 cm⁻¹.

IX. Second Attempt to Prepare 2-Methyl-1,3-dithiolane:

A sample of paraldehyde (70 g) was converted to acetaldehyde (bp 33°) using 3.5 ml of concentrated sulfuric acid

and 3.3 ml of water. The pure acetaldehyde (31 g, 0.755 mole) was reacted with 47.1 g (0.50 mole) of 1,2-ethanedithiol and no catalyst was needed for initiation of the reaction. Three main products were obtained from the pure acetaldehyde; the products were dried over calcium chloride and distilled:

Sample 59-1: bp $63-73^{\circ}/15\text{mm}$ (lit. $77^{\circ}/14\text{mm}$ ³⁵), probably impure 2-methyl-1,3-dithiolane.
 ir S-CH_2 , 2720 cm^{-1} ; S-CH_2 , 1430 cm^{-1} ; C-S , 683 cm^{-1} ; significant absorption at 1690 and 2550 cm^{-1} . (Fig. 25).
 nmr, ppm 4.7 (1,q), 3.38 (4,s), 2.87 (7,m), 2.11 (5,m), 1.72 (3,d) (Fig. 26)

Sample 59-2: bp $155^{\circ}/15\text{ mm}$
 ir S-CH_2 , 2720 cm^{-1} ; S-CH_2 , 1420 cm^{-1} ; C-S , 683 cm^{-1} ; significant absorption at 1690 , 2550 and 1150 cm^{-1} (Fig. 27).
 nmr, ppm 4.68 (1,q), 3.33 (4,s), 2.92 (3,m), 1.72 (3,d) (Fig. 28).

Sample 59-3: bp $162-170^{\circ}/15\text{mm}$
 ir S-CH_2 , 2710 cm^{-1} ; S-CH_2 , 1420 cm^{-1} ; C-S , 690 cm^{-1} ; significant absorption at 1690 and 2550 cm^{-1} (Fig. 29).
 An nmr spectrum was not available due to a break down of the instrument.

X. Final Attempt to Prepare 2-Methyl-1,3-dithiolane:

A pure sample of paraldehyde was used in this attempt. To 94 g (one mole) of 1,2-ethanedithiol were added 44 g (0.33 mole) of paraldehyde and one ml of boron trifluoride etherate, producing an exothermic reaction. The product was

cooled, washed with water, dried over calcium chloride and distilled. From this six products were separated, albeit not completely.

Sample 61-1: bp $77-92^{\circ}/30$ mm (lit. $77^{\circ}/14$ mm)³⁵), most likely 2-methyl-1,3-dithiolane.

ir S-CH₂, 2730 cm^{-1} ; S-CH₂, 1420 cm^{-1} ; C-S, 680 cm^{-1} ; significant absorption at 1690 and 2550 cm^{-1} (Fig. 31).

nmr, ppm 4.48 (1,q), 3.15 (,s), 1.52 (3,d) (Fig. 32).

Sample 61-2: bp $92-101^{\circ}/30$ mm

Sample 61-3: bp $106-112^{\circ}/30$ mm

Sample 61-4: bp $123-168^{\circ}/30$ mm

Sample 61-5 bp $206-216^{\circ}/30$ mm

Sample 61-6 bp $218-223^{\circ}/30$ mm

ir S-CH₂, 2730 cm^{-1} ; S-CH₂, 1420 cm^{-1} ; C-S 700 cm^{-1} ; significant absorption at 3510 , 2550 , 1710 cm^{-1} (Fig. 33).

nmr, ppm 4.21 (2,q), 3.00(16,s), 2.18 (4,m), 1.80 (6,d), 1.41 (1,d) (Fig. 34).

There is also a possibility of C-O absorption at 1150 cm^{-1} .

XI. A. First Attempt to Prepare 1,3-dithiolane:

When 1,2-ethanedithiol (47.1g, 0.5 mole) was heated in ten ml of benzene with 15 g (0.5 mole) of paraformaldehyde, a white solid was the major product, with or without the use of p-toluene sulfonic acid as the catalyst. A yield, after much drying in a vacuum oven, which probably accounts for any desired product and unreacted dithiol, of 33.2 percent was obtained of this white solid. A carbon-hydrogen-

analysis showed 33.7% C, 6.3% H; if the rest is assumed to be sulfur, the empirical formula would be $C_3H_6S_2$. This corresponds to the formula of a linear polymer, $(CH_2-S-CH_2CH_2-S)_x$. The sample melts at 118-119° (lit. 105-110°³⁶): ir S-CH₂, 2720 cm⁻¹; S-CH₂, 1430 cm⁻¹; C-S, 670 cm⁻¹ (Fig. 35). The nmr has not been taken for lack of a solvent, the search for which included toluene, methanol, ethyl acetate, water, carbon tetrachloride, amyl acetate, acetic acid, chloroform, cyclohexanone and dimethyl formamide. This compares with Gibson's description of the polymer he obtained.³⁶ (Sample 13-0)

B. Second Attempt to Prepare 1,3-Dithiolane:

Gaseous formaldehyde was bubbled through a benzene (100 ml) solution of 1,2-ethanedithiol (0.084 mole) and one g of p-toluene sulfonic acid. The product was then washed. A product was obtained, boiling at 67°/17 mm (lit. 65°/14mm³⁷) in a 22.4 percent yield, (sample 29-1).

The nmr spectrum shows an abundance of peaks, too complicated to make any sense of; there are two peaks that may indicate the presence of the desired product:

nmr, ppm 3.05 (s), 4.55 (s) (Figure 36).

The method of preparation followed here was suggested by Fuhrer and Gunthard, who claim a 90 percent yield.³⁸

C. Third Attempt to Prepare 1,3-Dithiolane:

Gaseous formaldehyde generated from paraformaldehyde was bubbled through a benzene (200 ml) solution of 1,2-ethanedithiol (0.2 moles) with 2.5 g p-toluene sulfonic acid as

catalyst. The product was washed with one M sodium hydroxide and water, then dried over calcium chloride. The solution was then distilled, and a 9.4 percent yield was obtained at $90^{\circ}/30$ mm (lit. $65^{\circ}/14$ mm ³⁷), (sample 33-1).

ir S-CH₂, 2680 cm⁻¹; S-CH₂, 1420 cm⁻¹; C-S, 680 cm⁻¹ (Fig. 37)
nmr, ppm 4.13 (2,s), 3.41 (4,s), (Fig. 38).

D. Fourth Attempt to Prepare 1,3-Dithiolane:

Gaseous formaldehyde generated from paraformaldehyde was bubbled through an acetic acid (100 ml) solution of 0.168 mole of 1,2-ethanedithiol. The product was washed with one M sodium hydroxide, water, and then distilled. The product was collected at $71-3^{\circ}/22$ mm in a 5.6 percent yield (0.97 g) (sample 65-1).

ir S-CH₂, 2830 cm⁻¹; S-CH₂, 1420 cm⁻¹; C-S, 680 cm⁻¹; significant absorption at 1685 cm⁻¹ (Fig. 39).
nmr, ppm 4.10 (2,s), 3.40 (4,s) (Fig. 40).

E. Fifth Attempt to Prepare 1,3-Dithiolane:

To one half mole (37.5 g) of aqueous formaldehyde (40%) were added 47.1 g (0.5 mole) of 1,2-ethanedithiol. The reaction took place without the use of a catalyst; it was afterwards heated for several hours to insure completion of the reaction, azeotroping off the water in the process. The solution was distilled and four products were actually obtained, the first being the impure 1,3-dithiolane, (sample 71-2), bp $78-90^{\circ}/26$ mm (lit $65^{\circ}/14$ mm ³⁷), in a 21.2 percent yield. Three other products remain in question.
ir (71-2) S-CH₂, 2850 cm⁻¹; S-CH₂, 1425 cm⁻¹; C-S, 680 cm⁻¹,

significant absorption at 2550 and 3350 cm^{-1} (Fig. 41).
 nmr, ppm 4.05 (2,s), 3.34 (4,s), other peaks indicate impurities, and these two indicate very strongly that the desired product is present. (Fig. 42).

XII. An Attempt at an Exchange with 2,2-Dimethyl-1,3-dithiolane and 3-Pentanone: To 13.4 g (0.1 mole) of 2,2-dimethyl-1,3-dithiolane were added 8.6 g (0.1 mole) of 3-pentanone and 0.2 ml of boron trifluoride etherate. These were heated and a fractionating column was to be employed. After an hour of refluxing, no acetone had distilled over.

XIII. An Exchange with 2,2-Diethyl-1,3-dithiolane and Formaldehyde, A. First Attempt: To (0.125 mole) 20.20 g of 2,2-diethyl-1,3-dithiolane were added (0.125 mole) 3.75 g of paraformaldehyde and 30 ml of benzene with 0.3 g of p-toluene sulfonic acid as catalyst.

The mixture was shaken and refluxed for one and one half hours. The solution steadily turned yellowish, then brownish. The product was distilled on this attempt, under vacuum, immediately losing some of the desired ketone. The solution definitely smelled of 3-pentanone, but difficulties demanded redistillation. The product came over at atmospheric pressure at about 90-100° (there were difficulties in excessive bumping) and a 38 percent recovery of 3-pentanone was obtained (sample 95-2),

ir C O, 1680-1740 cm^{-1} (Fig. 43); a comparison of this spectrum with that of pure 3-pentanone (Fig. 44), shows almost complete identity.

nmr, ppm 0.58 (6,t), 1.91

complete identity.

nmr, ppm 0.58 (6,t), 1.91 (4,q); there are a number of smaller peaks which might be attributed to starting materials, (Fig. 45).

The residue could not be distilled any further due to some apparent continuing reaction, noted through the deepening of the brownish color of the solution, and due to the excessive bumping.

B. Second Attempt: The same procedure was followed as in the above exchange attempt except that (0.375 mole) 60.60 g of the 2,2-diethyl-1,3-dithiolane was used, as well as three times the paraformaldehyde used in the first attempt. The solution was filtered before distillation, and the vacuum was not applied until after the ketone was drawn off. The ketone came off cloudy and low in temperature, so redistillation with a fractionating column was in order. Benzene came off at 80.5-82° and the impure ketone came off at 91-106°. The yield was extremely small, a matter of a few drops. A rough ir scan showed a large amount of ketone in the benzene fraction.

C. Third Attempt: This time the benzene was sacrificed as a solvent. To (0.125 mole) 20.20 g of 2,2-diethyl-1,3-dithiolane was added an excess (about 0.3 mole) of paraformaldehyde and 0.3 g of p-toluene sulfonic acid. The mixture was refluxed for about three hours; the solution was still yellowish, however. The mixture was then distilled and at 83° the first product came off yellowish, about 8.7 g, which

would be an 80.5 percent recovery if it were all ketone. However, redistillation produced about a 40 percent recovery, still impure, boiling at 95-100° (sample 107-1).

ir C=O, 1680-1720 cm^{-1} ; S-CH₂, 1420 cm^{-1} (Fig. 46);

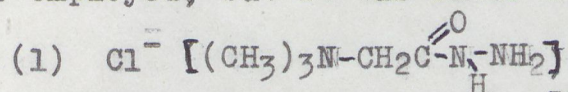
nmr, ppm 0.54 (t), 0.59 (t), 1.91 (q), 2.25 (q) (Figure 47).

The residue, however, was cooled and then distilled under reduced pressure, and 6.5 g of 1,3-dithiolane collected (sample 107-2), a 50 percent recovery, at 67°/15 mm.

ir S-CH₂, 2840 cm^{-1} ; S-CH₂, 1420 cm^{-1} ; C-S, 680 cm^{-1} ; C=O, 1700 cm^{-1} (Fig. 48). The carbonyl absorption is probably due to residue remaining in the condenser.

nmr, ppm 3.92 (2,s), 3.29 (4,s) (Fig. 49). Comparisons to previous data show this to probably be 1,3-dithiolane.

XIV. Attempt to Exchange 2,2-Diphenyl-1,3-dithiolane and Formaldehyde: The same procedure as above was used; no solvent was employed, an excess of paraformaldehyde was used. However, in trying to recover the ketone, Girard's T reagent, (1), was employed, but it was later found that this



reacts only very slowly with benzophenone³⁹, and so no ketone was recovered. The plan was to treat the product mixture with Girard's T reagent, which combines with ketones to form water-soluble compounds. This salt was then to be extracted with water and the ketone recovered by hydrolysis with hydrochloric acid.

Note: IR spectra were made on a Perkin-Elmer 727 infra-

red spectrometer, and NMR spectra were taken on a Varian Associates A-60 NMR spectrometer.

A comparison of typical ir bands in the 1,3-dithiolanes is made in Table 1, Appendix B, the ir spectra in Appendix A. A comparison of NMR spectra of the 1,3-dithiolanes is made in Table 2, Appendix D, the nmr spectra in Appendix C. Table 3, Appendix E, is a table of the dithiolanes and their physical properties.

DISCUSSION

Several interesting things have come out of the exchange. There is a definite indication that the diethyl ketone is regenerated when the 2,2-diethyl-1,3-dithiolane is reacted with paraformaldehyde, and that 1,3-dithiolane is formed. The nmr spectra of the regenerated ketone produced some interesting questions (Fig. 45,47):

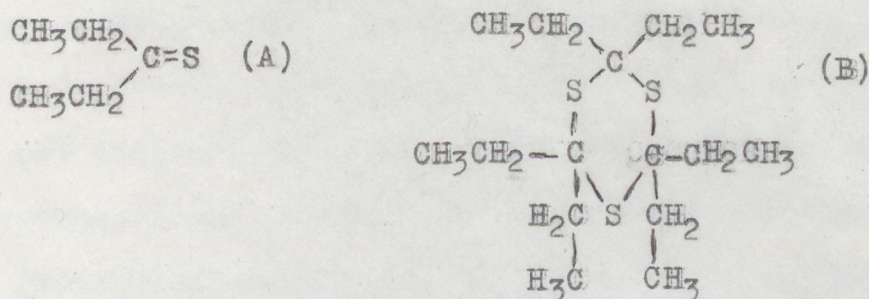
(1) the methyl peaks and the methylene peaks are very far upfield for such a close proximity to a carbonyl group; (methyl obs. 0.58 ppm, accepted 1-1.1 ppm; methylene obs. 1.91 ppm, accepted 2.35-2.4 ppm)⁴⁰. This might be due to a malfunction in the instrument. The TMS peak for these samples was also not observed. A reference diethyl ketone nmr spectrum could not be made because of a failure in the instrument. The ir spectrum seems to identify the product as diethyl ketone, however (Fig. 43,48).

(2) There seems to be a second set of methyl-methylene peaks at 0.55 ppm, 2.25 ppm respectively on Fig. 47, sample 107-1, the ketone fraction of the second exchange attempt. One can find essentially the same thing, only much weaker, in the nmr spectrum of the ketone fraction of the first exchange attempt at 0.61 ppm and 2.21 ppm respectively. If these are methyl and methylene peaks, they might originate from one of two things:

(a) 2,2-diethyl-1,3-dithiolane has methyl absorption at 1.16 ppm and methylene at 2.18 ppm. There is a small triplet at 0.91 ppm. That might account for this compound

in Fig. 45, sample 95-2, the ketone fraction from the first exchange attempt.

(b) The other possibility is tentatively the thioketone (A) or its trimer (B):



Mayer, Morgenstern, and Fabian⁴¹ have found that thioketone monomers, as well as trimers, can be formed from ketones in acid medium, as well as from ketals. However, gem-dithiols are the preferred product over the thioketones for cyclic ketones and the trimers are preferred for low molecular weight alkyl ketones. The boiling point of the diethyl ketone is given as 55-65°/57mm, the refractive index as 1.4776. The refractive index of diethyl ketone, taken in this laboratory, is 1.3934, that of the ketone fraction of the first exchange attempt, sample 95-2, is 1.4268, and that of the ketone fraction of the second exchange attempt is 1.458.

There is evidence in the ir of 95-2 (Fig.43) of C-S stretch at 680 cm⁻¹ and perhaps C=S absorption at 1040 cm⁻¹. The nmr methylene absorption would occur at 1.6 ppm and methyl, although no reference could be found for a methyl group of this environment, would probably lie around 0.8-1.0 ppm; these figures are of little use since the instrument

seemed to be malfunctioning. The ketone fractions of the exchanges seemed to smell of sulfur and the second exchange fraction was colored, as are the reported thioketones.

Other impurities are found in the nmr spectra of the ketone exchange products; in 95-2 and 107-1 absorption at 3.32 indicates 1,3 dithiolane. Three peaks in both mixtures were not identified; 2.67, 1.58, and 1.32 ppm; this could be because of the shift caused by the malfunction.

Impurities can be seen in the 1,3-dithiolane fraction of the exchange (Fig. 49, sample 107-2), such as 1.16 and 1.78 ppm, perhaps an indication of 2,2-diethyl-1,3-dithiolane or diethyl ketone, the latter suggested by the carbonyl absorption in the ir (Fig. 48).

The brown color of the solution of the exchange reaction remains in doubt. It does appear that the amount of brown colored substance increases as the ketone is withdrawn from the solution, but this may be pure coincidence with time.

Purification of the ketone is a very important step. Only when the product can be purified will the true worth, in percent recovery, be realized. Several things may be tried. Different solvents may be tried, so long as they are as neutral as benzene. Perhaps the difficulties lie in the particular boiling point of diethyl ketone, 102°, benzene, 80°, and water 100°. Perhaps 2,2-dimethyl-1,3-dithiolane should be tried next, taking care not to lose the product by evaporation. Better fractionating columns could be used. Matters might also be facilitated by neutralizing the solution

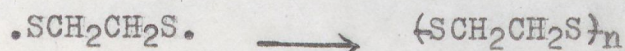
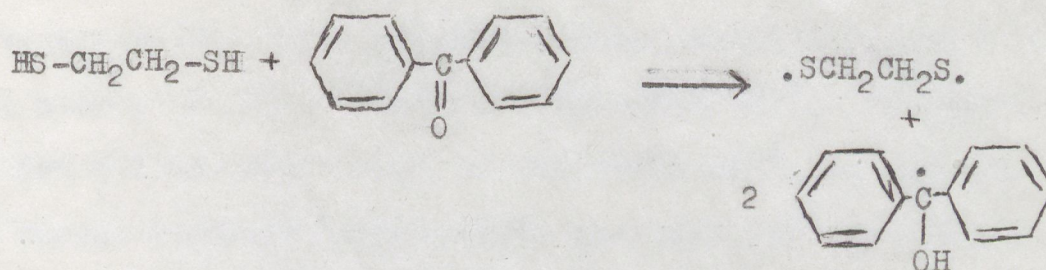
before distillation, as acid initiates the formation of the thioketones and the trimers, or perhaps the deep brown color; perhaps these are one and the same.

As per solid ketones, benzophenone was an unlucky choice. The exchange should be tried on the benzoylacetone thioketal, using Girard's T reagent. It was noted by Fieser³⁹ that Girard's T reagent reacted only very slowly with benzophenone. Another way to separate a solid ketone from the solution should be searched out, in the case of non-steroid carbonyl compounds.

The byproducts of the benzophenone reaction are interesting to speculate on. The insoluble floc (sample 47-1) formed in the first attempted preparation of the 2,2-diphenyl-1,3-dithiolane is still in question. It seems to have sulfur in it from the ir spectrum (p. 15), but there is also evidence of carbonyl. If an nmr could be taken, more could be said about the compound, but it is a solid, and no solvent could be found for it. One could almost make a case for some type of oxide of sulfur, as the $S=O$ absorption is in the 1070-1030 cm^{-1} range, and there is some small absorption noted in the spectrum of 47-1 (Fig. 9), but $S=O$ absorption is normally strong, and it isn't here.

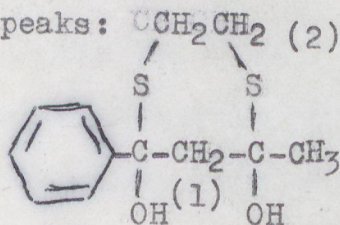
The brown powder (sample 89-1) formed when the dithiolane was made is of interest as well. An eight membered ring was suggested earlier, as was a polymer of similar composition (p.16). Sheffer has suggested the following: it is known that there is a transition of benzophenone to the triplet

state in the presence of light. It is possible, then for the following to happen:



This would account for the insolubility and for the C-H analysis.

The byproduct of the reaction of benzoylacetone with 1,2-ethanedithiol, sample 63-1, was interesting in that it seemed to react with DMSO upon standing, forming, in a matter of days, a bright, red-brown solution. It was this complication, plus the fact that DMSO was the only solvent found for 63-1, that makes the nmr spectrum questionable. It was suggested by Sheffer that the following structure could be assigned to it on the basis of a rough integration of the nmr peaks:



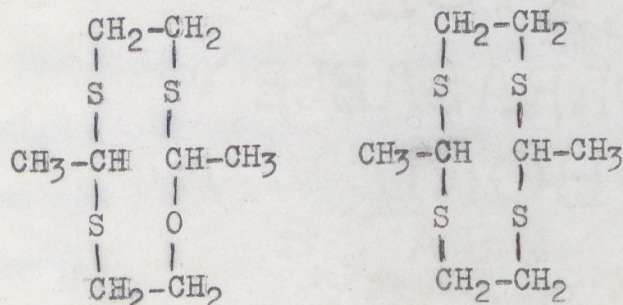
It is assumed in the explanation of the integration (p.17) that the methyl group hydrogen have perhaps the same absorption as the methylene (1) group hydrogen. There is a possibility for this as seen by the ir O-H absorption, weak as it is, at 3450 cm^{-1} (p. 17). A better picture can be

gained through a C-H analysis.

The products of the preparations of 2-methyl-1,3-dithiolane are extremely interesting, as the ir and nmr spectra are very similar. The ir spectra show absorptions about 1690, 2550, some at 1150, and some at 3420-3500 cm^{-1} . The absorption for S-H stretch occurs at 2600-2500 cm^{-1} , C=O absorption occurs anywhere between 1540 and 1870 cm^{-1} with dimerized aliphatic acids absorbing between 1665 and 1720 cm^{-1} ; C-O absorption can be from 1000 to 1300 cm^{-1} , with tertiary ethers absorbing from 1150 to 1185 cm^{-1} , and tertiary alcohols absorbing from 1120 to 1200 cm^{-1} . The absorption at 3420-3500 cm^{-1} is probably acidic or alcoholic -OH.⁴⁰

Acetaldehyde easily condenses with itself to produce an aldol. This process can continue for long chain lengths. Acetaldehyde also forms a cyclic compound, paraldehyde. The condensation products can dehydrate, to give unsaturated compounds. With all these possibilities it is reasonable to have such a gamut of compounds. Note: the the ir absorption for C=C is at 1670-1640 cm^{-1} .

It is feasible, because of the high reactivity of acetaldehyde and of 1,2-ethanedithiol that compounds such as the following rings could also be synthesized:

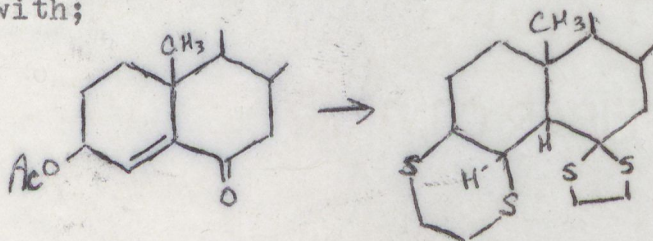


CONCLUSIONS

The final idea here is that the exchange does indeed work, the mechanism of which is still questionable. Further experimentation should be done with the exchange to try for optimum conditions, and to try to isolate the possible thioketone or its trimer. Changing solvents is one course of action. Using gaseous formaldehyde directly, trioxane, or perhaps methylal (methylal was reacted with 1,3-propanedithiol to give 1,3-dithiane)⁴² is another.

The future of the exchange may lie in steroid chemistry. According to Dauben⁴³ and his coworkers, a similar exchange involving dioxalanes is very useful in preparatory work of steroids, where the steroid dioxalane was prepared using an exchange with a simple dialkyl 1,3-dioxalane. The same thing might be tried with the dithiolanes.

If the exchange does work in this fashion, then it might be tried on something that Fieser⁴⁴ found difficulties with;



The dithiolane was prepared with ethanedithiol. The exchange, hopefully, would only react at the carbonyl site, or perhaps at the carbonyl in the acetate, which could be reversed.

Appendix A: IR spectra:

REMARKS

ORIGIN

PURITY

SPEED ~~Normal~~ NORMAL ☒ FASTSLITS ☒ NORMAL ☐ WIDEPHASE Liq. Neat

CONCENTRATION

THICKNESS AgCl cellsDATE 10/25/73OPERATOR J.G.

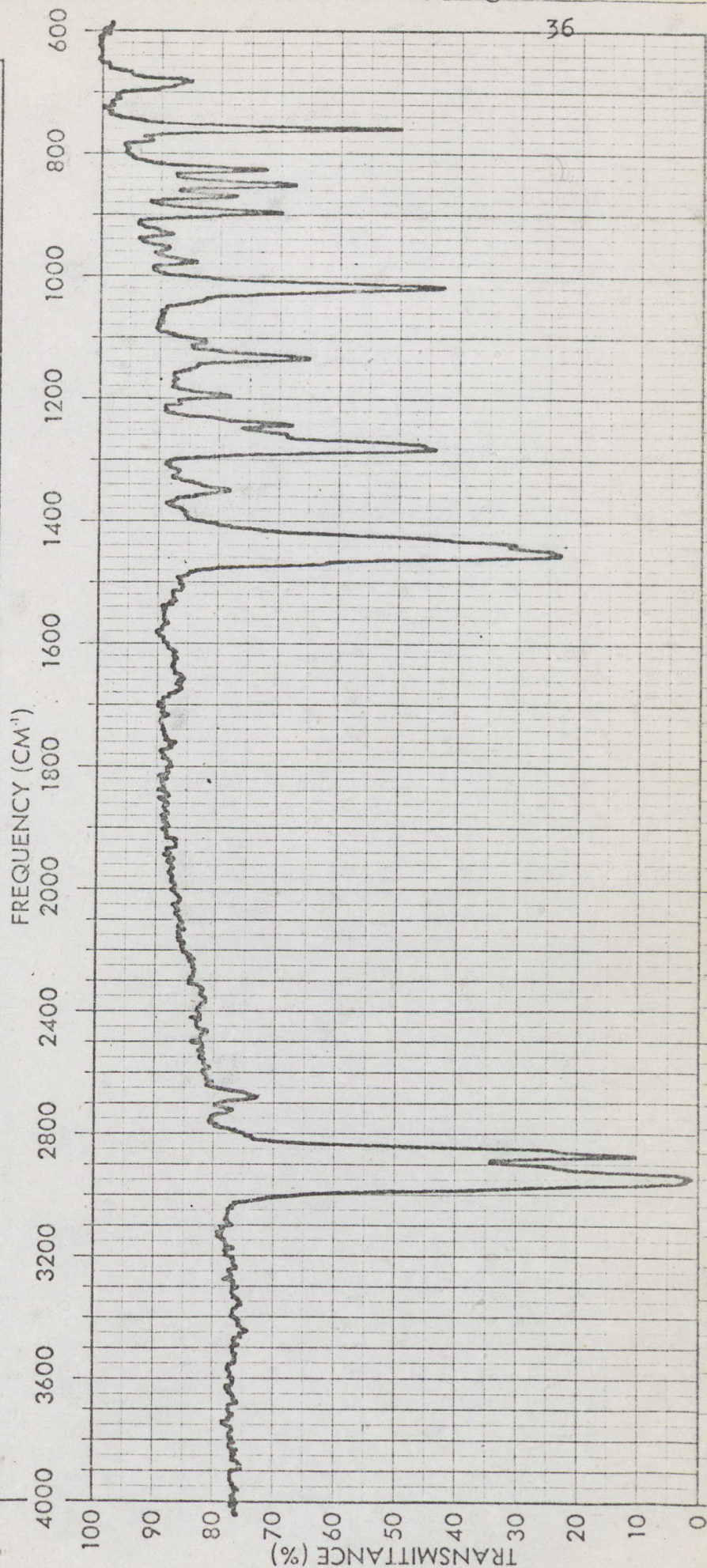
PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1

5-1

SAMPLE 2



PERKIN-ELMER

ORIGIN _____

PURITY _____

SPEED _____ NORMAL ☒ FAST _____SLITS _____ NORMAL ☒ WIDE _____

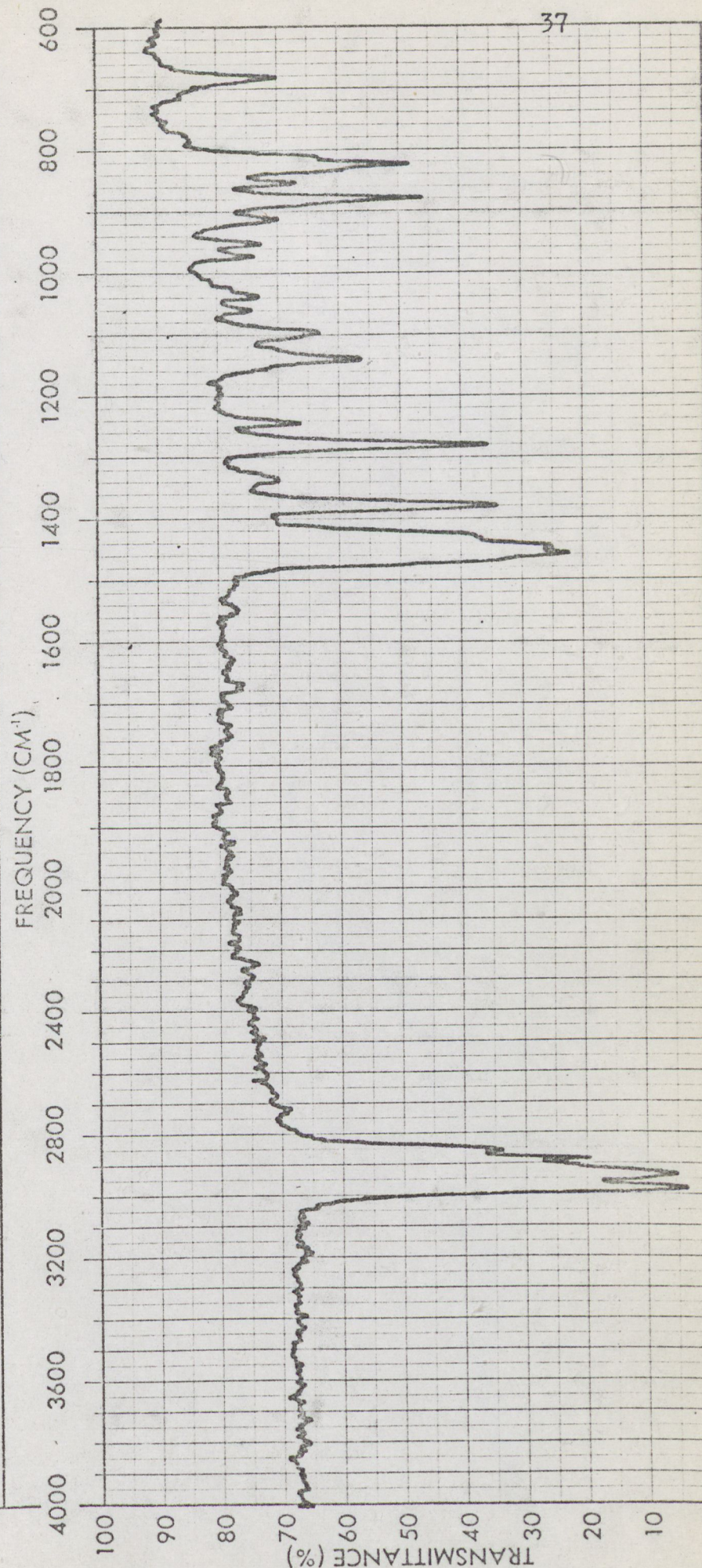
PHASE _____

CONCENTRATION *rest*THICKNESS *AgCl cells*DATE *10/25/73*OPERATOR *J.G.*

SPECTRUM NO. _____

SAMPLE 1 *53**29-2**et*

SAMPLE 2 _____



REMARKS

ORIGIN

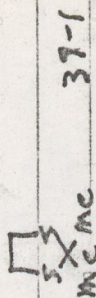
PURITY

SPEED NORMAL ☒ FASTSLITS NORMAL ☒ WIDEPHASE liquidCONCENTRATION NeatTHICKNESS AgCl cellsDATE 11/17/73OPERATOR J.G.

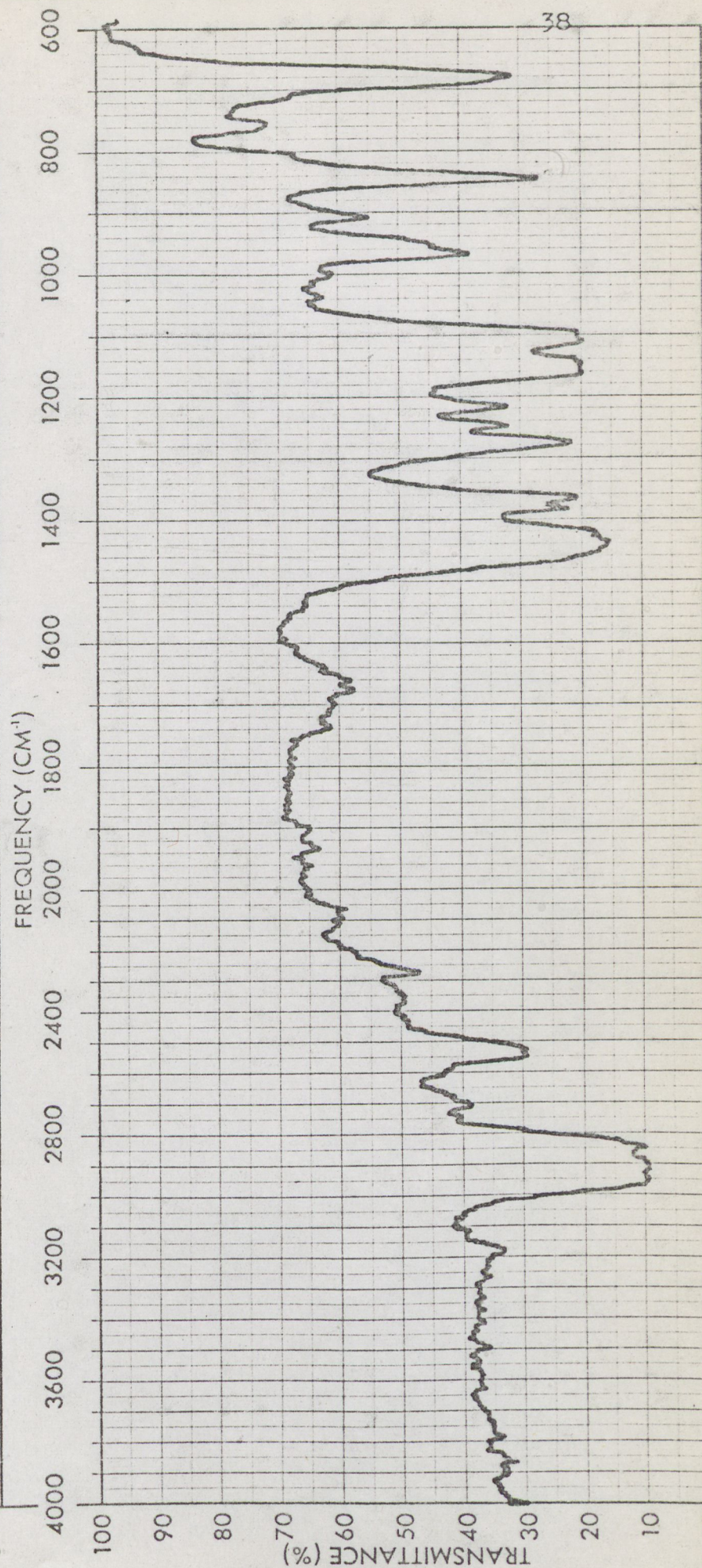
PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1


39-1

SAMPLE 2



REMARKS

ORIGIN

PURITY

SPEED NORMAL ☒ FASTSLITS NORMAL ☒ WIDE

PHASE New Sol Mull

CONCENTRATION

THICKNESS AgCl cells

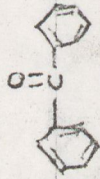
DATE 12/11/73

OPERATOR S.G.

PERKIN-ELMER

SPECTRUM NO. 47-2

SAMPLE 1



SAMPLE 2

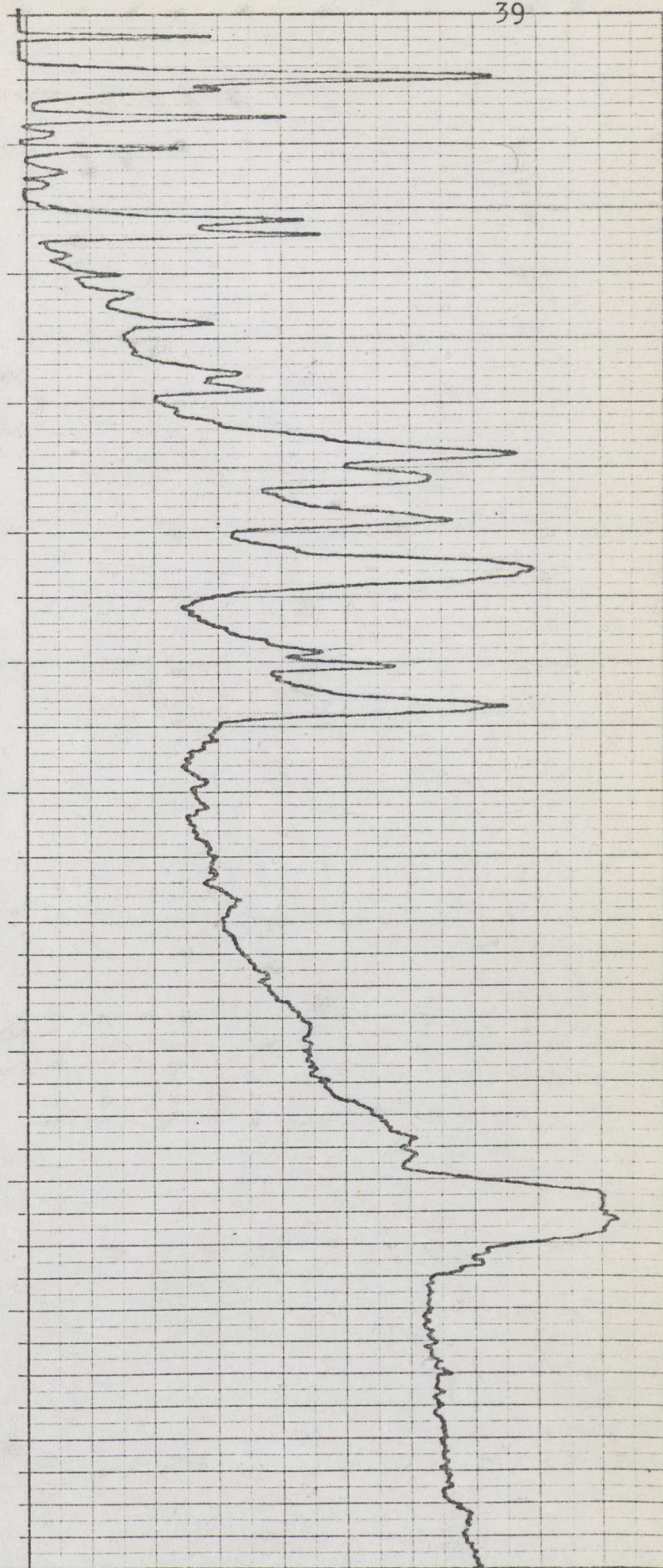
FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

TRANSMITTANCE (%)

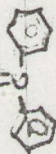
100 90 80 70 60 50 40 30 20 10 0

39



PERKIN-ELMER

SPECTRUM NO. _____

SAMPLE 1 Benzophenone

SAMPLE 2 _____

ORIGIN _____

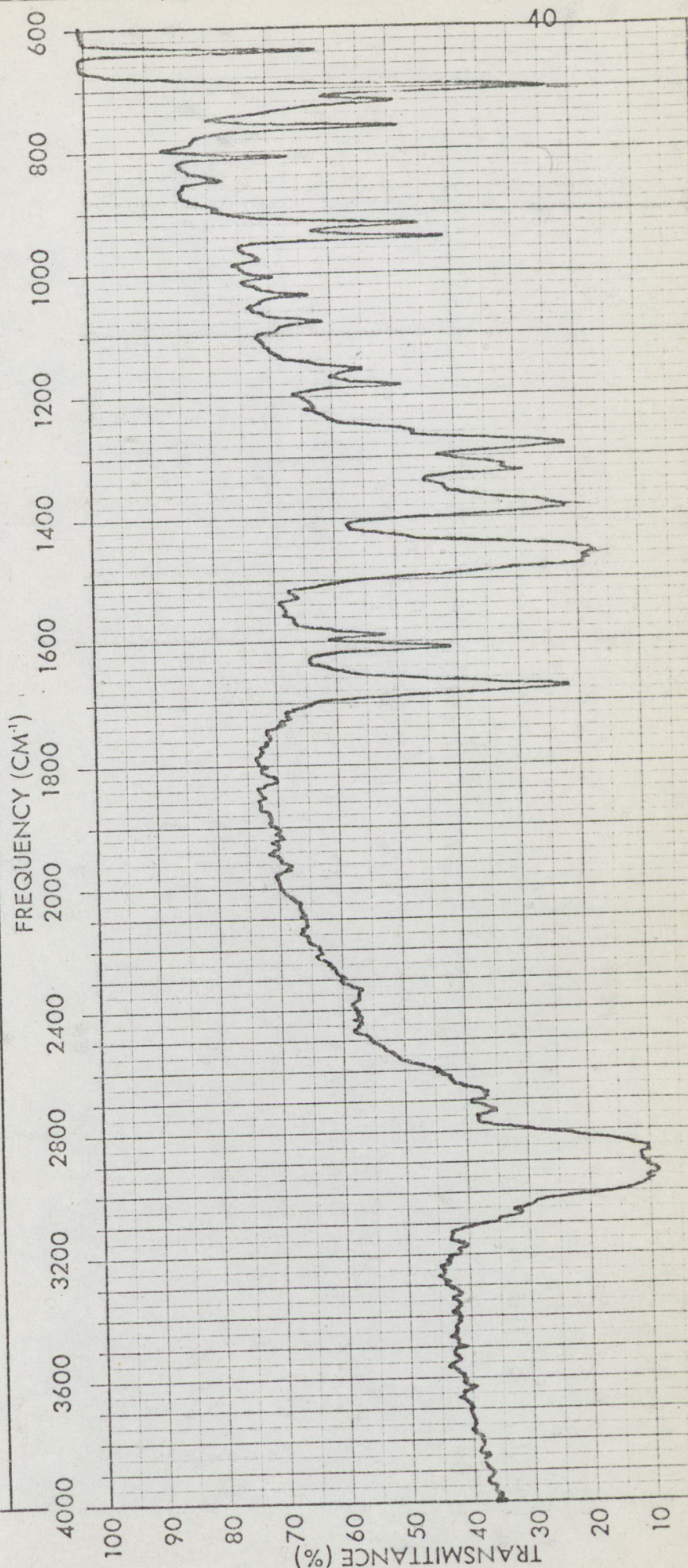
PURITY _____

SPEED _____ NORMAL ☒ FAST _____SLITS _____ NORMAL ☒ WIDE _____

PHASE _____

CONCENTRATION Nuzol MaltTHICKNESS AgCl CellsDATE 12/11/73OPERATOR J. G.

REMARKS _____



REMARKS

ORIGIN

PURITY

PHASE

CONCENTRATION

THICKNESS

DATE

OPERATOR

RECORDING CHARTS

GRAPHIC CONTROLS CORPORATION

BUFFALO, NEW YORK

PRINTED IN U.S.A.

SPECTRUM NO.

SAMPLE 1

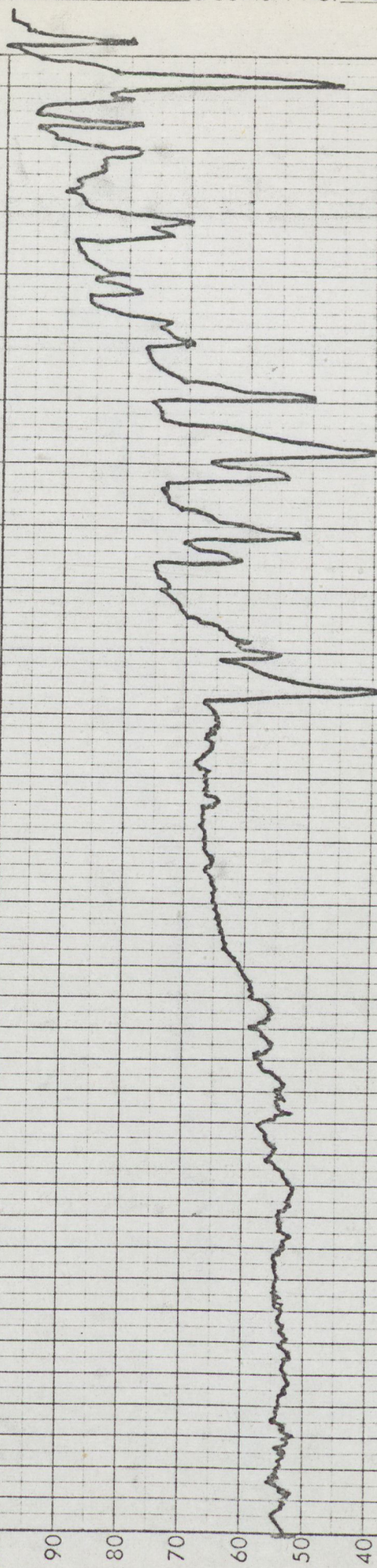
SAMPLE 2

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 650

TRANSMITTANCE (%)

100 90 80 70 60 50 40 30 20 10 0



PERKIN-ELMER

REMARKS

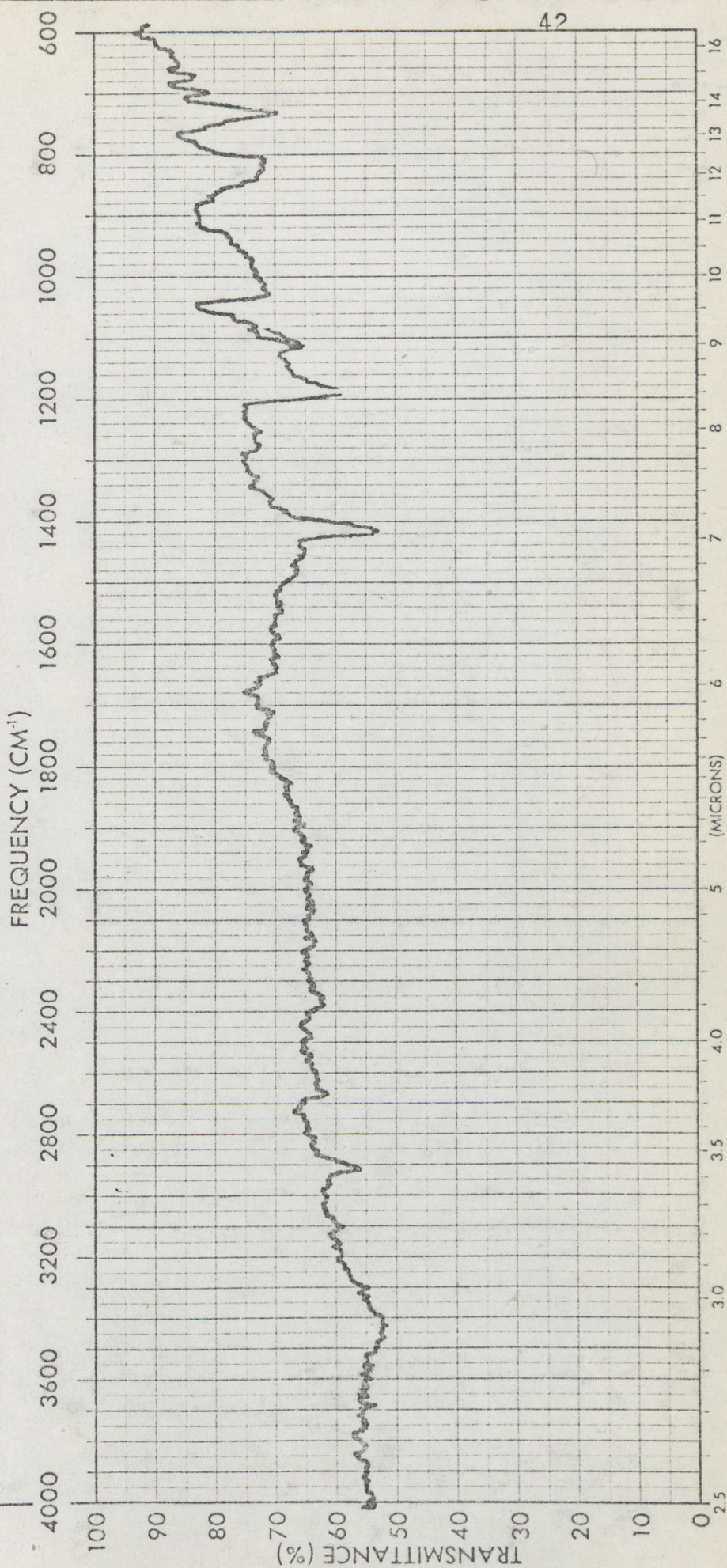
ORIGIN _____
PURITY _____
SPEED _____ NORMAL ☒ FAST _____
SLITS _____ NORMAL ☒ WIDE _____
PHASE _____ ☒ Br. pellet _____
CONCENTRATION _____
THICKNESS _____
DATE 1/10/74
OPERATOR J.G.

SPECTRUM NO. _____

SAMPLE 1 89-1

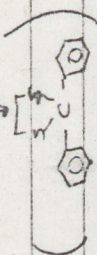
BY PRODUCT OF BENZOPHENONE

REXN.

SAMPLE 2 $\text{fS-CH}_2\text{CH}_2\text{-St}_x$ 

PERKIN-ELMER

SPECTRUM NO. 85-2

SAMPLE 1 $\text{H-S-CH}_2\text{CH}_2\text{H} + \text{C}_6\text{H}_5\text{I}$ 

SAMPLE 2

ORIGIN

PURITY

SPEED NORMAL ☒ FASTSLITS NORMAL ☒ WIDE

PHASE KBr pellet

CONCENTRATION

THICKNESS

DATE 1/10/74

OPERATOR J.G.

REMARKS

FREQUENCY (CM⁻¹)

600

800

1000

1200

1400

1600

1800

2000

2400

2800

3200

3600

4000

100

90

80

70

60

50

40

30

20

10

0

TRANSMITTANCE (%)

43

PERKIN-ELMER

REMARKS

ORIGIN

63-1

PURITY

SPEED

☒

NORMAL

FAST

SLITS

☒

NORMAL

WIDE

PHASE

CONCENTRATION 2.5% in CH₂Cl₂

THICKNESS matched cells

DATE 12/13/73 Gunther

OPERATOR

SPECTRUM NO.

SAMPLE 1

63-1

SAMPLE 2

FREQUENCY (CM⁻¹)

600

800

1000

1200

1400

1600

1800

2000

2400

2800

3200

3600

4000

TRANSMITTANCE (%)

100

90

80

70

60

50

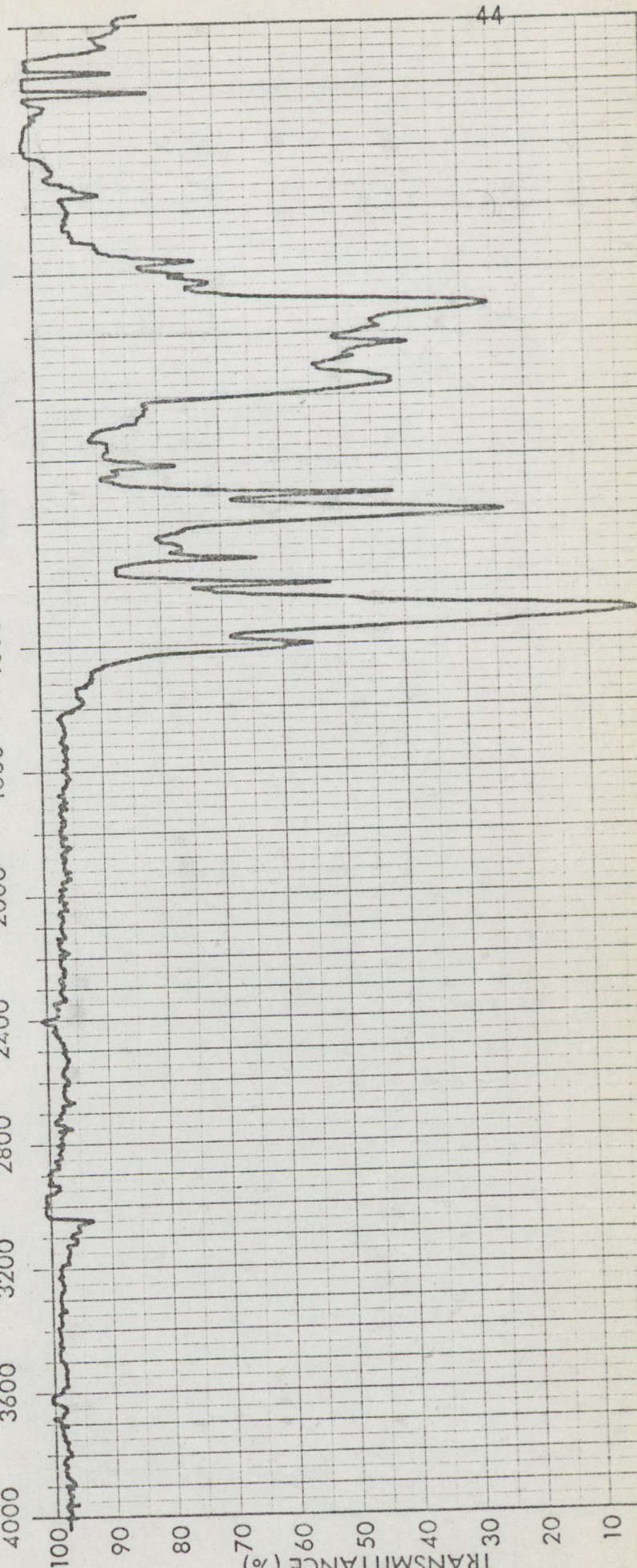
40

30

20

10

44



PERKIN-ELMER

REMARKS

ORIGIN

PURITY

SPEED

NORMAL ☒ FAST

SLITS

NORMAL ☒ WIDE

PHASE

KBr pellet

CONCENTRATION

THICKNESS

DATE

12/14/73

OPERATOR

J. G.

SPECTRUM NO.

SAMPLE 1

(03-1)

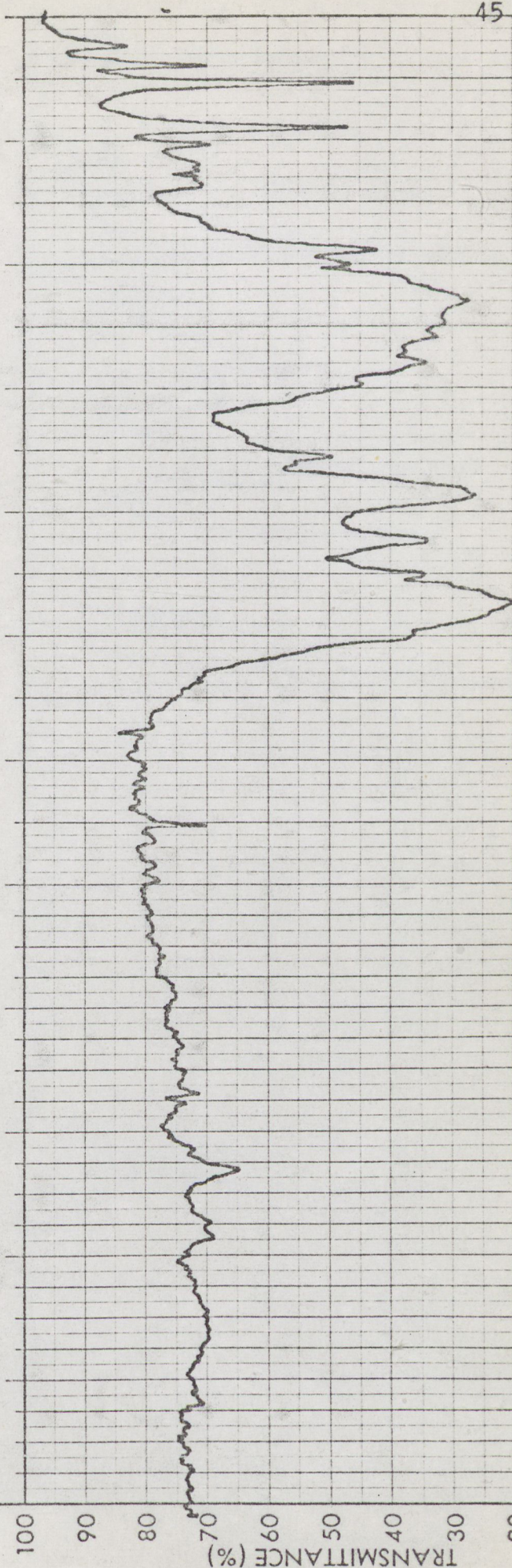
SAMPLE 2

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

TRANSMITTANCE (%)

100 90 80 70 60 50 40 30 20 10



PERKIN-ELMER

ORIGIN _____

PURITY _____

SPEED _____ NORMAL ☒ FAST _____SLITS _____ NORMAL ☒ WIDE _____

PHASE Chloroform Soln.

CONCENTRATION ~10%

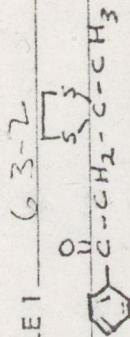
THICKNESS NaCl matched cells

DATE 12/11/73

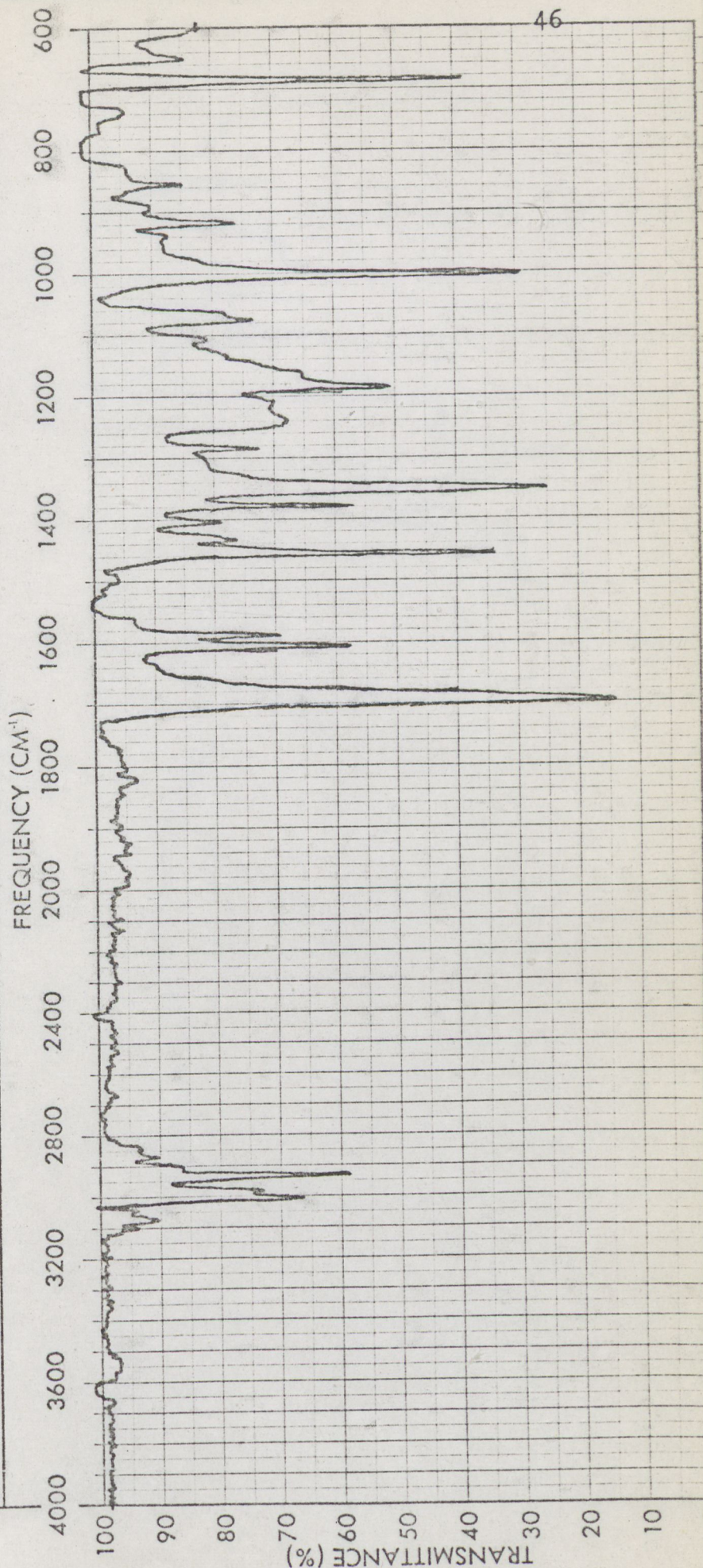
OPERATOR S.G.

SPECTRUM NO. _____

SAMPLE 1



SAMPLE 2 _____



PERKIN-ELMER

ORIGIN _____

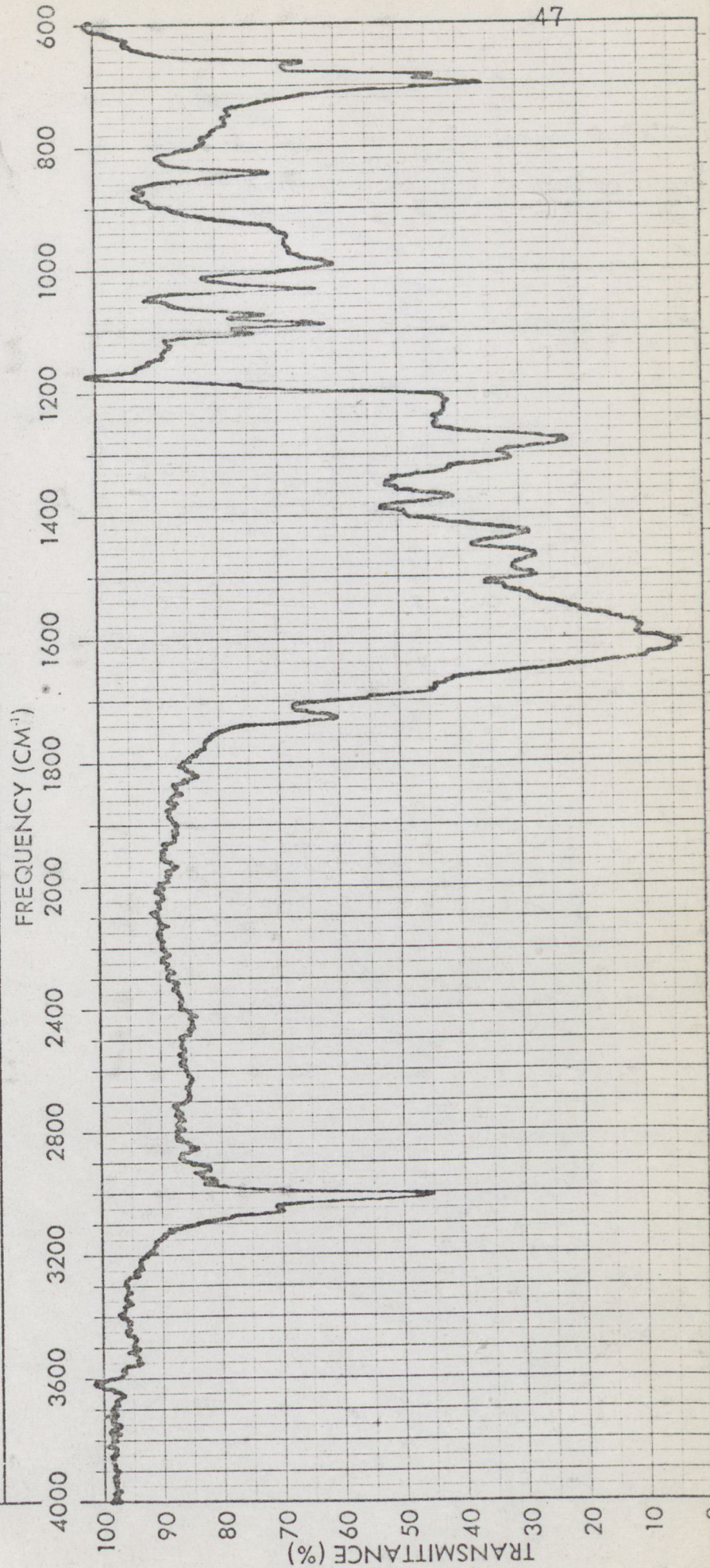
PURITY _____

SPEED _____ NORMAL ☒ FAST _____SLITS _____ NORMAL ☒ WIDE _____PHASE Chloroform soln.CONCENTRATION ~ 10%THICKNESS N x 11 matched cellsDATE 11/9/73OPERATOR J. G.

SPECTRUM NO. _____

SAMPLE 1 (10)1-benzoylacetone

SAMPLE 2 _____



PERKIN-ELMER

ORIGIN _____

PURITY _____

SPEED _____ NORMAL ☒ FAST _____SLITS _____ NORMAL ☒ WIDE _____

PHASE _____ liquid

CONCENTRATION _____ neat

THICKNESS _____ AgCl cells

DATE 11/9/73

OPERATOR J.G.

SPECTRUM NO. _____

SAMPLE 1 _____

53

H₂C=CH₂

41-1

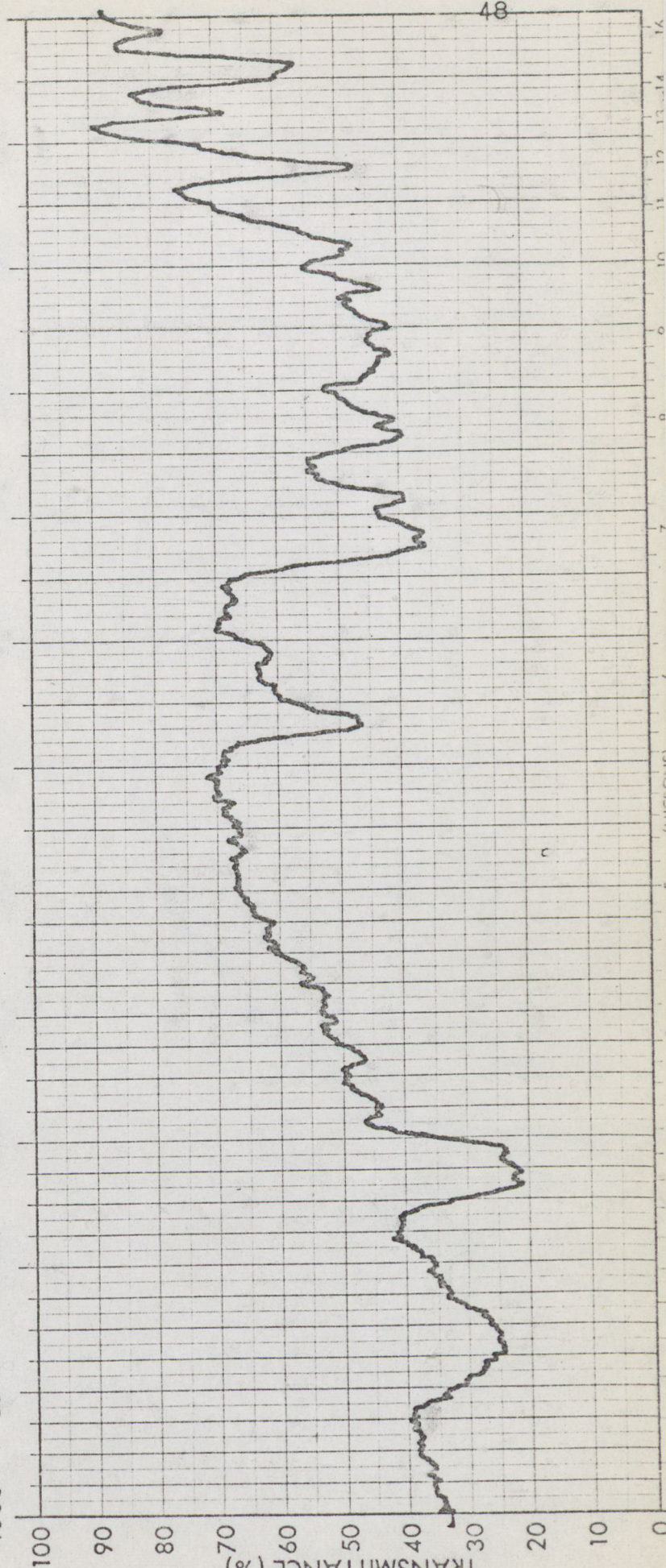
SAMPLE 2 _____

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

TRANSMITTANCE (%)

100 90 80 70 60 50 40 30 20 10 0



REMARKS

ORIGIN

PURITY

SPEED

NORMAL

FAST

SLITS

NORMAL

WIDE

PHASE

liquid

CONCENTRATION

neat

THICKNESS

AgCl cells

DATE

11/9/73

OPERATOR

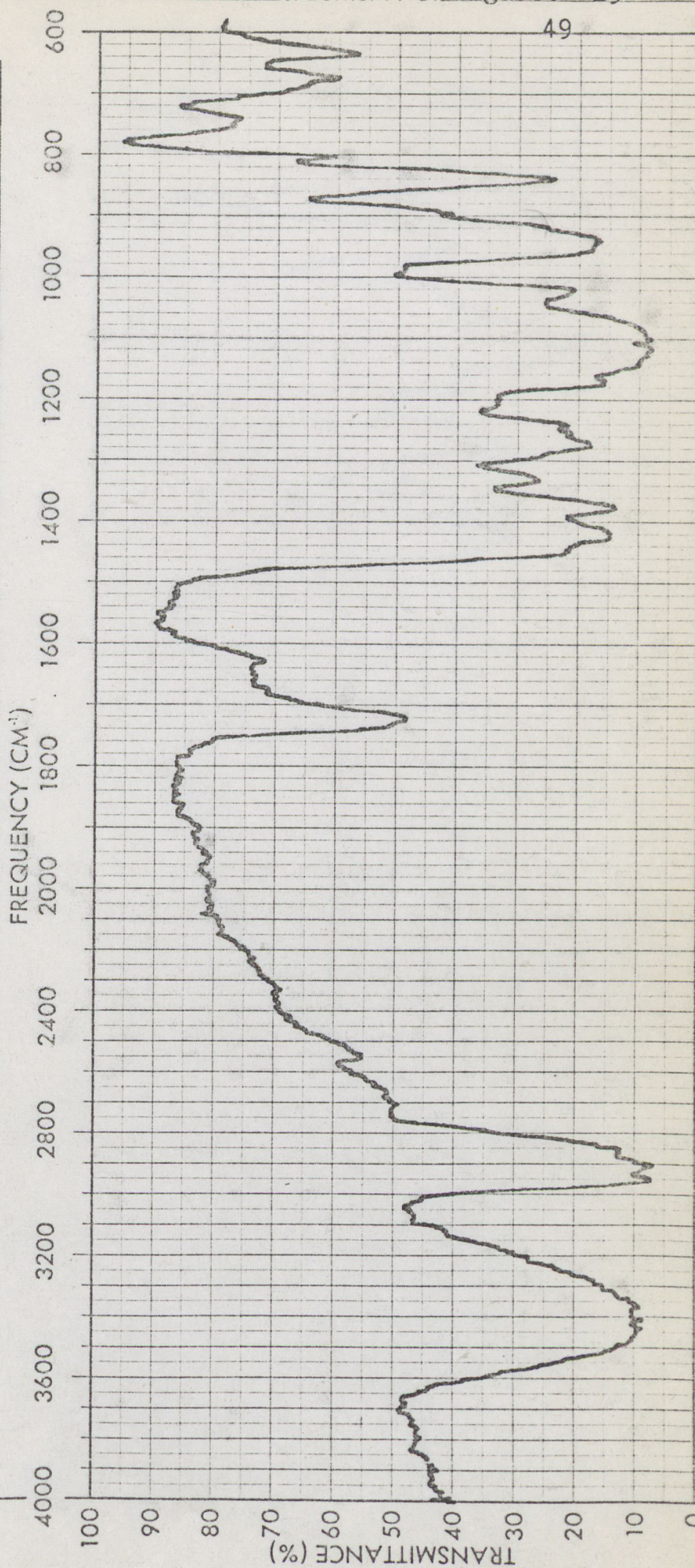
J.G.

PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1 41-3

SAMPLE 2



PERKIN-ELMER

REMARKS

ORIGIN

PURITY

SPEED NORMAL ☒ FASTSLITS NORMAL ☒ WIDE

PHASE liquid

CONCENTRATION neat

THICKNESS AgCl cells

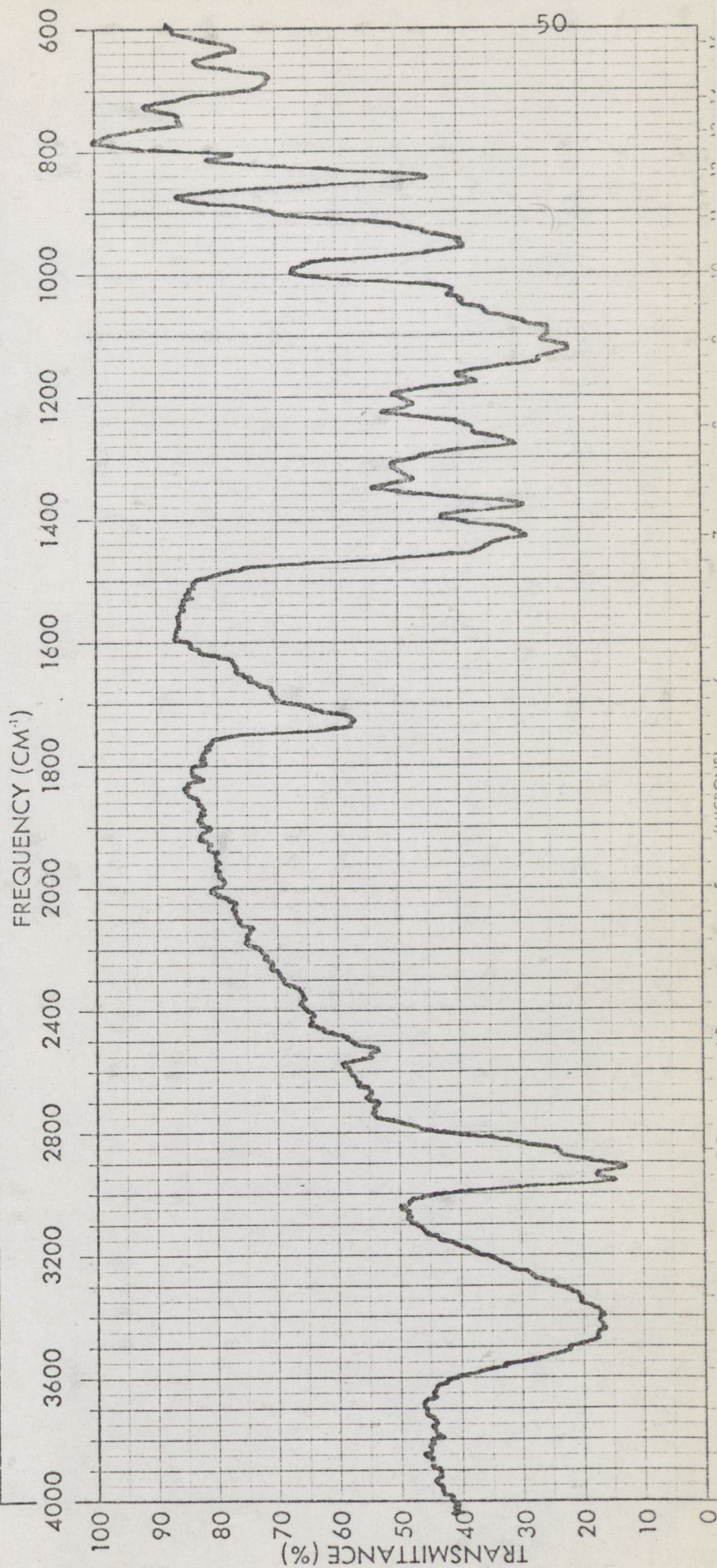
DATE 11/9/73

OPERATOR J. G.

SPECTRUM NO.

SAMPLE 1 41-4

SAMPLE 2



PERKIN-ELMER

REMARKS

ORIGIN

PURITY

SPEED

NORMAL

FAST

SLITS

NORMAL

WIDE

PHASE

liquid

CONCENTRATION

creat

THICKNESS

AgCl cells

DATE

11/9/73

OPERATOR

J.G.

SPECTRUM NO.

SAMPLE 1

41-5

SAMPLE 2

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

100

90

80

70

60

50

40

30

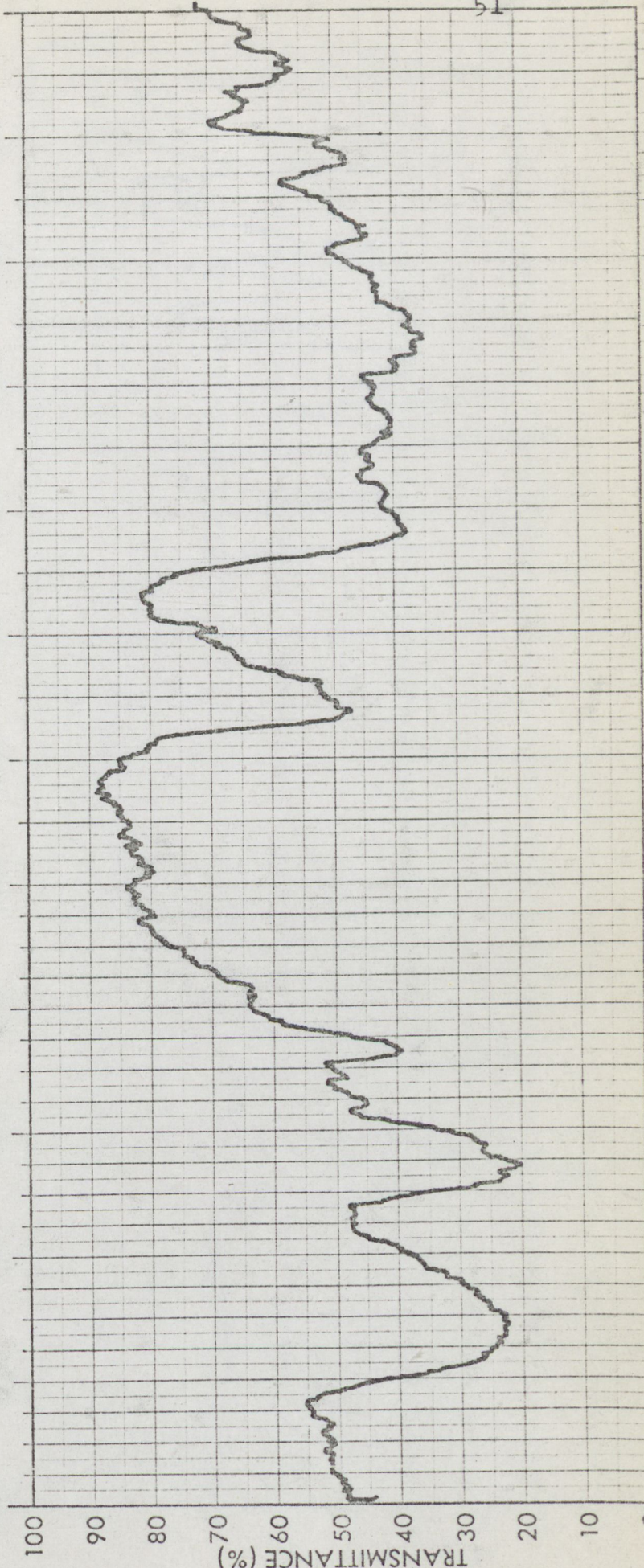
20

10

0

TRANSMITTANCE (%)

51



RECORDING CHARTS

GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
PRINTED IN U.S.A.

SPECTRUM NO. _____

SAMPLE 1

47-159-1

SAMPLE 2

33
H₂CN₂

ORIGIN _____

PURITY _____

PHASE

reat

CONCENTRATION _____

THICKNESS

AgCl cells

DATE

3/6/74

OPERATOR

J.G.

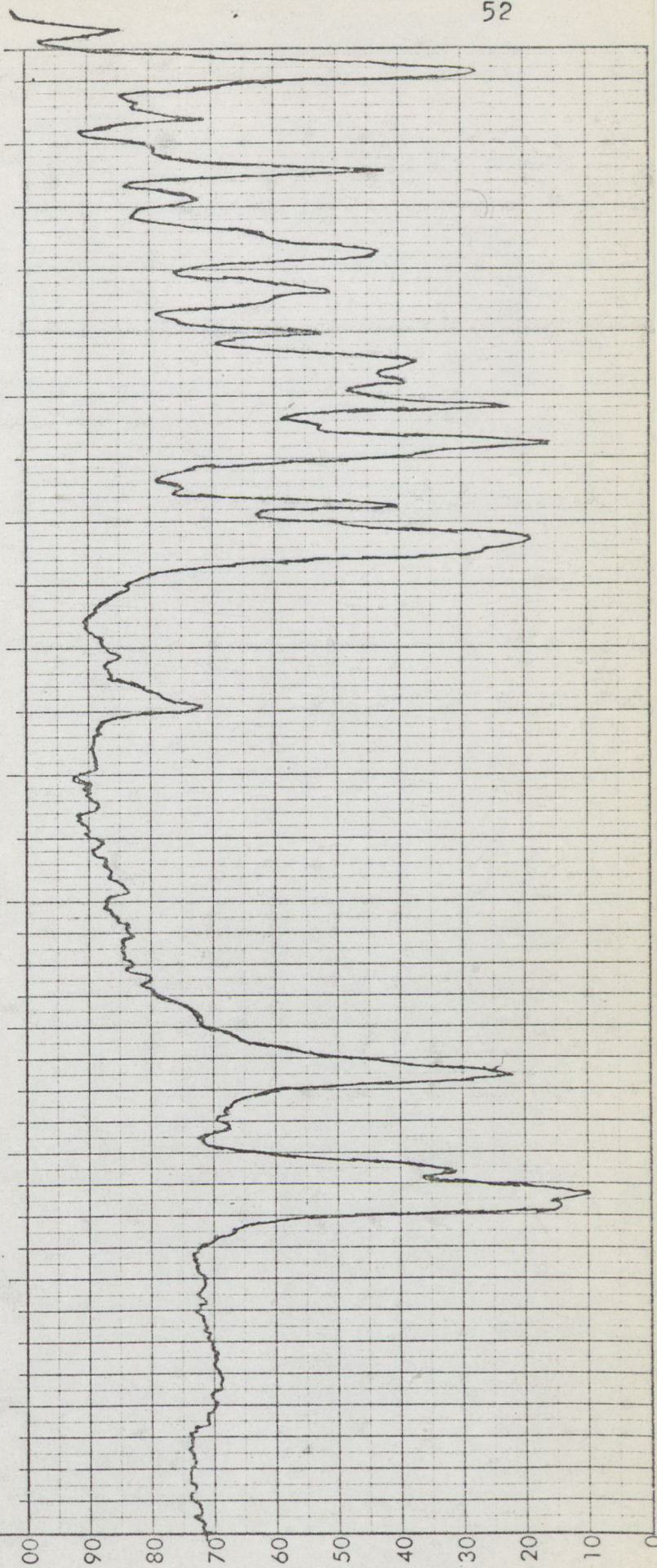
REMARKS

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 650

TRANSMITTANCE (%)

100 90 80 70 60 50 40 30 20 10 0



GRAPHIC CONTROLS CORPORATION
BUFFALO, N. Y. 14203
PRINTED IN U.S.A.

ORIGIN _____

PURITY _____

PHASE _____

CONCENTRATION _____

THICKNESS _____

DATE _____

OPERATOR _____

SPECTRUM NO. _____

SAMPLE 1 _____

SAMPLE 2 _____

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 650

TRANSMITTANCE (%)

100

90

80

70

60

50

40

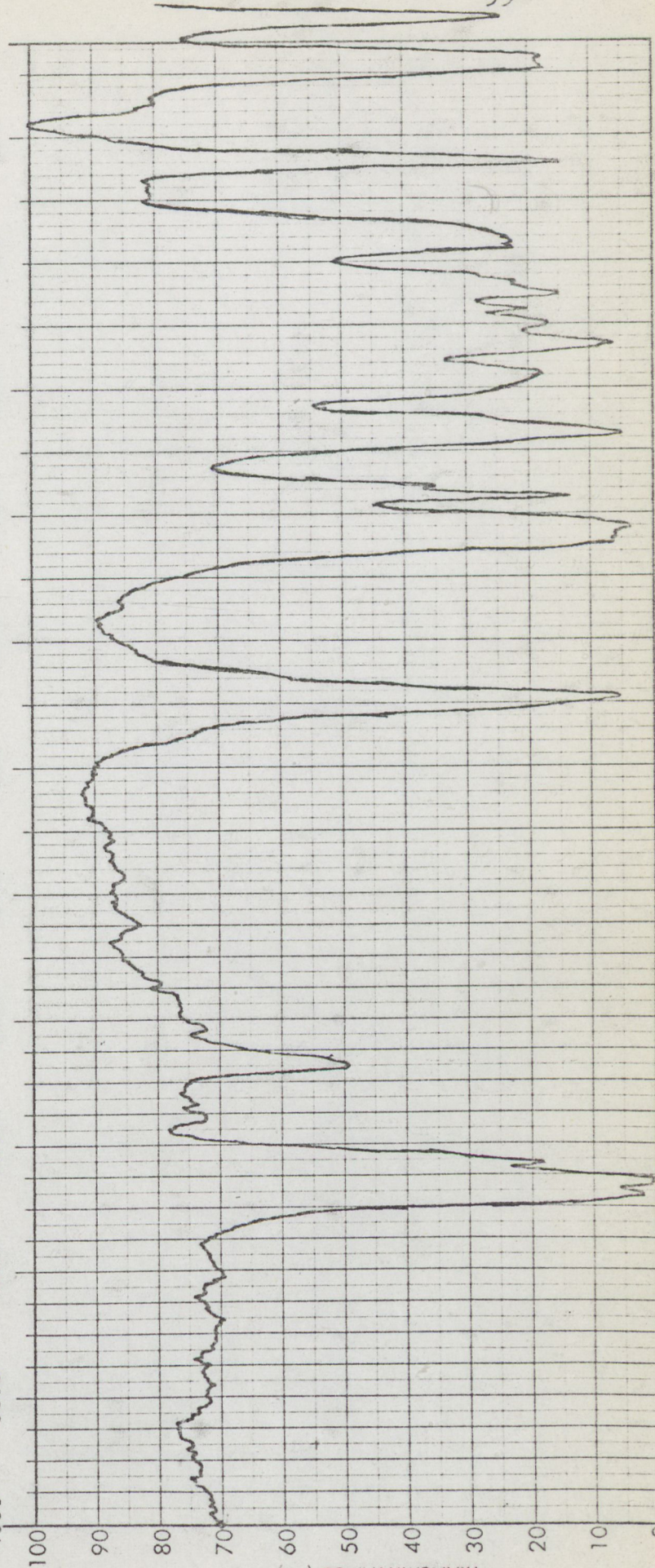
30

20

10

0

REMARKS _____



RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
PRINTED IN U.S.A.

SPECTRUM NO. _____

SAMPLE 1 59-3

SAMPLE 2 _____

ORIGIN _____

PURITY _____

PHASE _____

CONCENTRATION _____

THICKNESS _____

DATE _____

OPERATOR _____

heat

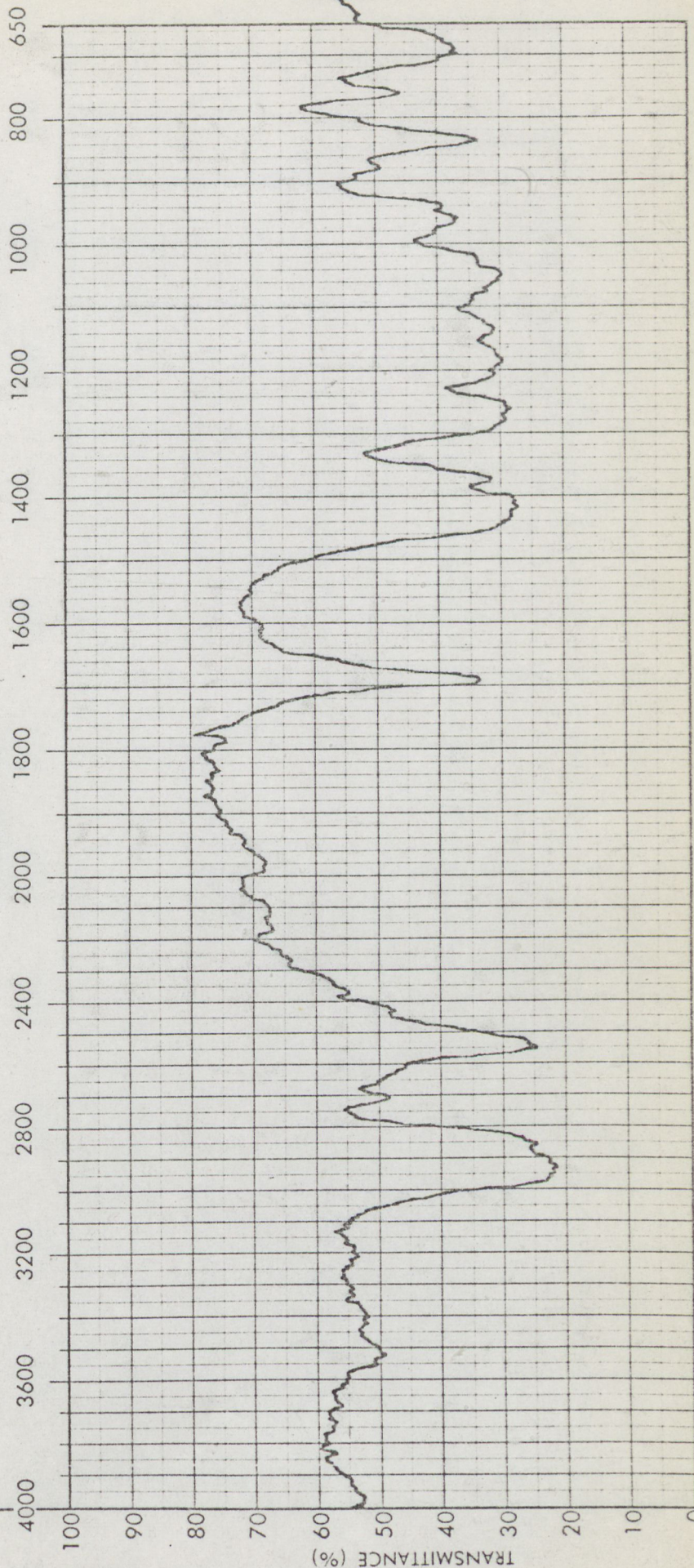
AgCl cells

3/6/74

J. G.

REMARKS

FREQUENCY (CM⁻¹)



RECORDING CHARTS

GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
PRINTED IN U.S.A.

REMARKS

ORIGIN

SPECTRUM NO.

PURITY

SAMPLE 1

PHASE

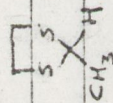
CONCENTRATION

THICKNESS

DATE

OPERATOR

61-1



SAMPLE 2

AgCl cells

3/6/74

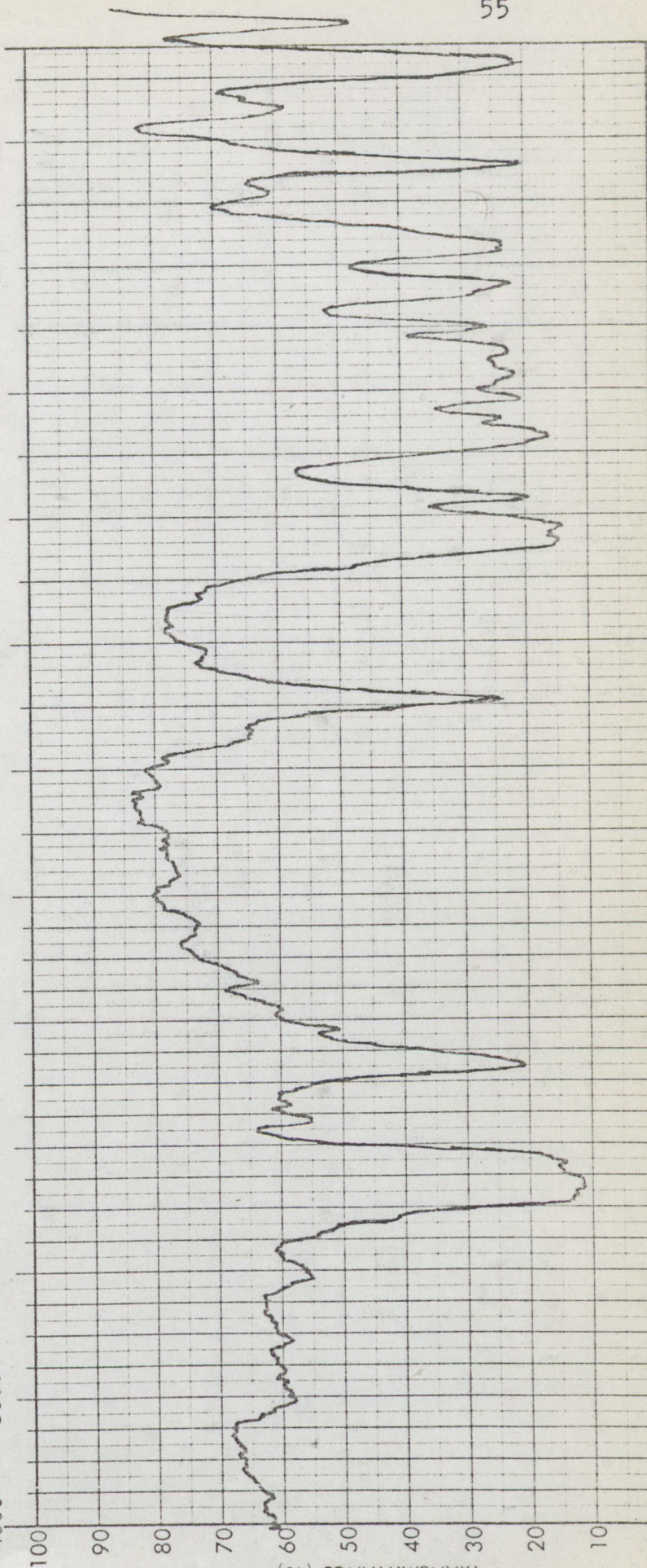
J.G.

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 650

TRANSMITTANCE (%)

100 90 80 70 60 50 40 30 20 10 0



RECORDING CHARTS

GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
PRINTED IN U.S.A.

ORIGIN _____

PURITY _____

PHASE _____

CONCENTRATION _____

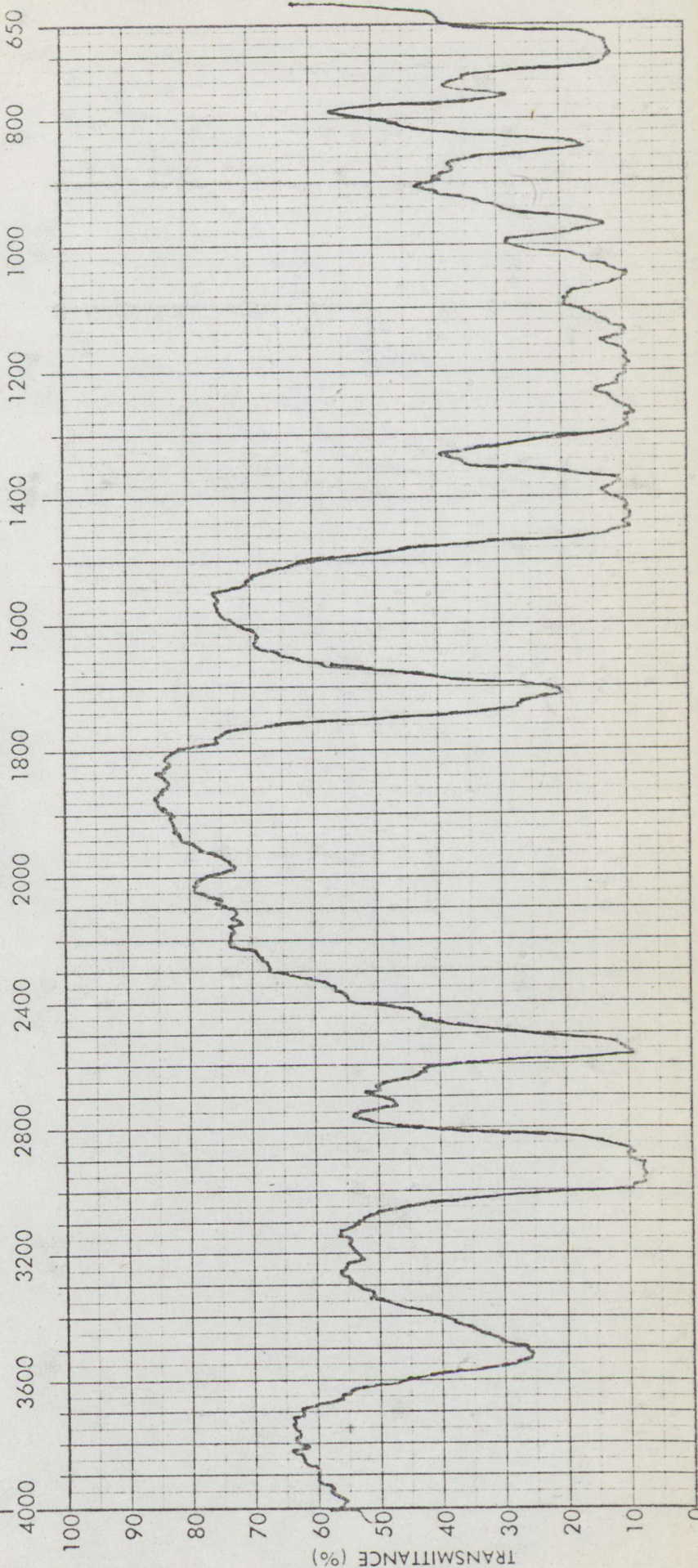
THICKNESS Ag Cl cellsDATE 3/6/77OPERATOR J.G.

SPECTRUM NO. _____

SAMPLE 1 61-6

SAMPLE 2 _____

REMARKS _____

FREQUENCY (CM⁻¹)

REMARKS

Solid sample -
PERMAPS LINEAR
POLYMER

ORIGIN _____

PURITY _____

SPEED _____ NORMAL ☒ FAST _____SLITS _____ NORMAL ☒ WIDE _____

PHASE _____ MULTIPLE - NO SOL

CONCENTRATION _____

THICKNESS _____ AgCl Cells

DATE _____ 10/25/73

OPERATOR _____ J. G.

PERKIN-ELMER

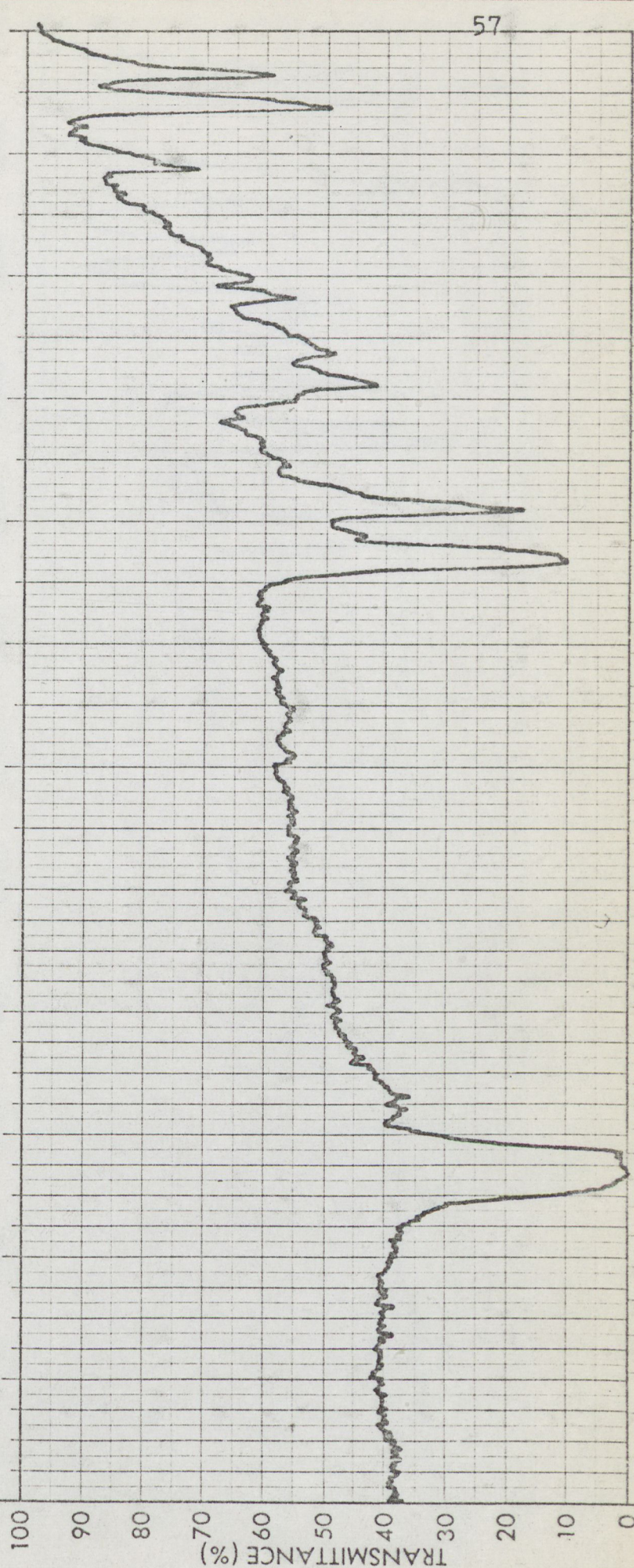
SPECTRUM NO. 13-0

SAMPLE 1 HS-CH₂-CH₂-SH + (CH₂O)_x →~~HS-CH₂-S-CH₂-CH₂-S-~~

SAMPLE 2 _____

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600



PERKIN-ELMER

REMARKS

ORIGIN

PURITY

SPEED ☒ NORMAL ☐ FASTSLITS ☒ NORMAL ☐ WIDE

PHASE

CONCENTRATION Heat

THICKNESS

DATE 12/13/73OPERATOR C. H. H. H.

SPECTRUM NO.

SAMPLE 1

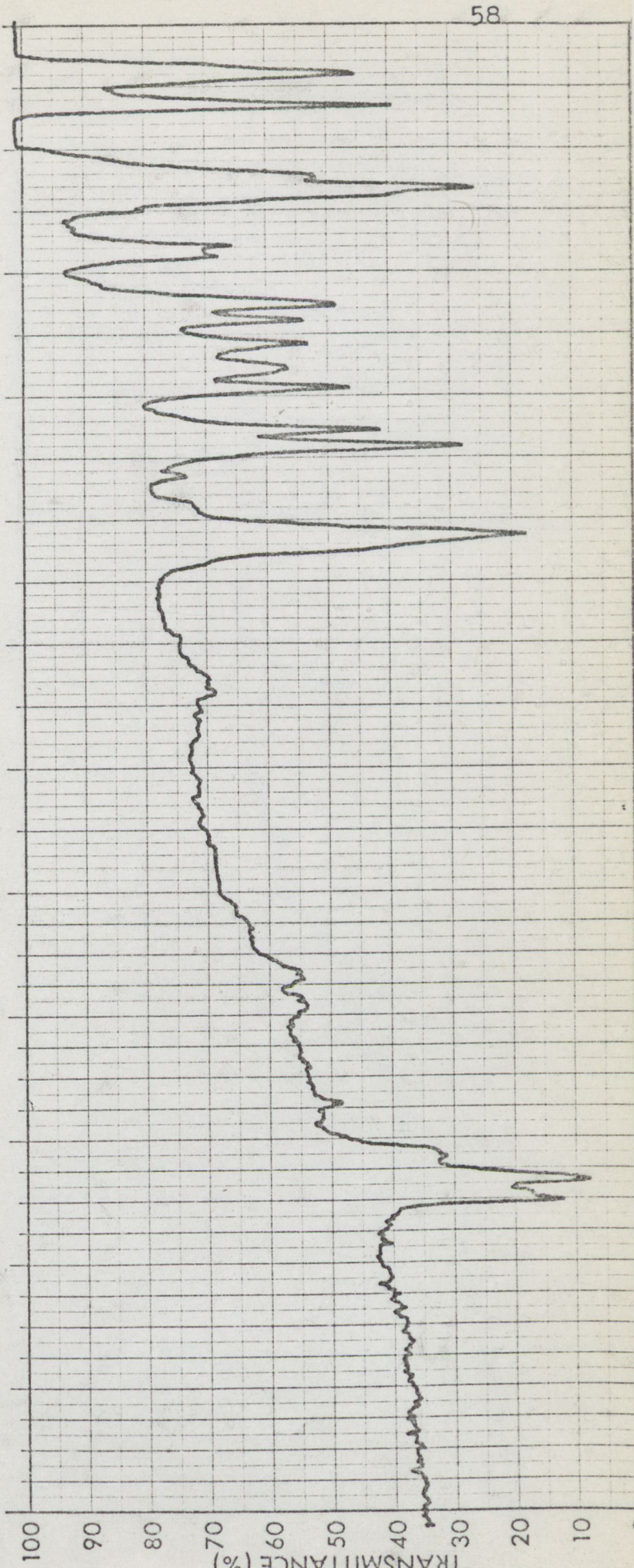
79-1 (33-1)CH₂Cl₂

SAMPLE 2

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

TRANSMITTANCE (%)



PERKIN-ELMER

REMARKS

ORIGIN _____

PURITY _____

SPEED _____ NORMAL ☒ FASTSLITS _____ NORMAL ☒ WIDE

PHASE _____ Heat - Liquid

CONCENTRATION _____

THICKNESS _____ AgCl cells

DATE _____ 12/11/73

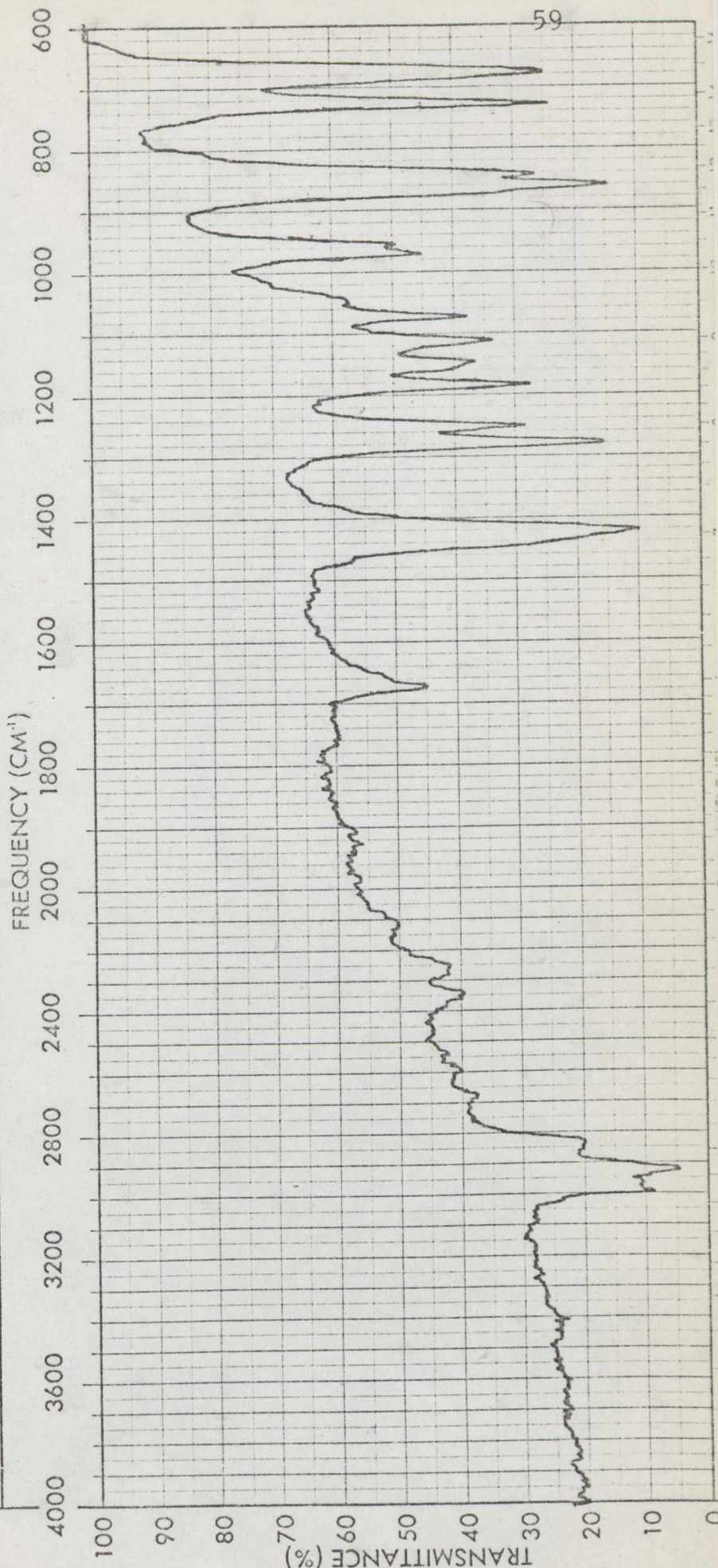
OPERATOR _____ S. G.

SPECTRUM NO. _____

SAMPLE 1 65-1



SAMPLE 2 _____



PERKIN-ELMER

REMARKS

ORIGIN

PURITY

SPEED NORMAL ☒ FASTSLITS NORMAL ☒ WIDE

PHASE LIQ.

CONCENTRATION NEAT

THICKNESS 8 cells

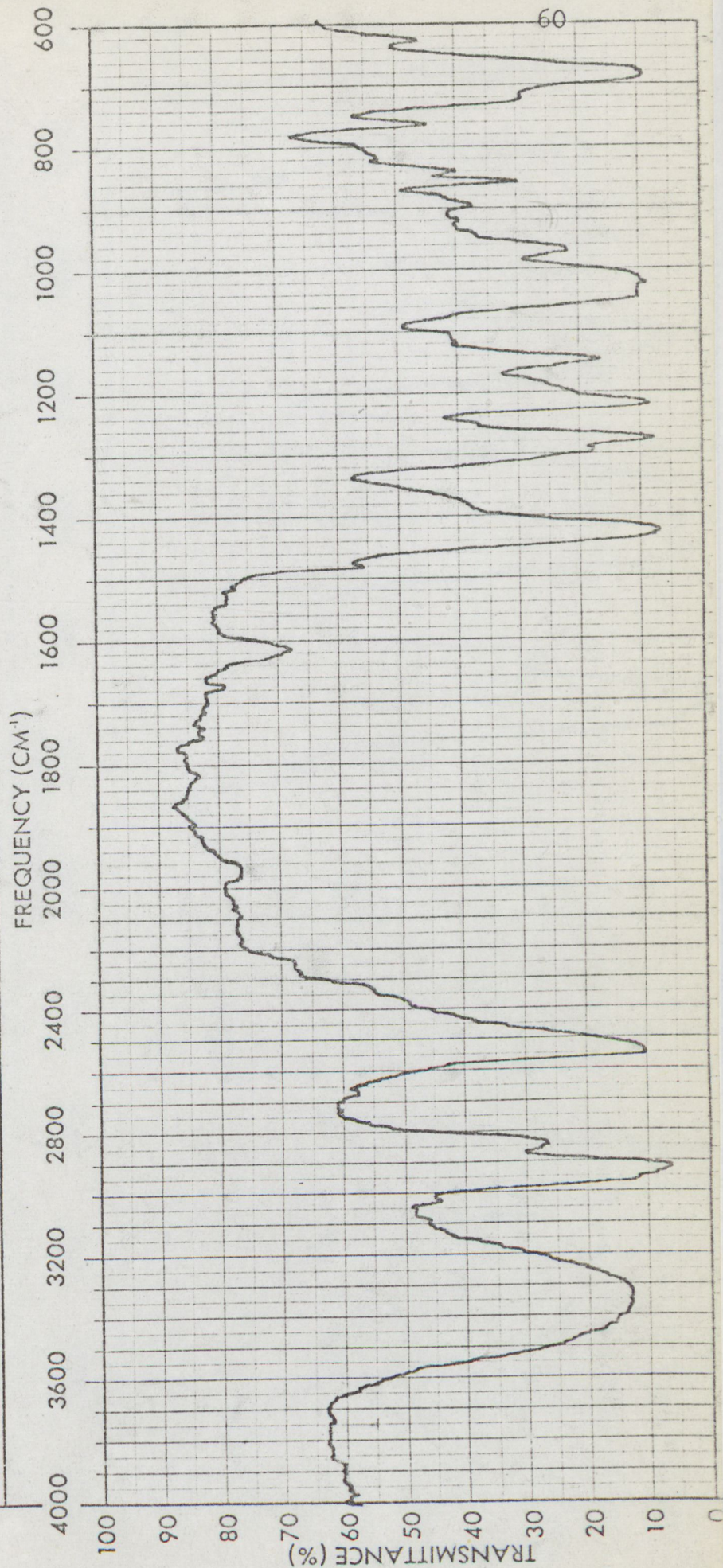
DATE 12/13/73

OPERATOR J.G.

SPECTRUM NO.

SAMPLE 1 71-2

SAMPLE 2



PERKIN-ELMER

REMARKS

ORIGIN

PURITY

SPEED NORMAL ☒ FASTSLITS NORMAL ☒ WIDE

PHASE

CONCENTRATION Neat

THICKNESS

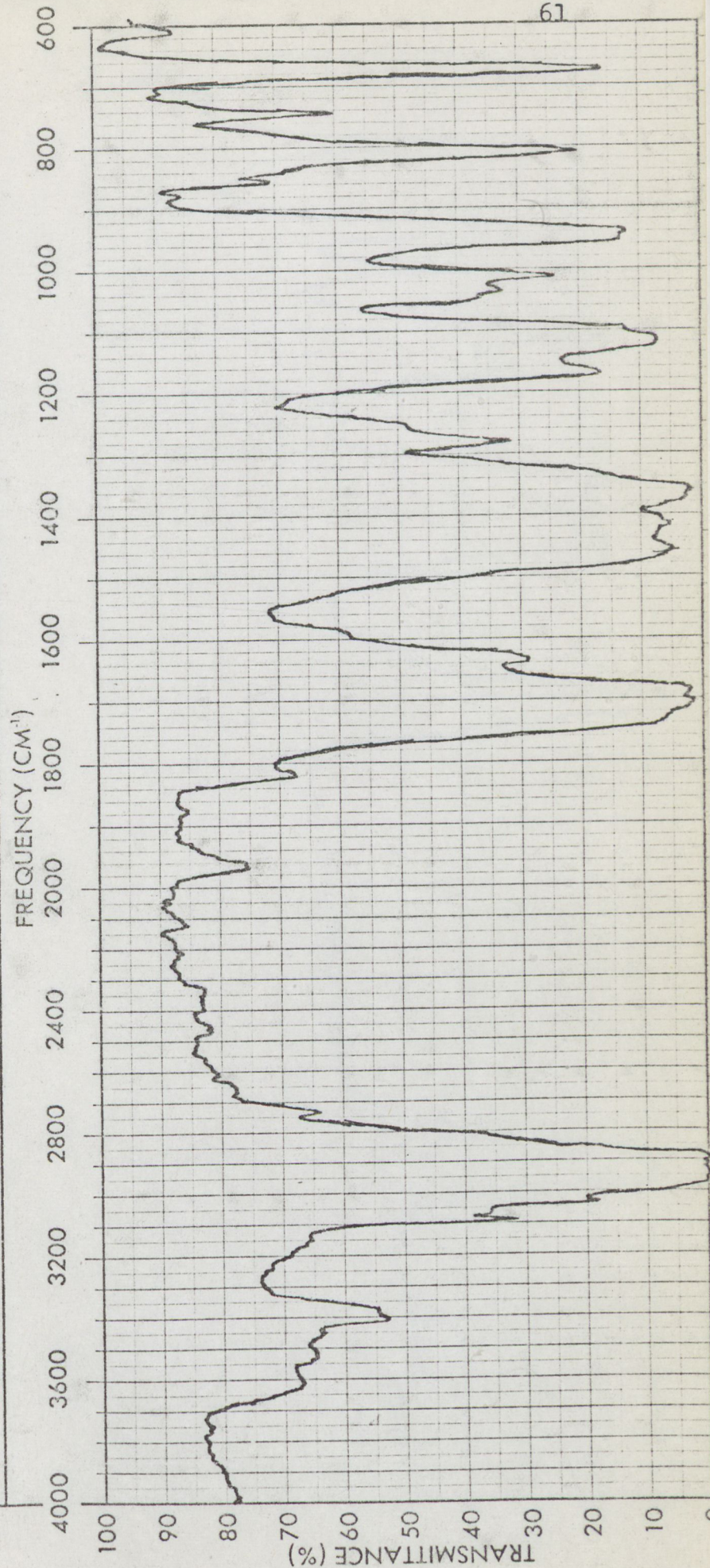
DATE

OPERATOR

SPECTRUM NO. 95-2

SAMPLE 1

SAMPLE 2



RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
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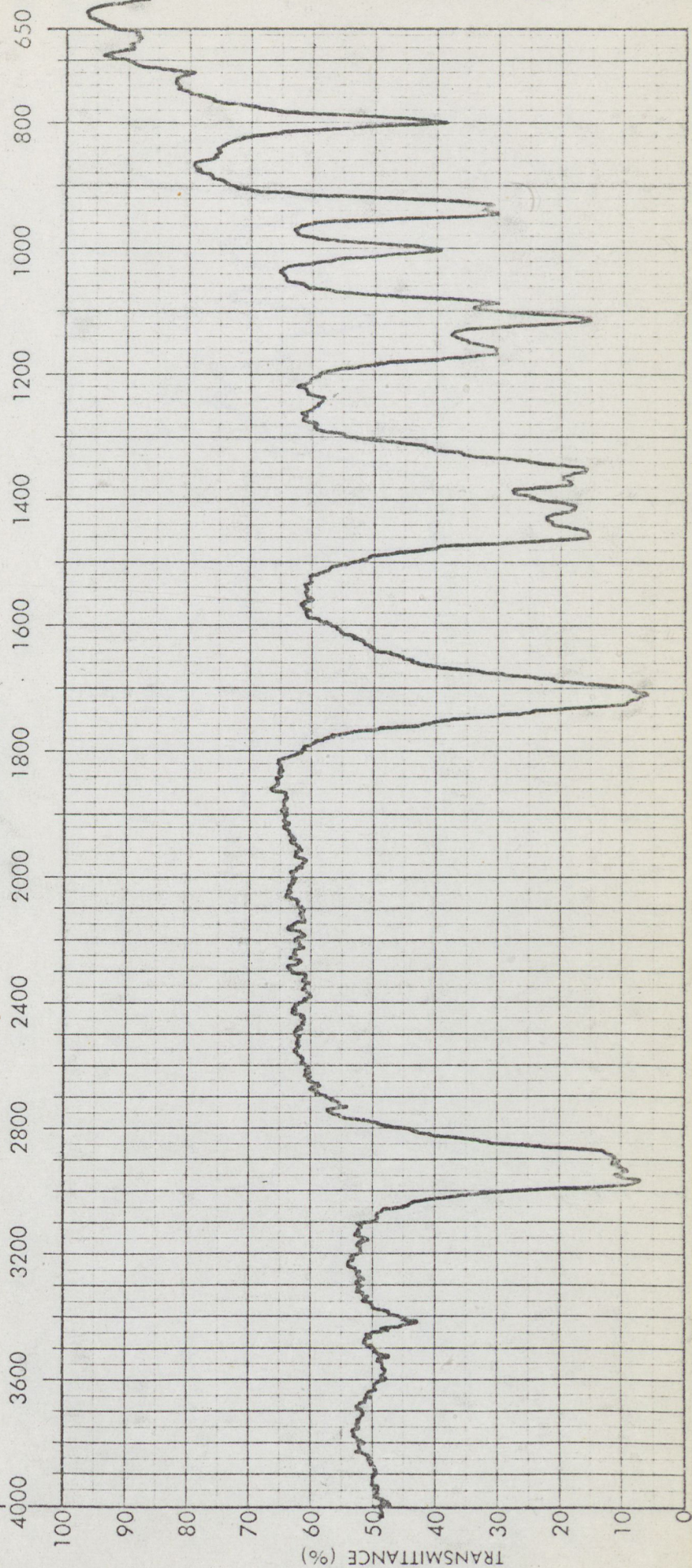
SPECTRUM NO. _____

SAMPLE 1 3-Pentanone

SAMPLE 2 _____

ORIGIN StockPURITY PracticalPHASE LIQCONCENTRATION NEATTHICKNESS AgCl cellsDATE 10/26/73OPERATOR J.G.

REMARKS _____

FREQUENCY (CM⁻¹)

PERKIN-ELMER

REMARKS

ORIGIN

PURITY

SPEED NORMAL X FAST

SLITS NORMAL X WIDE

PHASE

CONCENTRATION *rest*

THICKNESS

DATE 2/23/74

OPERATOR J. G.

SPECTRUM NO. 107-1

SAMPLE 1

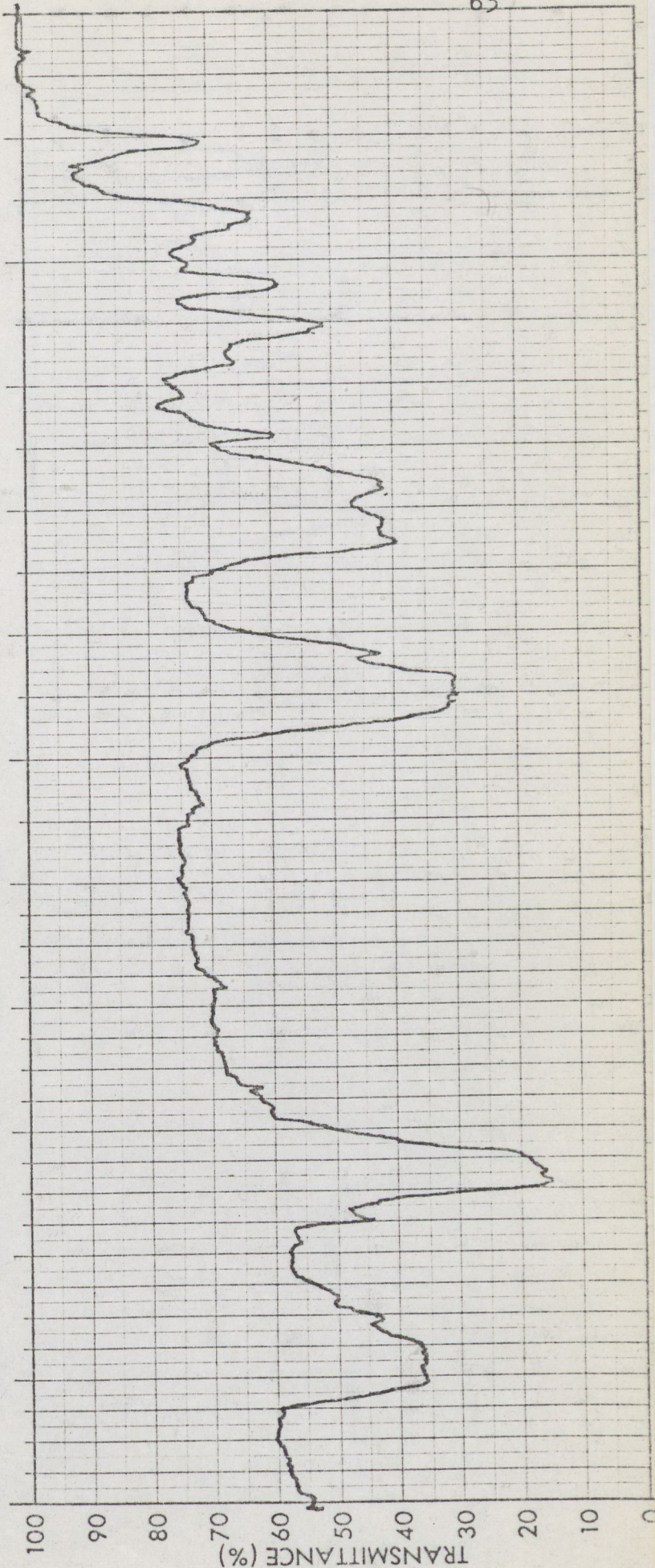
SAMPLE 2

FREQUENCY (CM⁻¹)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

TRANSMITTANCE (%)

100 90 80 70 60 50 40 30 20 10 0



PERKIN-ELMER

ORIGIN _____

PURITY _____

SPEED _____ NORMAL ☒ FAST _____SLITS _____ NORMAL ☒ WIDE _____

PHASE _____

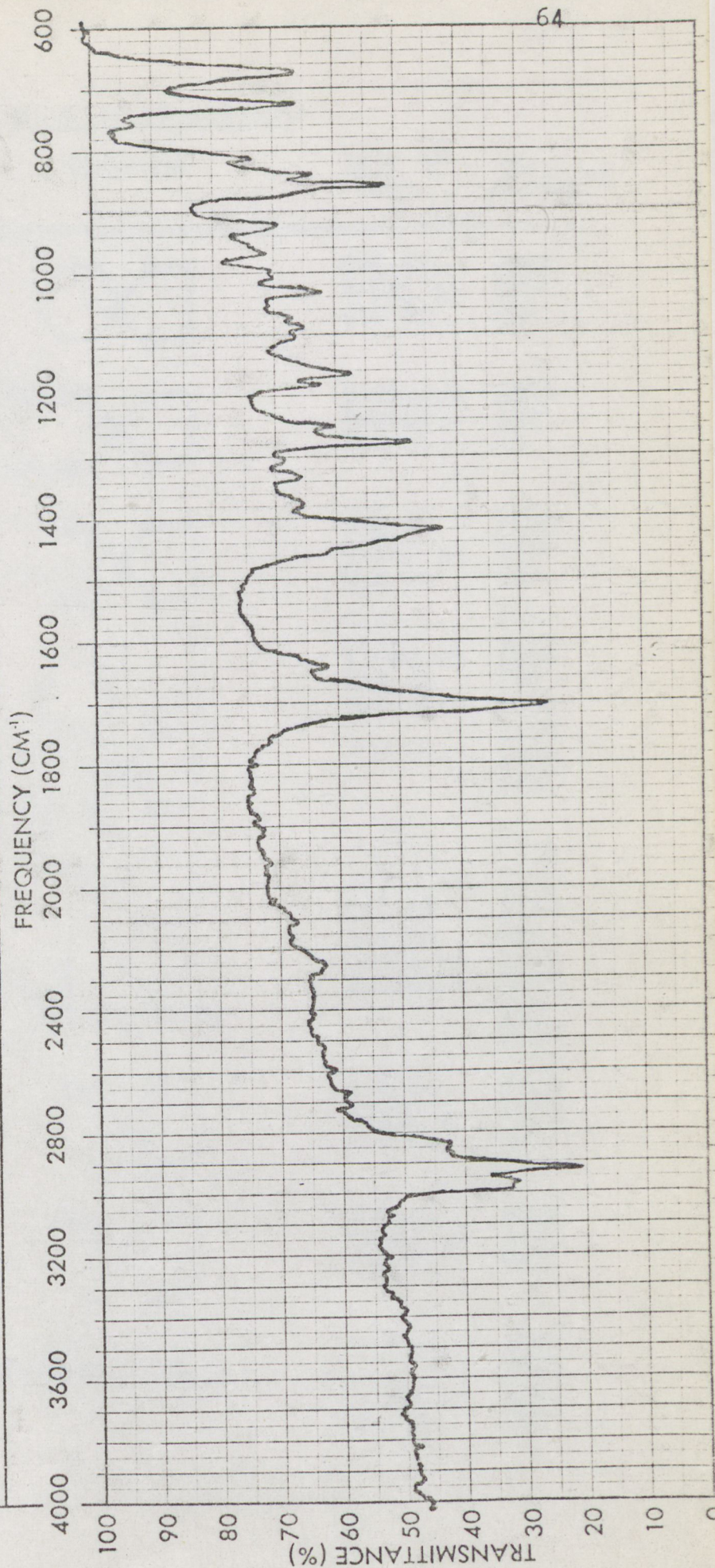
CONCENTRATION med

THICKNESS _____

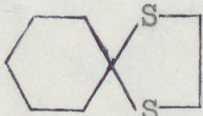
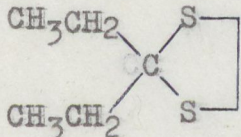
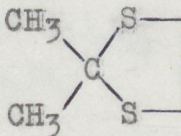
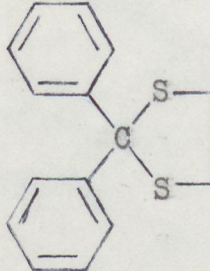
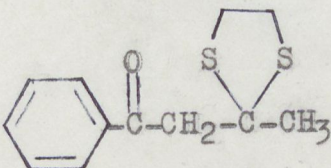
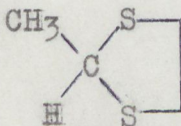
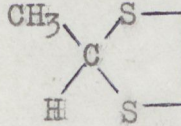
DATE 2/23/74OPERATOR J. G.SPECTRUM NO. 107-2

SAMPLE 1 _____

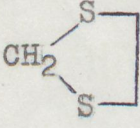
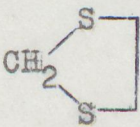
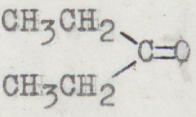
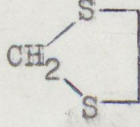
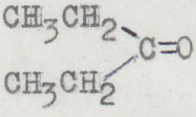
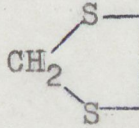
SAMPLE 2 _____



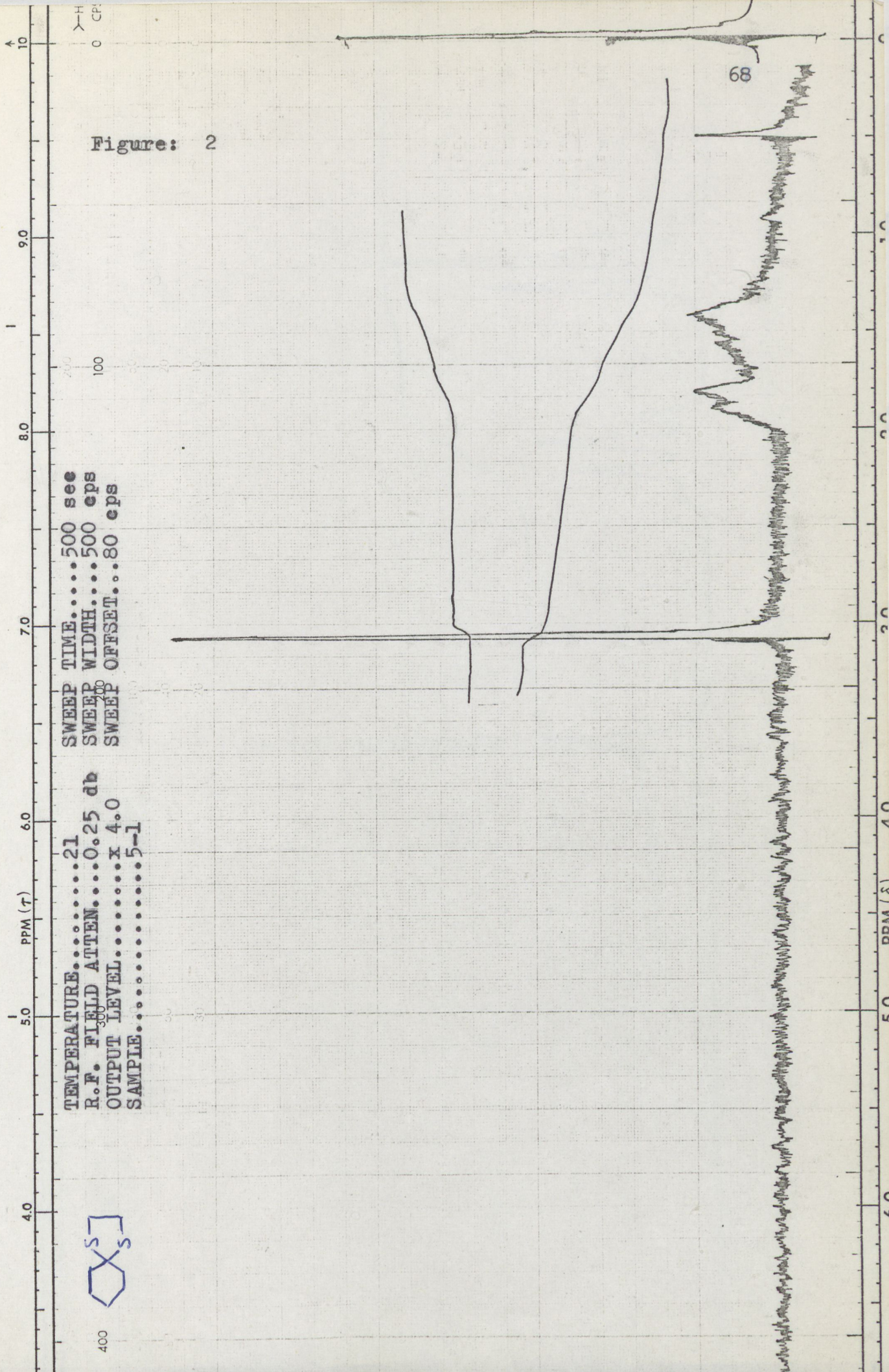
Appendix B: Interpretation of IR spectra:

| Fig. | Page | Sample | Compound | Type of Abs. | Abs. Band cm^{-1} |
|------|------|--------|---|--|--|
| 1 | 13 | 5-1 |  | C-H st S-CH ₂ sc C-S st | 2675 1450 680 |
| 4 | 14 | 29-2 |  | S-CH ₂ sc C-S st | 1425 690 |
| 5 | 14 | 39-1 |  | C-H st S-CH ₂ sc C-S st | 2700 1420 680 |
| 11 | 17 | 85-2 |  | S-CH ₂ sc C-S st Aromatic | 1420 697 3050 1600 1480 740 |
| 15 | 18 | 63-2 |  | C=O st C-S st S-CH ₂ sc Aromatic | 1700 685 1405 3000 740 1600 |
| 17 | 19 | 41-1 |  | C-H st S-CH ₂ sc C-S st | 2700 1430 680 |
| 25 | 20 | 59-1 |  | C-H st S-CH ₂ sc C-S st | 2720 1430 683 |
| 35 | 22 | 13-0 | $(\text{S-CH}_2\text{CH}_2\text{S-CH}_2)_x$ | C-H st S-CH ₂ sc C-S st | 2720 2675 1430 670 |

Appendix B (cont.)

| Fig. | Page | Sample | Compound | Type of Abs. | Abs. Bandcm ⁻¹ |
|------|------|--------|---|--|------------------------------|
| 37 | 23 | 33-1 |  | C-H st S-CH ₂ sc C-S st | 2680 1420 680 |
| 39 | 23 | 65-1 |  | C-H st S-CH ₂ sc C-S st | 2830 1420 680 |
| 43 | 24 | 95-2 |  | C=O st | 1680- 1740 |
| 41 | 24 | 71-2 |  | C-H st S-CH ₂ sc C-S st | 2850 1425 680 |
| 46 | 26 | 107-1 |  | C=O st | 1680- 1720 |
| 48 | 26 | 107-2 |  | C-H st S-CH ₂ sc C-S st | 2840 1420 680 |

Appendix C; NMR Spectra:

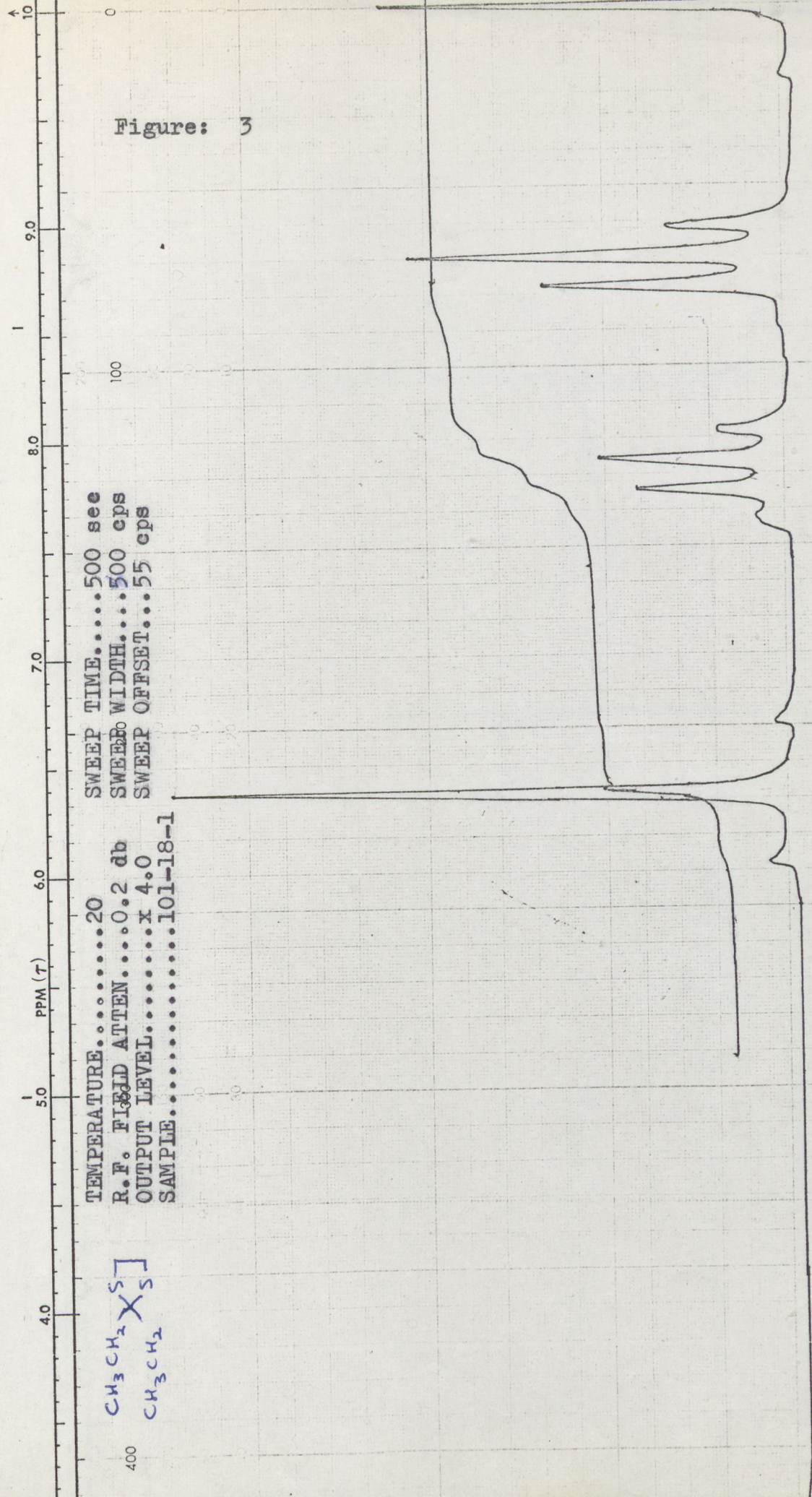


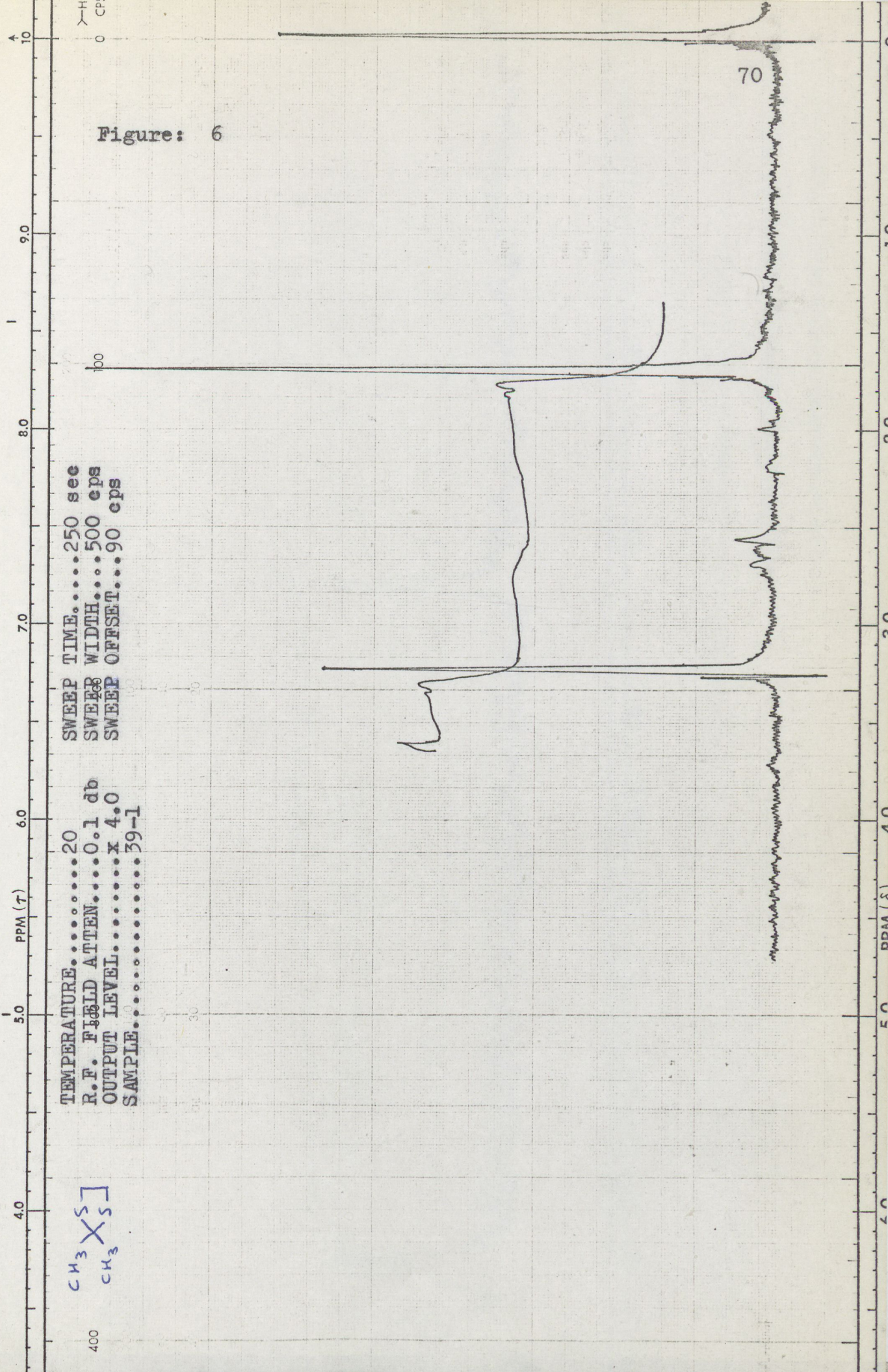
CH₃CH₂ X^S
CH₃CH₂ S

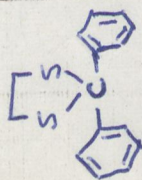
TEMPERATURE.....20
R.F. FIELD ATTEN.....0.2 db
OUTPUT LEVEL.....x 4.0
SAMPLE.....101-18-1

SWEEP TIME.....500 sec
SWEEP WIDTH.....500 cps
SWEEP OFFSET.....55 cps

Figure: 3



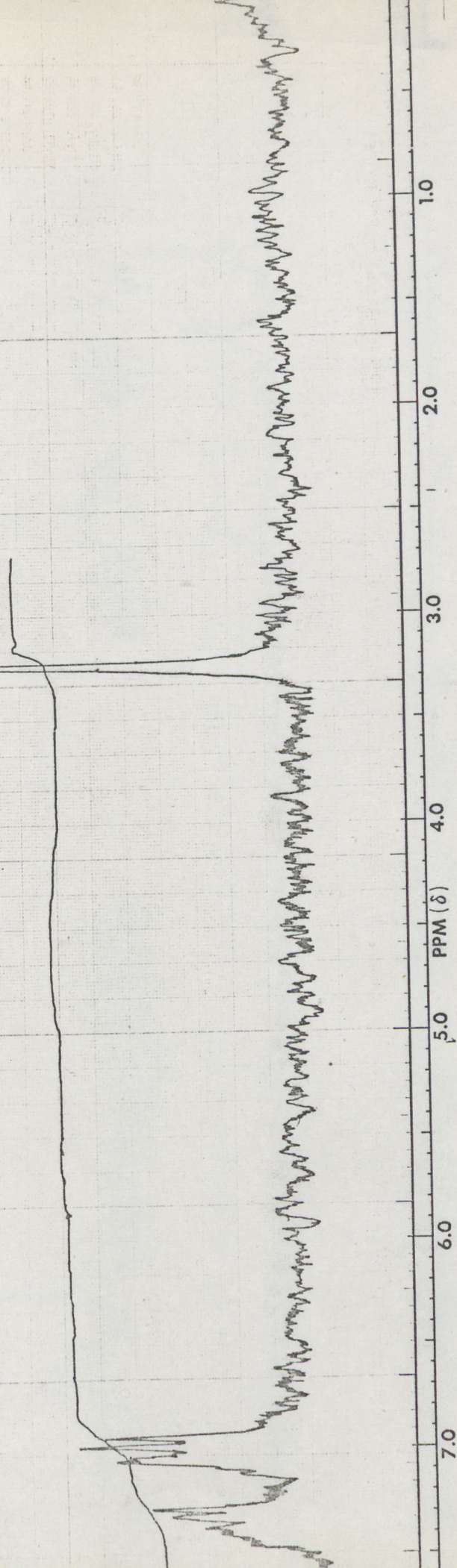




TEMPERATURE.....22
 R.F. FIELD ATTN.....0.4 db
 OUTPUT LEVEL.....x 3.2
 SAMPLE.....85-2

SWEEP TIME.....500 sec
 SWEEP WIDTH.....500 cps
 SWEEP OFFSET.....99 cps

Figure: 12



SOLVENT.....DMSO-6d
 TEMPERATURE.....20
 R.F. FIELD ATTEN.....0.4 db
 SAMPLE.....63-1

OUTPUT LEVEL....x 25.0
 SWEEP TIME.....500 sec
 SWEEP WIDTH.....500 cps

Figure: 14

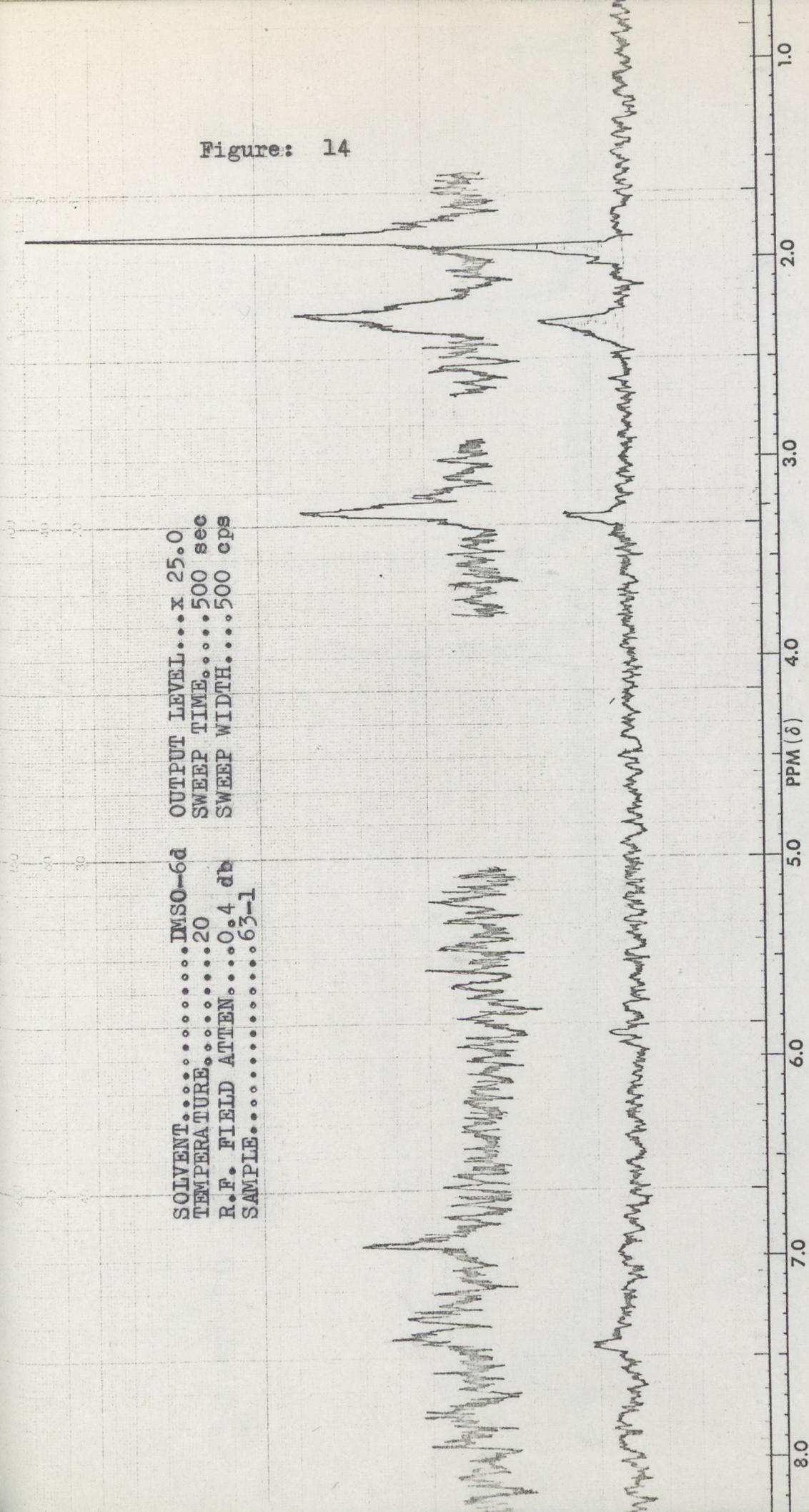


Figure: 16

TEMPERATURE.....22
R.F. FIELD ATTEN.....0.4 db
OUTPUT LEVEL.....x 20.0
SAMPLE.....63-2

SWEET TIME.....500 sec
SWEET WIDTH.....500 cps
SWEET OFFSET.....94 cps

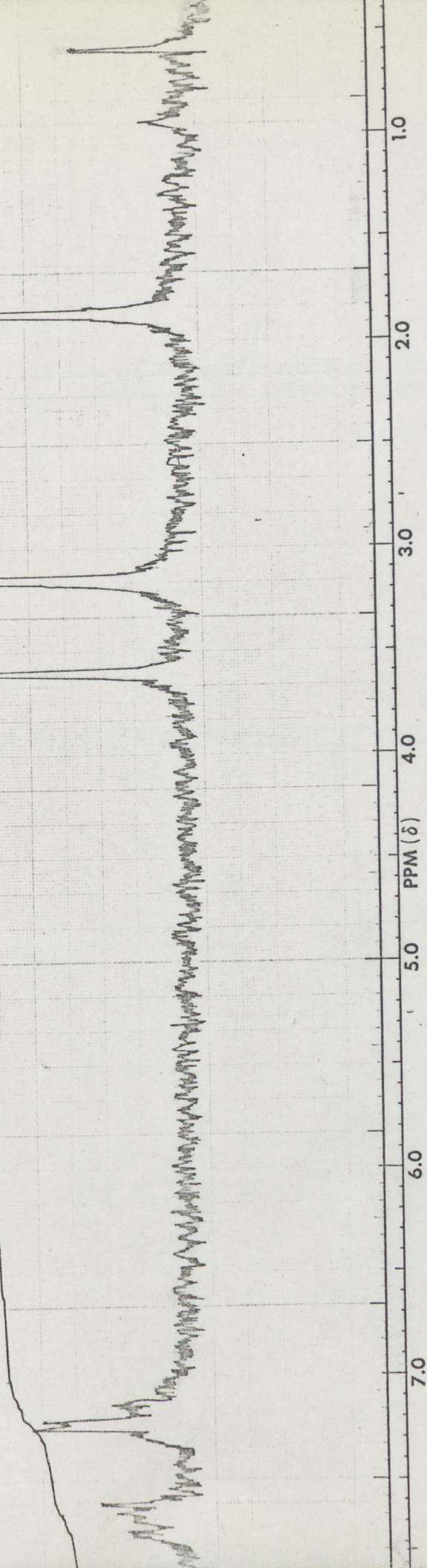
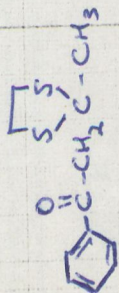
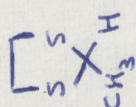
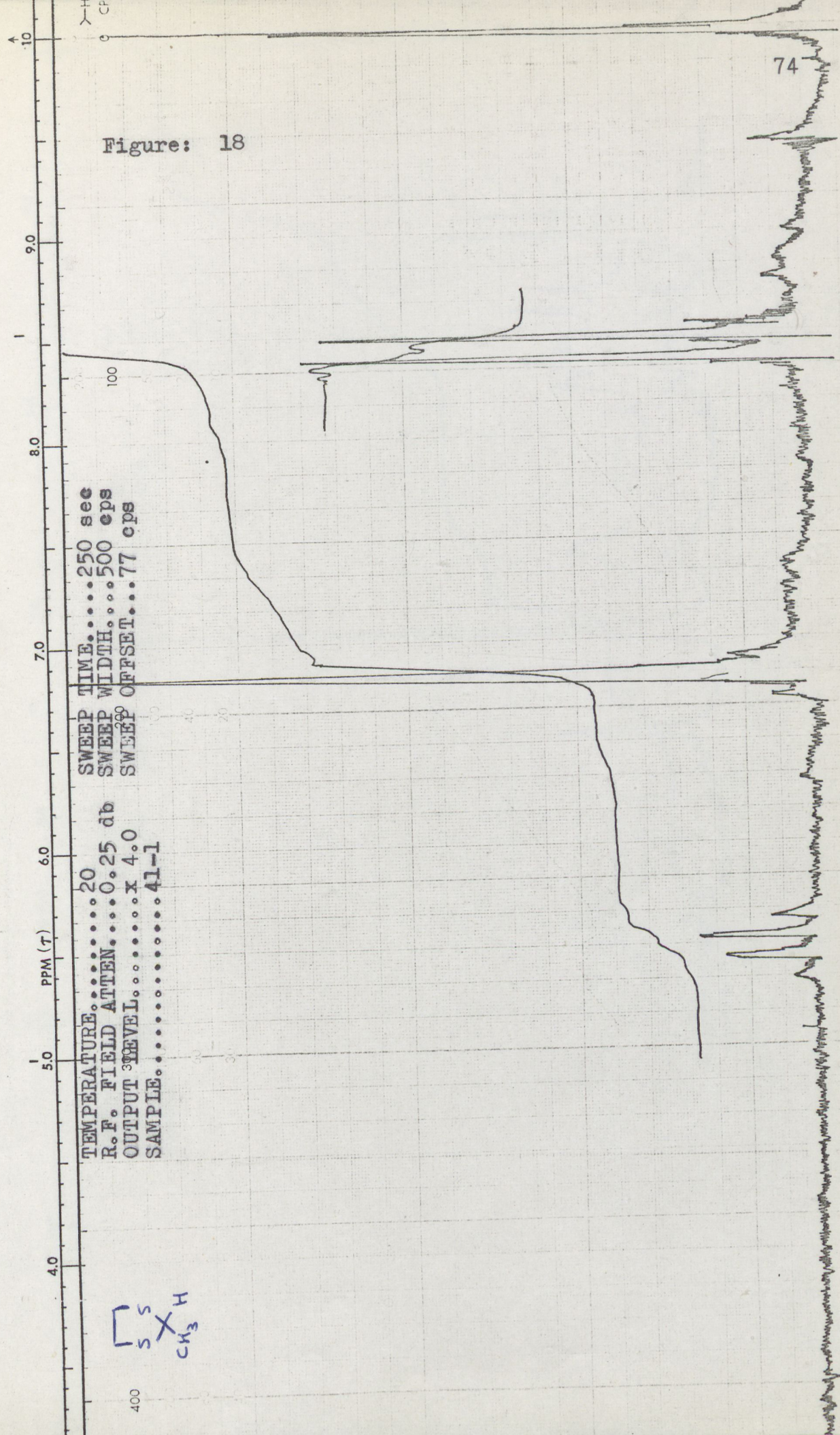


Figure: 18



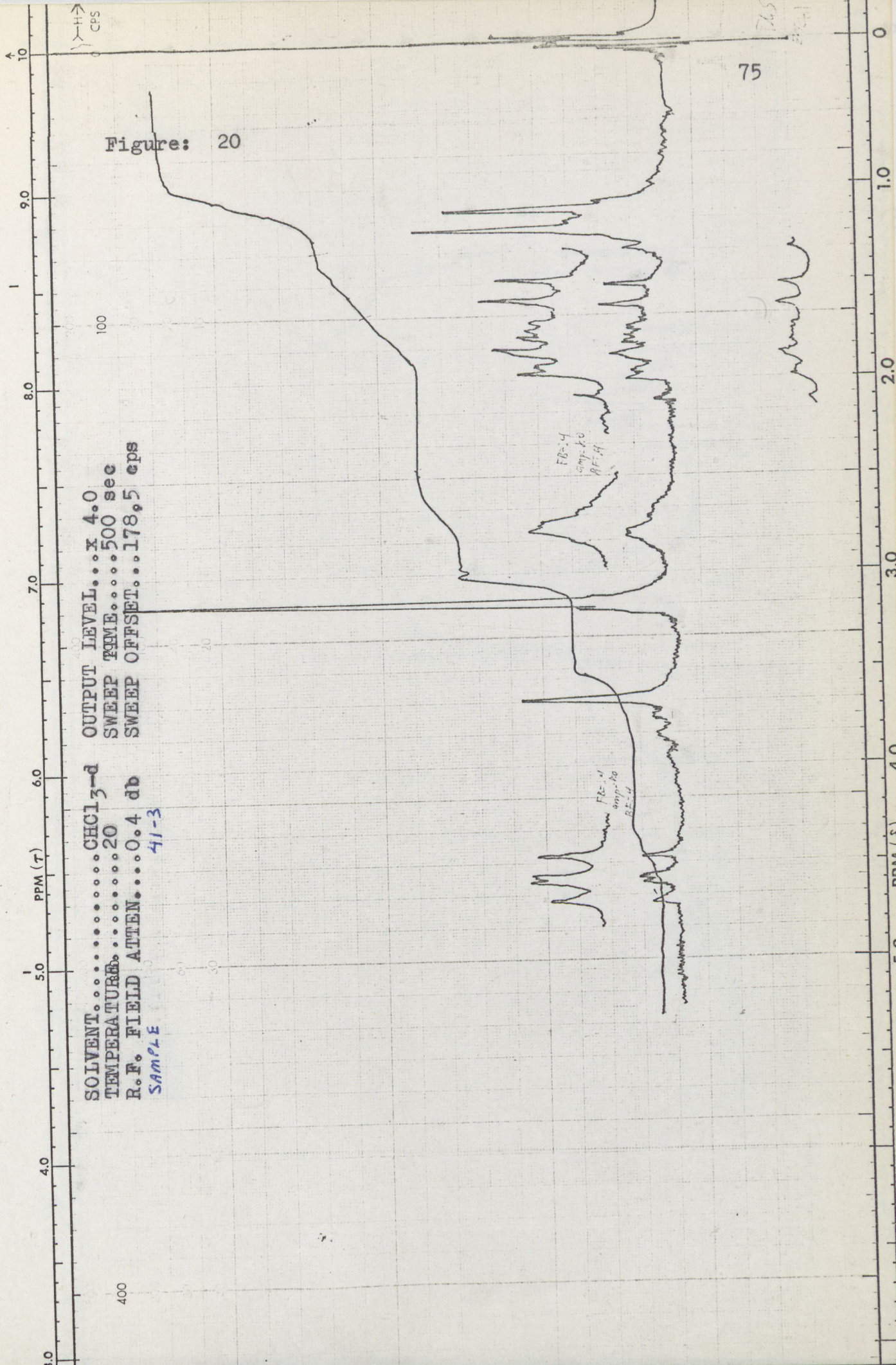


Figure: 22

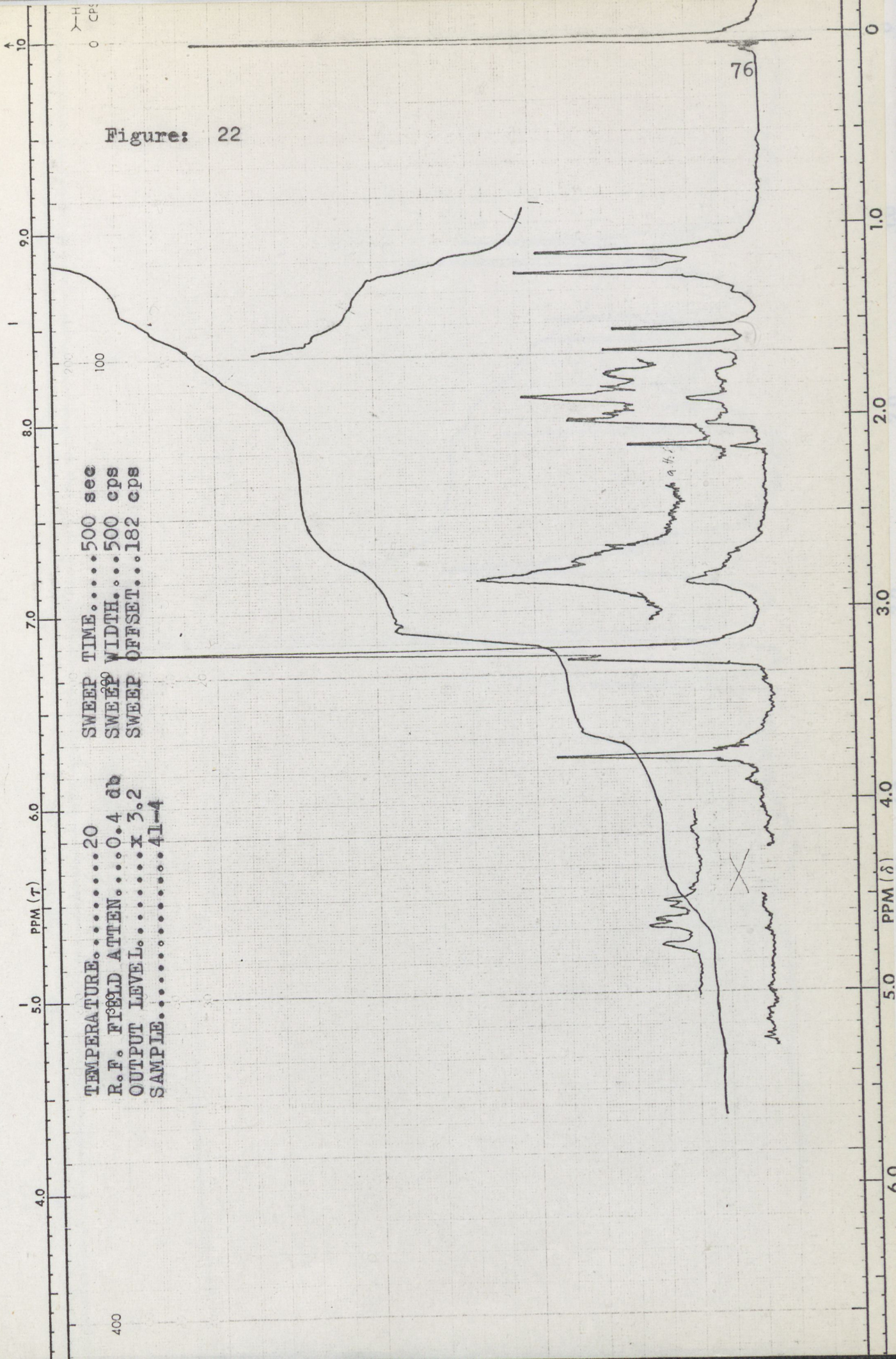
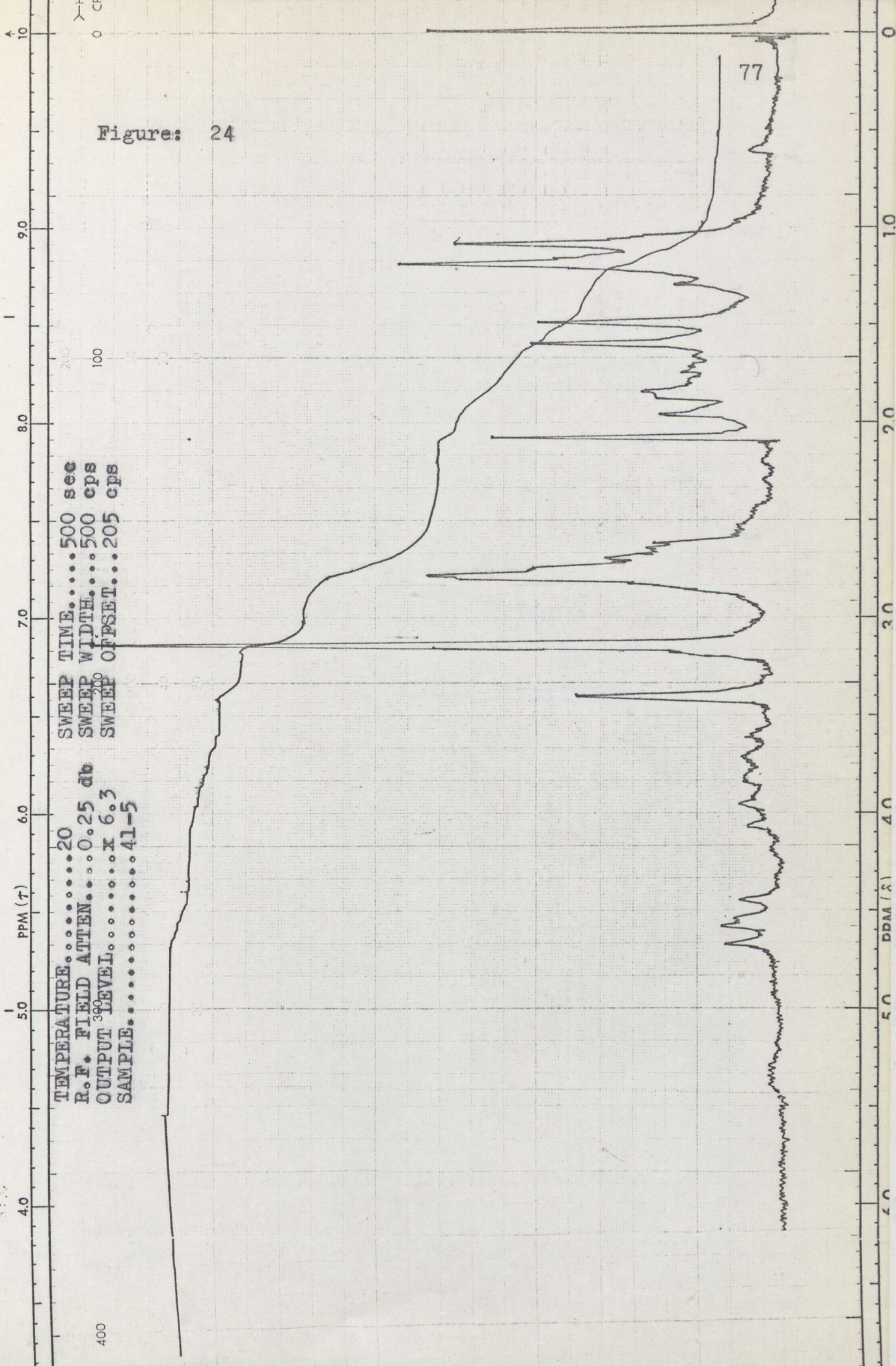
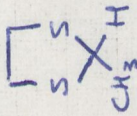


Figure: 24





4.0 5.0 6.0 7.0 8.0 9.0 10

TEMPERATURE.....20
 R.F. FIELD ATTN.....0.4 db
 OUTPUT LEVEL.....x 3.2
 SAMPLE.....59-1

SWEEP TIME.....250 sec
 SWEEP WIDTH.....500 cps

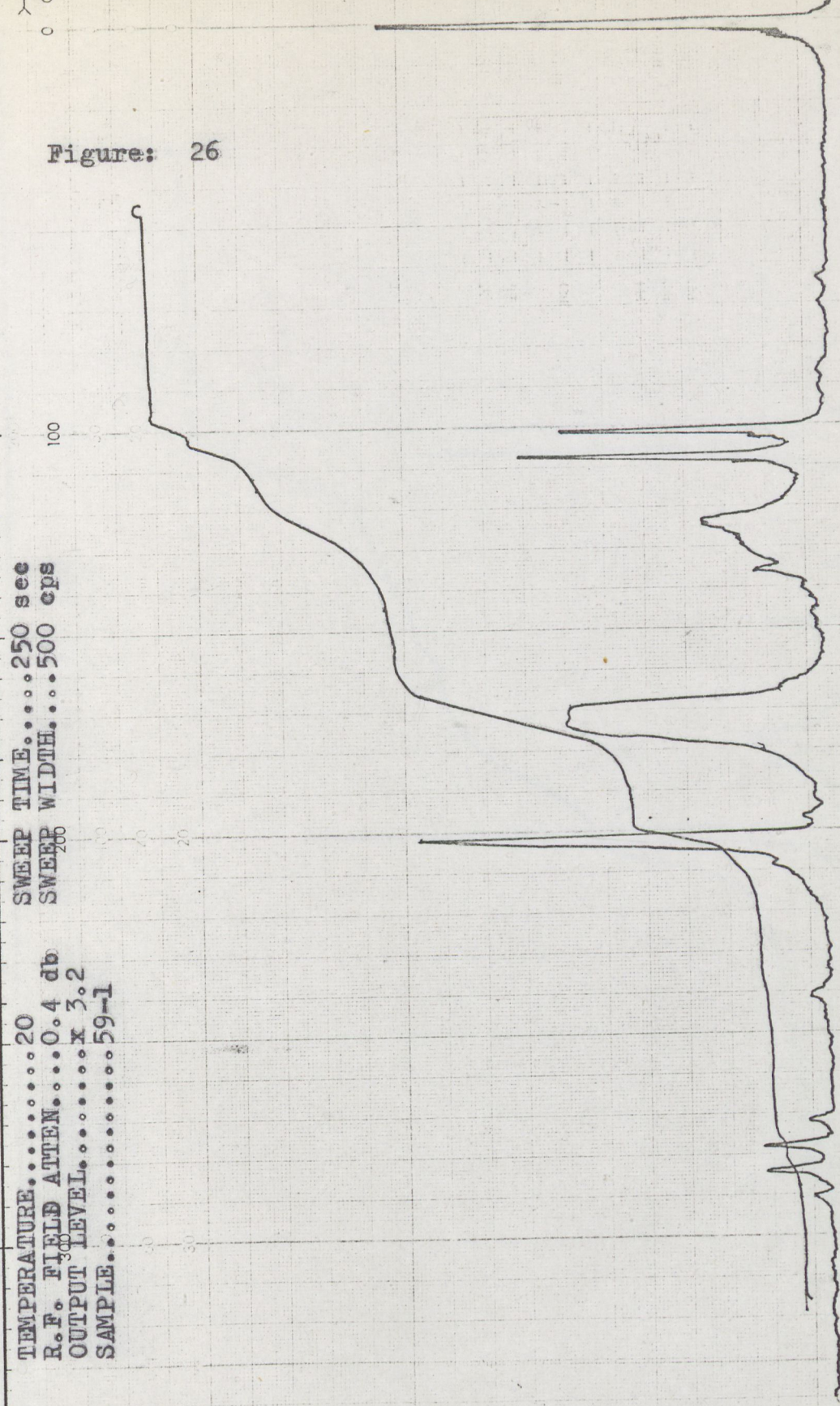
100

200

300

400

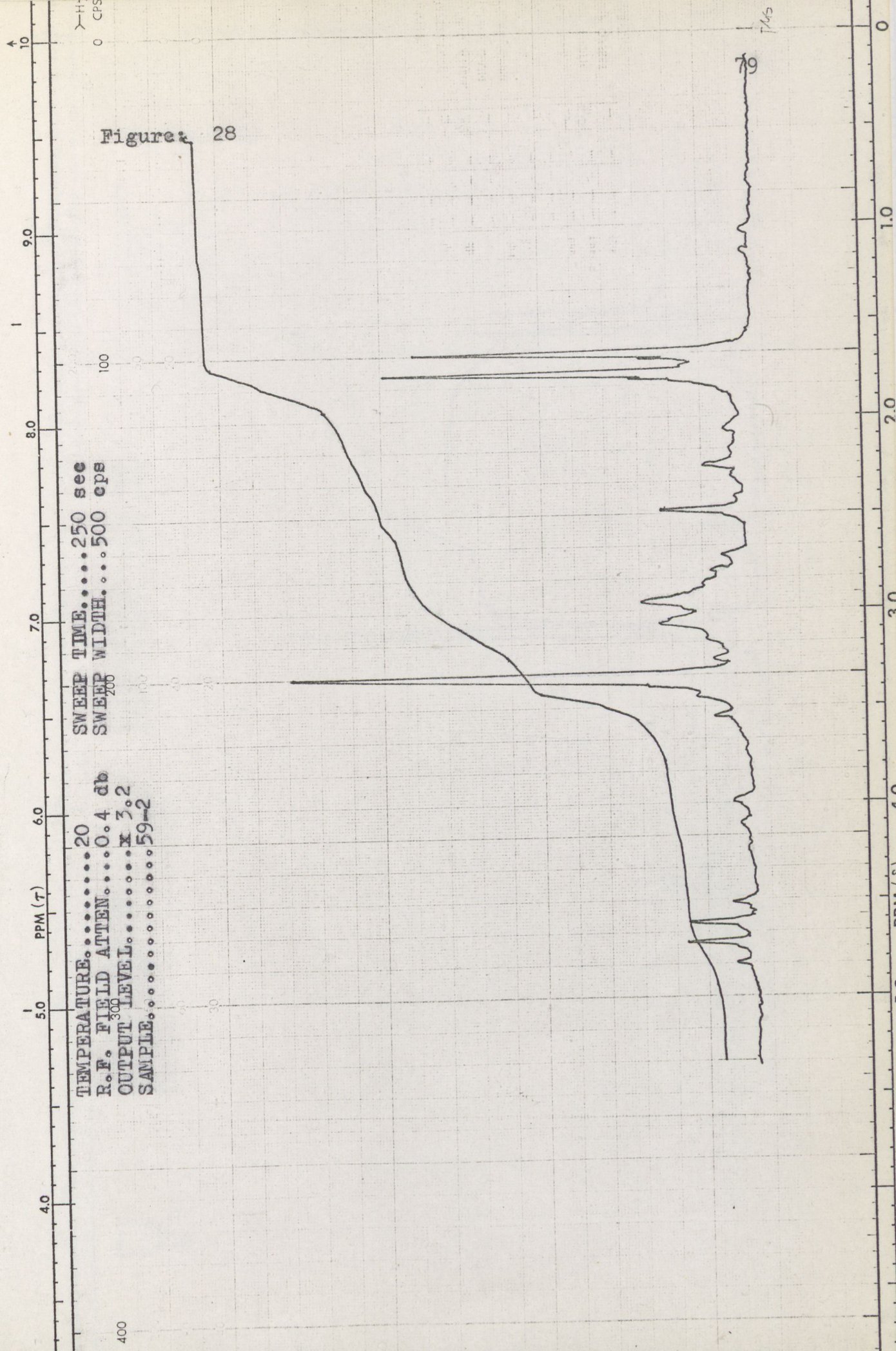
Figure: 26

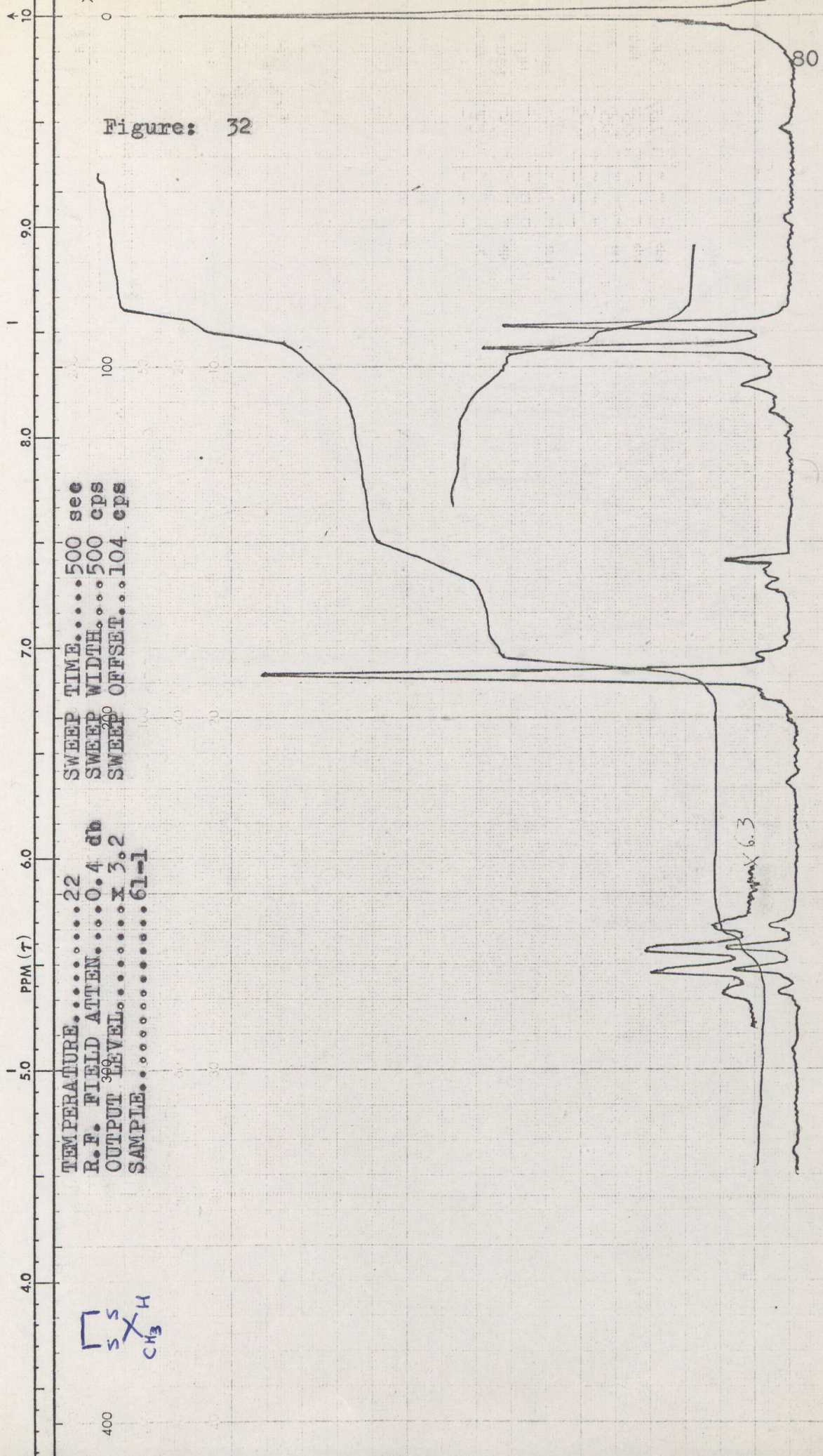
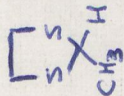


TEMPERATURE.....20
R.F. FIELD ATTN.....0.4 db
OUTPUT LEVEL.....x 3.2
SAMPLE.....59-2

SWEEP TIME.....250 sec
SWEEP WIDTH.....500 cps

Figure: 28





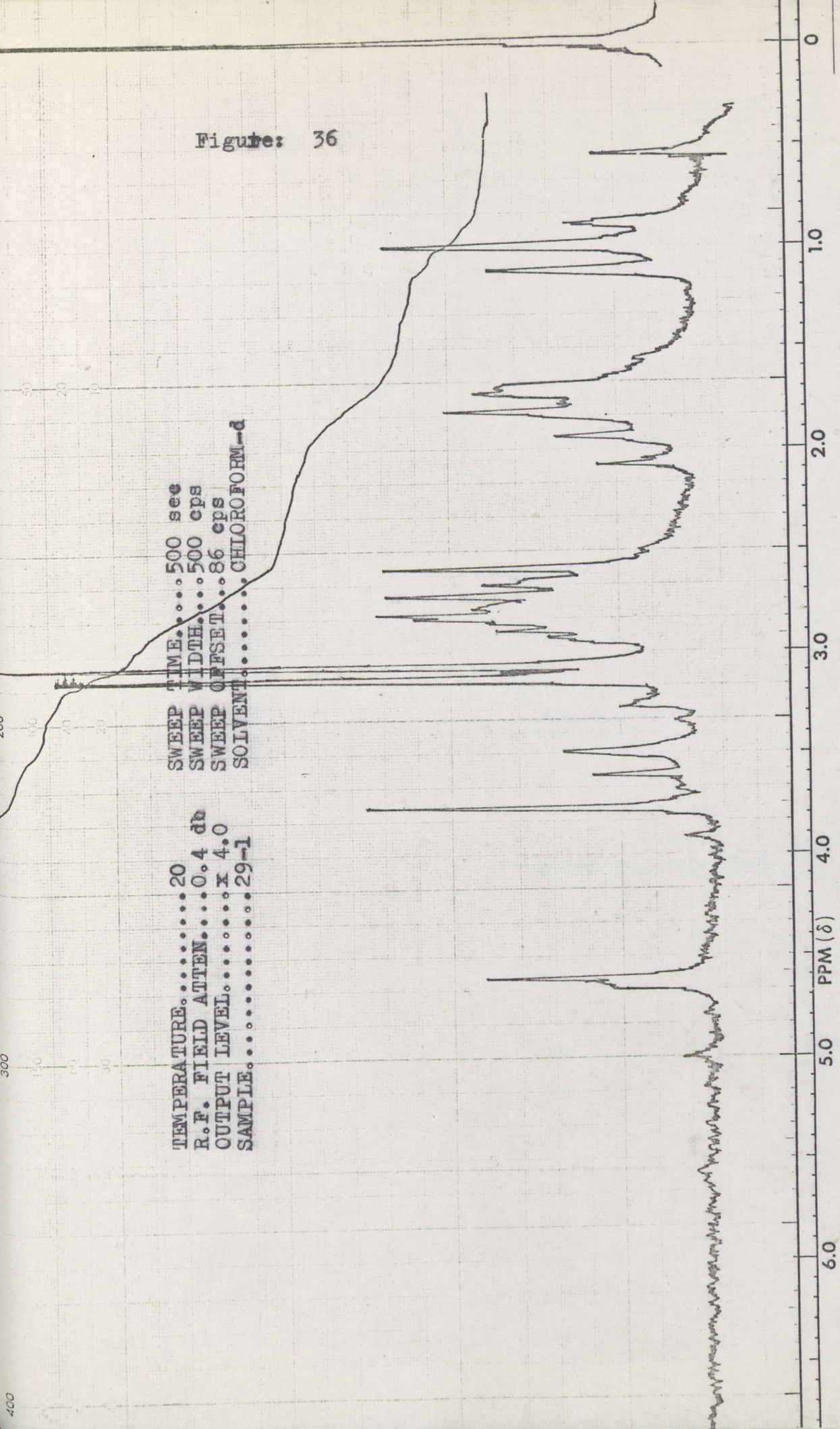
TEMPERATURE.....22
R.F. FIELD ATTN.....0.4 db
OUTPUT³⁰⁰ LEVEL.....x 4.0
SAMPLE.....61-6

SWEET TIME...500 sec
SWEET WIDTH...500 cps
SWEET ²⁰⁰ OFFSET...101 cps

Figure: 34

81

Figure: 36



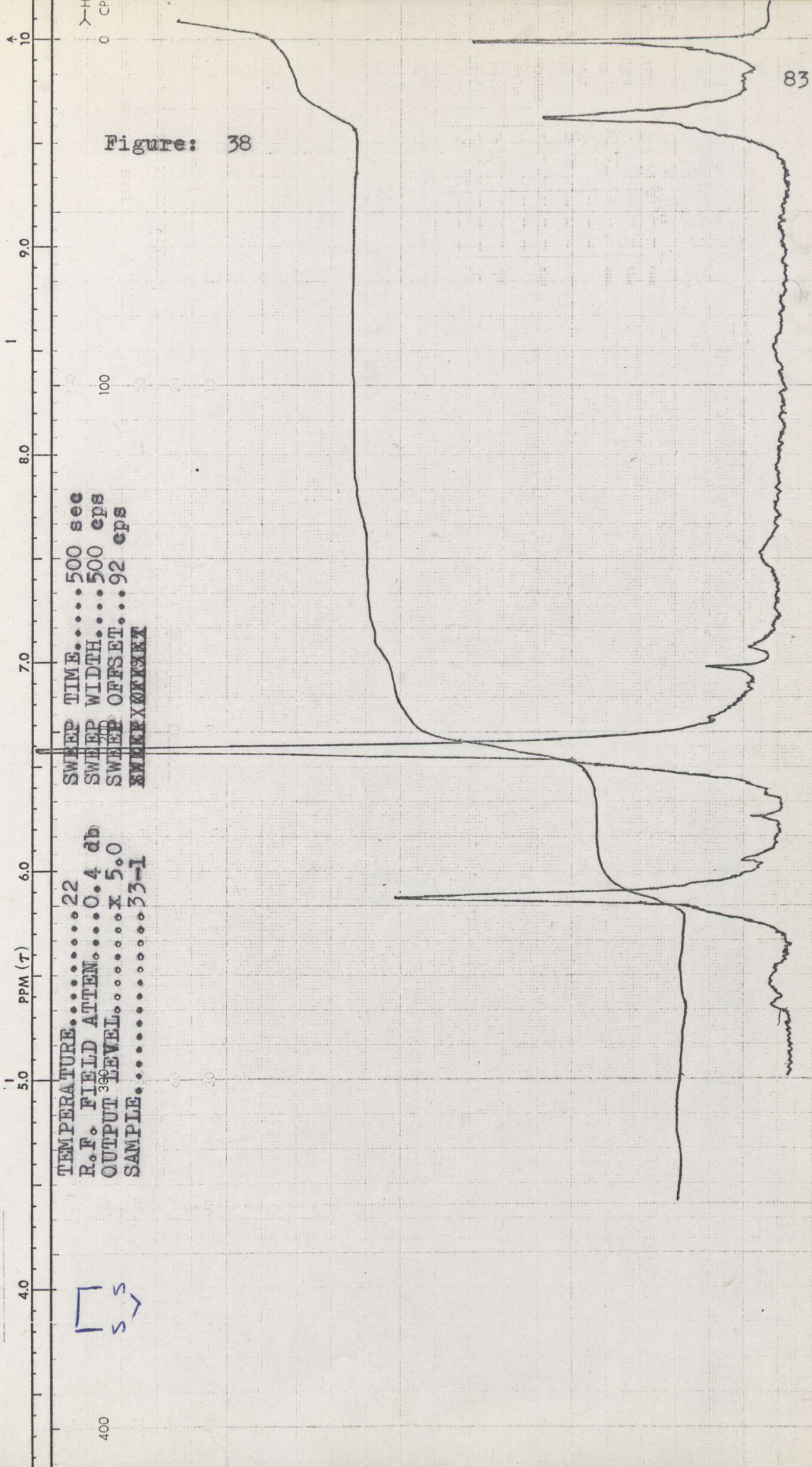
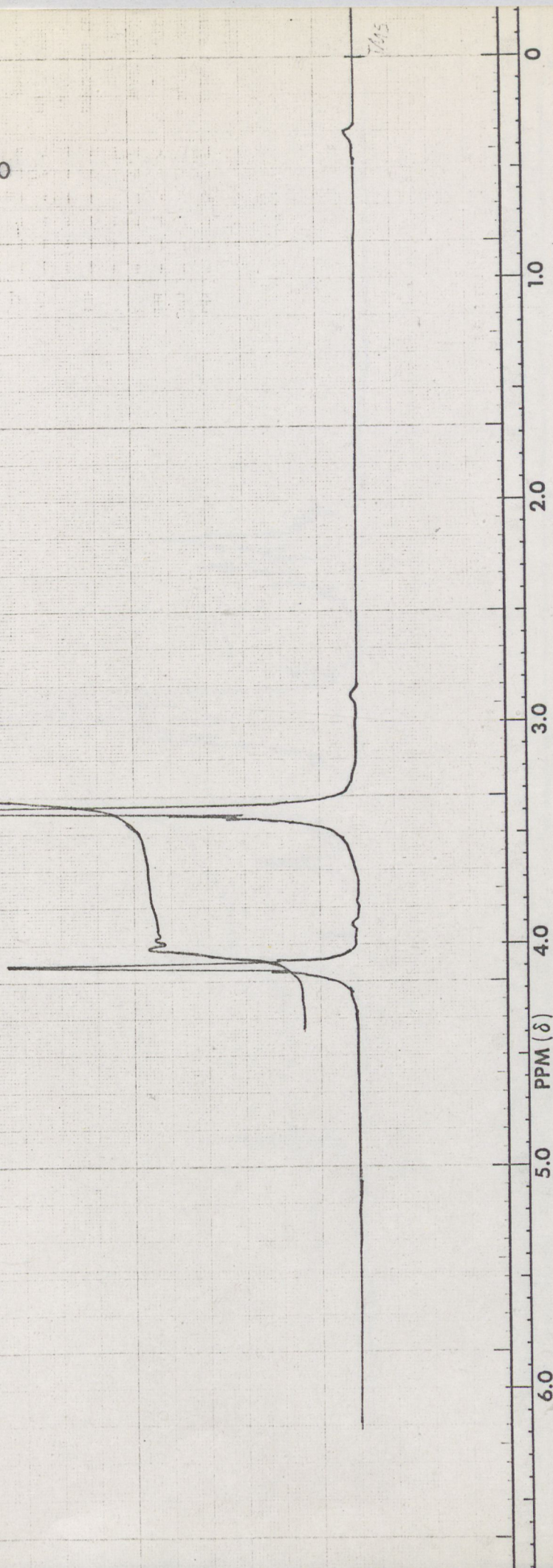


Figure: 40

TEMPERATURE.....22
R.F. FIELD ATTEN.....0.4 db
OUTPUT LEVEL.....x 1.0
SAMPLE.....65-1
SWEEP TIME.....500 sec
SWEEP WIDTH.....500 cps
SWEEP OFFSET.....99 cps

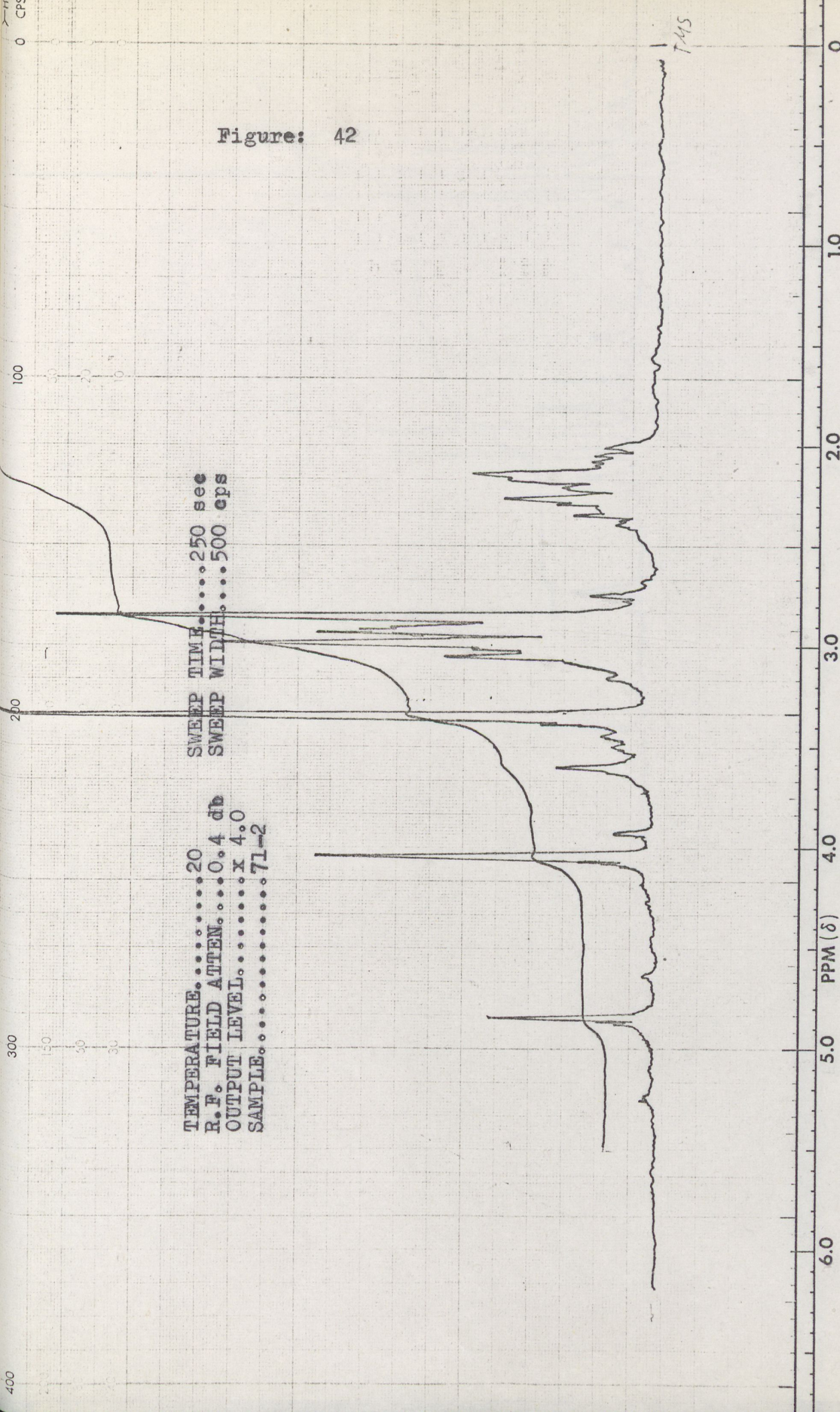
SS



TEMPERATURE.....20
R.F. FIELD ATTEN.....0.4 db
OUTPUT LEVEL.....x 4.0
SAMPLE.....71-2

SWEEP TIME.....250 sec
SWEEP WIDTH.....500 cps

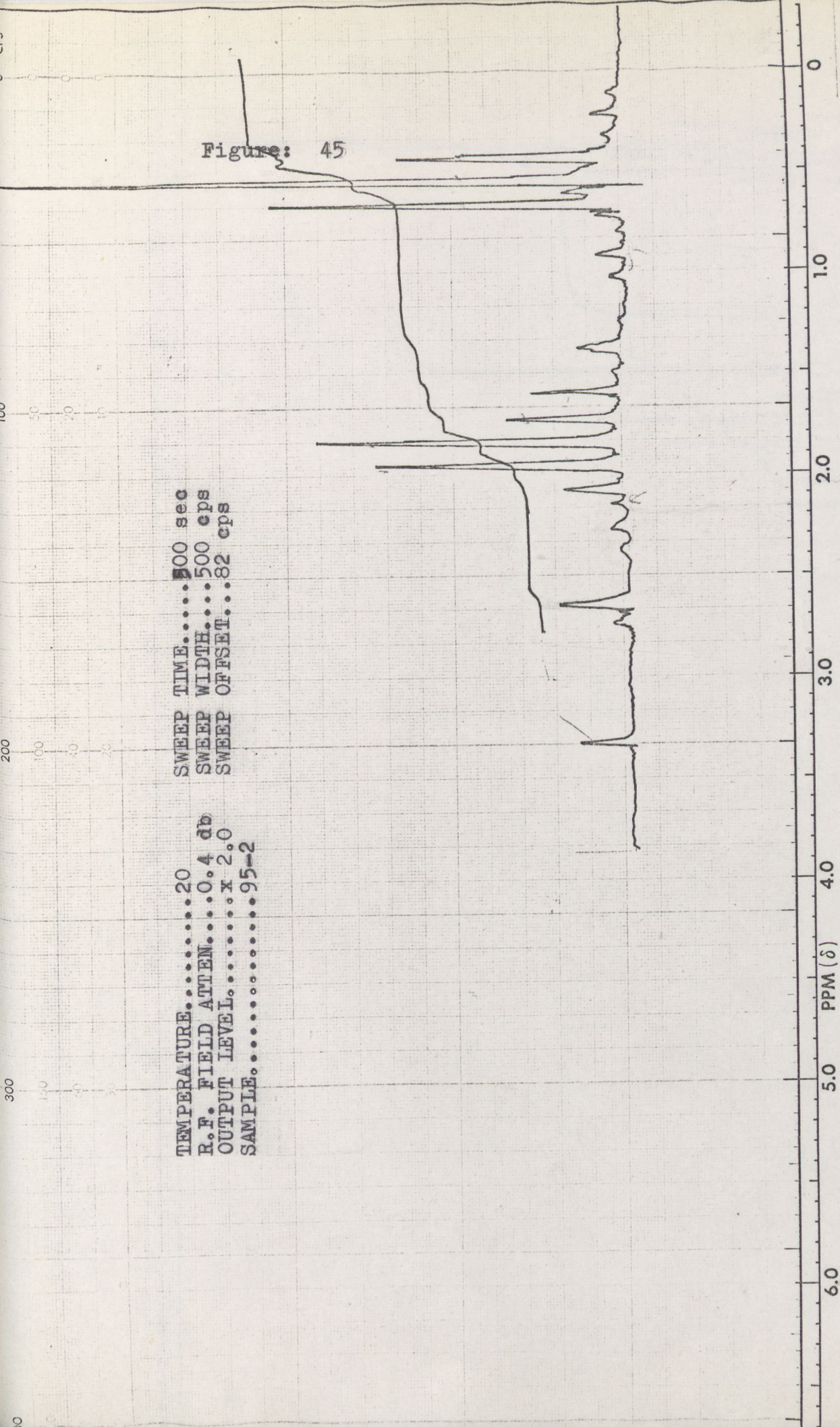
Figure: 42

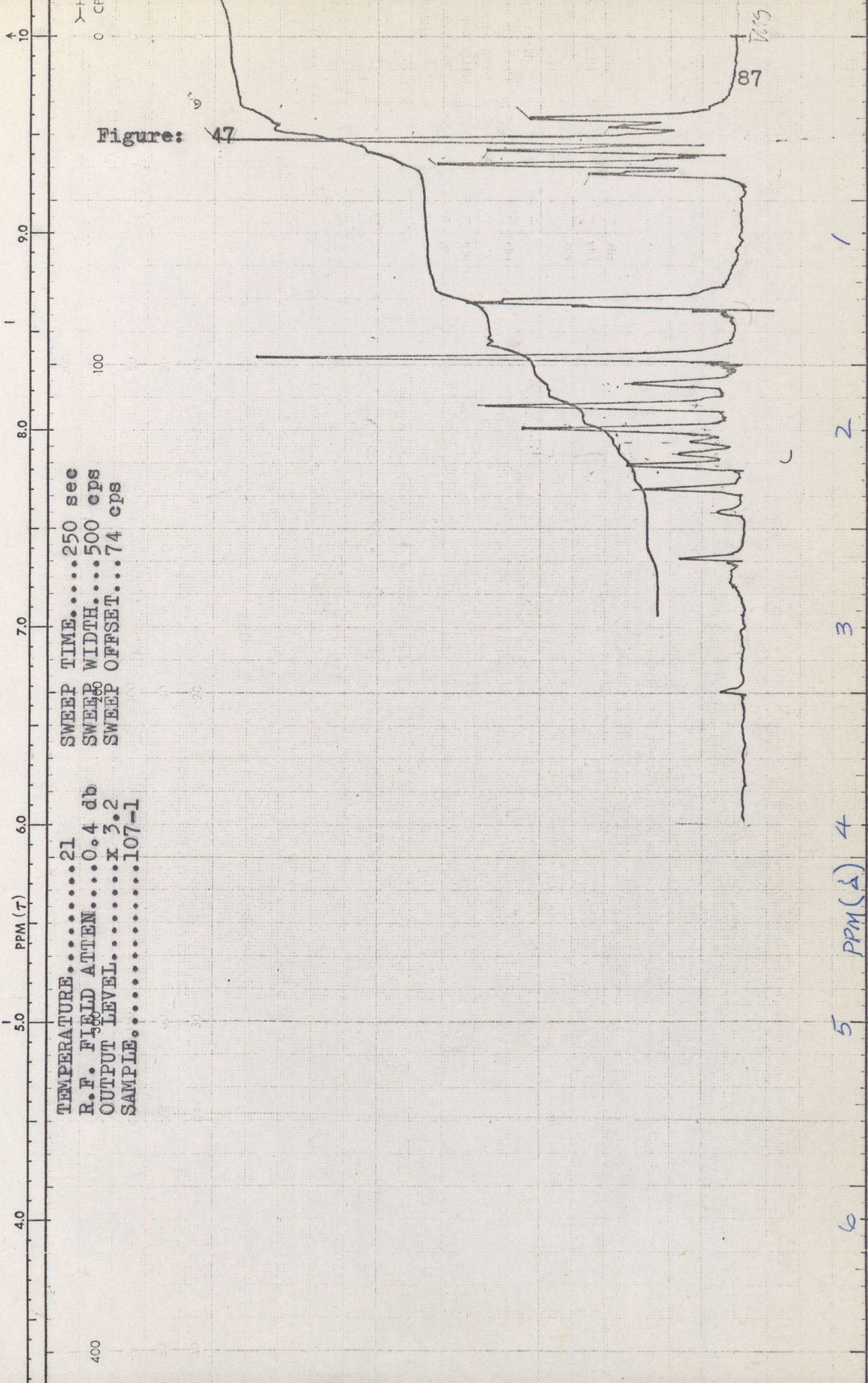


TEMPERATURE.....20
R.F. FIELD ATTEN.....0.4 db
OUTPUT LEVEL.....x 2.0
SAMPLE.....95-2

SWEEP TIME.....500 sec
SWEEP WIDTH.....500 cps
SWEEP OFFSET...82 cps

Figure: 45





| | |
|-----------------------|--------|
| TEMPERATURE..... | 20 |
| R.F. FIELD ATTEN..... | 0.4 db |
| OUTPUT LEVEL..... | x 1.0 |
| SAMPLE..... | 107-2 |

SWEET TIME...250 sec
SWEET WIDTH...500 cps
SWEET OFFSET...74 cps

Figure: 49

88

1
2
3
4
5
6

ppm(δ)

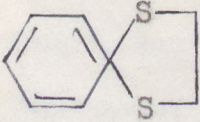
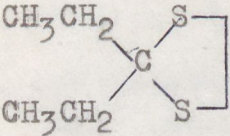
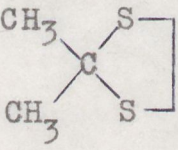
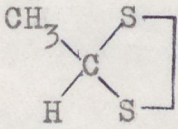
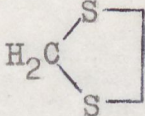
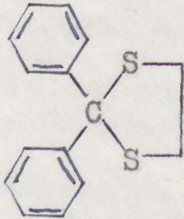
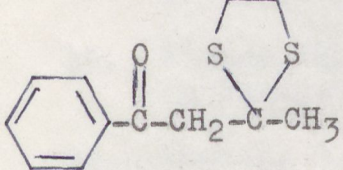
Appendix D: Interpretation of NMR spectra:

| Fig. | Page | Sample | Compound | Peak | Type of H |
|------|------|----------|----------|------------------------------|-------------------------|
| 2 | 13 | 5-1 | | 3.06 1.82 1.41 | a b c |
| 3 | 13 | 101-18-1 | | 3.6 2.18 1.16 | a b c |
| 6 | 14 | 39-1 | | 3.21 1.7 3.21 1.7 | a b a b |
| 12 | 17 | 85-2 | | 3.25 7.15 | a Aromatic |
| 16 | 18 | 63-2 | | 1.88 3.15 3.61 7.42 | a b c Aromatic |
| 18 | 19 | 41-1 | | 3.15 4.5 1.55 | a c b |
| 32 | 21 | 61-1 | | 3.15 4.48 1.52 | a c b |

Appendix D (cont.)

| Fig. | Page | Sample | Compound | Peak | Type of H |
|------|------|--------|--|--------------|-----------|
| 36 | 22 | 29-1 | $ \begin{array}{ccc} & \text{S}-\text{CH}_2 & \\ & & \\ \text{(b) } \text{H}_2\text{C} & & \text{(a)} \\ & & \\ & \text{S}-\text{CH}_2 & \end{array} $ | 3.05 4.55 | a b |
| 38 | 23 | 33-1 | $ \begin{array}{ccc} & \text{S}-\text{CH}_2 & \\ & & \\ \text{(b) } \text{H}_2\text{C} & & \text{(a)} \\ & & \\ & \text{S}-\text{CH}_2 & \end{array} $ | 3.41 4.13 | a b |
| 40 | 23 | 65-1 | $ \begin{array}{ccc} & \text{S}-\text{CH}_2 & \\ & & \\ \text{(b) } \text{H}_2\text{C} & & \text{(a)} \\ & & \\ & \text{S}-\text{CH}_2 & \end{array} $ | 3.40 4.10 | a b |
| 42 | 24 | 71-2 | $ \begin{array}{ccc} & \text{S}-\text{CH}_2 & \\ & & \\ \text{(b) } \text{H}_2\text{C} & & \text{(a)} \\ & & \\ & \text{S}-\text{CH}_2 & \end{array} $ | 3.34 4.05 | a b |
| 49 | 26 | 107-2 | $ \begin{array}{ccc} & \text{S}-\text{CH}_2 & \\ & & \\ \text{(b) } \text{H}_2\text{C} & & \text{(a)} \\ & & \\ & \text{S}-\text{CH}_2 & \end{array} $ | 3.29 3.92 | a b |
| 45 | 25 | 95-2 | $ \begin{array}{ccc} & \text{CH}_3-\text{CH}_2 & \text{(b)} \\ & & \\ \text{(a)} & & \text{C=O} \\ & & \\ & \text{CH}_3-\text{CH}_2 & \end{array} $ | 0.58 1.91 | a b |
| 47 | 26 | 107-1 | $ \begin{array}{ccc} & \text{CH}_3-\text{CH}_2 & \text{(b)} \\ & & \\ \text{(a)} & & \text{C=O} \\ & & \\ & \text{CH}_3-\text{CH}_2 & \end{array} $ | 0.54 1.91 | a b |

Appendix E: Physical Properties of 1,3-Dithiolanes:

| Compound | mp | | bp | | Yield% |
|---|-------------|-----|----------------|----------|--------|
| | obs | lit | obs | lit | |
|  | | | 132/24mm | 1107/5mm | 85 |
|  | | | 105/22mm | | 76 |
|  | | | 66-70/ 18mm | 89/14mm | 66 |
|  | | | 68-80/ 20mm | 77/14mm | 17 |
|  | | | 67/17mm | 65/14mm | 22.4 |
|  | 103- 104 | 106 | | | 64.5 |
|  | 70 | | | | 10 |

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