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TUNNEL DENIAL STUDY

Final Report

By
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Franklin Institute Research Laboratories

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13. ABSTRACT

Under Work Assignment No. 1 of Contract DAAD05-72-C-0113 by the Franklin Institute Research Laboratories (FIRL) for the U. S. Army Land Warfare Laboratory, the feasibility of disseminating o-chlorobenzal malononitrile (CS) as a two-component aerosol system was studied. The rate of CS formation from o-chlorobenzaldehyde (OCBA) and malononitrile (MN) with and without catalyst was followed using gas liquid chromatography (GLC). Having demonstrated the above feasibility Work Assignment No. 6 involved control of the rate of reaction in such a manner as to keep the concentration of CS above that which is considered incapacitating (10-20 mg/m^3). Encapsulation of the reactants was studied as a method of controlling the rate.

The object of the study is to develop a method of controlling the rate of reaction in an enclosed space, such as a tunnel, in such a manner as to produce CS in an effective concentration over a minimum period of six months.

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FOREWORD

This report is submitted in compliance with contractual requirements as directed by the U.S. Army Land Warfare Laboratory, Aberdeen Proving Ground, Maryland, under Contract No. DAAD05-72-C-0113. Mr. Harold H. Rosen, Biological Sciences Branch, served as Technical Supervisor for the work, and we would like to acknowledge his insights and assistance during the project.

Principal Investigator for the program at the Franklin Institute Research Laboratories was Mr. F. J. Sweeney, Research Chemist, Materials and Physical Sciences Department. Other FIRL personnel contributing significantly to the program were Miss Florence Serafin, Research Chemist, Dr. Peter Francis, Director of the Materials and Physical Sciences Department and Mr. William Collins, Director, Electrical Engineering Department.

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1. INTRODUCTION

There is at present no completely satisfactory method for denying the reuse of tunnels. Destruction by explosives creates a logistic problem as well as generally requiring that the tunnel be entered to implace the explosives. Treatment with CS does not deny the tunnel for a long enough period.

It is the objective of this study to devise a system for the *in situ* generation of CS from o-chlorobenzaldehyde and malononitrile (with or without catalyst) by disseminating the two components as an aerosol and to study the rate of formation and decay of CS.

Once this objective is realized, methods for controlling the rate in such a manner as to maintain physiologically active concentrations of CS (10-20 mg/m^3) over a period of six months are to be investigated.

2. CONCLUSIONS

1. It is possible to generate CS in situ at a rapid rate by separately spraying the two components that form CS into an inclosed space at room temperature and pressure.

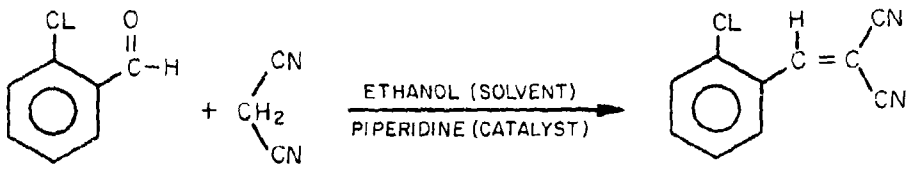
2. The method described above produces a peak concentration in about 2.5 hours and remains above the effective concentration for six hours.

3. It is possible to encapsulate o-chlorobenzaldehyde in relatively stable micro-capsules from which it can be released by rupture of the capsules to react with aqueous malononitrile at room temperature and pressure.

4. Encapsulation and the two-component system for generation of CS provide a good possibility for achieving the goal of maintaining an effective concentration of CS in a tunnel or bunker for a significant period of time. This method should be pursued further.

3. THEORETICAL

The preparation of o-chlorobenzal malononitrile in 95% yield was reported in 1928 by Corson and Stoughton[1]. The compound is prepared by condensing o-chlorobenzaldehyde with malononitrile using piperidine as a catalyst, and absolute ethanol as solvent.



In 1959, S.R. Eckhaus, et al.[2] studied percent yield of CS as a function of solvent, temperature, pH and reaction time. They found the following conditions to be optimal:

a) Solvent - 30% aqueous ethanol or isopropanol
b) Temperature - 50°C
c) pH - 6.5
d) Reaction time - 30-40 minutes

These results were of some value to us since we are to disperse the reagents as two separate aerosols, one containing the o-chlorobenzaldehyde, the other containing malononitrile. Formation of CS would then depend on: collision of two or more aerosol droplets, containing each of the reactants, reaction of OCBA and MN in this droplet, and finally evaporation of the solvent to form an aerosol particle of CS.

4. SELECTION OF ANALYTICAL TECHNIQUE AND INITIAL EXPERIMENTS

4.1 SPECTROPHOTOMETRY

It was at first decided to follow the course of reaction between OCBA and MN by measuring the increase in CS absorbance in the ultraviolet. This was to be done by aspirating the chamber and trapping the effluent or by washing the chamber walls with a suitable solvent. The solution would then be taken up to known volume and its U.V. spectrum recorded. The concentration of CS could then be calculated using the Beer-Lambert Law.

We ran U.V. absorption spectra on our Cary 14 recording spectrophotometer. The absorption maximum for o-chlorobenzal malononitrile is 298 mμ; that for o-chlorobenzaldehyde is 250 mμ. As expected, malononitrile has no intense absorption maximum in the U.V. region (see appendix).

4.2 GAS CHROMATOGRAPHY

Although the U.V. absorption for OCBA and CS are well separated and suitable for analysis of one in the presence of the other, the possibility of further reaction taking place during washing and dilution of samples prompted us to consider gas chromatography (GC) as the analytical technique. The GC method has several advantages: it is much more rapid (20-30 min./analysis); easily quantitated; there is no need to make dilutions, and with a gas tight syringe one can sample directly from the vapor space in the chamber.

Investigation of the literature yielded data for GC analysis of CS[2]. Two 5.5 ft. x 1/4 in. glass columns packed with 10% QF-1 on 60/80 mesh Gas-Chrom Q were purchased from Applied Science Laboratories and installed in our Beckmann GC-45 equipped with flame ionization detectors.

(Due to a prior commitment of the Beckman GC-45, we later switched to our Hewlett-Packard model 810 research chromatograph using essentially the same conditions.)

Standardization and retention time data was taken using sclutions of CS, OCBA and MN in ethylacetate. It was found that diethylphthalate, used as a fogging agent and diluent, emerged from the column too close to the CS peak during programmed G.C. runs. Isothermal conditions gave separation but increased analysis time considerably. We decided to omit diethylphthalate in our spray formulations and use methylene chloride alone since good fogs could still be obtained without diethylphthalate.

We made several calibration runs using reagents of different concentration. After the run the peak area was measured by triangulation, then normalized to account for attenuation changes. In an effort to simplify analysis of raw data, we made up a solution of CS in ethylacetate so that 1 μL of the solution was equivalent in response to a 5.0 ml gas sample of physiologically active concentration (20 mg/m^3). Thus, at any time we could see the response from a physiologically active concentration simply by injecting one microliter of this standard solution. This was done each time any parameter was changed, and intermittently to check the flame ionization detector response.

By this technique we could easily detect 5 nanomoles of CS and OCBA. Malononitrile, however, being highly polar had a high retention time and emerged as a broad peak. By sampling 5.0 ml of the vapor above closed containers of CS and OCBA, we observed excellent responses; but the chromatograms were not reproducible due to condensation on the syringe. A thorough washing with methylene chloride, then heating the syringe to 50°C before sampling and injection, alleviated this problem. Although several temperature programs were tried and used, we found the best to be isothermal at 65°C for 2 min. then increased to 200°C in 16 minutes and holding for 4 minutes. Using this program CS emerges in about 16.5 minutes.

4.3 DESIGN OF THE TEST CHAMBER

The actual test chamber is a modified 5-liter 3-neck flask. A ground glass female joint was sealed to the bottom of the flask and connected in series to a trap filled with chloroform and a critical orifice to limit the flow of purge gas. The outlet from the critical orifice was connected to a rotary vacuum pump (Figure 1). Originally we had intended to spray the reagents in the flask, allow a specified time for reaction, then aspirate the contents into a solvent trap. The solution would then be subjected to further analysis for CS. Further development prompted us to alter our sampling technique. As described in the text, two further modifications were necessary. First, the bottom joint was removed and two heated glass extensions were placed on two of the joints. The third joint was sealed with a rubber septum. Secondly, we replaced the two heated tubes with one 24" long (Figures 2 and 3) and sealed the other openings with rubber septa.

4.4 PRELIMINARY EXPERIMENTS

Initially we decided to spray the two reagents and the catalyst into the test chamber, and after a specified time the aerosolized CS would be aspirated into the trap and analyzed. Also, we wanted an estimate of how much CS condensed on the walls of the flask.

Since the solvents reported by Eckhaus, et al.[2] for the reaction were all highly polar, we conducted an experiment using hexane, a non-polar solvent - the objective being to find a solvent wash in which no further reaction would take place. Thus, to 50 ml of .01 M malononitrile in reagent grade hexane was added 50 ml of 0.01 M o-chlorobenzaldehyde and a drop of piperidine. After about 30 seconds, the solution became cloudy and the physiological effect of CS could be realized.

Several other relatively non-polar solvents were tried (pentane, ether, benzene) all of which showed the same effect. It became evident that we could not determine quantitatively the amount of CS formed *in situ* by aspirating the chamber contents into a solvent trap since further reaction would take place during work-up and analysis.

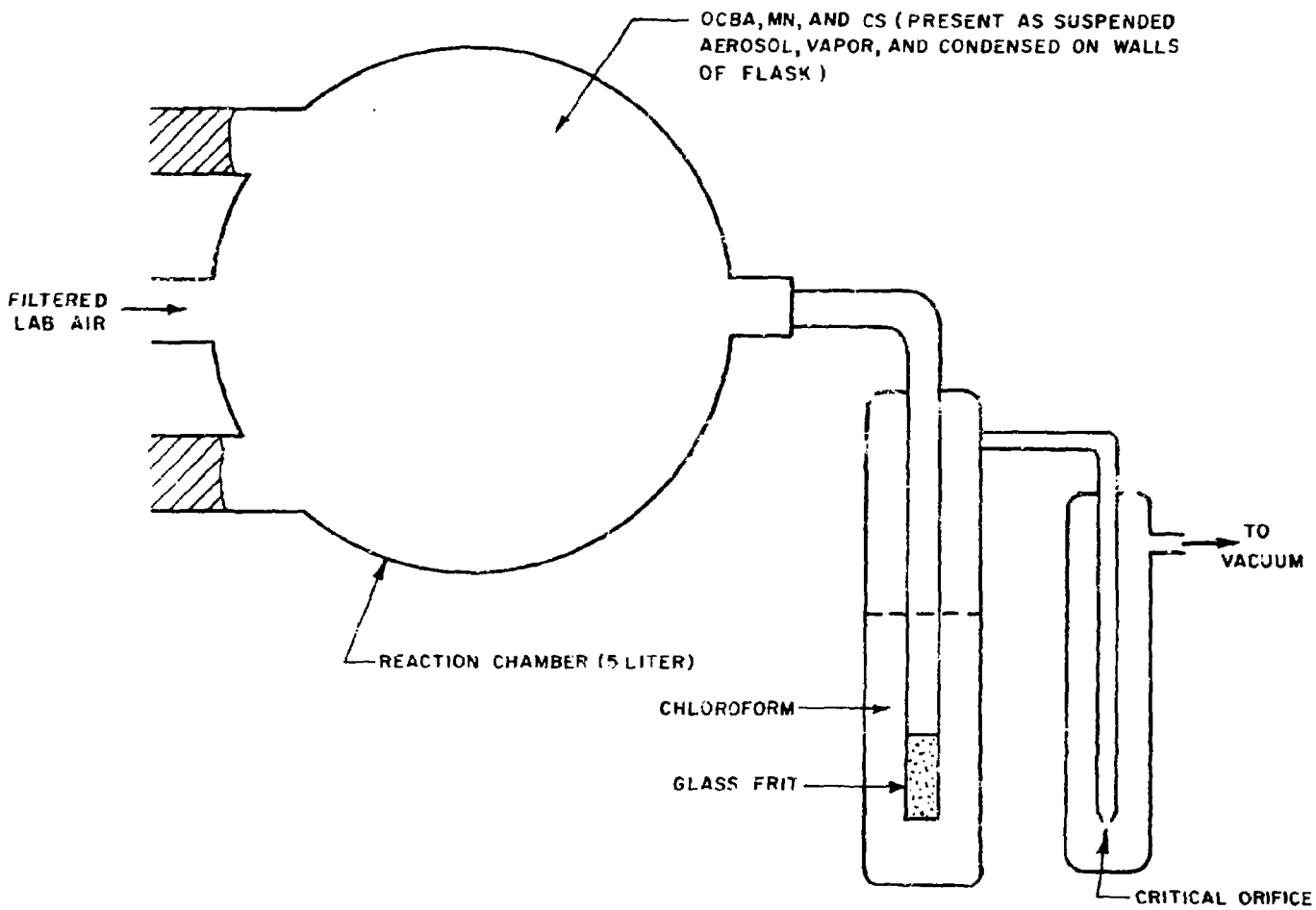


Figure 1. Test Chamber

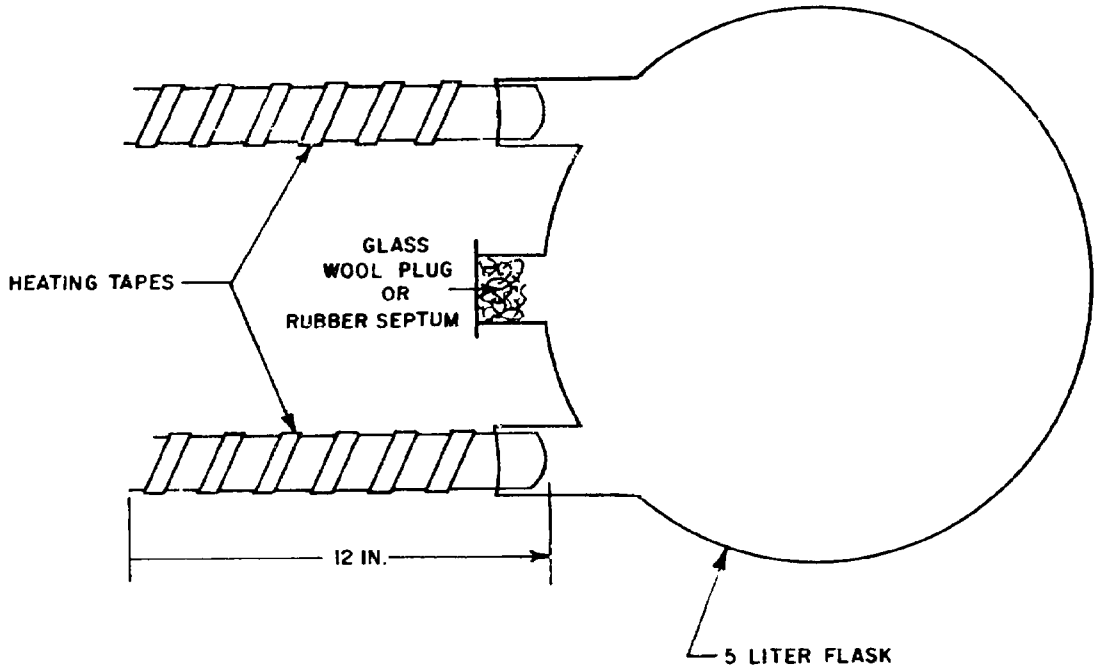


Figure 2. Test Chamber (First Modification)

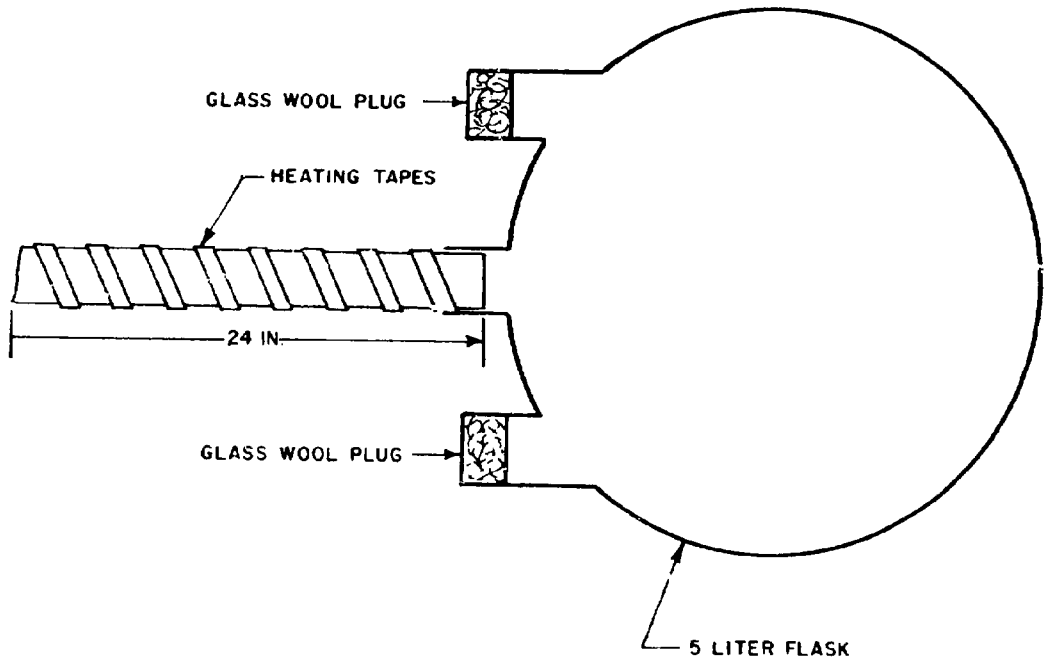


Figure 3. Test Chamber (Second Modification)

5. EXPERIMENTAL

Having found a reliable analytical procedure and having modified test chamber, we were now ready to start our experiments. Several trial runs were made using equimolar concentrations of MN (6.6 g/50 ml solvent) and OCBA (14.1 g/50 ml solvent) - first in diethylphthalate methylene chloride 1:1, then in methylene chloride. Before spraying the two glass extension tubes were heated to 270-290°C and the center outlet of the flask was plugged loosely with glass wool. The reagents were sprayed concurrently through the heated tubes for about 15 seconds until a very dense fog could be observed in the flask. Thorough mixing of the two sprays was evidenced by the vigorous swirling and vortexing of the fog in the flask. Quantities of reagents were estimated by weighing the sprayers before and after spraying. Upon completion of the spraying operation, the heated tubes were replaced by glass stoppers and the center neck closed with a rubber septum. The first chromatogram was run immediately using a 5.0 ml sample in a warmed gas-tight syringe, and every 20 minutes thereafter. Immediate formation of CS was observed by a peak at the proper retention time in the first chromatogram.

However, within 45 minutes the fog in the flask settled with concomitant decrease in CS concentration. At no time did the CS in the fog reach physiologically active level. In order to decrease the aerosol particle size and give a more durable fog, the concentration of reagent solutions was doubled. Using the same spraying procedure outlined above we have increased the fog duration to 55-60 minutes but concentration of CS was still far below active.

A further modification of the chamber was suggested by Mr. Hal Rosen, contract supervisor. In order to more closely simulate actual field conditions, the two 12" heated tubes were replaced by one 24"

long, and the reagents were sprayed in one at a time. With this modification we were able to obtain usable although somewhat erratic data. For example, three runs were made:

In the first run, approximately 300 mg of MN and 700 mg of OCBA were sprayed into the flask in methylene chloride solution - no catalyst was used.

In the second run, approximately 5 mg of piperidine was introduced into the chamber through the heated tube. The concentration of OCBA and MN was the same as in the uncatalyzed run.

In the third run, the piperidine was sprayed through the cool port. Again OCBA and MN concentration was 700 mg and 300 mg respectively. Chromatograms were run every 20 minutes for the first 4 hours and hourly thereafter.

Results from the first run are shown in Table 1 and Figure 4. The area of a chromatogram corresponding to a physiologically active concentration is plotted horizontally. It can be seen that CS concentration reaches physiologically active concentration in about 1.5 hour, maximum concentration in 2.5 hours, then rapidly falls below active concentration after 6 hours.

The concentration of CS in catalyzed runs never reached physiologically active levels. Also, after 24 hours a brown film could be seen on the walls of the flask. This film was not present in the runs without catalyst. A portion of this oily material was dissolved in acetone and injected into the chromatograph. Several peaks emerged but none correspond to CS.

Again we sprayed approximately 300 mg of MN and 700 mg of OCBA in methylene chloride solutions without catalyst in an attempt to duplicate previous results.

As Figure 5 shows, maximum concentration is reached immediately and the decay of CS is almost linear (see also Table 2). Active concentration persisted for only 50 minutes. This differs considerably from the

TABLE 1

Time (Hours)	Peak Area (mm^2)	Attenuation	Normalized Peak Area (Atten. x 8)
0 (start)	1463	2	366
2.0	975	8	975
3.5	1596	8	1596
8.5	1674	4	824
22.5	1120	2	280
26.5	1040	2	260
67.5	899	2	225
74.5	1245	2	311

TABLE 2

Time (Minutes)	Peak Area	Attenuation	Normalized Peak Area
0	416	128	6656
20	455	64	3640
40	476	32	1904
60	270	16	540

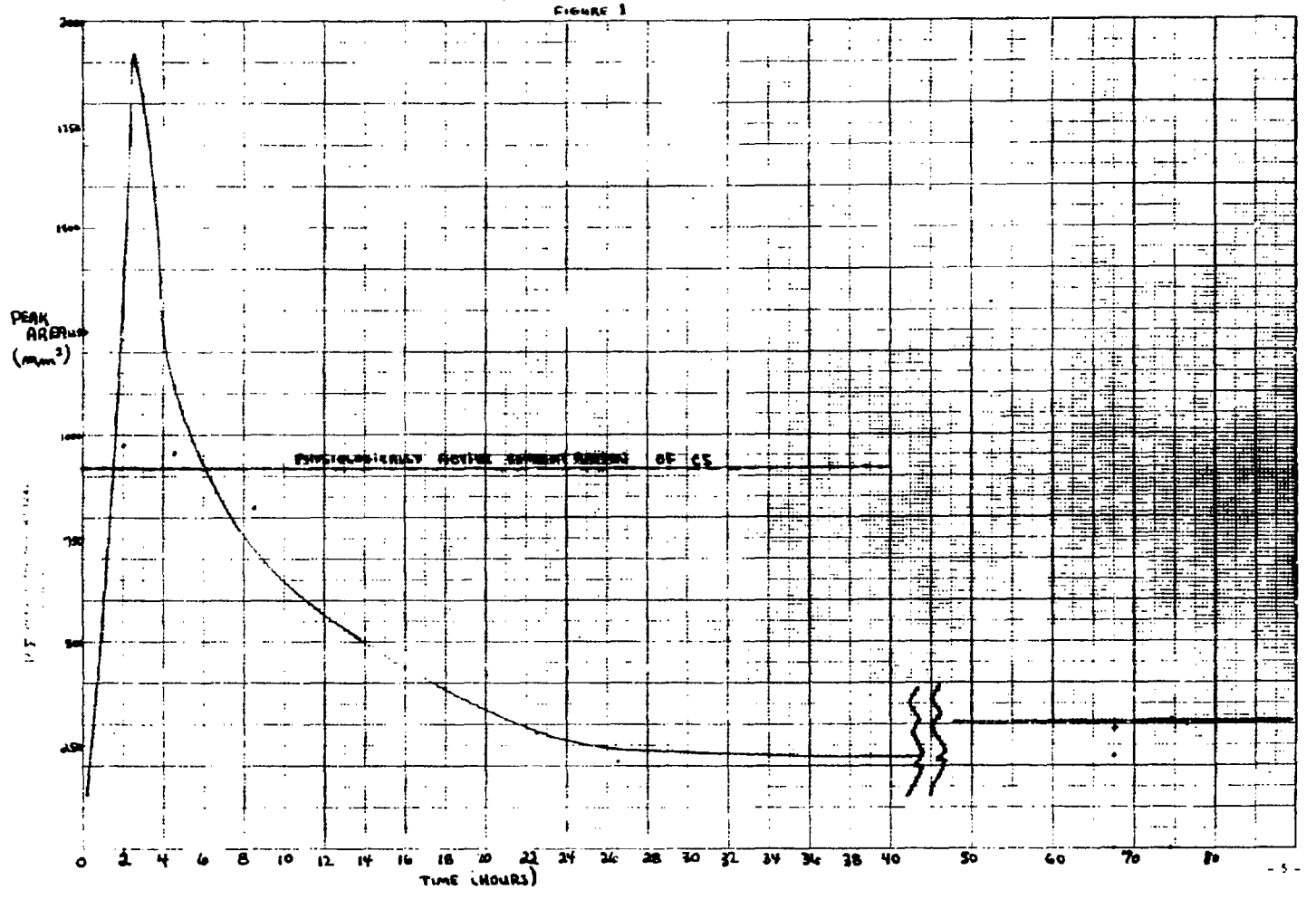


Figure 4. MN and OCBA in Methylene Chloride (No Catalyst)

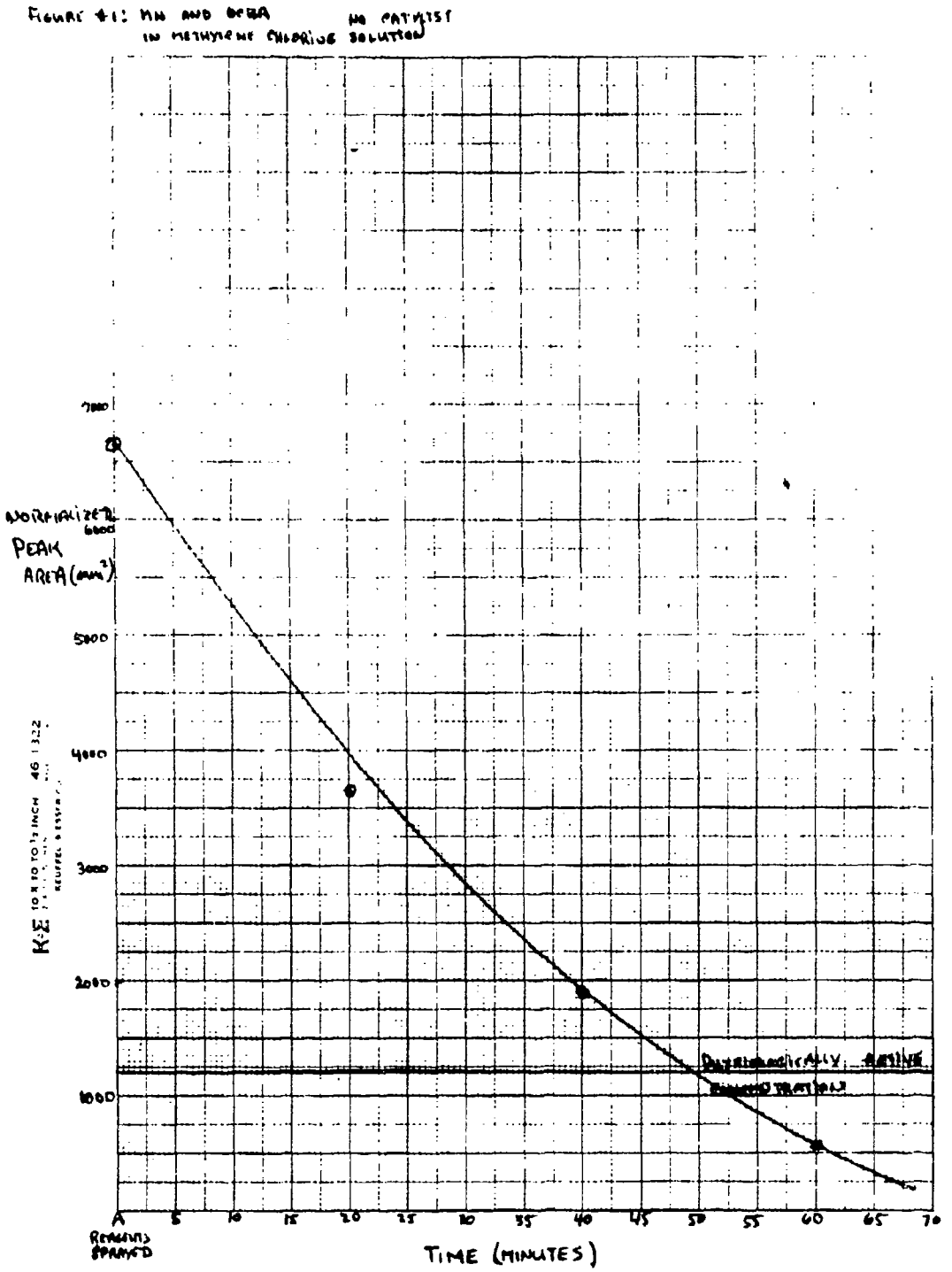


Figure 5. MN and OCBA in Methylene Chloride (No Catalyst)

first run wherein maximum concentration was reached in 2.5 hours, and activity persisted for 6 hours. Since all other parameters were constant, this difference can be attributed to the extreme difficulty of spraying exactly the same quantities of reactants into the chamber repeatedly.

The next experiments show the results of two other base catalysts. Thirty milligrams of pyridine were added to the reaction flask prior to spraying the reactants (Figure 6, Table 3). Again maximum concentration was reached immediately but dropped below active levels in about 2 hours. Next 30 mg of n-butylamine were added to the methylene chloride solution of orthochlorobenzaldehyde and sprayed through the heated tube (Figure 7, Table 4). So instead of depending on evaporation of the base from the walls of the chamber for catalytic activity, it is originally present as an aerosol with the reactants. In this system maximum concentration is reached immediately after (or during) spraying but it dropped much more quickly. Figure 7 shows the initial concentration of CS to be about 10 times that of the first two runs. This was attributed to increased sensitivity resulting from cleaning of the G.C. flame ionization detector. This conclusion was reached through observation that the response from the standard solution was also about 10 times higher.

5.1 MICROENCAPSULATION

On July 7, 1972, discussions were held with Mr. H. Rosen of LWL. The opinion was reached that although we have successfully demonstrated the feasibility of on-site generation of CS from the reactants, with or without catalyst, the problem remaining is to ensure the concentration remains physiologically active for longer periods of time. We decided to investigate the possibility of microencapsulating one or both reagents in a polymer which is friable enough to rupture when disturbed, or through which the reactants can diffuse.

Another possibility considered was encapsulating (or embedding) the CS in microcapsules made from a water soluble polymer. These

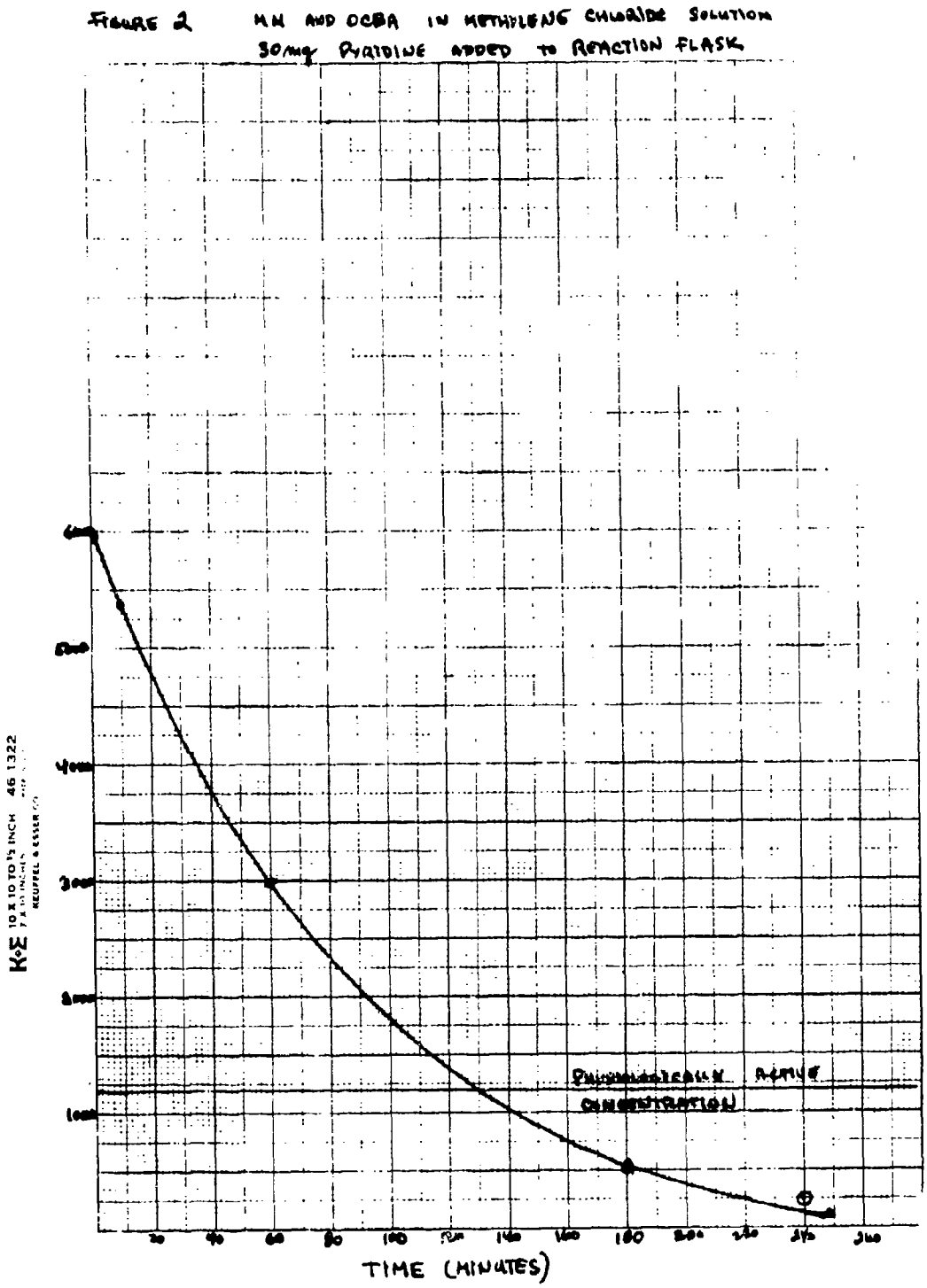


Figure 6. MN and OCBA in Methylene Chloride, 30 mg Pyridine Added

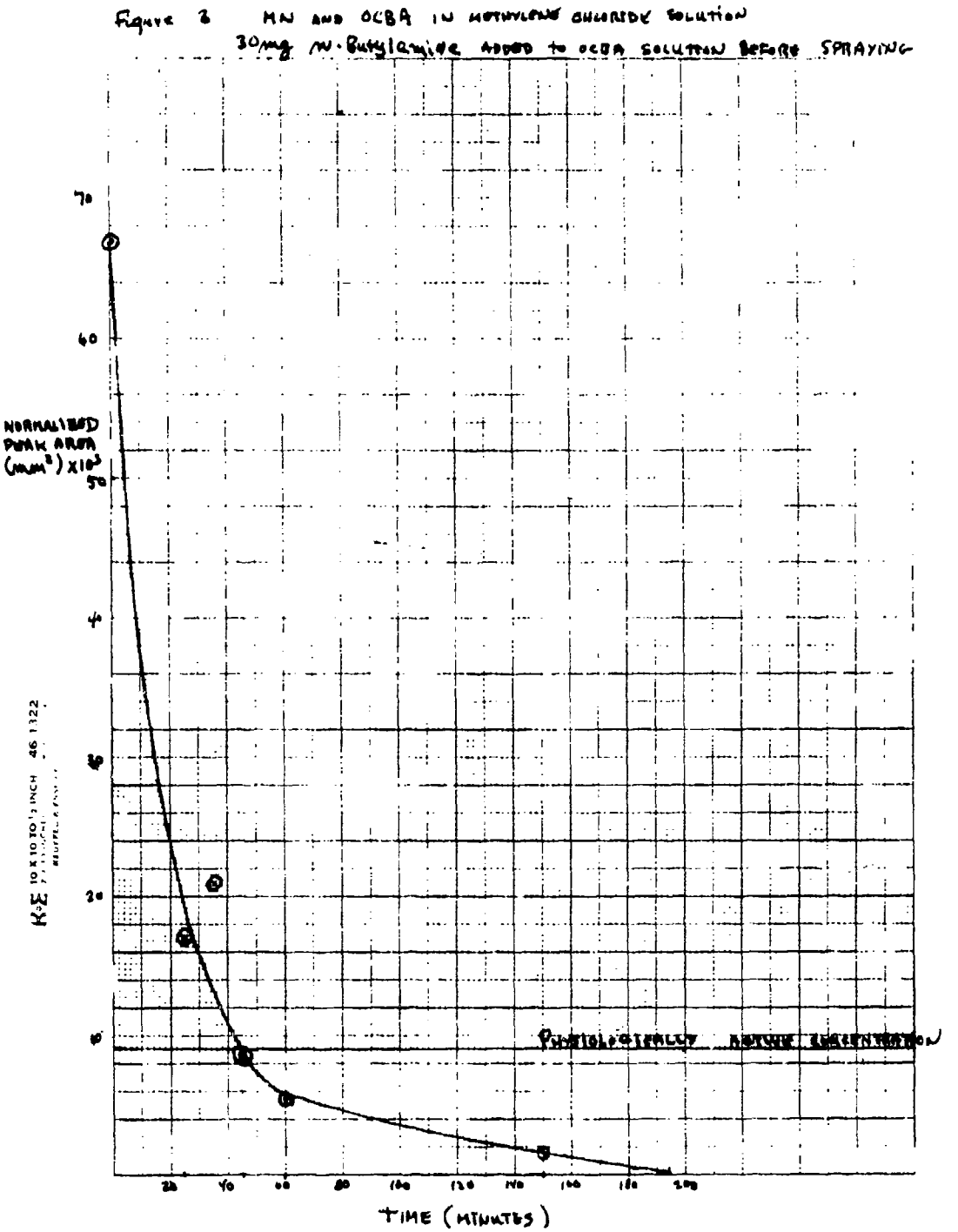


Figure 7. MN and OCBA in Methylene Chloride Solution, 30 mg n-Butylamine Added

TABLE 3

Time (Minutes)	Peak Area	Attenuation	Normalized Peak Area
0	750	64	6000
10	430	1000	5375
60	2950	8	2950
180	499	8	499
240	238	8	238

TABLE 4

Time (Minutes)	Peak Area	Attenuation	Normalized Peak Area
0	8375	64	67,000
25	538	256	17,200
35	658	128	21,056
45	1040	64	8,320
60	675	64	5,400
150	396	32	1,584
180	138	32	500

capsules when disturbed would enter the mucuous membrane, dissolve and release their contents. This approach was rejected since studies on encapsulation had been done at Edgewood Arsenal.

Microcapsules can be made by a technique involving interfacial polymerization. A solution of a diacidchloride such as sebacoyl chloride in chloroform or carbon tetrachloride is emulsified by stirring in a Waring blender at high speed. To this mixture an aqueous solution of a diamine such as hexamethylene diamine and a small amount of emulsifier is added dropwise. Polymerization takes place at the interface of the two immiscible solvents and only there, forming small spherical shells of polyamide. Organic materials can be incorporated into the spheres by dissolving them in the nonaqueous phase (see Figure 8). Initial experiments with the above system looked encouraging. We encapsulated OCBA by dissolving it in a carbon tetrachloride solution of sebacoyl chloride. To this was added a solution of hexamethylene diamine in water. Polymerization took place immediately resulting in a slurry of milk white polyamide microcapsules. Examination under a scanning electron microscope revealed the presence of spherical capsules approximately 35 microns in diameter with amorphous polymer interspersed (Figures 9 and 10).

A brief review of the most recent patent literature yielded another promising technique for microencapsulation. Water immiscible organic oils can be encapsulated by selective coagulation of an aqueous solution of egg albumin around the oil. This yields a water suspension of the oil encapsulated in albumin microcapsules (U.S. Patent 3,406,119). We have adapted this technique for encapsulating OCBA. In a typical run 10 grams of egg albumin were dissolved in 200 ml of water at room temperature. Five drops of G.E. silicone antifoam 60 were added. Next, a suspension of 0.5 g of activated carbon in 20 ml of OCBA was added. (The carbon was added to absorb infrared energy.) The mixture was emulsified in a Waring blender with rapid stirring, and heated to 70°C with an infrared lamp. Heat treatment causes selective coagulation of

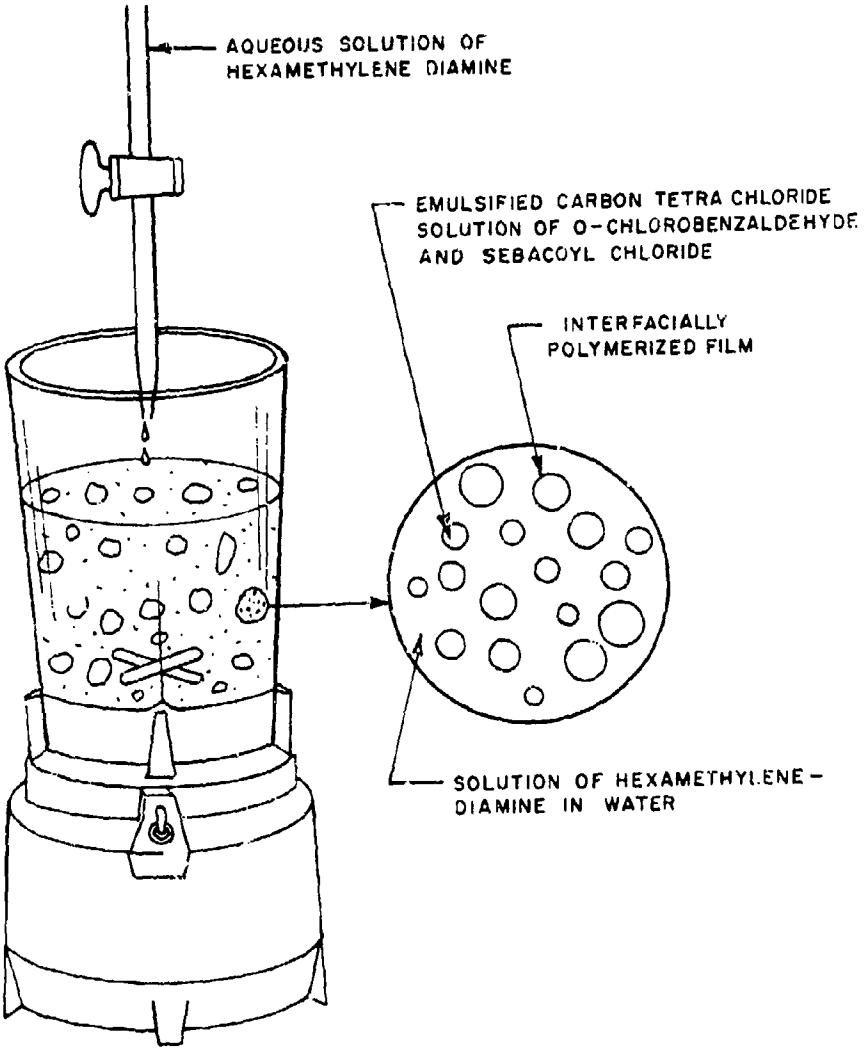


Figure 8. Apparatus for Microencapsulation Via Inter-Facial Polymerization

Figures 9 and 10. Scanning Electron Micrographs of Microcapsules

the albumin around the organic droplets since they contain the carbon which absorbs the infrared energy. The capsules were filtered and washed with water, water-isopropanol (50:50), water isopropanol (25:75) and finally isopropanol (neat). A slurry of the capsules was deposited on ceramic beads used for ball milling, either by dipping the beads or spraying the capsules on the beads, and allowed to air dry. They were placed in a septum stoppered container. The vapor space was sampled periodically and tested for the presence of OCBA. G.C. analysis showed a small peak corresponding to OCBA, probably due to a residual film on the outside of the capsules or slow diffusion through the capsule walls. The coated ceramic beads were then tumbled in their container in order to break the capsules and release their contents. Again the vapor was sampled. The peak corresponding to OCBA was increased twentyfold indicating OCBA had indeed been encapsulated and was released when the capsules were broken. Next we sprayed an aqueous solution of MN on the encapsulated OCBA. After air drying overnight, the sprayed ceramic beads were put in a stoppered container. Analysis of the vapor showed no indication of CS and a slight responce for OCBA. However, after tumbling, the capsules were broken and the OCBA and MN reacted. Sampling at this stage indicated presence of CS. Heating the entire chamber for 2 minutes at 100°C ruptured more of the capsules and increased reaction rate as shown by a 25fold increase in CS concentration after heating and equilibration of the chamber at room temperature.

Attempting to more closely simulate actual field conditions, we next sprayed an aqueous suspension of OCBA capsules into the chamber, which contained 250 gm of sand, ensuring that the walls were completely covered. The inside of the flask was air dried with the aid of a stream of compressed air (3 days). After drying, a solution of 25 ml of 10% MN in methylene chloride was sprayed through the heated tube. In the catalyzed experiment, 50 µl of piperdine was added to the MN solution immediately before spraying. The system was again air dried. After drying, some ceramic beads were added and the flasks were slowly rotated to break the capsules. Chromatograms, immediately after rotation,

showed no evidence of CS in both catalyzed and uncatalyzed runs. However, after allowing the capped containers to sit for two weeks, sampling of the vapor space did give a small peak for CS although the concentration was far below active.

Also, extracting the sand with a small amount of acetone showed presence of CS.

Unfortunately, neither time nor funds would enable us to study the encapsulation technique further. Several questions remain unanswered; for example, in the experiment with sand in the chamber, we are not sure whether the sand acts to inhibit the reaction or whether CS formed is strongly absorbed on it. It is strongly urged that this technique be further investigated as a possible means of tunnel denial. For example, if CS could be incorporated into a "timed release" microcapsule in such a manner as to release its contents over a period of time, there would be no need of generating CS from a two component system. This could be realized by encapsulating CS in degradable polymers of increasing molecular weight. The lower molecular weight polymers would tend to degrade first yielding CS immediately. By adjusting the molecular weight of the encapsulating polymer, one could theoretically "stretch out" the release of CS over any desired length of time.

6. REFERENCES

1. B.B. Corson and R.W. Stoughton, J. Am. Chem. Soc. *50*, 2829 (1928).

2. S.R. Eckhaus, E.L. Baratto, and R.E. Meuser, CWL Technical Memorandum 31-83, July 30, 1959.

APPENDIX A

INSTRUMENTATION

Gas Chromatographs: Chromatograms were run on either a Beckman G.C. 45 or Hewlett Packard Model 810 research chromatograph.

Detector - Flame Ionization

Carrier Gas - Helium

Carrier Flow - 90 ml/min

Inlet Temperature - 180-200°C

Detector Temperature - 210-220°C

Spectrophotometer - Cary 14 grating spectrophotometer

ULTRAVIOLET SPECTRA
(See Figures 11 and 12)

(a) Malononitrile

0.0106 g malononitrile dissolved in 100 ml ethyl alcohol (95%). One ml of this solution was diluted to 10.0 ml and one ml of the resulting solution diluted to 10 ml to give a 1.6×10^{-5} molar solution.

(b) o-Chlorobenzaldehyde

0.0668 g o-chlorobenzaldehyde dissolved in 50 ml ethyl alcohol (95%). One ml of this was diluted to 10 ml and one ml of the resulting solution was diluted to 10 ml to give a 9.6×10^{-5} molar solution.

(c) o-Chlorobenzalmalononitrile

0.0462 g o-chlorobenzalmalononitrile dissolved in 50 ml ethyl alcohol (95%). One ml of this solution was diluted to 50 ml and one ml of this resulting solution diluted to 50 ml to give a 2.0×10^{-6} molar solution. Each of these solutions was scanned from 200 mμ to 340 mμ on our Cary 14 spectrophotometer. The absorption maxima for each is indicated below.

Extinction coefficients were not calculated.

Compound	λ max
o-chlorobenzalmalononitrile	298 mμ
o-chlorobenzaldehyde	252 mμ
malononitrile	No λ max

GAS CHROMATOGRAMS
(See Figures 13, 14 and 15)

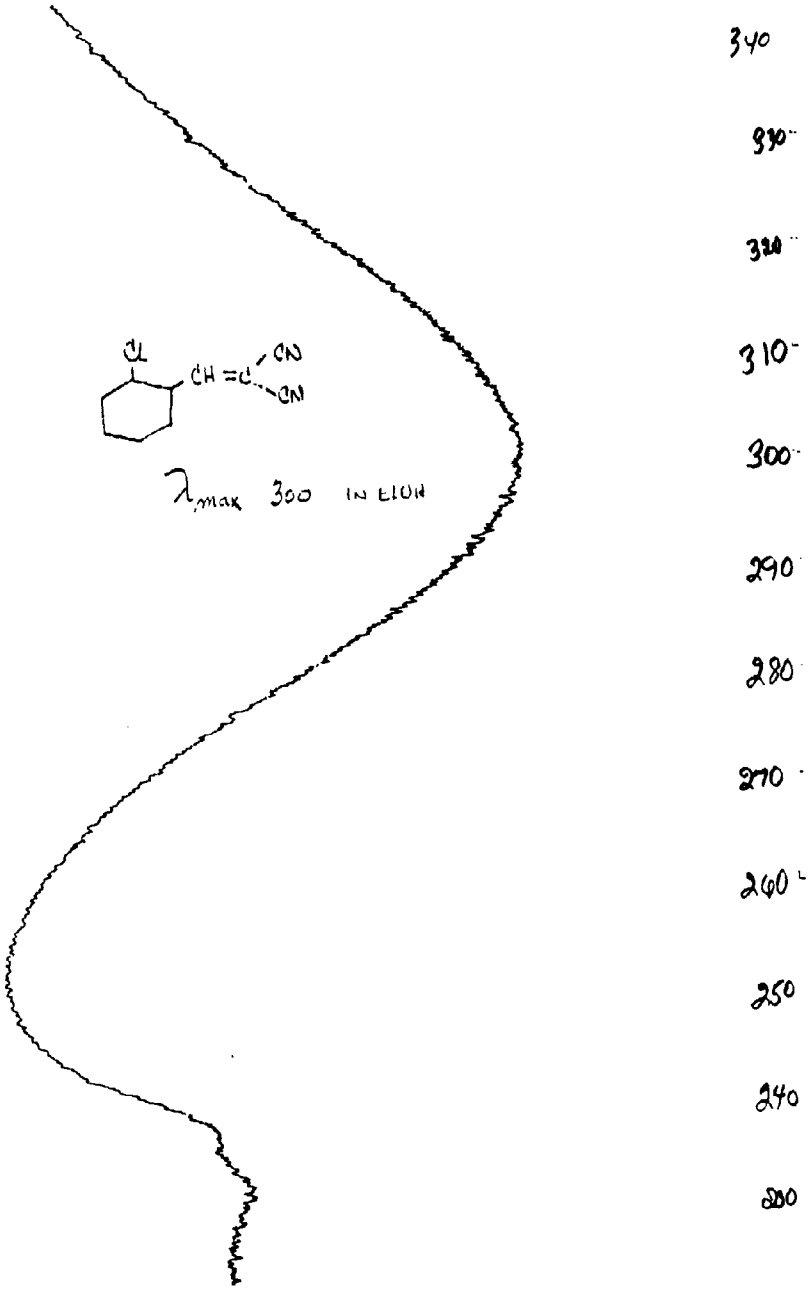


Figure 11. U.V. Spectra of CS

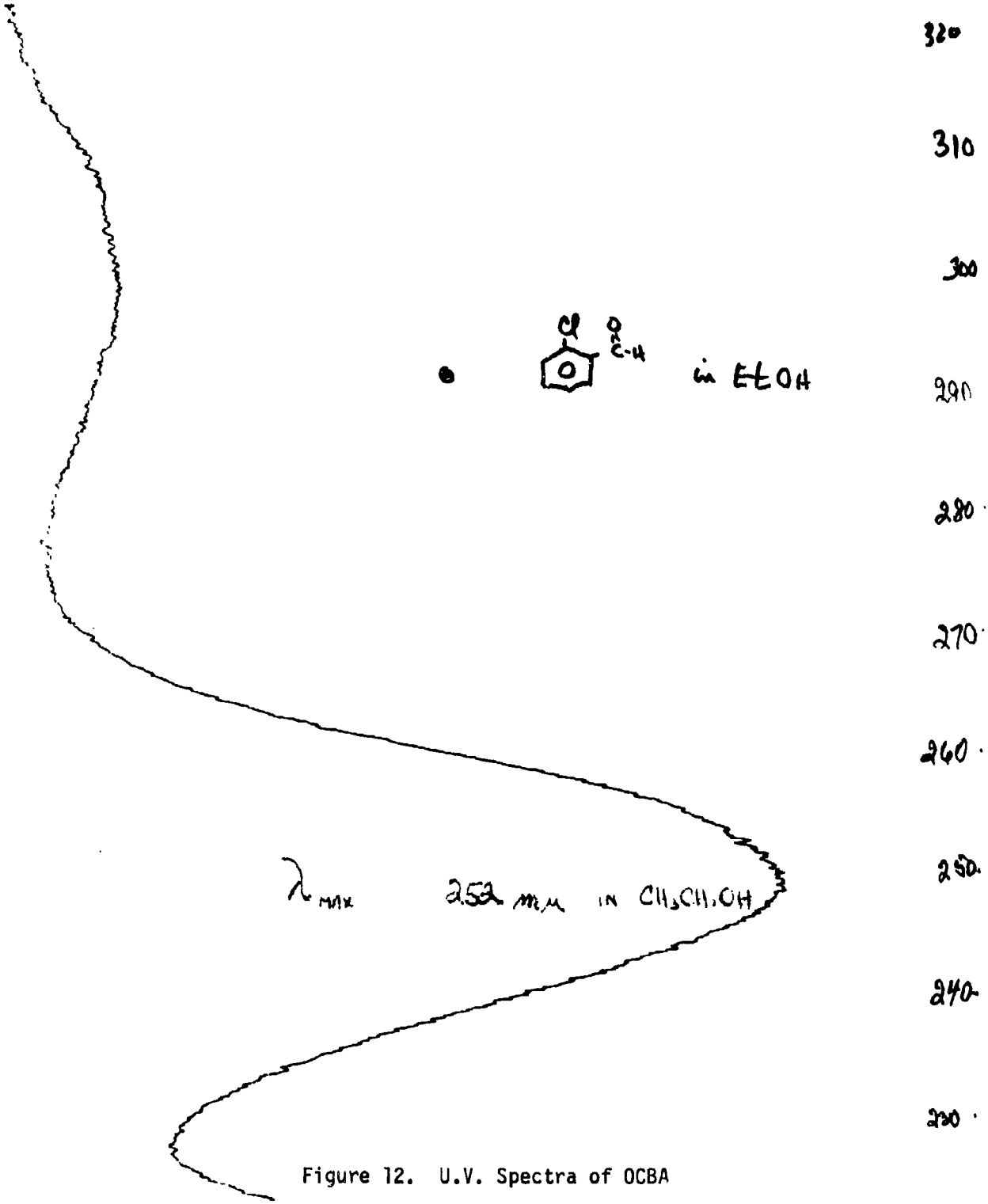


Figure 12. U.V. Spectra of OCBA

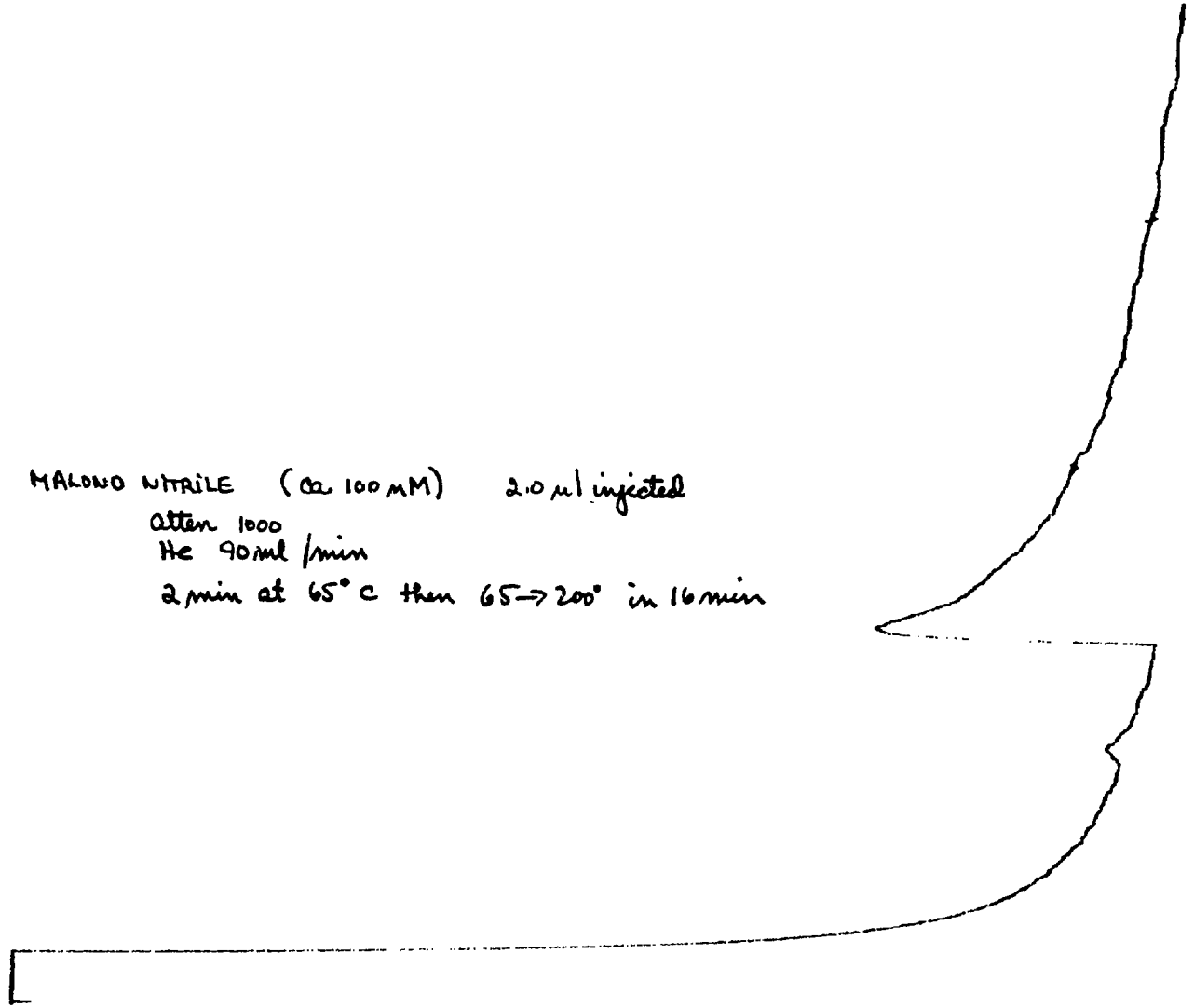


Figure 1 ram of MN

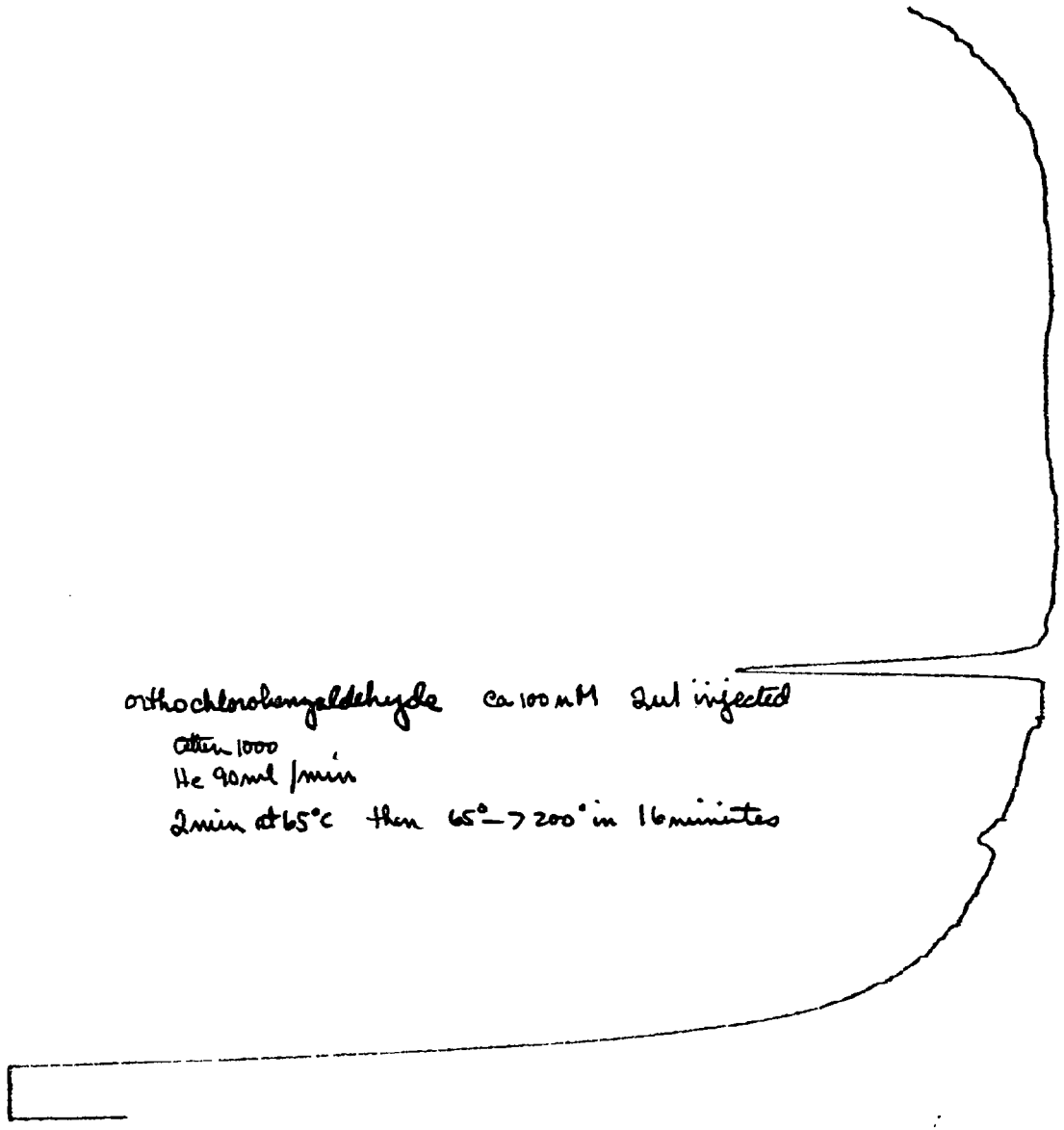


Figure 14. Gas Chromatogram of OCBA

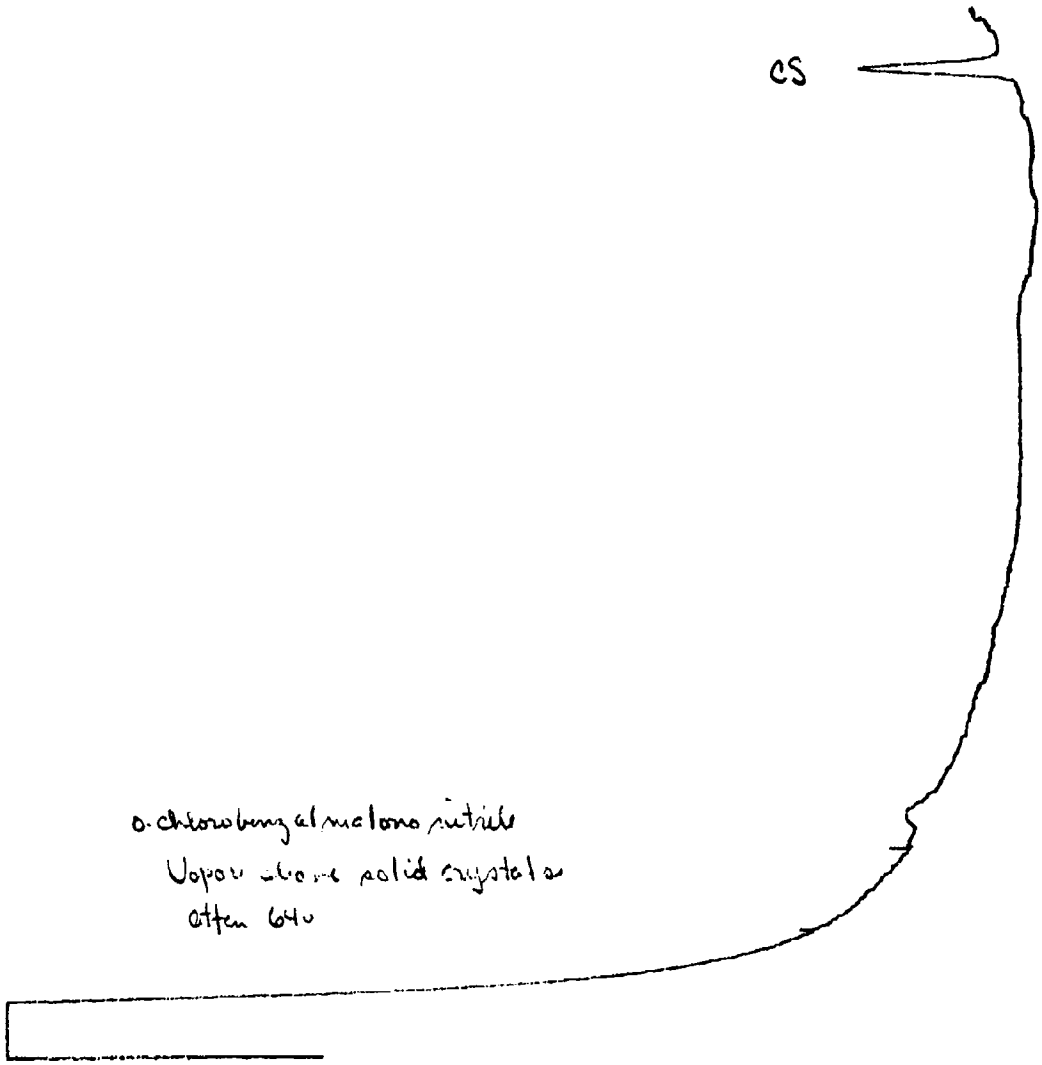


Figure 15. Gas Chromatogram of CS

APPENDIX B

REAGENTS AND SUPPLIES

Malononitrile was purchased from Eastman Kodak and recrystallized from water before use. Orthochlorobenzaldehyde was purchased from Eastman Kodak and vacuum distilled. Orthochlorobenzalmalononitrile was kindly supplied by Mr. H. Rosen, LWL and used as received. All the purified compounds showed single peaks on gas chromatographic analysis. All other solvents and reagents were A.C.S. reagent grade.

Prepacked glass GLC columns, 5.5 ft. x 1/4 in. O.D., packed with 10% QF-1 on 60/80 mesh Gas Chrom Q were purchased from Applied Science Laboratories, State College, Pa.

Sprayers were of the type used in thin layer chromatography, purchased from A. H. Thomas, Philadelphia, Pa.