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The Use of Arsenic Trichloride as a Solvent in NMR Spectrometry

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THE USE OF ARSENIC TRICHLORIDE
AS A SOLVENT IN NMR SPECTROMETRY

by


Philip Wills Haines UC 1967

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

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This Thesis

Submitted by

Philip Wills Haines

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

John G. Lamer

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THE USE OF ARSENIC TRICHLORIDE AS A SOLVENT IN NMR SPECTROMETRY

I. INTRODUCTION

Since Union College has had its Nuclear Magnetic Resonance Spectrometer, a great many organic compounds have been analyzed. Several more might have been identified if they could have been dissolved in a suitable solvent. The expense of deuterated solvents and the lack of suitable solvents for some compounds have led to the consideration of inorganic compounds for use as solvents.

Szymanski (1) has published an article dealing with the use of antimony trichloride (SbCl_3) and arsenic trichloride (AsCl_3) as solvents, primarily for infra-red spectroscopy, but secondarily for NMR spectra as well. He does not go into any detail, but merely suggests the usefulness of these compounds as solvents and lists two groups of compounds; those reacting with SbCl_3 and giving altered spectra, and those not reacting, giving essentially unchanged spectra. The following is a partial listing of these groups:

A. UNREACTIVE COMPOUNDS:

Benzene
Acetone
Naphthalene
Tetra-anisylethylene
Succinic acid
Anisic acid

Phenyl acetic acid
p-nitrobenzoic acid
Resourcinol
Naphthol
Propylene
2,4 di-hydroxyacetophenone

B. REACTIVE COMPOUNDS:

Trimethyl amine	Benzoic anhydride
Triethyl amine	Cholesterol
Dimethyl aniline	3,4 toluene diamine
o-aminophenol	Organo phosphorous acids

Olah (2) has also reported the use of inorganic solvent media, having analyzed reaction mixtures with NMR in a mixture of Antimony (V) flouride and sulfur dioxide.

In the case of all previously considered solvents for NMR, both the nature of the solvent and the relative concentration of sample to solvent affect the chemical shift of protons. This is especially true of hydroxyl and amine protons. These factors, however, do not affect the spin coupling constants or splitting patterns of known spectra. It was hoped that this would be the case with the inorganic solvent to be investigated.

II. EXPERIMENTAL

SbCl_3 and AsCl_3 were considered likely choices for study, and AsCl_3 was chosen for the initial work since it is a liquid at both magnet temperature and room temperature, while SbCl_3 is a solid at both temperatures.

A Varian A-60 NMR spectrometer operated at ambient magnet temperature was used for all measurements. Spectra were taken of a number of compounds from both of Szymanski's groups in both a standard solvent and AsCl_3 , and also neat if the compound was a liquid. The spectra taken in standard organic solvents (or D_2O) were to be considered as standards and the spectra taken in AsCl_3 were to be judged against these standards.

In order to avoid concentration effects on the chemical shift, an attempt was made to run each sample at approximately the same concentration in each solvent. This proved to be difficult since certain compounds were only slightly soluble in one solvent or the other. Nevertheless, uniformity was maintained in so far as was practical.

Each spectrum was run at the highest possible or practical gain setting with a sweep width of 500 hz./sec. Peaks with a shift greater than 500 hz./sec. were included in inserts. Integral curves were taken wherever feasible and desirable.

Tetramethyl silane (TMS) is the standard NMR reference peak, and this was used in the AsCl_3 spectra and all standard

spectra except those taken in water. DSS was used as a reference in water.

From the unreactive group, spectra of the following compounds were taken in both a standard solvent and AsCl_3 :

Acetone
Acetic Acid
Benzene
Naphthalene
Resorcinol
o-Naphthol
Propylene glycol

Phenyl acetic acid was run in CDCl_3 , but was insoluble in AsCl_3 . Anisic acid was run in DMSO but was insoluble in AsCl_3 . Succinic acid and p-Nitrobenzoic acid defied adequate solution in any solvents.

From the reactive group, spectra of the following compounds were taken in both standard and inorganic solvents:

Triethyl amine
Dimethyl aniline
Benzoic anhydride

N-butyl amine was run to supplement the above group. Aniline reacted in AsCl_3 to form a solid product which could not be analyzed by NMR, and o-aminophenol defied solution in either solvent.

Several of the liquid samples were also analyzed neat.

III. OBSERVATIONS

Arsenic trichloride is magnetically active, so it should have a NMR spectrum, but it should appear at an entirely different field strength from that in the A-60. It seemed necessary, however, to analyze the sample of AsCl_3 which was to be used. This spectrum was taken at the maximum feasible amplitude. (Figure 1) This spectrum shows two peaks, at 458 hz./sec. and 464 hz./sec. These peaks appear in the midst of the aromatic range but they are of relatively low strength, so they would not be likely to give trouble with respectable sample concentrations and normal amplitude settings. These peaks were attributed to the presence of impurities in the AsCl_3 , which was quite old, and of unknown original purity. Water has been considered, but there are two peaks, rather sharp, and at quite fixed chemical shift. No further attempt was made to identify the peaks.

The unreactive compounds as a group exhibited essentially identical properties, so that they can be discussed in general terms. Chemical shifts seem to be affected slightly, most peaks being shifted a greater distance from TMS. In some cases, these shifts could be explained by concentration differences, but in the case of benzene, the shift of 24 hz./sec. would seem to be due to the AsCl_3 .

Spin coupling constants in the unreactive group, where observable, were strictly maintained. Reduced sharpness was observed in some peaks or groups, such as naphthlene.

The greatest observable effect of AsCl_3 in the

unreactive group involved the hydroxyl protons of naphthol and propylene glycol. Figure 2 shows the spectrum of naphthol in CDCl_3 and AsCl_3 . In the CDCl_3 spectrum, the hydroxyl peak is not located, although the entire spectrum was scanned separately. (1000--0 Hz./sec.). In AsCl_3 , there is a relatively sharp hydroxyl peak at 4.75 ppm. This is suitably located in the range for phenols, which is given as 7.1--4.2 ppm. (3)

Propylene glycol, a liquid, was run in three states: neat, in CDCl_3 , and AsCl_3 . These three spectra are shown in figures 3 and 4. Clearly, there is a considerable difference between the patterns presented in all three cases. The hydroxyl peak, which appears at 3.4 ppm in the neat form, and at 3.8 ppm in CDCl_3 is shifted to 7.1 ppm in AsCl_3 . Also, while the methyl peak doublet is only slightly shifted the other two peaks for the protons bound to the hydroxyl carbons and merged in a family of small peaks from 3.5-4.2 ppm in AsCl_3 . Clearly, identification of this AsCl_3 spectrum by the usual means would be quite difficult.

In the reactive group of compounds, an entirely different set of circumstances was found. First, the process of dissolution of almost all of the reactive compounds in AsCl_3 involved an obvious and definite chemical reaction. This reaction produced bubbling and spattering and evolved both heat and dense white fumes. In most cases

the reaction left a liquid product, but in the cases of piperidine, pyrrolidine, and aniline, the reaction of two liquids produced a solid product, which was clearly not suitable for analysis.

The spectrum of benzoic anhydride (Figure 5) is changed less than any other in this group. There was a nominal change in the chemical shift and the major spin coupling constants were unchanged. What did change slightly was the splitting pattern, which was increased in complexity. As can be seen, there are additional splits in two of the four major peaks. Since splitting is caused by neighboring magnetically active atoms, the possibility of a new atom on the molecule, namely arsenic in some form, must be considered. This possibility will be considered more fully later.

Normal butyl amine is another case of a reaction that is not easily identified. Comparison of the two spectra (Figure 6) taken in CCl_4 and AsCl_3 show a vast change in the character of the molecule with the presence of AsCl_3 . (The spectrum of the neat liquid was also taken and is essentially identical to that in CCl_4 .) The amine protons in CCl_4 give a sharp peak at 1.3 ppm. In AsCl_3 , this peak is shifted to 7.3 ppm. The alkyl peaks are broadened in AsCl_3 , which is unusual for alkyl peaks, and three tiny new peaks appear at 3.7, 3.85, and 3.95 ppm. The general broadening is typical of hydroxyl and amine hydrogens in

general, and indicates rapid proton exchange, which is unlikely in alkyl groups, but can occur.

The two most clear cut cases are N,N-dimethyl aniline and triethyl amine. (Figures 7 and 8) In both cases, chemical shift increased significantly although the major spin coupling constants remained the same. The difference was most easily observed in the splitting patterns. In both cases, the protons on the carbons adjacent to the nitrogen showed secondary splitting as if a magnetically active atom were attached to the nitrogen. Such an additional atom on the nitrogen could also be responsible for the increased chemical shift.

In the triethyl amine, it is difficult to classify the additional splitting to determine the number of additional atoms on the nitrogen. In the case of dimethyl aniline, however, the situation is more obvious. The singlet methyl peak at 2.85 ppm in CDCl_3 is shifted to 3.2 ppm and split into a doublet, indicating a magnetically active atom on the nitrogen. The very wide split, perhaps into two separate peaks rather than a doublet could be explained by steric rotation hindrance caused by a bulky group bonded to the nitrogen, creating slightly different environments for the two methyl groups.

Some consideration must now be given to the reaction which occurs between the amines and AsCl_3 . The evidence indicates, as might be expected, that the nitrogen atom is

the reactive site on the amines. Since the protons on carbons adjacent to the nitrogen are split, we know that the new substituent must be magnetically active, but since it gives no spectrum of its own, the substituent is almost certainly the arsenic. In the primary and secondary amines, protons can be replaced, but this does not seem to be the case, and in the tertiary amines, there is no proton to replace. The evidence also eliminates the possibility of alkyl groups being replaced. This leaves us with the possibility of a reaction producing something analogous to an ammonium salt, i.e. $R_3NAsCl_2^+ Cl^-$.

Most reported reactions of halo-arsenic compounds with amines or ammonia suggest the substitution of an amine hydrogen with arsenic, which has lost a halogen.(4) and (5) Also, arsenic trichloride reacts with diphenyl amine to produce phenarsazine chloride, with arsenic attached to carbon in the rings.(6)

Phosphorous trichloride and trialkyl amines react to form the addition product R_3NPCl_3 , which should give spectra identical to those observed, if the same reaction occurs in the arsenic case. This reaction seems to explain the data best.(7)

IV. PROBLEMS

In addition to the obvious problems of too much reaction or too little solution, a definite problem was encountered with the AsCl_3 which could be of great importance and considerable expense in practical applications. All the sample tubes used with AsCl_3 or stored for cleaning near others used with AsCl_3 developed very inert deposits of paramagnetic material, apparently arsenic salts. This made it almost impossible to use these tubes since erratic results were obtained and peaks were broadened and split, and tuning, if achieved, could not be maintained.

Nitric acid, the cleaning agent previously used, was ineffective in removing these deposits. Ethanolic potassium hydroxide and chromic acid both gave equally disappointing results. Aqua regia (hydrochloric acid and nitric acid) finally removed at least a major portion of the deposits, enabling the tubes to be used.

Cleaning was accomplished in a large tube closed at one end. The sample tubes were placed open end down in the tube and covered with cleaning agent. The tube was sealed and evacuated by a water aspirator. When the vacuum was broken gently, cleaning agent flowed up into the tubes. This was repeated several times before the tubes were rinsed with water, acetone, and finally chloroform by the same procedure. The tubes were blown out with nitrogen to dry them.

V. CONCLUSIONS

Based on the evidence presented, it is felt that arsenic trichloride will find only limited usefulness as an NMR solvent. Certain substances will dissolve in AsCl_3 while they will not dissolve in conventional solvents, and these substances may be run in AsCl_3 to advantage if they are not of the reactive type.

Arsenic trichloride may be useful, however, in an application previously not considered. This application is based on its reaction with amines. Since AsCl_3 reacts with and affects the spectrum of amines, it may be extremely useful for structure confirmation in complex amines, or for structure determination in unknowns. Further work could be done with other nitrogen compounds to determine usefulness in these cases. Work could also be done with the unreactive group to catalogue the changes in chemical shift for different groups and classes in AsCl_3 , increasing its usefulness as a solvent for general use.

Arsenic trichloride will probably never replace the standard organic solvents for NMR, but for certain purposes it may prove to be quite useful.

FIGURE 1

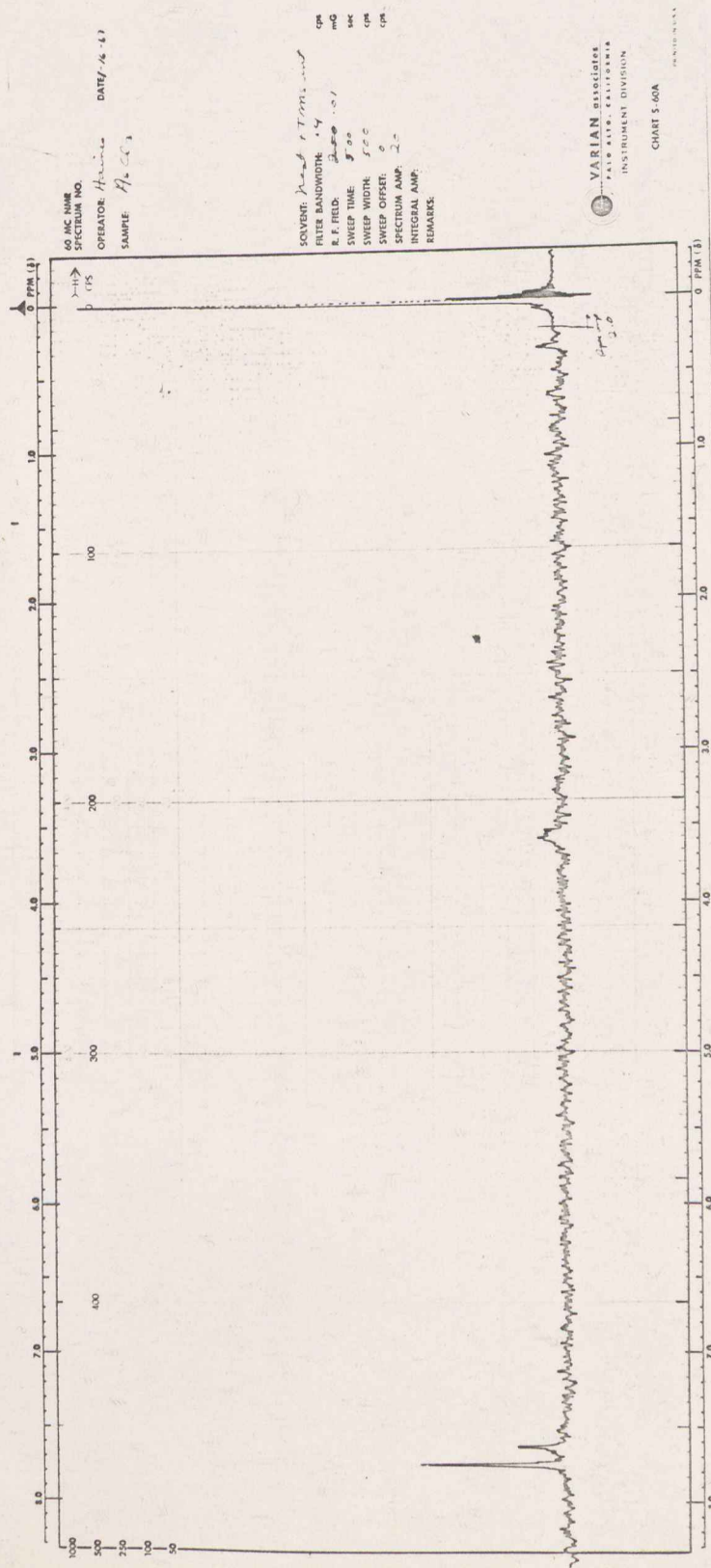


Figure 2

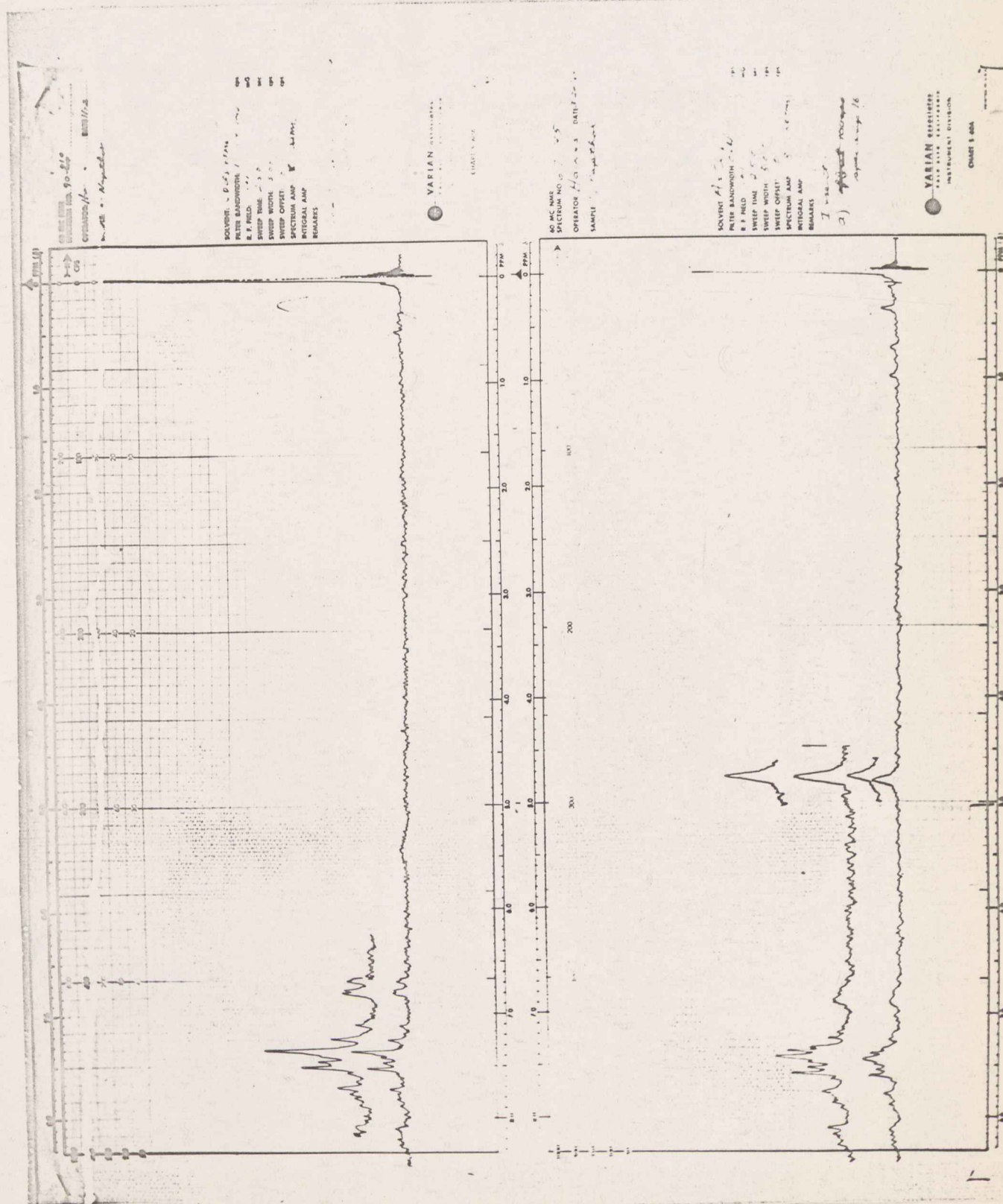


FIGURE 3

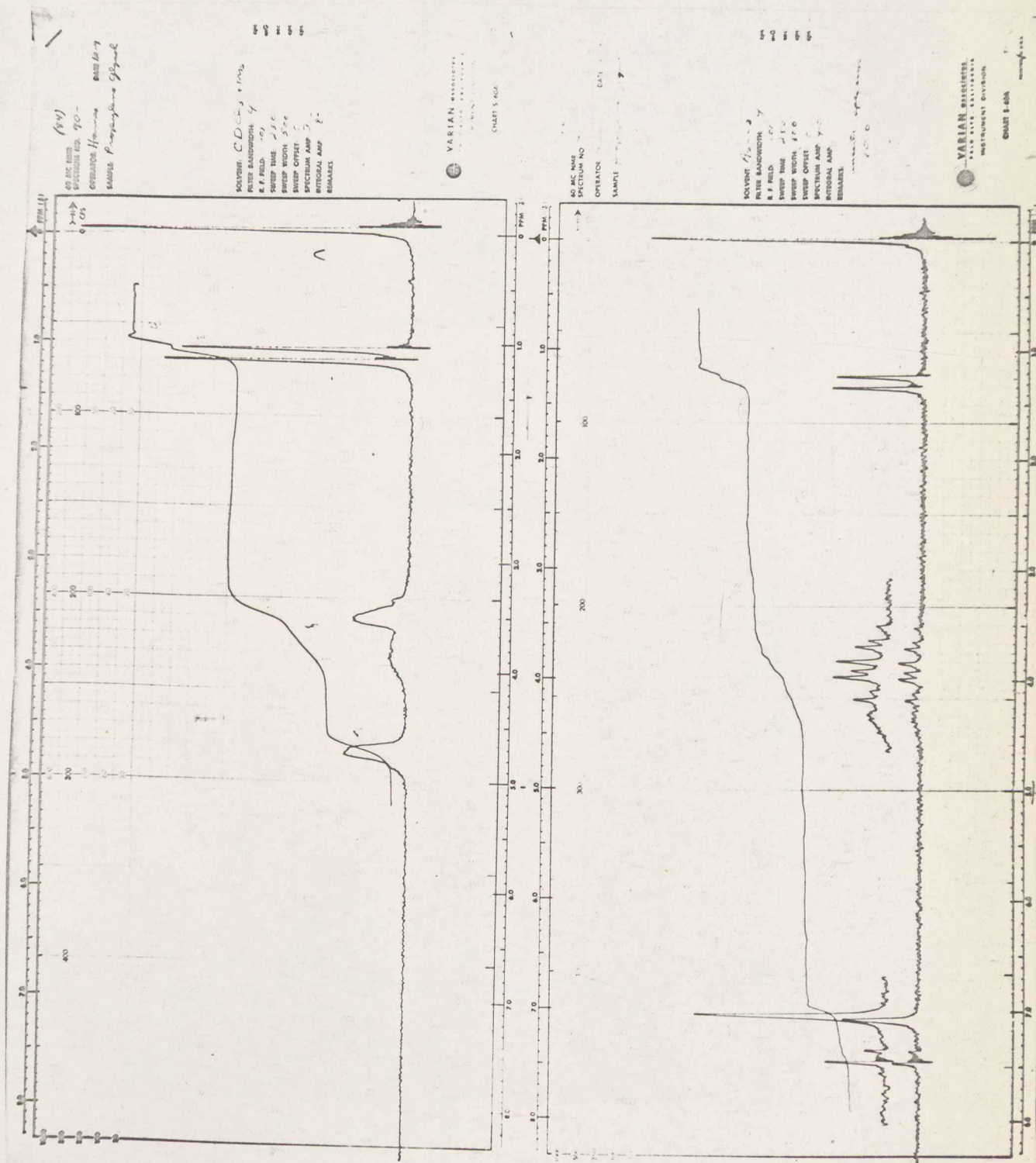


FIGURE 4

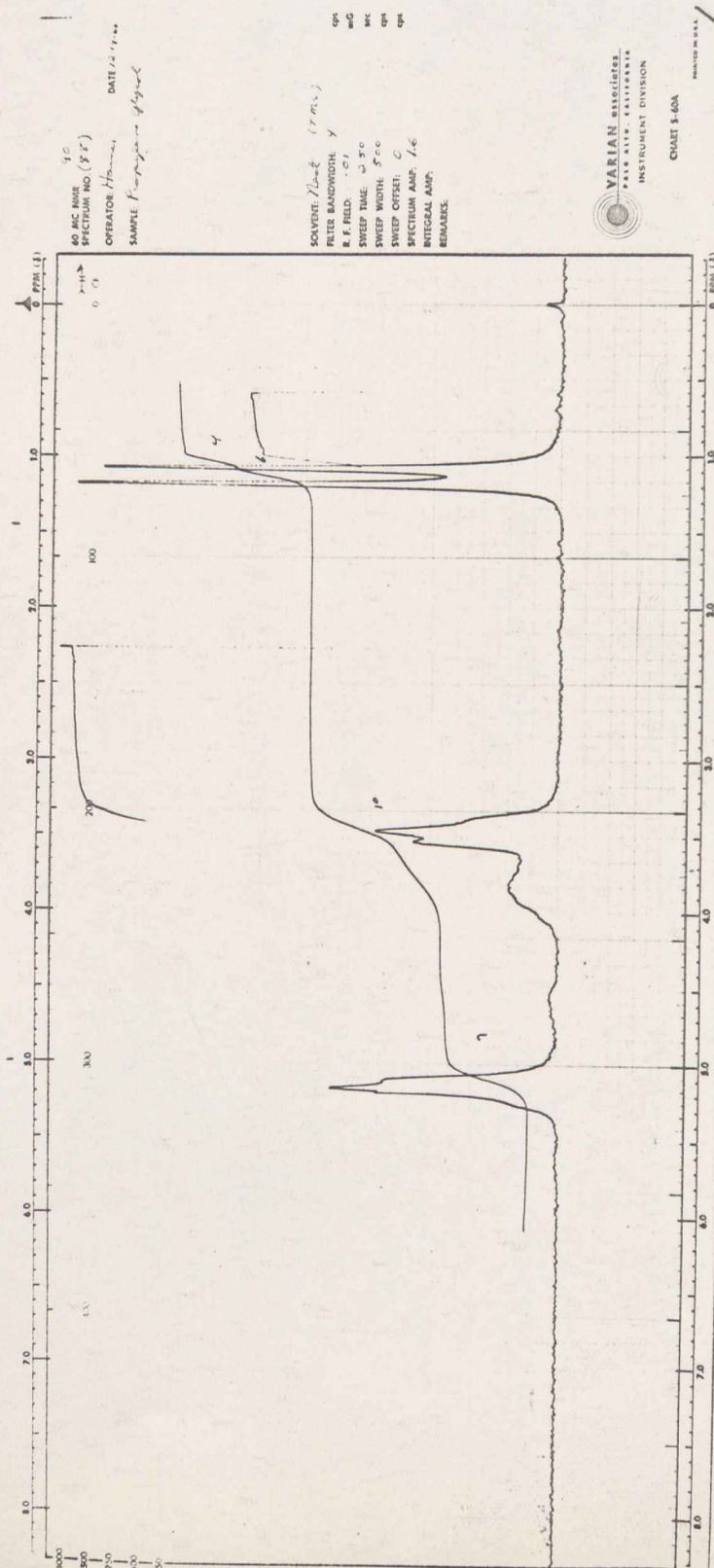


FIGURE 5 a

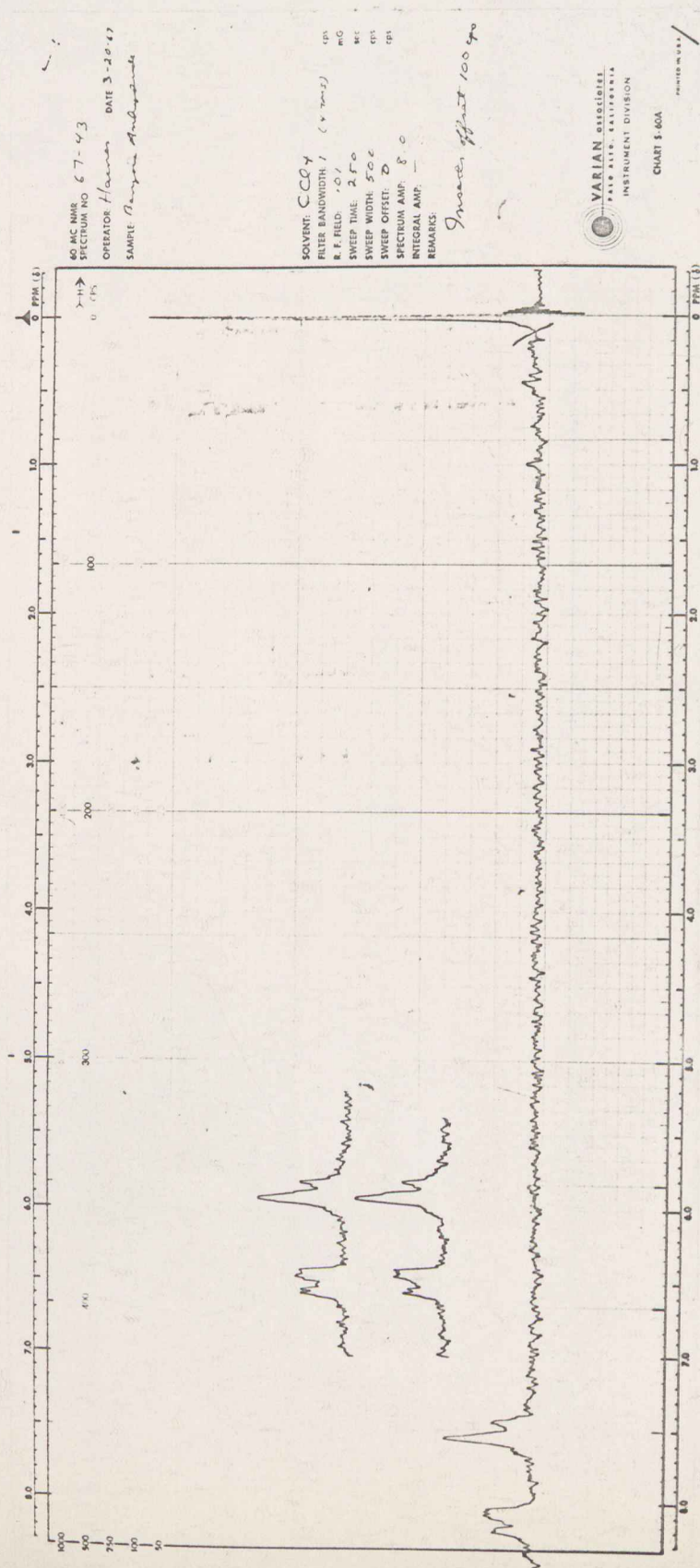


FIGURE 5 b

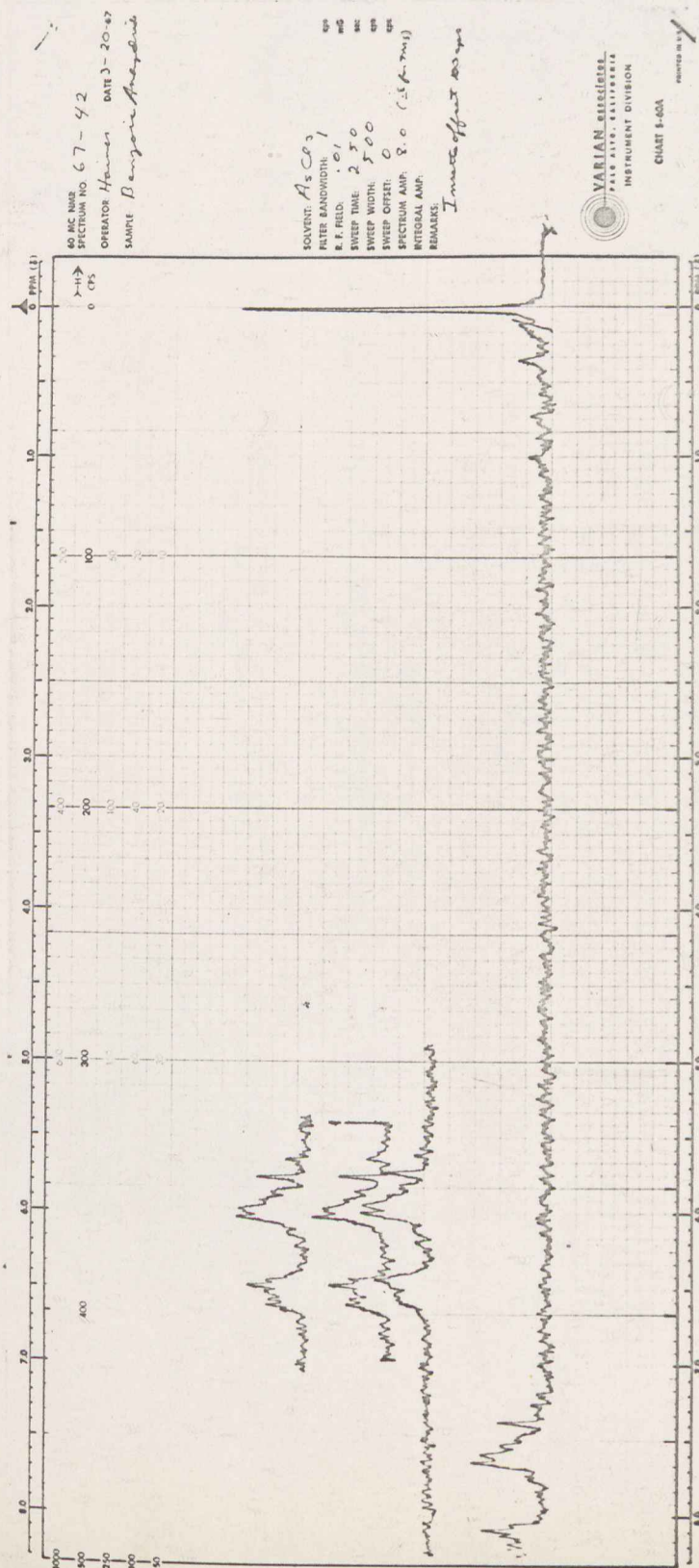


FIGURE 6

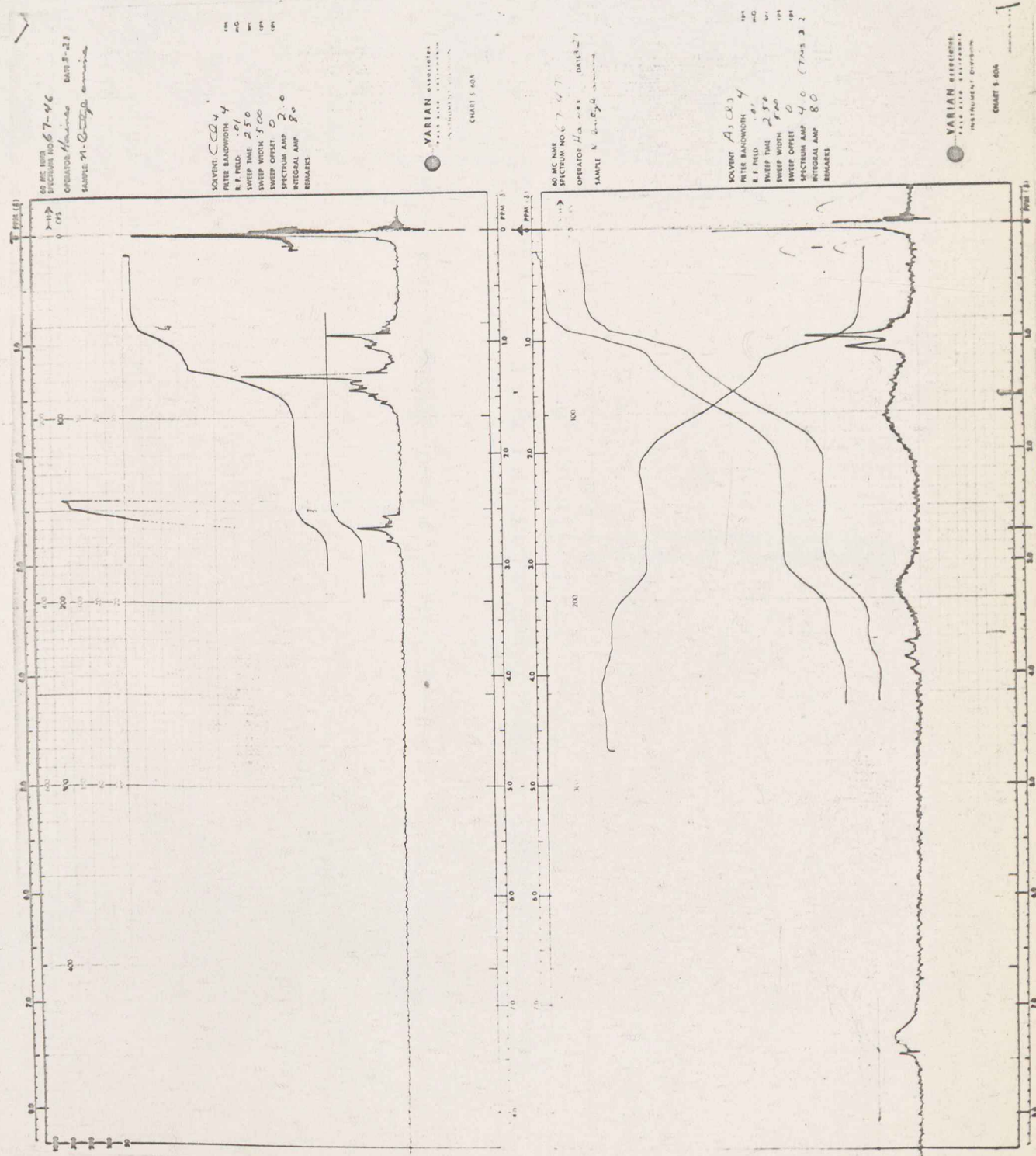
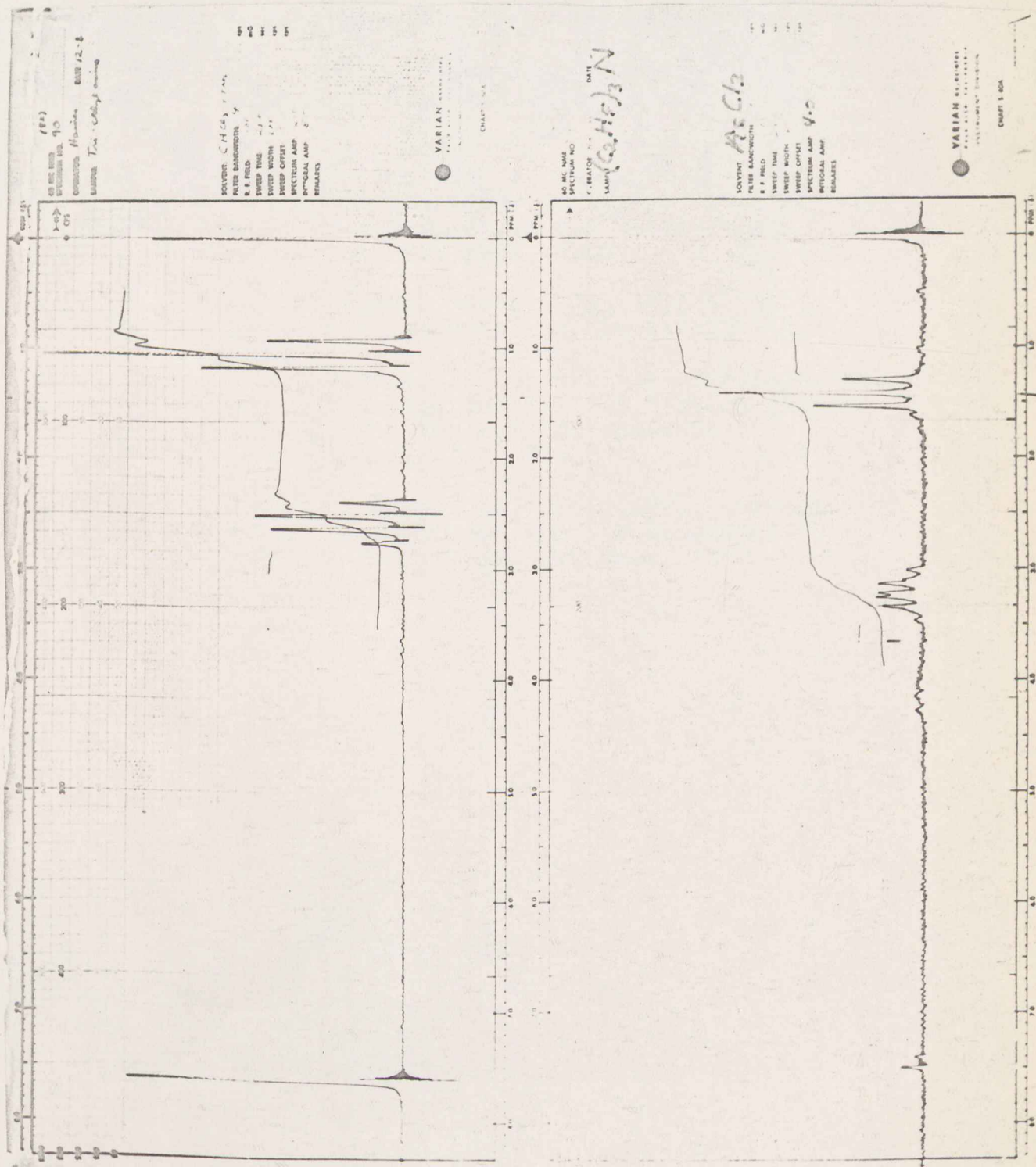


FIGURE 8



BIBLIOGRAPHY

1. Szymanski, H.; Analytical Chem. 37, 617-18 (1965).
2. Olah, G.A.; J. Am. Chem. Soc. 89, 711, (1967).
3. Silverstein and Bassler, "Spectrometric Identification of Organic Compounds," 87, John Wiley and Sons, New York, 1964.
4. Cullen, W.R. and H.J. Emeleus; J. Chem. Soc. (London) p. 372, (1959) through "Advances in Organo Metallic Chemistry" edited by F.G.A. Stone and Robert West, vol. 4, Academic Press, New York, 1966.
5. Doak, G. O.; J. Am. Pharm. Assoc., 24, 453, (1935), through "Advances in Organometallic Chemistry," (Op. Cit.).
6. Mann, F.G.; "The Heterocyclic Derivatives of Phosphorous, Arsenic, Antimony, Bismuth, and Silicon," Wiley (Interscience), New York, 1950 through "Advances in Organometallic Chemistry," (Op. Cit.)
7. Trost, W. R.; Can. J. Chem., 32, 356 (1954), through John R. Van Wazer, "Phosphorous and its Compounds," Vol. I, Interscience Publishers, New York, 1958.