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The detection of pesticide residues in water supplies

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THE DETECTION OF PESTICIDE RESIDUES IN WATER SUPPLIES

by

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UC
Thesis

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INTRODUCTION

The use of organic chemicals as pesticides has increased greatly in recent years and continues to do so, since these pesticides offer advantages of greater effectiveness, more selectivity, and lower toxicity to mammals, than the previously used inorganic pesticides, such as arsenic compounds. The problem of pollution of water supplies by these pesticides becomes more important with this increasing usage, and with the increasing pressures on our water resources. Pesticides may find their way into water supplies by various means, such as runoff of rain water from crop land or other pesticide-treated land, direct application to bodies of water, for aquatic weed or algae control, and by accidents in the application of pesticides to adjacent land areas, as in aerial spraying.

Sensitive analytical methods are needed for the detection of pesticides in water supplies, since biological activity persists, in some cases, to extremely low concentrations. Fish kills have been reported at insecticide concentrations as low as 10 parts per billion (12). Benzene hexachloride, an insecticide, gives a disagreeable taste to drinking water at concentrations of 20 parts per billion (12).

This study undertook to develope methods for the identification and quantitative measurement of Dalapon, 2,2-dichloropropionic acid, a herbicide manufactured by the Dow Chemical Company, and Systox, a mixture of O,O - diethyl, O-(2-ethylthioethyl) thiophosphate and O,O-diethyl, S-(2-ethylthioethyl) thiophosphate, an insecticide manufactured by the Chemagro Corporation.

The steps of the proposed method are, extraction of the pesticide from a water sample with an organic solvent, isolation of the pesticide from other extracted compounds by a vapor phase chromatograph and fraction collector, identification of the pesticide by infra-red analysis, and quantitative measurement using either the response of the chromatograph detector or the infra-red spectrophotometer.

HISTORICAL

Infra-red radiation was discovered in 1800 by Sir Willaam Herschel, but little use was made of this portion of the electromagnetic spectrum until Julius in 1892 demonstrated the relation between the structure of organic molecules and their infra-red spectra. This work was confirmed and extended by Coglenz (10). Since the '30's, when organic chemists began to explore the use of infra-red as a means of identification and functional group analysis, the progress in instrumentation and theoretical understanding of infra-red spectrophotometry has been rapid (6,7).

The Russian botanist Tswett first used the techniques of chromatography to separate plant pigments on an adsorbent column. His work was largely ignored until 1931, after which the techniques of chromatography were rapidly developed. The possibilities of chromatography in the vapor state were suggested in 1941, but little use was made of this method until the '50's. James and Martin (8,9) made a fundamental contribution to the develoepement of vapor phase chromatography by the developement of partition columns in 1952. Since then, vapor phase chromatography has been found applicable to a great many problems of qualitative and quantitative analysis (11).

A literature search discovered no methods for the analysis of Dalapon or Systox in water samples. Coulson et al. (3) have studied the chromatography of several pesticides, including Systox, and have developed apparatus for the determination of chlorinated pesticide residues, using vapor phase chromatography for purification, followed by combustion and microcoulimetric

determination of their chloride content. Goodwin et al. (5) have used vapor phase chromatography, with argon ionization detection, to determine Aldrin and Dieldrin residues in vegetable extracts. Zweig et al. (14) used vapor phase chromatography and infra-red spectrophotometry to isolate and measure Thiodan residues.

Sumiki and Matsuyama (13) have published a method for the determination of traces of Parathion in water, using infra-red spectrophotometry. Rosen and Middleton (12) have developed a method for the detection of chlorinated insecticides in water, using a carbon filter for the collection of samples, adsorption chromatography for purification, and infra-red spectrophotometry for identification. Large volumes of water can be passed through the carbon filter to give sensitivities in the part per billion range.

THEORETICAL

Infra-red radiation is that portion of the electromagnetic spectrum with wavelengths from approximately 2 to 25μ. The spectral region from 0.7 to 2μ is known as the near infra-red, and the region from 25 up to about 150μ is known as the far infra-red. These regions are divided at rather arbitrary points; the figures vary with different sources.

Atoms in a molecule are in continuous vibrating motion with respect to one another, and different frequencies are associated with each mode of vibration. Different molecules have different characteristic sets of vibrational frequencies. These frequencies fall in the same range as those of infra-red radiation (10). Wavelengths of infra-red radiation corresponding to a molecular vibration will be absorbed by the molecule, so that a plot of wavelength vs. the absorption of infra-red light will give a specific pattern for each molecular specie, from which it can be identified.

According to the Beer-Lambert Law (4), the intensity of a beam of monochromatic radiation decreases exponentially as the concentration of absorbing material increases, or

$$\log \frac{I_o}{I} = A = abc$$

I_o- intensity of the incident light.

I - intensity of the transmitted light.

A - absorbance or optical density.

a - absorbancy index of the absorbing substance at a fixed wavelength.

b - thickness of the absorbing layer.

c - concentration of the absorbing substance.

The absorption of infra-red light can be used for quantitative measurements of absorbing substances, since the absorbancy index, a, is a constant for a given substance at a fixed wavelength, and can be calculated from the absorbance of solutions of known concentration.

An infra-red spectrophotometer measures and records the absorption of light in the infra-red region. The essential parts of an infra-red spectrophotometer are the source, sample holder, monochromator, receptor, and measuring circuitry.

Sources of infra-red radiation are the Globar, a silicon carbide rod, and the Nernst glower, a rod of rare earth oxides bonded together. These rods are heated electrically to 1200-2000°C. and give off radiations approaching those of an ideal black body radiator.

The sample holder consists of some material transparent to infra-red light, arranged so that a known thickness of absorber can be placed in the beam of light. Rock salt is commonly used, since this material does not absorb appreciably in the 2-15μ range.

The monochromator consists of a dispersing device, such as a prism or diffraction grating, which, with associated optical and mechanical components, allows only a narrow range of wavelengths to strike the receptor. The selection of the prism material depends on the range of wavelengths to be covered. Rock salt prisms are usually used in the 2-15μ region.

Receptors commonly used are the bolometer, or resistance thermometer, and the thermocouple. Light striking the thermo-

couple is converted to an electric current. The current produced to drive a pen recorder. The recorder chart paper is driven linearly with time, and by proper settings of the chart drive system and the monochromator, a record of absorbance vs. wavelength is made.(10)

The principles of vapor phase chromatography are similar to those of liquid-liquid partition chromatography, except that the mobile phase is compressible, producing a gas velocity gradient along the column (8).

The vapor phase chromatograph consists of a long column filled with a non-volatile substance, either solid or liquid coated on an inert support. The column is contained in an insulated, thermostatted compartment, so that close regulation of the column temperature is possible. A liquid sample, injected at the head of the column with a hypodermic syringe, is vaporized, and swept through the column by a stream of carrier gas, such as hydrogen, helium, or nitrogen. Each component of the sample moves through the column at a rate determined by the column temperature, gas flow rate, and the component's interactions with the moving gas phase and the stationary phase. These interactions involve the vapor pressure of the component at the operating temperature, and the polarity of the component and the stationary phase. The length of time a compound is retained in a column is a constant at constant temperature and flow rate. As the components emerge from the column, they are detected and the detector signal is recorded.

Various means of detection have been developed. The thermal conductivity detector is frequently used. One form of this

detector consists of a Wheatstone bridge using thermistors in two arms. The thermistors are heated by current flowing through the bridge, and cooled by the flow of gas around them. One thermistor is placed ahead of the sample inlet so that only the pure carrier gas flows around it. The other thermistor is at the outlet of the column. When the carrier gas alone flows around it, both thermistors have the same temperature, and the bridge can be balanced by adjusting its other two arms, which consist of a potentiometer. When a component emerges, the thermal conductivity of the gas mixture decreases, and the temperature and resistance of the outlet thermistor change. This unbalances the Wheatstone bridge. The unbalance signal is amplified and recorded as a function of time. A precision attenuator in the circuit allows the signal to be kept on the recorder scale.

The vapor phase chromatograph can be used qualitatively, measuring the retention time of a compound and comparing it with those of known compounds determined with the same operating conditions. By recovering a compound as it leaves the column, purification and concentration of the compound can be achieved. Quantitative measurements are also possible, since the area under the detector trace is proportional to the concentration of the compound causing the signal. For sharp, well-defined peaks, the peak height is proportional to concentration.

APPARATUS AND REAGENTS

APPARATUS

1. Perkin-Elmer Model 21 double beam automatic recording spectrophotometer. Nernst glower source, NaCl prism monochromator.
2. 0.10 mm. NaCl sample holders.
3. Cenco-Hyvac vacuum pump.
4. Perkin-Elmer Model 154-C vapor phase chromatograph, with thermal conductivity detector and automatic recorder.
5. Perkin-Elmer Type R, 1 meter x ½ inch chromatograph column. Stationary phase - polypropylene glycol of average molecular weight 550, coated on diatomaceous earth.
6. Perkin-Elmer Type R, 2 meter x 1 inch preparative chromatograph column. Stationary phase - same as above.
7. Hypodermic syringes, with luer-lok fittings, sizes 50 microliter and 2 ml.
8. Hypodermic needles, sizes #20 and #27.
9. Two-way valve, with luer-lok fitting, for outlet of chromatograph.

REAGENTS

1. Dalapon, 98%, Dow Chemical Co.
2. Systox, analytical standard, Chemagro Corp.
3. Chloroform, U.S.P.
4. Carbon tetrachloride, U.S.P.
5. Carbon disulfide, tech.
6. Hydrochloric acid, conc., C.P.
7. Calcium chloride, anhydrous.
8. Helium, 99.9%, Matheson Co.

EXPERIMENTAL

PROCEDURES AND DATA

Infra-red spectra of Dalapon and Systox were run in carbon disulfide (tech.), carbon tetrachloride (USP) and chloroform (USP). The solvents were dried over Ca Cl_2 before use. Solutions containing about 5% (w/v) of a pesticide were made up with each solvent and were transferred to the 0.10 mm. NaCl sample cell with a medicine dropper. The samples were run with the appropriate pure solvent in the reference cell. Little difference was noted in the details of the spectra in the different solvents. Spectra were also run of the solvents alone against an air path. Chloroform was selected for further infra-red investigations, for reasons of safety, and because its absorption peaks did not interfere with those of either pesticide. Spectra of Dalapon and Systox in chloroform are shown in Fig. 1 and 2.

At the wavelengths of maximum absorbance, 5.80 and 9.95μ for Dalapon and Systox, respectively, the absorbance of series of standard solutions was measured (Tables 1,2) and plots of absorbance vs. pesticide concentration were prepared (Fig. 3,4).

Table 1. Dalapon, absorbance at 5.80μ vs. concentration.

g. Dalapon/ 100 ml. $CHCl_3$	$A_{5.80\mu}$
0.60	0.094
1.20	0.169
1.87	0.281
2.39	0.360
4.78	0.650

Table 2. Systox, absorbance at 9.95 μ vs. concentration.

g. Systox/ 100 ml. $CHCl_3$	$A_{9.95\,\mu}$
0.69	0.132
1.38	0.280
2.76	0.560

Investigations of the chromatography of the pesticides were made with the 1 meter x $\frac{1}{4}$ inch Type R column. Aliquots of standard pesticide solutions in chloroform were injected into the chromatograph with a 50 λ hypodermic syringe. Data on the effect of the flow rate of the helium carrier gas on the retention time (t_R) of the pesticides could not be obtained, since the flow-meter on the chromatograph was inoperative during the course of the project. The effect of column temperature on the pesticide retention time is shown in Table 3.

Table 3. Column temperature and retention time of Dalapon and Systox.

Column Temp. °C.	He pressure p.s.i.	Dalapon, t_R, min.	Systox, t_R, min.
100	25.0	5.95	---
124	23.7	2.8	13.4
150	25.0	1.4	5.6
175	26.2	0.75	2.7

The response of the thermal conductivity detector as a function of pesticide concentration was measured by injecting aliquots of standard pesticide solutions and measuring the height of the pesticide peak on the chromatograph recorder. The effect of column temperature on the sensitivity of the detector for Dalapon was also investigated.

Table 4. Peak height vs. Dalapon concentration.

λ 4.78% Dalapon injected	ν Dalapon injected	Peak Height 100° C. 24.5 psi.	Peak Height 150° C. 24 psi.
5	239	----	12.1
10	478	10.8	26.8
15	717	----	38.0
20	956	21.7, 21.0, 21.7, 21.8	50.8
30	1434	32.3	----
40	1912	43.3	----
50	2390	53.9	----

These data are plotted in Fig. 5, as peak height vs. Dalapon injected.

Table 5. Peak height vs. Systox concentration.

λ 5.25% Systox injected	ν Systox injected	Peak Height 150° C. 25 psi.
20	1050	2.1
30	1570	3.4
40	2100	4.8
50	2625	6.0

The next phase of the project was the extraction of the pesticides from water samples. Asample size of one liter was chosen for convenience. For Systox, the following procedure was developed. The sample ss shaken in a 1 liter separatory funnel with three successive portions, of 20, 10, and 5 ml., of chloroform. Each portion is shaken for two minutes. After separation of the phases, the portion is drained into a 50 ml. suction flask. The combined portions are evaporated to about 8 ml., using suction from an aspirator, and gentle heating,

provided by immersing the suction flask in a 250 ml. beaker of warm water. The extract is transferred to a 10 ml. volumetric flask, rinsing the suction flask several times with chloroform, and made to volume. Several pieces of $CaCl_2$ are added to the volumetric flask to dry the extract.

Standard samples were prepared by adding 2 ml. of 5.25% Systox in chloroform to one liter of tap water, then shaking vigorously. These samples were put through the procedure described, and the absorbance of the 10 ml. extract was measured at 9.95μ. Standard solutions were prepared by diluting 2 ml. of the 5.25% Systox to 10 ml. in chloroform, and the absorbances of these solutions were measured along with the samples. Table 6 shows the recoveries of Systox obtained with this procedure.

Table 6. Recovery of Systox from water samples.

Sample No.	Systox added, g.	$A_{9.95\mu}$ Sample	$A_{9.95\mu}$ Std. Soln.	% Recovery
1	0.105	0.187	0.215	87
2	"	0.174	"	80
3	"	0.183	0.218	84
4	"	0.192	"	88
5	"	0.182	0.214	85
6	"	0.184	"	86

Attempts to increase the recovery of Systox by the use of larger portions of solvent were unsuccessful. Extracting with three 25 ml. portions of chloroform gave the recoveries listed in Table 7.

Table 7. Recovery of Systox from water samples.

Sample No.	Systox added, g.	A9.95μ Sample	A9.95μ Std. Soln.	% Recovery
7	0.105	0.200	0.218	92
8	"	0.163	"	75
9	"	0.159	"	68
10	"	0.171	"	71

A similar extraction procedure was developed for Dalapon. 100 ml. of conc. HCl is added to the sample, to repress the dissociation of Dalapon and favor its extraction into chloroform. The acidified sample is shaken with three 25 ml. portions of chloroform. Each portion is shaken for two minutes. The portions are combined in a125 ml. Erlenmeyer flask and evaporated to about 8 ml., using suction and gentle heating as in the Systox procedure. The extract is transferred to a 10 ml. volumetric flask and made to volume with chloroform, then dried by the addition of $CaCl_2$ to the flask.

Standard samples containing 0.096 g. of Dalapon were made up by adding 2 ml. of 4.78% Dalapon in chloroform to tap water in the separatory funnel, then shaking the funnel vigorously. These samples were then put through the procedure described. The Dalapon content of the chloroform extracts were measured with the chromatograph, using the 1 meter x $\frac{1}{4}$ inch column. 50λ aliquots of the dried extracts were injected into the chromatograph, and the height of the Dalapon peak was measured. Standard solutions containing 0.096 g. of Dalapon in 10 ml. of chloroform were prepared and determined with the samples. The chromatograph was operated at 100° C. The pressure varied

from 24 to 25 p.s.i. for different sets of determinations. Table 8 shows the recoveries obtained.

Table 8. Recovery of Dalapon from water samples.

Sample No.	Dalapon added, g.	Peak height, sample	Peak height, standard	% Recovery
1	0.096	11.0	12.0	92
2	"	10.5	"	88
3	"	11.6	12.2	95
4	"	10.7	"	88
5	"	10.0	12.0	83
6	"	10.3	"	86
7	"	12.0	12.5	96
8	"	11.4	"	91

For the purification of the pesticides, the 2 meter x 1 inch preparative column was used in the chromatograph. Aliquots of up to 2 ml. of chloroform solutions of the pesticides were injected, using the 2 ml. hypodermic syringe. To trap the pesticides as they emerged from the column, a valve, which directed the gas stream either to the atmosphere or to a trapping device, was attached to the outlet of the chromatograph. When the pesticide emerges, the gas stream is led through a #20 hypodermic needle attached to the valve into a 3 ml. test tube containing chloroform. Evaporation of the chloroform cools the test tube and condenses the pesticide vapor. $CaCl_2$ is added to the solution, and after drying, the solution is drawn up into the 2 ml. hypodermic syringe, and transferred to a 0.10 mm. NaCl cell for infra-red analysis.

The effects of column temperature and helium pressure on the separation of Dalapon and chloroform by the preparative column were investigated. For Dalapon, the operating conditions chosen were 120°, 20 psi. Trapping of Dalapon starts at 4.8 min. after injection, and continues for 4 minutes. Fig. 6 shows a chromatogram obtained when 0.2 ml. of 4.78% Dalapon was injected into the chromatograph. Fig. 7 shows an infra-red spectrum of a sample of Dalapon which had been chromatographed and trapped. 0.5 ml. of 4.78% Dalapon was injected, with the chromatograph at the operating conditions described. The volume of the trapped pesticide solution was 0.4 ml.

Attempts to recover Systox with the trapping devide described were unsuccessful. With the chromatograph operating at 150°, 20 psi., aliquots of up to 2 ml. of 5.25% Systox were injected. Trapping started at 4.2 min. after injection and continued for 11 minutes. Infra-red spectra of the trapping solutions showed none of the characteristic absorption bands of Systox.

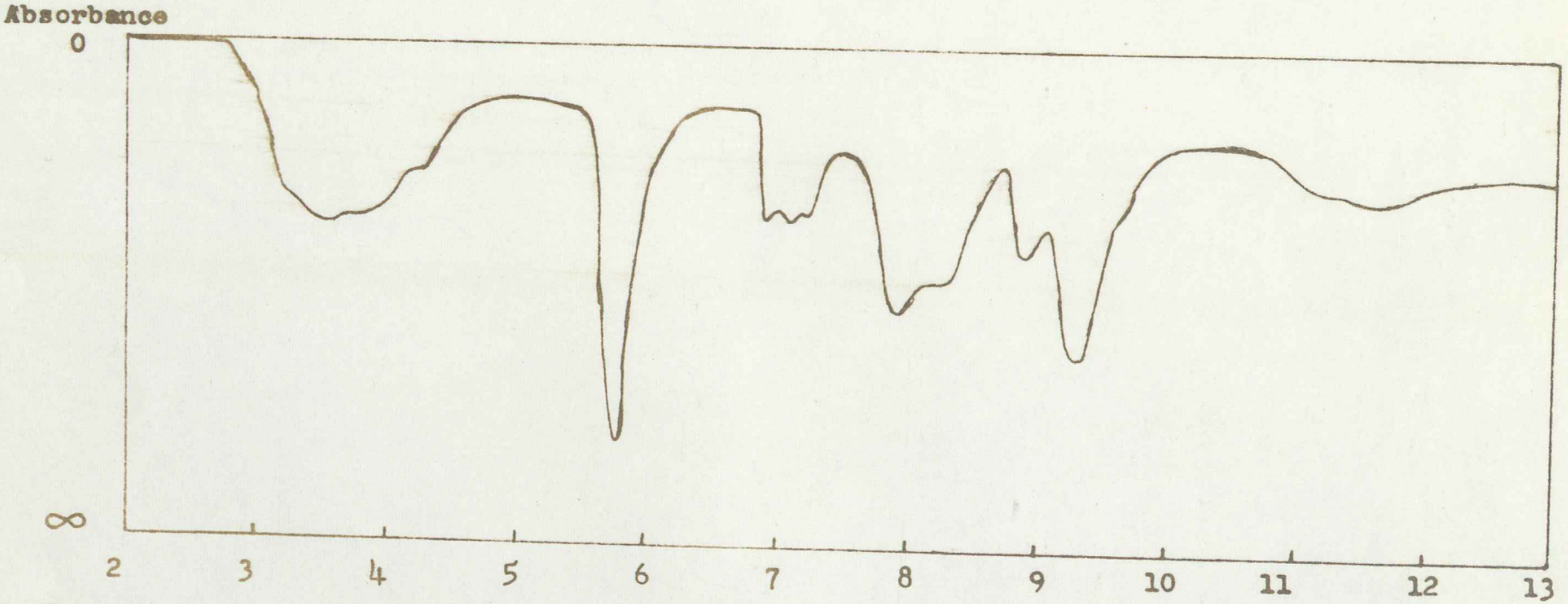


Fig. 1. Infra-red spectrum of Dalapon.

4.78 % (w/v) Dalapon in $CHCl_3$.

0.10 mm. absorbing layer.

Instrument operating conditions; Response 1, Gain 4, Speed 3.5, Suppresion 0.

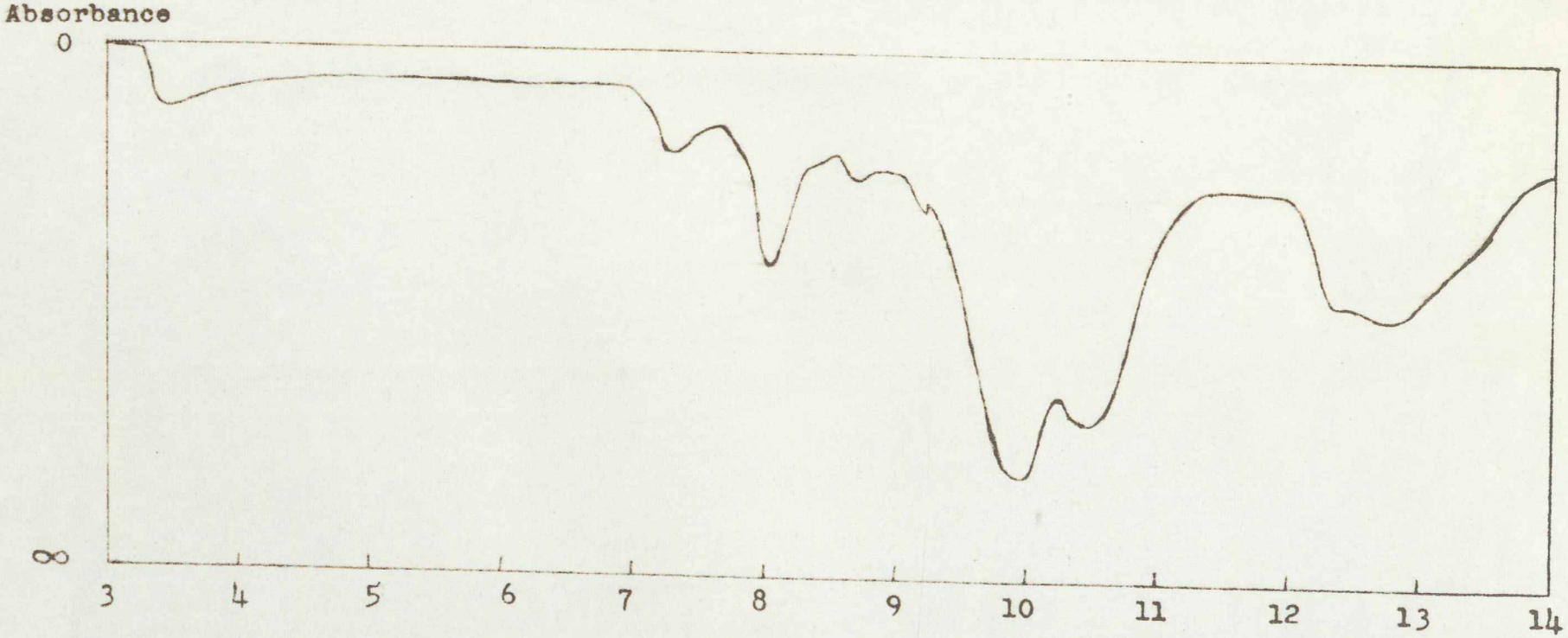


Fig. 2. Infra-red spectrum of Systox

4.54 % (w/v) Systox in $CHCl_3$.

0.10 mm. absorbing layer.

Instrument operating conditions; Response 1, Gain 4, Speed 4, Suppresion 0.

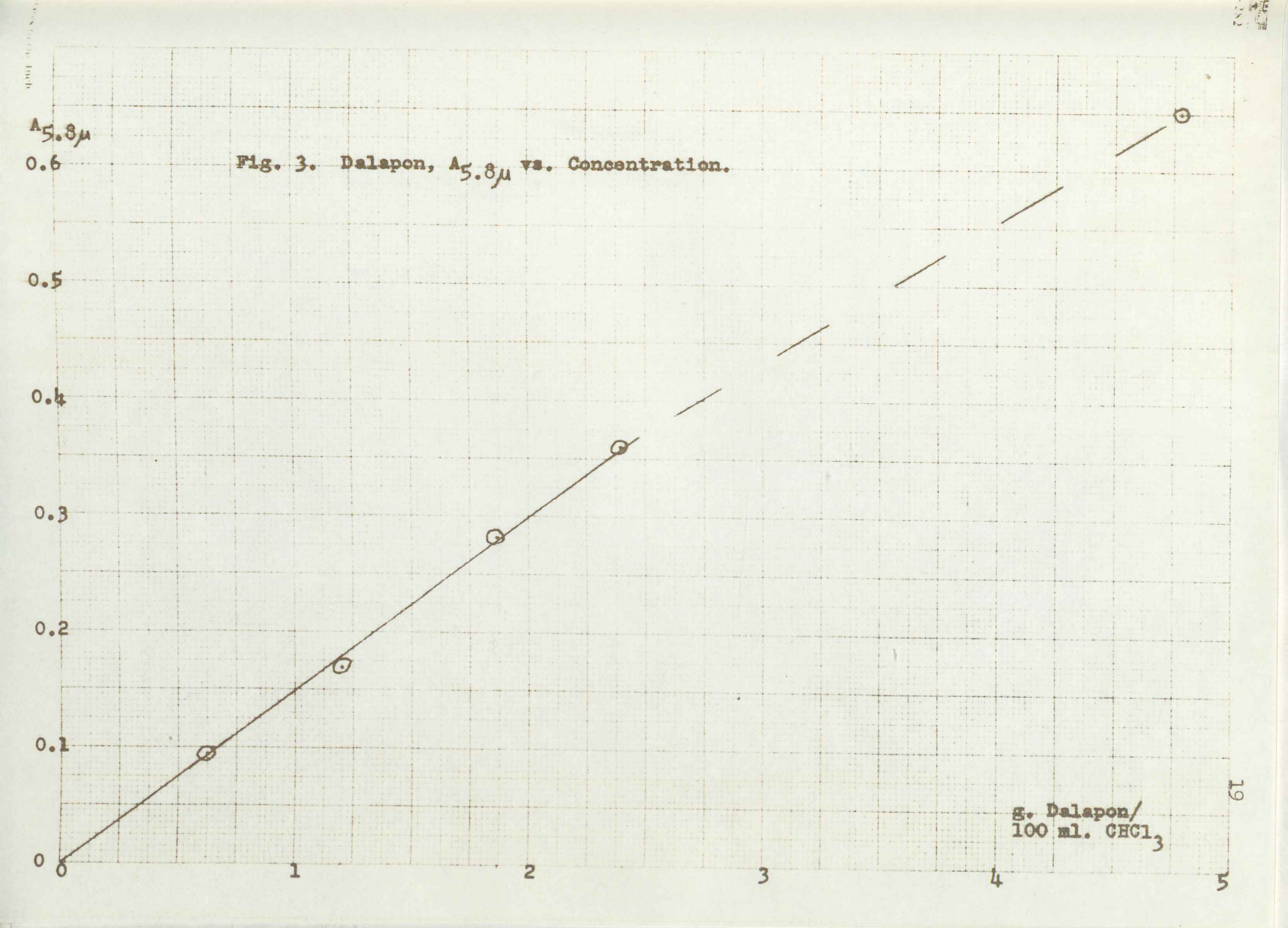
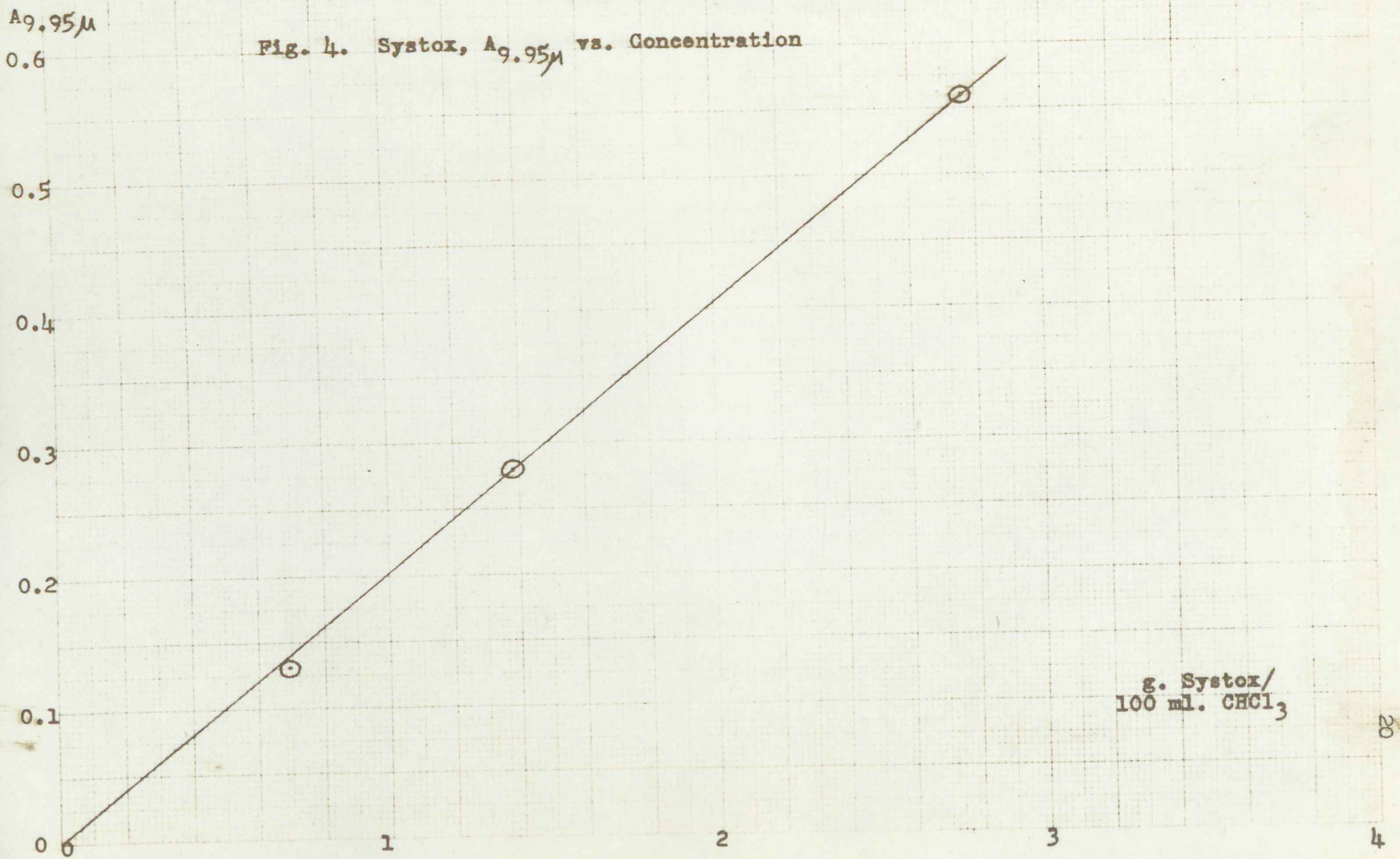


Fig. 3. Dalapon, $A_{5.8\mu}$ vs. Concentration.

Fig. 4. Systox, $A_{9.95\mu}$ vs. Concentration



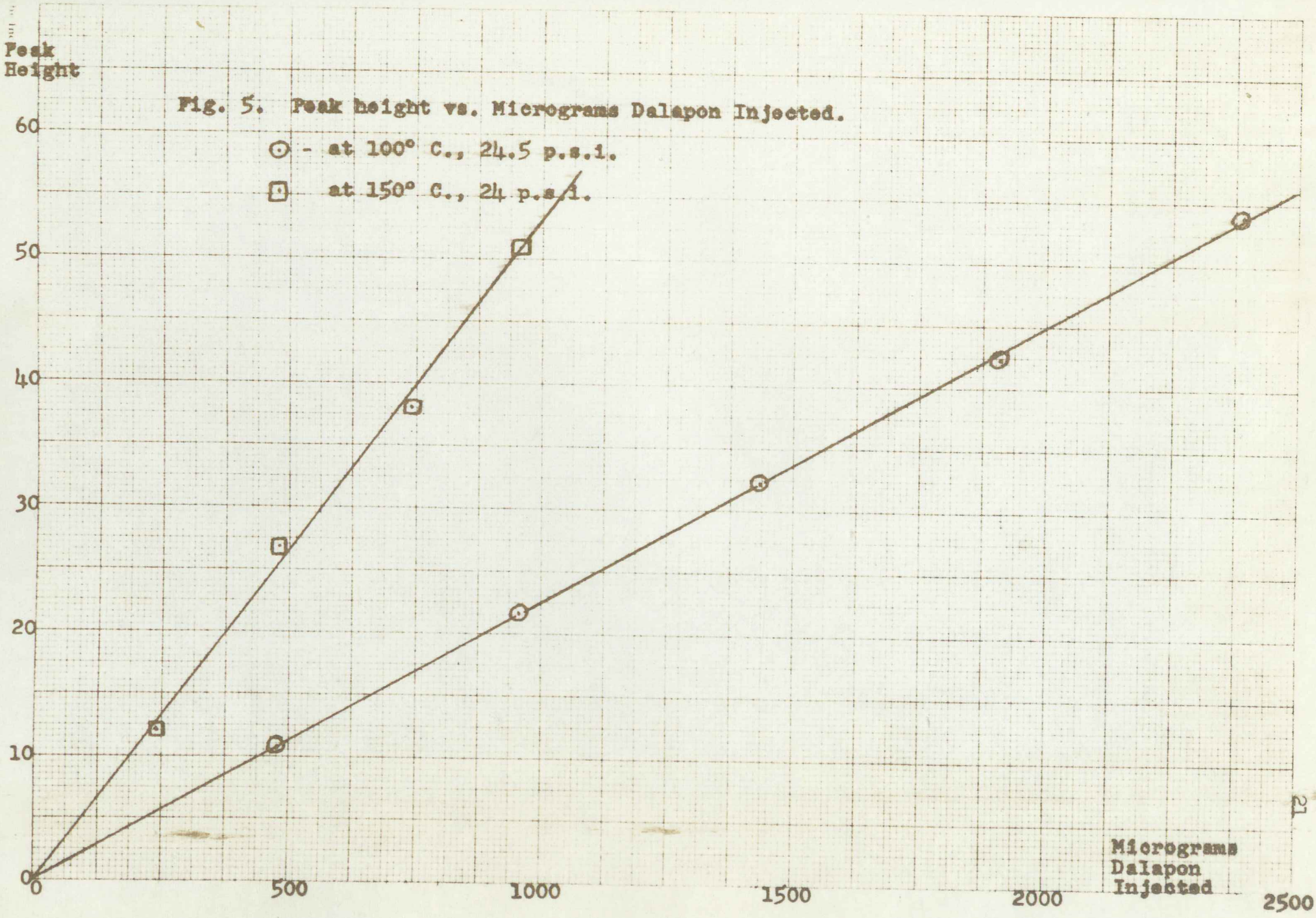


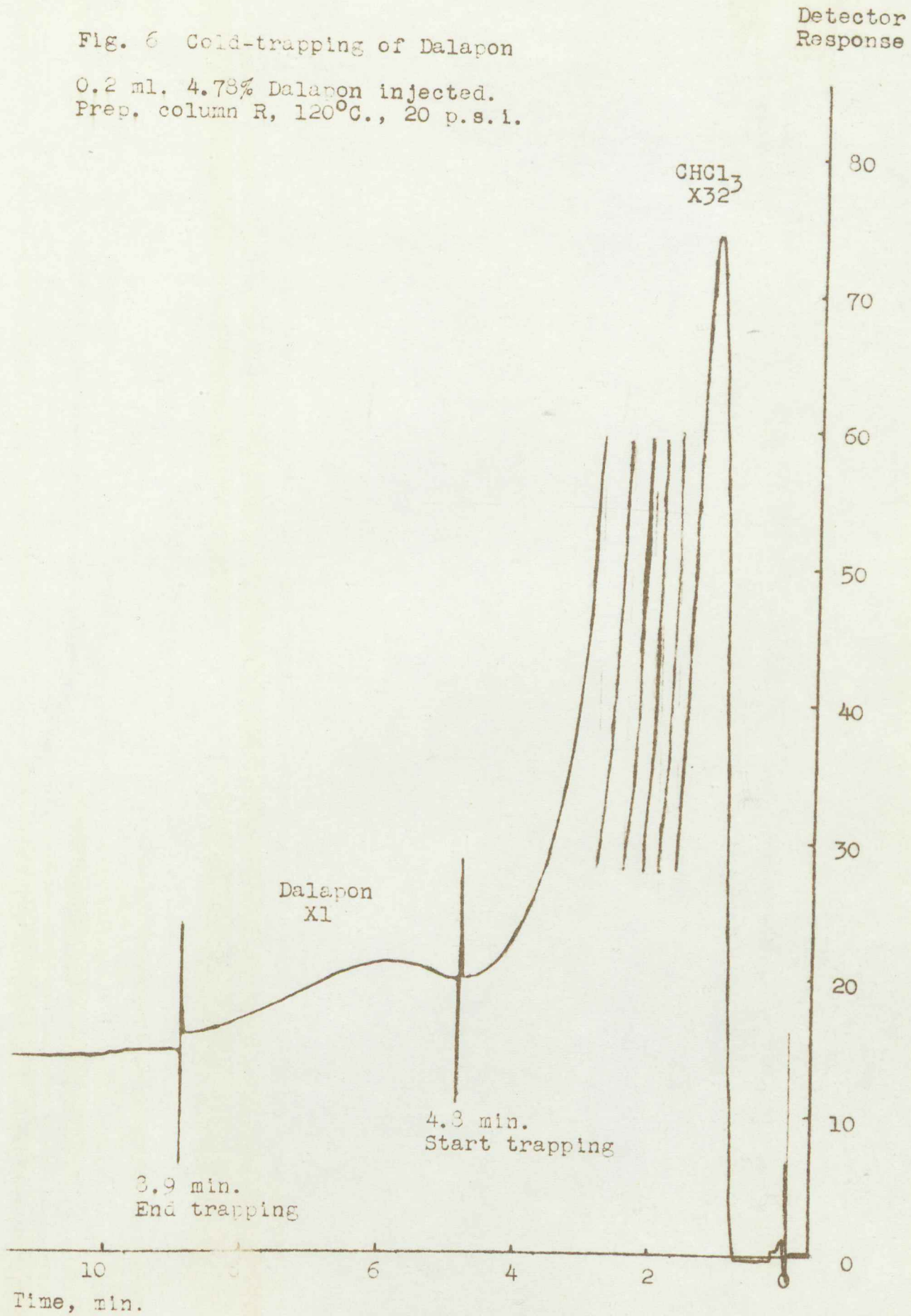
Fig. 5. Peak height vs. Micrograms Dalapon Injected.

⊙ - at 100° C., 24.5 p.s.i.

⊡ - at 150° C., 24 p.s.i.

Fig. 6 Cold-trapping of Dalapon

0.2 ml. 4.78% Dalapon injected.
Prep. column R, 120°C., 20 p.s.i.



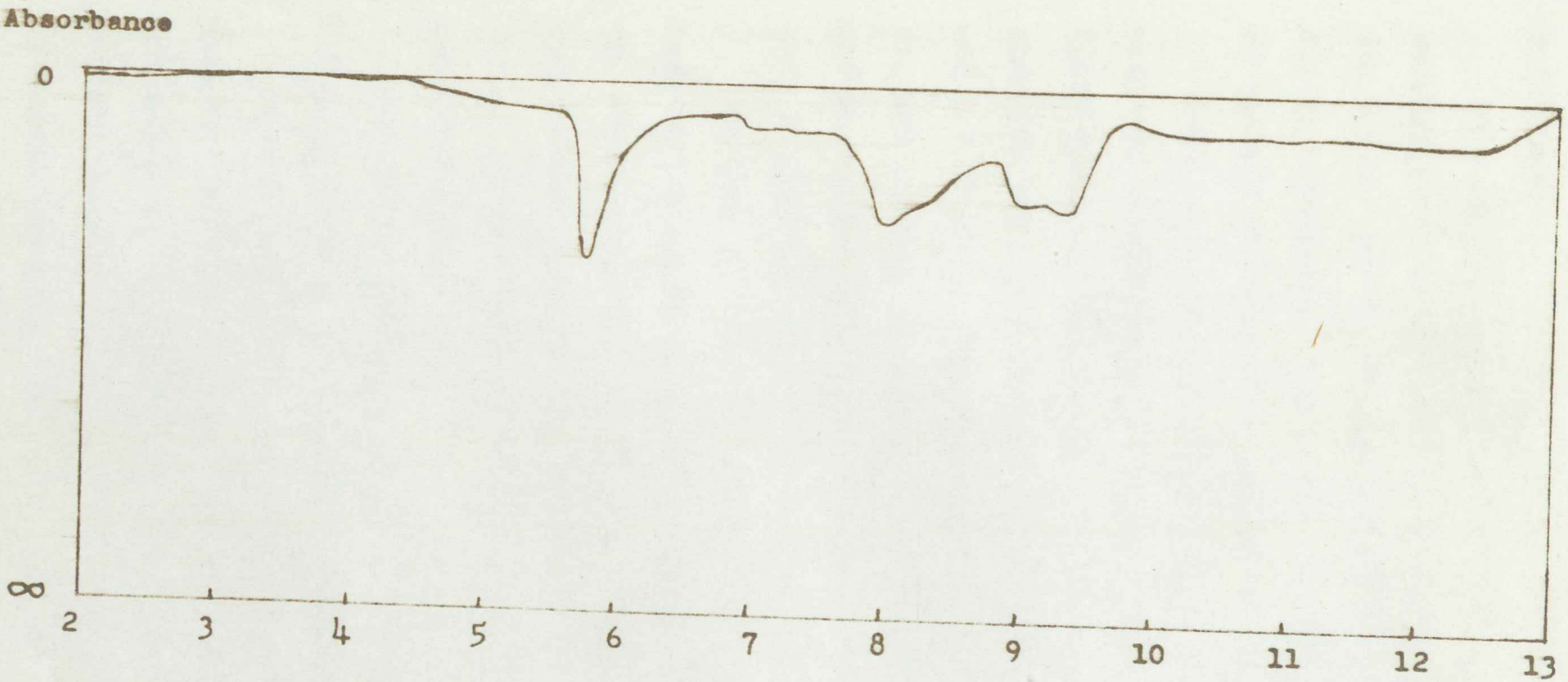


Fig. 7. Infra-red spectrum of Dalapon

Dalapon trapped from V. P. C.

0.5 ml. of 4.78% Dalapon injected; collected in 0.4 ml.

0.10 mm. absorbing layer.

Instrument operating conditions; Response 1, Gain 4, Speed 4, Suppression 0.

DISCUSSION

At a column temperature of 100°, minor peaks appear in Dalapon chromatograms at 4.0 and 8.6 minutes. Chromatograms of the chloroform used showed no corresponding peaks. These are probably due to impurities in the Dalapon. Similar impurity peaks appear at 1.8 and 3.2 minutes in Systox chromatograms at 150°.

Attempts were made to resolve a mixture of Dalapon and Systox with the chromatograph at 150°. A solution of 3.14% Dalapon and 7.82% Systox in chloroform was made up. When aliquots of this solution were chromatographed, peaks were observed at 1.8, 3.2, and 5.7 minutes. The expected peak for Dalapon at 1.4 minutes did not appear. No explanation is offered for this phenomenon, and no further investigations of it were made, except to verify that Dalapon had been added to the solution.

The data in Table 4, and Fig. 5, show a linear relation between the amount of Dalapon injected into the chromatograph and the response of the thermal conductivity detector. The peak heights measured for replicate 956 amounts of Dalapon show that a reproducibility of ± 2% can be obtained from the chromatographic determination.

The average recovery of Dalapon from water samples containing 0.1 g./l. is 90%, from the data presented in Table 8.

From the data obtained, the minimum amount of Dalapon detectable by the procedures used can be calculated. The assumptions are made that the extraction efficiency remains 90% at lower Dalapon concentrations, that 100λ of the 10 ml. chloroform extract is chromatographed, and that a peak height of 5 units is the smallest measureable. If the chromatograph is operated at 150°,

24 psi., 90γ of Dalapon will cause a peak 5 units high.

$$\frac{90\gamma}{100\lambda} = \frac{9000\gamma}{10 \text{ ml.}}$$

$$\frac{9000\gamma}{0.90} = 10{,}000\gamma \text{ in the sample.}$$

$$\frac{10{,}000\gamma}{1000 \text{ g.}} = 10 \text{ ppm., minimum measureable amount in a 1 liter sample.}$$

Since the resolution, or separating power, of the chromatograph decreases with increasing operating temperatures, other pollutants in a sample may interfere with the Dalapon determination at 150°. Operation of the chromatograph at lower temperatures will increase the resolution, at the expense of sensitivity. A similar calculation, based on the operation of the chromatograph at 100°, 24.5 psi., gives a minimummeasureable amount of 24 ppm. Dalapon in a 1 liter sample.

To calculate the recovery of Dalapon in the purification and cold-trapping procedure, the data for the solution whose spectrum is plotted in Fig. 7 is used. The absorbance of the solution is 0.186 at 5.8μ. This corresponds to a Dalapon concentration of 1.23%. Since the volume of this solution is 0.4 ml. and 0.5 ml. of 4.78% Dalapon was chromatographed,

$$\frac{0.5 \times 4.78}{0.4} - 5.97\%, \text{ theoretical Dalapon concentration.}$$

$$\frac{1.23}{5.97} \times 100 - 20.5\% \text{ recovery of Dalapon.}$$

To calculate the minimum identifieable amount of Dalapon, it is assumed that a 5 ml. aliquot of the 10 ml. chloroform extract is chromatographed, that the recovery of Dalapon through the trapping process is 20.5%, and that the final volume of the Dalapon solution obtained is 0.2 ml, which is sufficient to fill the 0.10

mm. NaCl cell. A 1% solution is assumed to be the most dilute which will give an identifieable infra-red spectrum.

0.2 x 0.01 = 0.002 g. Dalapon in the trapped solution.

$\frac{0.002}{0.205}$ = 0.01 g./5 ml. = 0.02 g. in the 10 ml. extract.

$\frac{0.02}{0.90}$ = 0.022 g. in the original sample.

$\frac{0.022 \text{ g.}}{1000 \text{ g.}}$ = 22 ppm., minimum identifieable amount in a 1 liter sample.

A compArision of Tables 6 and 7 shows that increasing the volume of chloroform decreases the recovery of Systox from water samples. This is probably due to the greater losses of Systox in the evaporation of the larger volume of solvent. To see what loss occurs in the evaporation, 0.105 g. of Systox in 25 ml. of chloroform was evaporated as described in the procedure, and made to a 10 ml. volume. The absorbance of this solution was 0.202 at 9.95μ. The expected absorbance is 0.217. This represents a loss of 7% of the Systox on evaporation.

Calculations for the minimum measureable amount of Systox are based on its absorbance at 9.95μ, since the thermal conductivity detector proved very insensitive to Systox. An absorbance of 0.05, corresponding to a 0.25% Systox solution, is taken as the smallest measureable. It is assumed that the extraction efficiency remains 85% at lower concentrations, and that interferences absorbing at 9.95μ are absent, or can be compensated for.

10 x $\frac{0.25}{100}$ = 0.025 g. Systox in the 10 ml. extract.

$\frac{0.025}{0.85}$ = 0.029 g. or 29 ppm in the 1 liter sample

The identification of Systox residues would be possible only

if other pollutants present in a sample did not interfere with an infra-red spectrum run on the 10 ml. extract. The concentration of Systox in the sample would have to be considerably higher than 29 ppm. for an identifiable spectrum to be obtained.

The poor recoveries of both compounds in the purification procedures indicate that more work is needed on this step of the methods. It should be possible to develope more efficient trapping devices, such as a test tube chilled in a dry ice-acetone bath, but no investigations toward this end were carried out.

The small response of the thermal conductivity detector to Systox, and the poor recovery of Systox in the purification procedure may be due to incomplete elution of this substance from the column material used. No other column materials were studied in this project, however.

The necessary steps for the identification and measurement of Dalapon in water have been explored in sufficient detail to propose them as a method for residue analysis. A method using these procedures would suffer from a lack of sensitivity, but could be useful in measuring high local concentrations of Dalapon, such as might result from its application to land areas adjacent to bodies of water.

In similar circumstances, the procedures developed for Systox may be useful for analyses, but because of the lack of sensitivity and of a means of identification except at high concentrations, they cannot be proposed as a general analytical method.

More sensitive detectors are available for the vapor phase chromatograph. In particular, flame ionization detection offers

a sensitivity approximately 100 times that of thermal conductivity detection. With such a detector, the sensitivity of the proposed method for Dalapon can be extended to concentrations below 1 ppm. Determination of Systox by the chromatograph would become feasible.

The procedures investigated are by no means completely developed, but the results obtained are encouraging, and show that vapor phase chromatography and infra-red spectrophotometry are applicable to the analysis of Dalapon and Systox.

SUMMARY

The increased use of pesticides has made desirable the development of sensitive analytical methods for their detection in water. Studies were made of the possibilities of the use of vapor phase chromatography and infra-red spectrophotometry for the analysis of two pesticides, Dalapon and Systox. Methods of extraction, identification, and quantitative measurement were developed to some extent. Dalapon can be measured at concentrations of 10 ppm., and identified at concentrations of 22 ppm., in a one liter sample. Systox can be measured at concentrations of 29 ppm. in a one liter sample, but a satisfactory method of identification was not found.

Sensitivities can be increased by using different detectors, such as the flame ionization detector, with the vapor phase chromatograph.

The investigation of different column materials and trapping procedures may produce a method for the identification of Systox residues.

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