LABORATORY EVALUATION OF HIGH-TEMPERATURE DESTRUCTION OF KEPONE AND RELATED PESTICIDES

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LABORATORY EVALUATION OF HIGH-TEMPERATURE
DESTRUCTION OF KEPONE AND RELATED PESTICIDES

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Surplus, unwanted, and highly hazardous pesticides pose safety hazards to the public and are potential sources of environmental contamination. The study reported herein presents thermal decomposition data for several pesticides based on a specially designed laboratory technique.

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PREFACE

The serious environmental contamination of the manufacturing facility, sewage treatment works, and nearby environs by the pesticide Kepone required attention to proper disposal techniques. After all disposal alternatives had been considered, the need to develop supporting data for the chosen technology became evident. As discussions progressed, it became more apparent that high-temperature controlled incineration offered a good potential for successful disposal. Thermal degradation data for Kepone were not available, however, and would have to be generated.

During this period researchers at the University of Dayton Research Institute were developing a thermal oxidation apparatus for determining the thermal behavior for a wide variety of pesticides. Responding to an urgent request from the Special Kepone Task Force, the researchers embarked on a high-intensity, short-turnaround project on Kepone. Within 3 months, by early Spring of 1976, substantial data were developed and a special technical report submitted to the EPA Project Officer for distribution to involved parties. This report has subsequently formed the data base in support of planned pilot plant burns of Kepone and Kepone-contaminated sludge.

ABSTRACT

The serious problems concerning Kepone manufacturing operations in
the Hopewell, Virginia, area have been widely publicized. Disposal problems
and environmental cleanup associated with Kepone found in soil, water,
sewage sludge, etc. have been substantial. Thermal disposal was considered
to be a primary means for solving this disposal problem. However, basic
high-temperature data on Kepone were lacking; accordingly, this study was
aimed at providing necessary information.

Thermal destruction testing was conducted with three pesticides: Kepone,
Mirex, and DDT. A specialized laboratory technique incorporating a two-
stage quartz system was developed. It is important to note that in this system
the pesticide was first converted to the gas phase, then exposed to the high-
temperature destruction conditions. Critical parameters of temperature and
residence time were accurately measured. Both the Kepone and DDT mole-
cules, at a residence time of ∼1 second, were essentially destroyed at
500°C; however, Mirex, at the same residence time, required 700°C for
destruction.

CONTENTS

FIGURES

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ACKNOWLEDGMENTS

SECTION I

INTRODUCTION

The problems associated with the safe disposal of unwanted or hazardous pesticides has been recognized for several years. Recently, the pesticide Kepone has received national attention for various reasons [1, 2]. Suffice it to say that Kepone is a chlorinated carbon with a carbonyl group; that it is toxic and probably bioaccumulative; it is suspected of being a carcinogen; and that it closely resembles the pesticide Mirex that has been shown to be thermally stable [3].

Prior to the initiation of this study, there existed no reported thermal decomposition data for Kepone. This report is primarily concerned with the high temperature destruction of Kepone, with DDT and Mirex being used as comparative analogues. DDT has been the most studied compound as far as thermal decomposition is concerned, while Mirex is thermally stable and very close in molecular structure to Kepone. The exact chemical structures are shown in Figure 1.

This study was designed to provide data from which requirements can be assigned for the thermal disposal of Kepone. Accordingly, the specific objective of the laboratory effort was to establish destruction temperature characteristics of the vaporized pesticides at preselected residence times. A major part of this program involved examinations of the gas phase destruction behavior of the selected pesticides for completeness of destruction and identification of decomposition products while in a controlled-flow, high-temperature air environment. The work was performed utilizing special instrumentation designed by University of Dayton Research Institute (UDRI) personnel. The pesticides selected for study were also evaluated by standard thermoanalytical techniques of thermogravimetry (TG) and differential thermal analysis (DTA).

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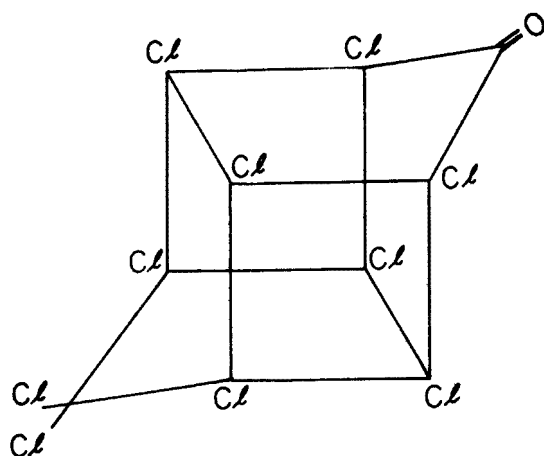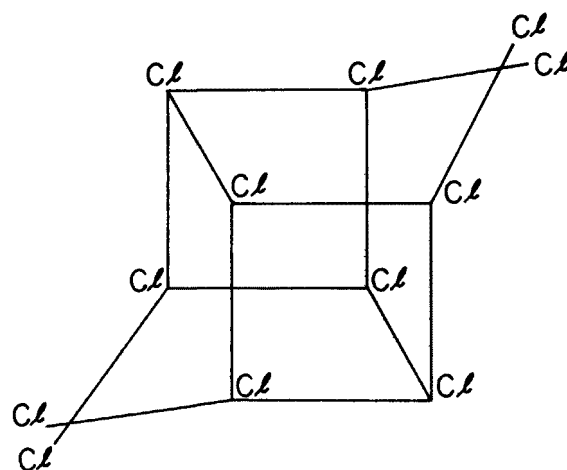
KEPONE

MIREX

p,p'-DDT
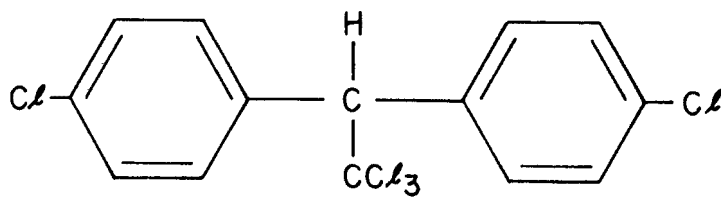
Figure 1. Chemical Structures.

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SECTION II
CONCLUSIONS

1. A laboratory technique was developed for determining the thermal destruction characteristics of pesticides. Results for Kepone, Mirex, and DDT showed that the parent molecule for each was essentially destroyed at a one second residence time and a temperature range of 500°C-700°C, depending on the pesticide.

2. Kepone was found to be slightly more thermally stable than DDT. Therefore, based on the conclusions of others that established a two second residence time and 1,000°C temperature requirement for safe incineration of DDT, the results of this research show that any incineration of Kepone should, at least, meet the aforementioned requirements for DDT.

3. Analyses showed major decomposition products to be hexachlorocyclopentadiene and hexachlorobenzene (HCB) for both Kepone and Mirex. These products were formed in different thermal regions; and trace (but detectable) levels of HCB were still present at 900°C.

4. Residence time was found to be important in the thermal decomposition of Kepone at a temperature predetermined to be a reactive region.

5. Differential Thermal Analysis (DTA) showed no thermal reaction areas (exotherms or endotherms) above 600°C. These findings are contradictory to results reported by others.

6. This laboratory-scale technique can be used to develop quick response thermal stability baseline data for organic materials posing environmental disposal hazards, and for which no previous thermal data exist.

7. This study clearly demonstrated that the chemical nature of the effluent products is dependent on the temperature and residence time that the basic molecule experiences. Thus, precise analytical data which identify and quantify decomposition and/or recombination products, with respect to these two parameters, are necessary for establishing guidelines for safe thermal disposal of hazardous materials.

SECTION III
SIGNIFICANCE OF LABORATORY INVESTIGATION

The objective of the study discussed in this report was to obtain laboratory test data that could be applied to a large-scale system for the thermal disposal of Kepone and similar pesticides. The rather unique approach utilized in this study permitted the gathering of basic thermal destruction data under controlled residence times.

In this study, the laboratory data were obtained by subjecting pure pesticides to a two-step destruction process. First, the pesticide was vaporized at a low temperature, 200°C to 300°C; then the gas phase sample was passed through a high-temperature quartz tube. The distinct advantage of this laboratory approach is that thermal destruction data can be obtained while both temperature and residence time are being controlled and accurately measured. This contrasts sharply with large-scale conditions where the pesticide would be introduced as a solid or liquid, and often as a mixture containing foreign materials such as organic solvents or inorganic solid supports. In this situation, attainment of a given temperature is hindered by the fact that the necessary phase changes of the pesticide must occur even while the insulating and possible retentive effects of inorganic sorbents are being overcome. Under such conditions, the measured reaction chamber temperature will not reflect the true temperature that the pesticide molecule actually experiences. Also, accuracy of residence time measured in the large-scale system suffers from the shortcomings graphically displayed and discussed in Section IV.

This laboratory study clearly showed that the complicated chemical nature of pesticide thermal destruction products is strongly dependent on the temperature and residence time that the pesticide encounters. Therefore, it is most important to acquire precise analytical data which identify and quantify decomposition products relative to exposure temperature and residence time. The above laboratory approach is ideally suited for obtaining these basic data which are needed to insure <u>logical</u> decision making in the thermal disposal of pesticides.

SECTION IV

LABORATORY APPROACH

In order to determine the high-temperature destruction characteristics of an organic molecule, it is necessary to obtain precise information on certain crucial parameters. It is important that the system temperature be accurately determined, along with the residence time, i.e., the time interval during which the molecule experiences the destructive temperature. Another critical parameter that must be fulfilled in such an evaluation is that there be an adequate supply of air so that the destruction takes place in an oxidative environment, as opposed to an atmosphere containing insufficient oxygen. Lastly, an important factor is the composition of the high-temperature environment, e.g., water content, presence of other gases, and interfering materials such as clays, fillers, organic sorbents, etc.

The laboratory approach to establishing a pesticide's high-temperature, non-flame destruction characteristics has certain distinct advantages. First, if one examines the pure pesticide, no interferences are encountered from other materials. Second, the composition of the high-temperature environment can be precisely established by using compressed air of known quality and employing in-line filters to remove water, oil, and other foreign materials. Next, by using a technique whereby a small sample of pesticide is gradually vaporized; and, then passed through a high-temperature zone, one is assured of an excess of oxygen, thus avoiding the possibility of a pyrolytic reaction occurring. Further, it is possible to evaluate the behavior of the pure pesticide on the molecular level. By vaporizing the pesticide prior to its exposure to the high-temperature environment, one can be assured, based on the kinetic theory of gases [4], that pesticide molecules do indeed experience the actual average temperature. Finally, the laboratory evaluation of a pesticide's destruction characteristics can be accomplished quickly and economically with minimum environmental risk.

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It is important to note that during incineration of a pesticide formulation, a certain amount of energy must be applied just to change the incorporated pesticide from its usual state (whether it be solid or liquid) to the gas phase. These phase transitions, apart from requiring additional energy, also require an undefined amount of exposure time to the high-temperature source. Therefore, it is almost certain that in the case of the incineration of pesticide formulations, some pesticide molecules do not encounter the prescribed incineration temperature. In short, even through the temperature within a chamber is known, it does not necessarily mean that all substances within that chamber have indeed attained thermal equilibrium. However, if all of the substances in the chamber are in the gas phase, one can safely assume that the individual molecules have (with sufficient time exposure) achieved the average temperature of that environment.

For similar reasons, the laboratory evaluation of a pesticide's residence time is considerably simplified over that of measuring residence time in a large scale unit. When a gas is passed through a lengthy narrow-bore flow path (in the laminar flow region), radial dispersion can be neglected and the main factor affecting the residence time distribution is longitudinal diffusion. However, for large diameter, mixing chamber, or multichamber flow paths, radial dispersion is the major factor effecting the variation in residence time of the transported molecule [5]. Figure 2 depicts the residence time distributions for pesticides passing through the two different flow paths. The exact contour of these generalized profiles would be dependent upon the nature of the flow, i.e., laminar or turbulent, and other factors such as wall composition [6] and surface finish. However, in general, residence time can be accurately measured with a narrow-bore flow path, whereas for the large diameter flow path, molecular residence time can, at best, only be approximated. This situation can be illustrated by observing in Figure 2a that some pesticide molecules can pass through the large diameter flow path
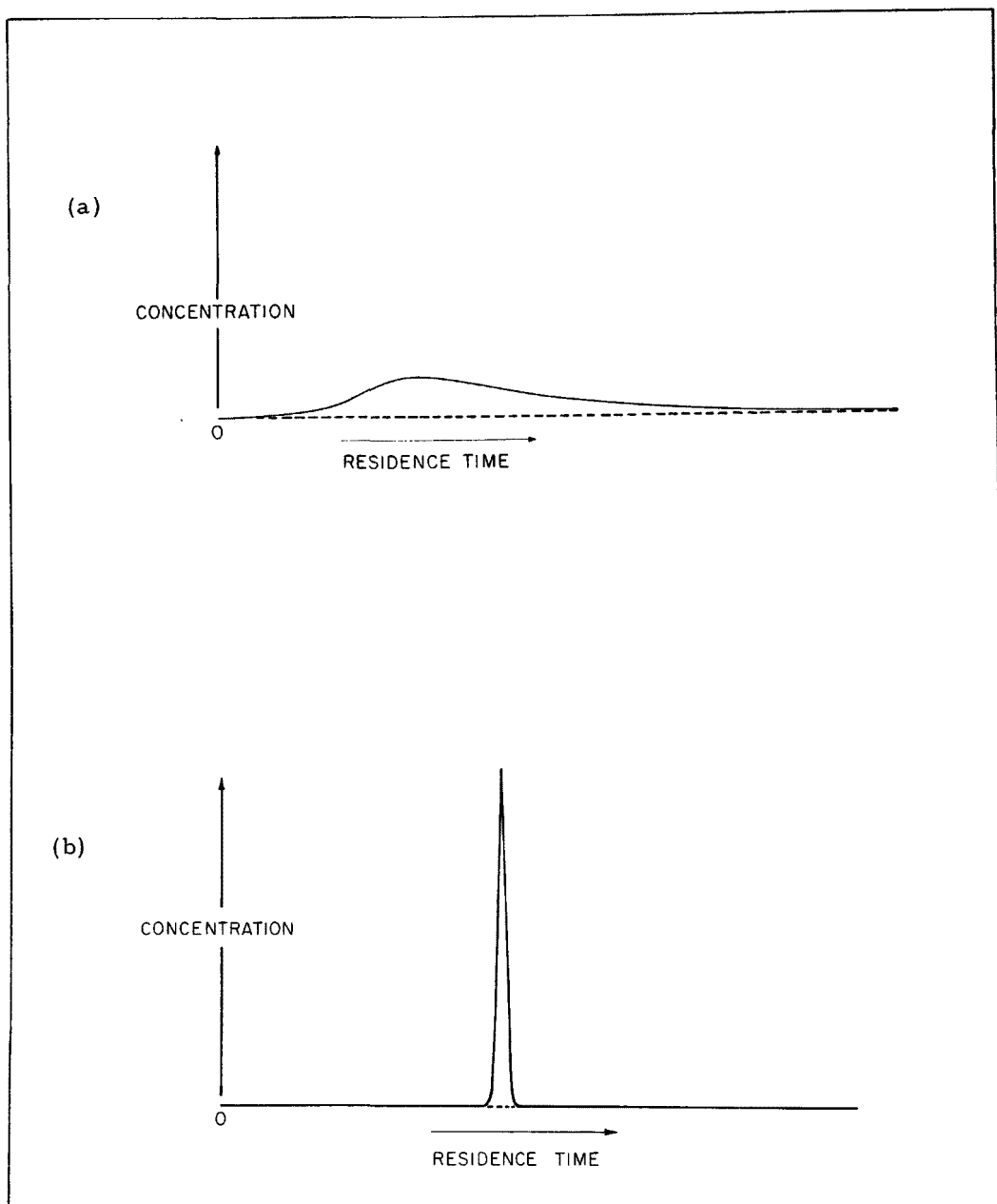
Figure 2. Residence Time of Gas Phase Molecules.
(a) Large Diameter, Mixing Chamber, or Multichamber
     Flow Path.
(b) Narrow-Bore Flow Path.

in a very short time; while some molecules, as evidenced by the asymptotic behavior of the right-hand side of the same curve, can remain in the high-temperature region for an extended period of time.

Two approaches were considered for obtaining high-temperature destruction data on the pesticides: (1) a discontinuous system where the thermal stressing of the pesticide, and product analysis are separate, and (2) a closed, continuous system incorporating both thermal stressing and product analysis. In the discontinuous system, the effluent sample is trapped, then removed from the thermal processor and inserted into the gas chromatograph for analysis. In a closed, continuous system, the thermal processor would be connected to the gas chromatograph. A decision was made to go with the discontinuous system, as it would be simpler to develop, and a logical first approach for acquiring the desired data.

Proceeding with this approach, Kepone, Mirex, and DDT were evaluated in a series of tests where the pesticide was first vaporized and then transported through a narrow-bore, high-temperature zone by a controlled flow of air. In this way, average temperature and residence time were firmly established. These tests were conducted at a series of temperatures ranging approximately from 250°C to 900°C. Also, the effluent from each high-temperature test was passed through a trapping medium and the collected fraction was subsequently analyzed by gas chromatography. In addition to the foregoing investigation, standard examinations by TG and DTA were utilized to acquire basic thermal data on each pesticide.

SECTION V

EXPERIMENTAL

Description of Samples

This study was concerned primarily with the behavior of the pure pesticide; therefore, only samples of known purity were used. Kepone, Mirex, and DDT reference standards were obtained from the National Environmental Research Center, Research Triangle Park, North Carolina. The pesticide reference standards were examined in a series of high-temperature destruction tests and were also subjected to thermogravimetric analysis (TG). Mirex and DDT samples obtained from Applied Science Laboratories, State College, Pennsylvania were investigated by differential thermal analysis (DTA). The sample used for the DTA of Kepone was obtained by recrystallizing an 80 percent Kepone formulation supplied by the project officer. As these pesticides are solids at room temperature, it was necessary to dissolve them with a volatile solvent. Subsequently, a mixture of acetone and benzene (50:50 by volume) was selected for dissolving the three pesticides.

Before conducting any tests, the reference standard pesticides from Research Triangle Park were examined by gas chromatography using both a nonpolar column (OV-1) and a moderately polar column (1.5% OV-17 + 1.95% QF-1). These samples were also analyzed by two different detection methods; namely, hydrogen flame ionization detection (HFID) and electron capture detection (ECD).

As the DDT sample was a mixture of isomers, numerous peaks were observed, although the sample did appear to contain approximately 80% p,p'-DDT and 20% o,p'-DDT. The Mirex reference standard was found to be very pure and in all cases yielded a single chromatographic peak. The

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Kepone sample showed only a single peak when examined by HFID, however, when examined by ECD, trace levels were observed of substances considerably heavier than Kepone.

Thermal Analysis

Before conducting the high-temperature destruction tests, it was considered desirable to obtain some basic thermal analysis data on the three pesticides. Accordingly, each pesticide was subjected to a thermogravimetric analysis. These TG analyses were conducted with a Fisher Series 100 thermogravimetric instrument. Small quantities of pesticide (approximately 2 mg) were tested while a flow of 60 ml/min of dried air was passed through the sample region. Each sample was programmed from room temperature to approximately $900^{\circ}C$ at the rate of $10^{\circ}C$ per minute. The TG tracings for the reference standard pesticides are shown in Figures 3, 4, and 5.

It was found from duplicate tests that TG repeatability was good; and, also, that there was no visible residue in the platinum sample container upon completion of any of the tests. The TG tracings for Mirex and DDT showed essentially an increasing rate of evolving material which suggests a simple evaporation of the pesticide. The TG tracing for Kepone shows an early weight loss between 30° and $50^{\circ}C$. Upon investigating this further, it seems apparent that the submitted Kepone sample contained Kepone hydrate. Thus, this early weight loss represents the evolution of water.

For the three pesticides, the indicated temperatures corresponding to the completion of evaporation are aligned in the same order as the molecular weights of the pesticides. That is, DDT is thermally removed first, followed by Kepone and then Mirex.
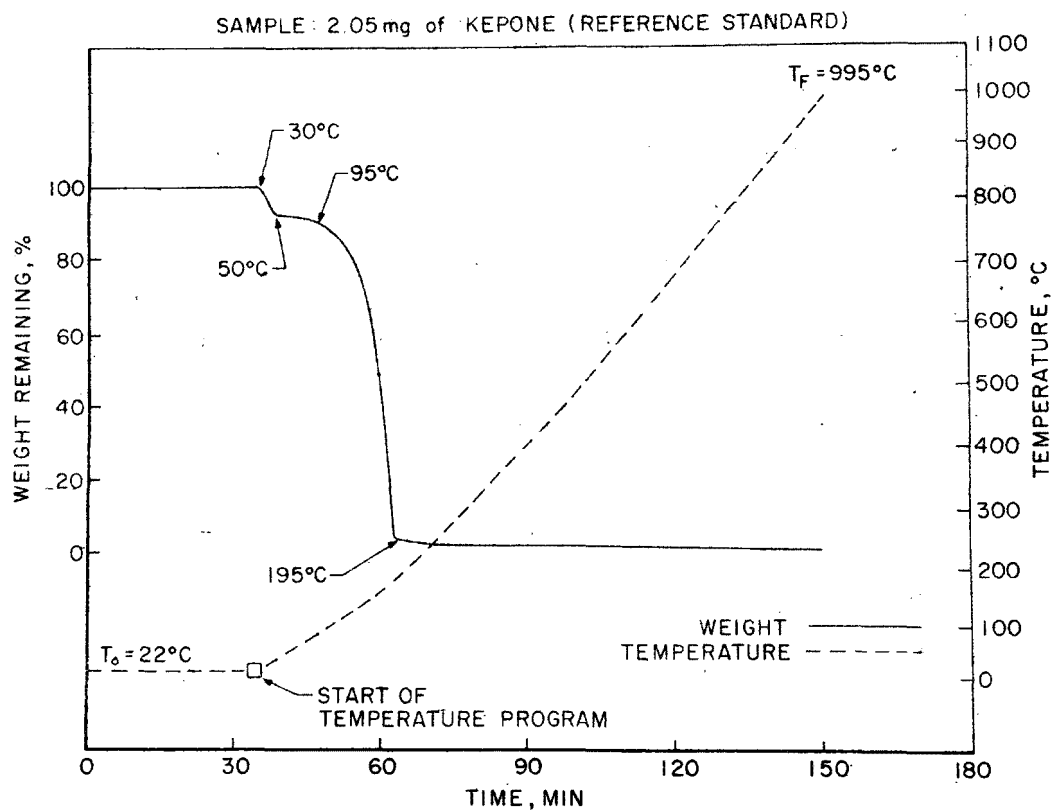
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SAMPLE : 2.05mg of KEPONE (REFERENCE STANDARD)

Figure 3. TG Analysis of Kepone.

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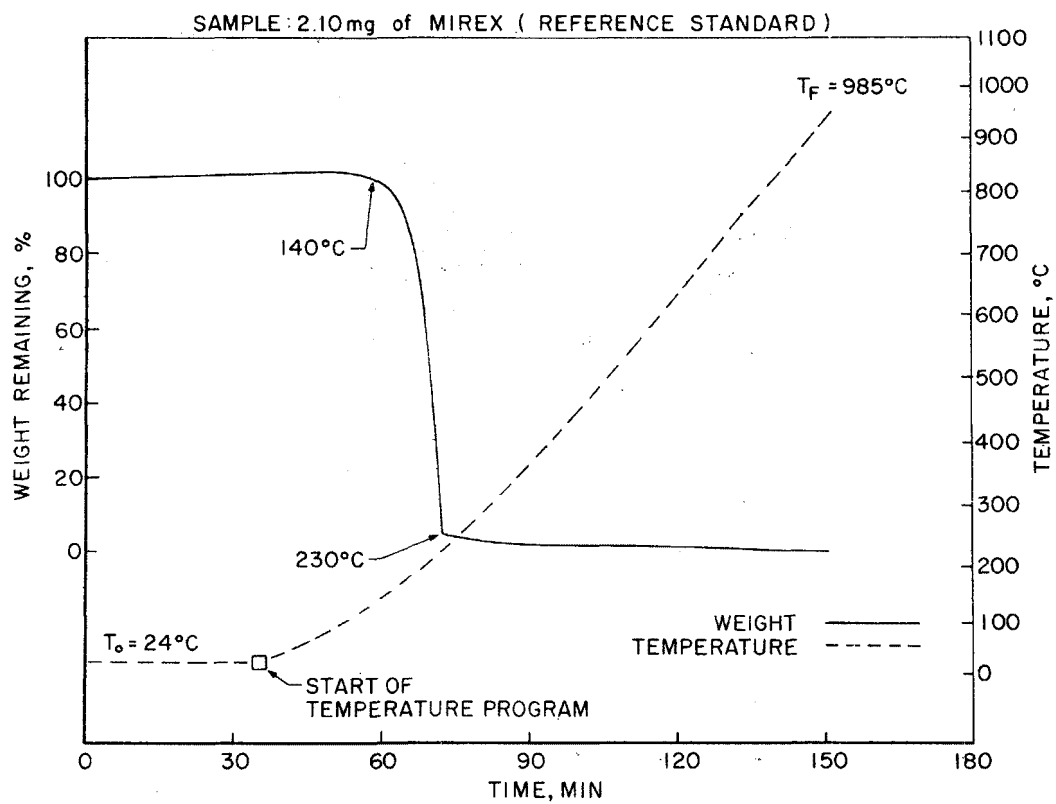
Figure 4. TG Analysis of Mirex.
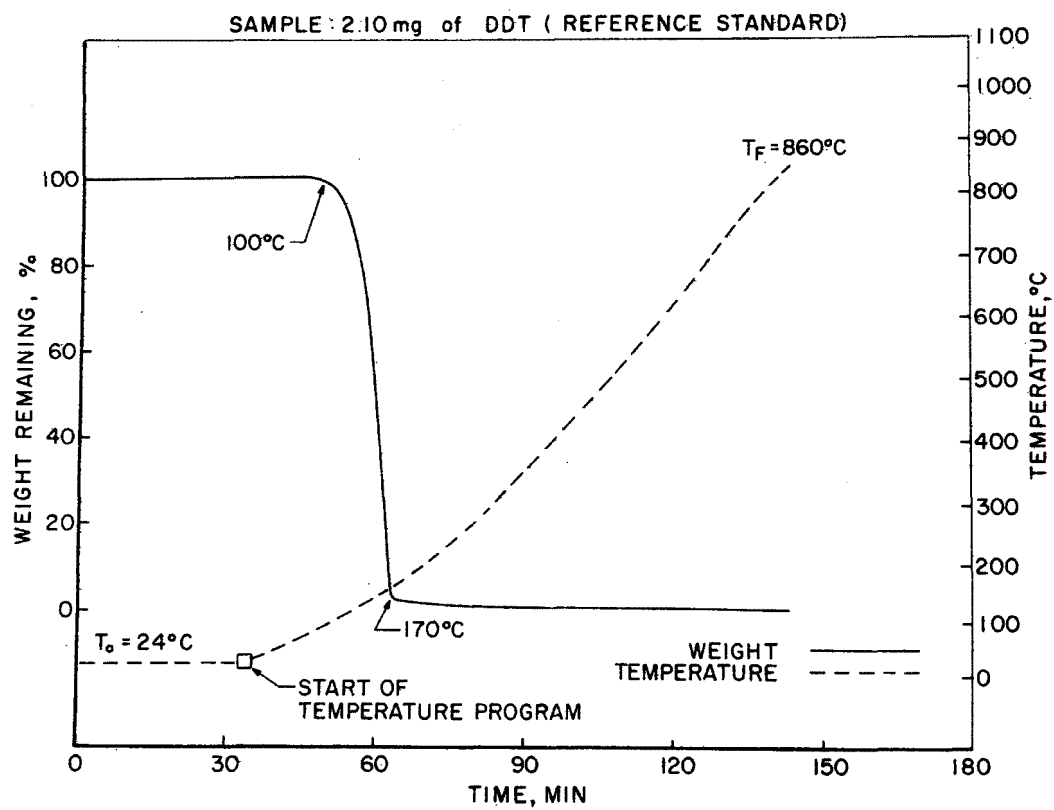
Figure 5. TG Analysis of DDT.

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Samples of Kepone, Mirex, and DDT were also subjected to differential thermal analysis. These tests were conducted with a DuPont 900 DTA apparatus which utilized a purging air atmosphere. The DTA results will be presented and discussed in Section VI.

Quartz Tube Apparatus

Figure 6 is a schematic of the high-temperature quartz tube apparatus that was designed and assembled for the examination of pesticides. An important component in this apparatus is the folded quartz tube which is contained in a Lindberg furnace, type 55035A.

Two quartz tubes of different bore size were fabricated for this work. Both tubes had an effective length, when positioned in the furnace, of 84 cm. By using a mercury plug displacement method [7], the average inside diameters of the finished, folded tubes were found to be 0.80 mm and 2.14 mm, respectively.

Upstream of this folded quartz tube is a special sample holder which is shown in Figure 7. With the use of a 10 microliter syringe and following suggested procedure [8], a known quantity of pesticide can be readily deposited on the sand blasted region of the sample holder. The solvent quickly evaporates, leaving the pure pesticide on the rough Pyrex surface. This device is then inserted into a chamber upstream of the high-temperature quartz tube. Next, this chamber is heated to the extent necessary to vaporize the pesticide; whereupon, the gas phase pesticide is swept through the high-temperature tube.

An effluent trap is located at the outlet of the high-temperature tube. A sketch of the basic trap is shown in Figure 8. This lengthy Pyrex tube (22.5 cm) is connected to the quartz tube outlet with a special Swagelok

A. COMPRESSED AIR, BREATHING QUALITY GRADE

B. TWO STAGE PRESSURE REGULATOR

C. "HYDROPURGE" FILTER

D. FLOW CONTROL VALVE

E. PRESSURE TRANSDUCER

F SAMPLE HOLDER, PYREX

G. HEATED INLET CHAMBER

H QUARTZ TUBE

I. HEATED OUTLET CHAMBER

J EFFLUENT TRAP, TENAX-GC OR CHARCOAL

K. FLOW METER
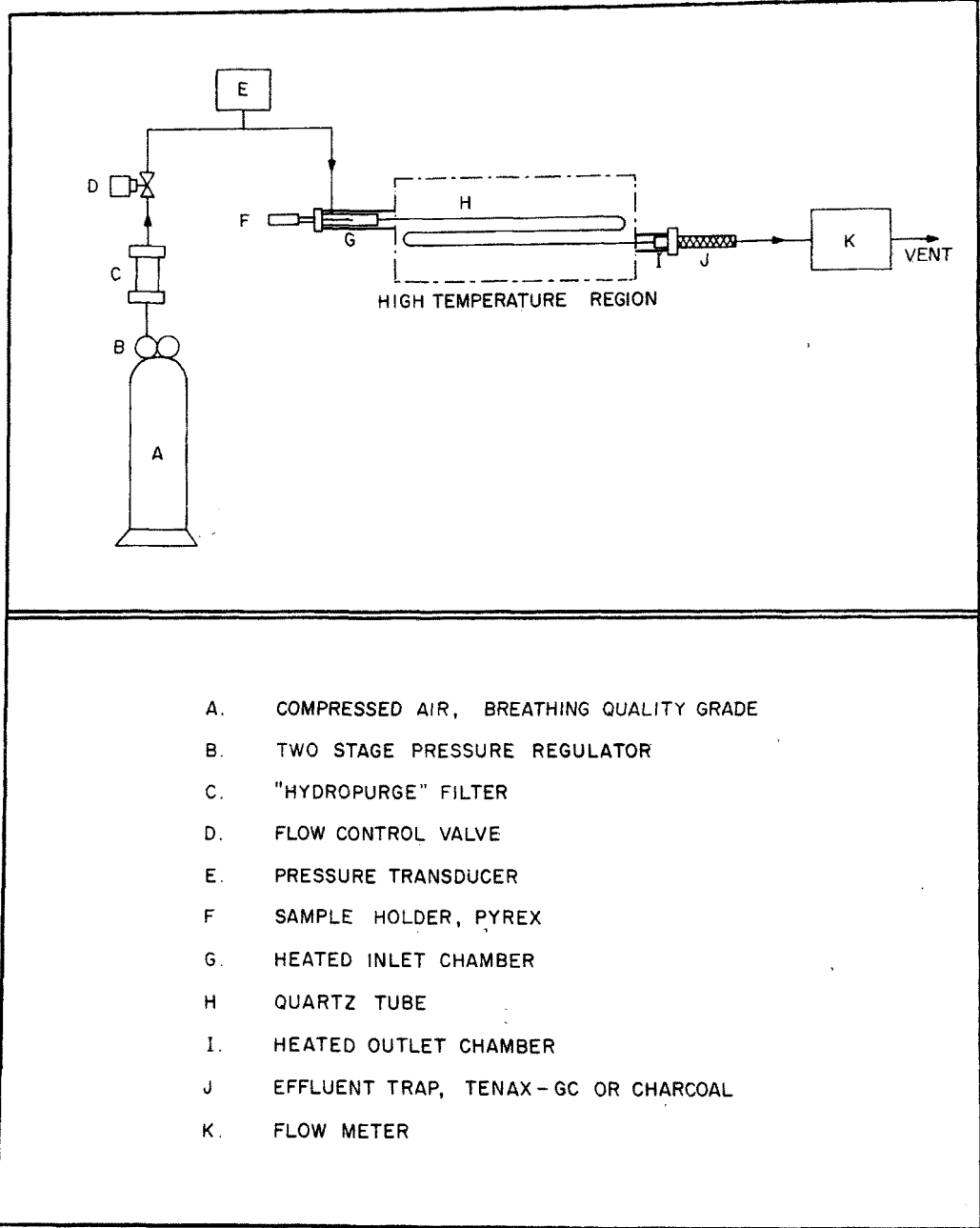
Figure 6. Schematic of Quartz Tube Apparatus.

SAMPLE DEPOSIT REGION
2.0 cm BY 0.4 cm DIAMETER
(SAND BLASTED)

GAS-TIGHT SEAL
(3-SILICONE O-RINGS)

HANDLE

PYREX ROD
25 cm BY 0.6 cm

ADJUSTABLE
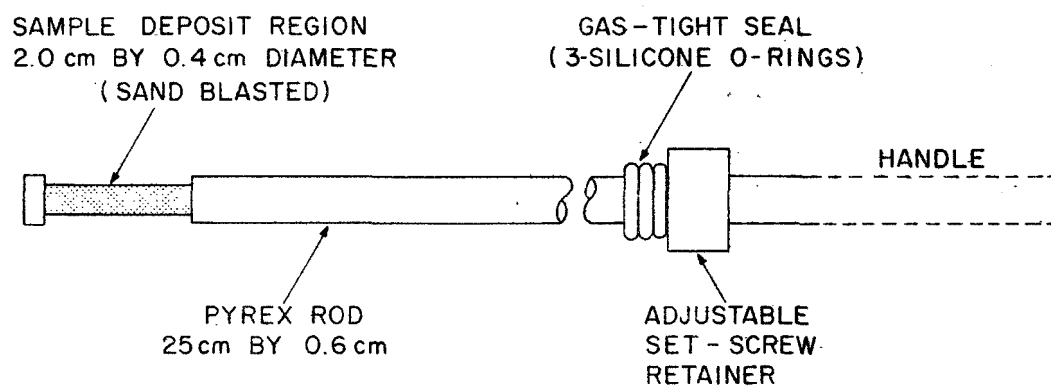SET - SCREW
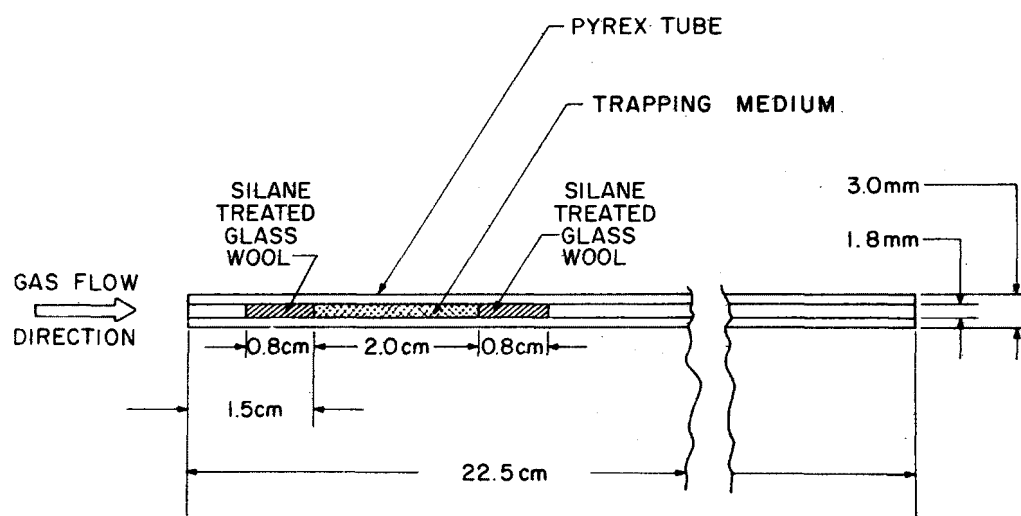RETAINER

Figure 7. Sample Holder.

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Figure 8. Effluent Trap.

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reducer union containing a Teflon sleeve. A gas tight seal is obtained with the use of Vespel ferrules. The outlet of the trapping medium tube approaches ambient temperature.

During this study, different trapping media were employed. Tenax-GC was found to be an excellent trapping medium for the three pesticides and their larger fragmentation products. Tenax-GC, a porous polymer, is currently commercially available in 35/60 and 60/80 mesh sizes. Also, this material has a desirable feature in that it can be readily, thermally desorbed [9-16]. Traps prepared with the 60/80 mesh Tenax-GC particles performed quite well and did not present an excessive pressure drop. Also, a 2.0 cm length of Tenax-GC was sufficient to obtain quantitative recoveries of the pesticides. However, acetone and benzene were not quantitatively retained at the typical trap inlet temperature of approximately 300°C. Charcoal [17, 18] was also used as a trapping medium in this study, and was found to be an excellent trapping material for these three pesticides.

Other important components in this high-temperature destructive apparatus are a Porter flow control valve (model number VCD-1000), a differential pressure transducer, two Blue M model APH-500 temperature indicators which continually display the temperatures of the inlet and outlet chambers, and a specially fabricated soap-bubble flowmeter for measuring the system's outlet flow rate. The gas used in this study was breathing-quality compressed air which was passed through an Applied Science Laboratories Hydro-Purge filter. The average temperature in the high-temperature furnace was continually monitored by the digital readout from a compensated chromel-alumel thermocouple.

From the sketch shown in Figure 9, it is seen that the pressures, temperatures, and volumes in this system can be related according to the ideal gas law as,

19
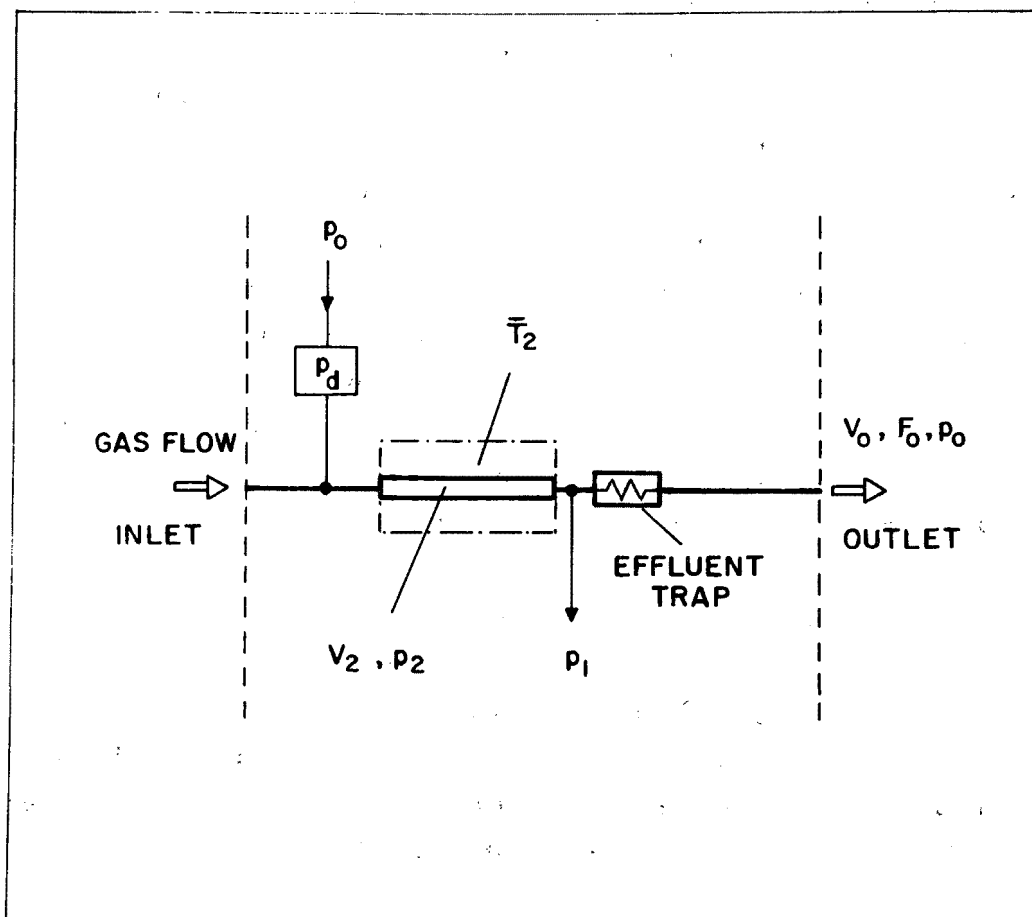
Figure 9. Sketch of Pressure, Volume, and Temperature Relationship in Test System.

$$\frac{V_2 P_2}{T_2} = \frac{V_o P_o}{T_o} \ , \qquad\qquad\qquad \text{(V. 1)}$$

where V is volume, p is pressure, and T is temperature. The subscript 2 denotes the quartz tube interior, while the subscript o represents the ambient outlet conditions.

Due to the extremely low pressure drop posed by the open quartz tube, and the comparatively high pressure drop presented by the packed small particle effluent trap, the differential pressure p_d can be expressed as

$$p_d = p_2 - p_o = p_1 - p_o \ . \qquad\qquad\qquad \text{(V. 2)}$$

Now, volume flow F can be written as

$$F = \frac{V}{t} \ , \qquad\qquad\qquad \text{(V. 3)}$$

where t is time, equation (V. 1) can be rewritten as

$$\frac{V_2 P_2}{T_2} = \frac{F_o t P_o}{T_o} \ , \qquad\qquad\qquad \text{(V. 4)}$$

or

$$\frac{\pi r^2 L P_2}{T_2} = \frac{F_o t P_o}{T_o} \ , \qquad\qquad\qquad \text{(V. 5)}$$

where r and L are the tube radius and length, respectively. Therefore, it is seen that time, or in this case residence time, can be written simply as

$$t_r = \left(\frac{\pi r^2 L}{F_o}\right)\left(\frac{T_o}{\overline{T}_2}\right)\left(1 + \frac{P_d}{P_o}\right) \ , \qquad\qquad (V. \ 6)$$

where t_r represents the calculated mean residence time of a substance in the quartz tube interior.

Special measurement equipment is required to measure the outlet flow, the temperature of the quartz tube, and the upstream differential pressure. Specifically, the outlet flow is measured with a small bore soap-bubble flowmeter having an in-line water saturator [19]. This device was fabricated in the University Glass Shop and incorporated a calibrated volumetric pipette in the design. The average temperature of the quartz tube was determined by measuring the axial temperature profile in the Lindberg furnace and then determining the location of a point within the furnace which would represent the average temperature. This point was found to be at a location 9 cm from the axial midpoint of the furnace. The temperature profile for the contained, folded quartz tube is shown in Figure 10. This thermal information was obtained with a chromel-alumel thermocouple which was used to measure the temperature at 1 cm increments along the tube furnace axis. The average temperature that a pesticide will encounter during its gas phase traverse through the quartz tube will be represented by $\overline{T}_2$ as shown in Figure 10.

The pressure within the quartz tube is difficult to measure. A low pressure gage, such as a Bourdon gage, customarily exhibits high degrees of inaccuracy, along with a large mechanically induced hysteresis. Consequently, a very precise pressure transducer was utilized for measuring the differential pressure at the inlet to the quartz tube. This pressure transducer (see Figure 11) was found to be extremely accurate, linear, and
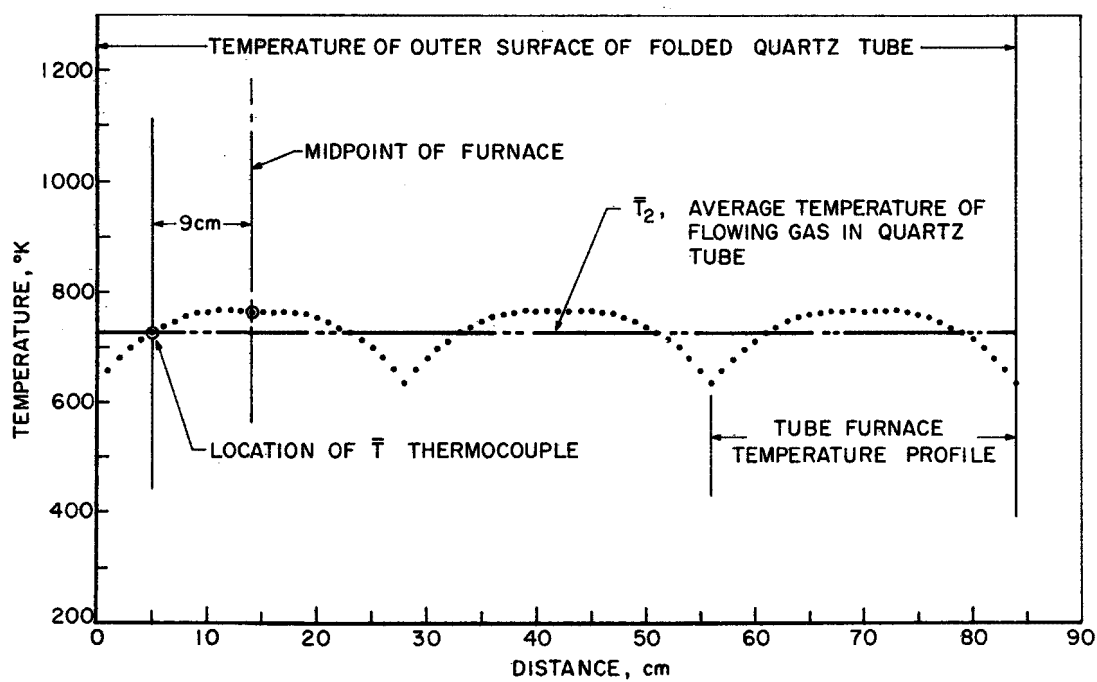
Figure 10. Temperature Profile of Quartz Tube Furnace.

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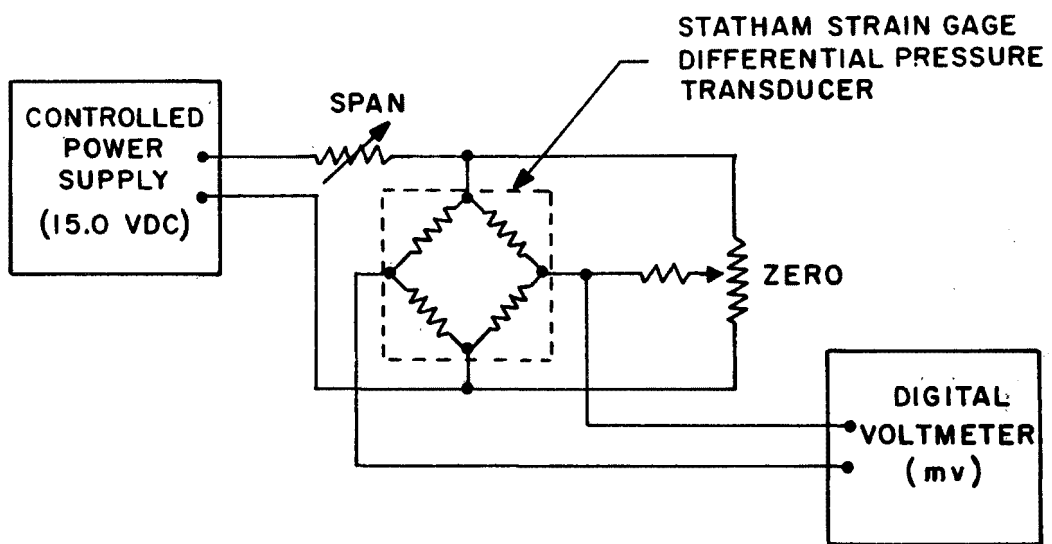
Figure 11. Electrical Schematic of Pressure Transducer.

exhibited no hysteresis. The output from the pressure transducer was displayed on a digital millivoltmeter. Throughout this study it was observed that the differential pressure varied with the particle size of the trapping medium and the linear gas velocity.

The determination of mean residence time was subjected to an error analysis which is described in Appendix I. Essentially, as a result of this error analysis, it was found that mean residence time can be accurately determined provided F_o, $\overline{T}_2$, and p_d are also measured with accuracy.

Even though the mean residence time can be accurately determined, additional information is needed concerning the distribution of the residence times of different molecules. The residence time distribution of the pesticide molecules can be studied in the same manner as if they entered the quartz tube as a concentrated narrow pulse (Appendix II). Also, the behavior of different molecular weight substances at different temperatures has been investigated. It was found that different molecular weights (different pesticides) produced only a very small effect on the respective residence time distribution; however, the residence time distribution was found to be strongly dependent upon temperature, as described in Appendix II. Even so, a fairly small tolerance can be applied to the mean residence time and still envelope the rapidly migrating molecules.

Once the pesticide molecules, or fragments and products thereof, have passed through the high-temperature quartz tube, they are trapped in, or on, the sorbing medium of the effluent trap. This trap is then removed from the high-temperature apparatus. A quantitative standard is then deposited in the trap (4.0 μg of n - octadecane in a 50:50 vol mixture of acetone and benzene). The contents are then subjected a programmed temperature gas chromatographic analysis using a modified Tracor 550 Instrument.

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The injector of this gas chromatograph has been modified so that it will accept the Pyrex tube containing the trapping medium and its sorbed sample. Modifications to the chromatograph have been made so that thermal desorption of the trapping medium can be conducted while it is positioned just upstream of the column packing (see Figure 12). This is accomplished with the use of a cartridge heater embedded in an aluminum block which surrounds the inlet region of the glass column. By heating this inlet region to $260^{\circ}C$ for 10 minutes, complete desorption of the trapped effluent is accomplished. This desorption is made with the chromatographic oven at room temperature; therefore, the products are swept from the trapping medium and deposited on the inlet portion of the packed column.

After a suitable thermal desorption time (10 minutes), the chromatographic oven is closed and the temperature is programmed to $260^{\circ}C$ at the rate of $14^{\circ}C$ per minute. It has been found that the 1.8 meter length OV-1 column efficiently elutes Kepone, Mirex, DDT, and their various decomposition products when this GC procedure is used. (With this trapping and thermal desorbing technique, essentially quantitative transfer of the three pesticides was achieved.)

Charcoal can be substituted for the Tenax-GC in the effluent trap; however, the trap must then be chemically desorbed, rather than thermally. Accordingly, after selecting suitable solvents, the charcoal trap was chemically desorbed and the contents analyzed with a gas chromatograph using either HFID or ECD. This form of effluent trapping and chemical desorption was performed for the three pesticides at the highest temperature studied, namely $900^{\circ}C$.

The effect of residence time on the high-temperature degradation was also of interest. With the high-temperature quartz-tube apparatus, Kepone was examined at a region of high thermal degradation, namely in the vicinity of
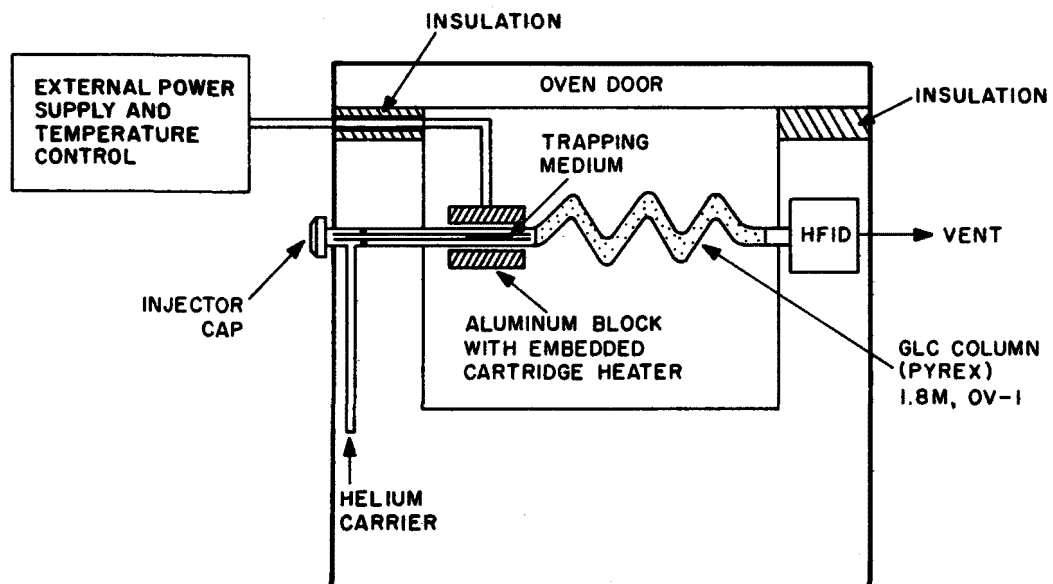
Figure 12. Interior of Modified Tracor 550.

420° to $440^\circ C$. At temperatures less than this, Kepone was passed through the quartz tube essentially intact. At higher temperatures, Kepone was observed to decompose rapidly. Accordingly, samples of Kepone were subjected to three successive tests at a constant $\overline{T}_2$ of $433^\circ C$, but with different residence times. The trapped effluents from these three tests were then analyzed. The effect of Kepone residence time at $433^\circ C$ was then evaluated from the effluent data.

SECTION VI

RESULTS AND DISCUSSION

High-Temperature Vapor Phase Destruction

Samples of each pesticide were subjected to a series of high-temperature destruction tests. The trapped effluent from each test was then analyzed by GC as described by the conditions listed in Figure 13. Typical chromatograms corresponding to thermally stressed Kepone, Mirex, and DDT are shown in Figures 14, 15, and 16, respectively. The entire series of chromatograms corresponding to the examination of Kepone is presented in Figure 17. This figure shows, in sequential chromatogram form, the thermal destruction of Kepone at temperatures up to $910^{\circ}C$.

In this laboratory work, it was felt desirable to obtain the entire series of analytical data at a fixed detection sensitivity so that the display of the various chromatograms could be more easily compared. Consequently, signal attenuation was maintained constant throughout the work. The quantitative data were obtained from GC peak height measurements -- the preferred method [20, 21] when one is comparing partially superimposed GC elution profiles.

The compiled GC data obtained with HFID and the Tenax-GC trapping medium are given in Table I. From these data, thermal destruction plots were prepared for Kepone, Mirex, and DDT. These plots are presented in Figures 18, 19, and 20, respectively. Also, Figure 21 shows a direct comparison of the high-temperature destruction of Kepone, Mirex, and p,p'-DDT.

Before proceeding with the presentation of further results, it is interesting to note that Mirex undergoes a considerable degradation in the vicinity of

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┌─────────────────────────────────────────────────┐
│         GAS CHROMATOGRAPHIC CONDITIONS          │
├─────────────────────────────────────────────────┤
│                                                 │
│  Instrument        Tracor 550                   │
│  Analyst         W. Rubey                       │
│  Date       3-15-76                             │
│  Column:                                        │
│     tubing material    Pyrex                    │
│     tubing length  1.8        meters            │
│     tubing bore     3.5       mm                │
│  Stationary Phase  OV-1 Silicone                │
│     weight   3%                                 │
│  Support  Chromosorb-W, HP Grade                │
│     mesh   100/120                              │
│  Carrier Gas  Helium                            │
│     inlet pres          1.8      abs  atm       │
│     linear velocity    10        cm/sec         │
│     outlet flow         65       ml/min         │
│  Chart Advance      0.5          cm/min         │
│  Read Out       1.0          mv  full scale     │
│  Sample     Pesticides                          │
│     size      Noted                             │
│  Detector  HFID                                 │
│     range  10⁻⁹ AFS                             │
│     attenuation   16                            │
│  Gas Flows, ml/min                              │
│     hydrogen       50                           │
│     air           350                           │
│     split ratio      none                       │
│  Temperatures, °C                               │
│     detector    320                             │
│     injector    RT                              │
│     column:                                     │
│        initial    40                            │
│        final    260                             │
│        progam rate      14        °C/min        │
│  Sample Solvent  Acetone + Benzene              │
│     concentration    Noted       % solvent      │
│                                                 │
└─────────────────────────────────────────────────┘
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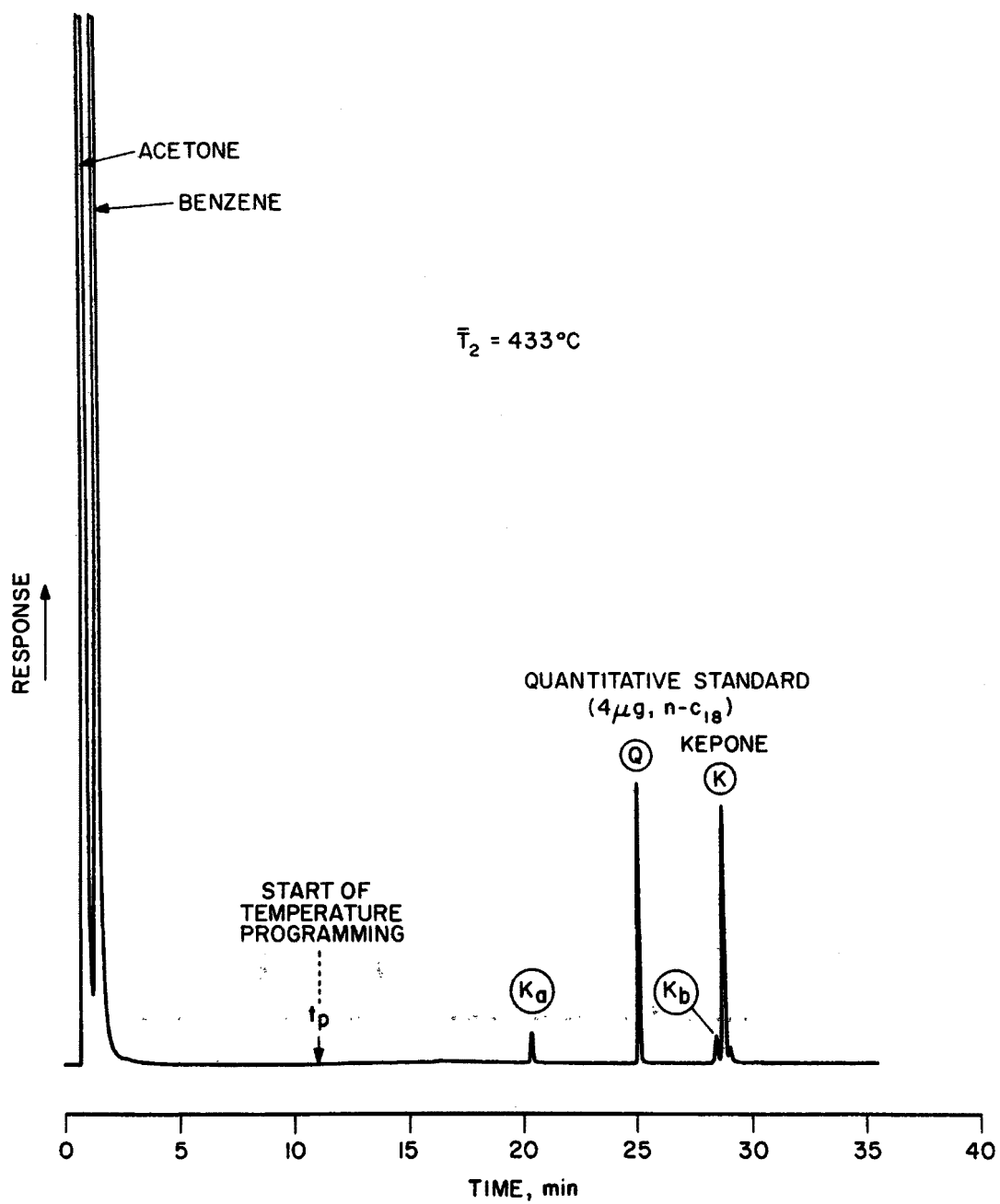Figure 13. Programmed Temperature GC Analysis Conditions.

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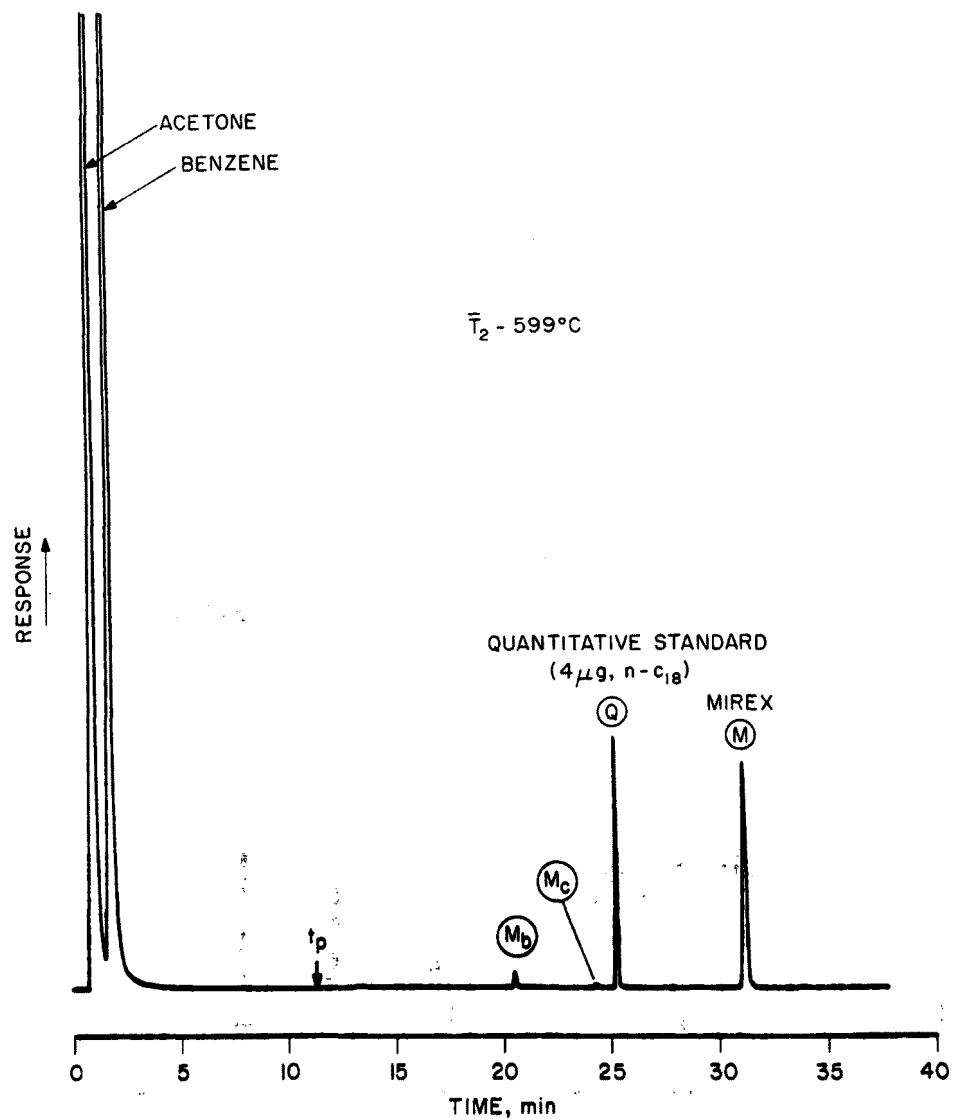Figure 14. Chromatogram of Thermally Stressed Kepone.
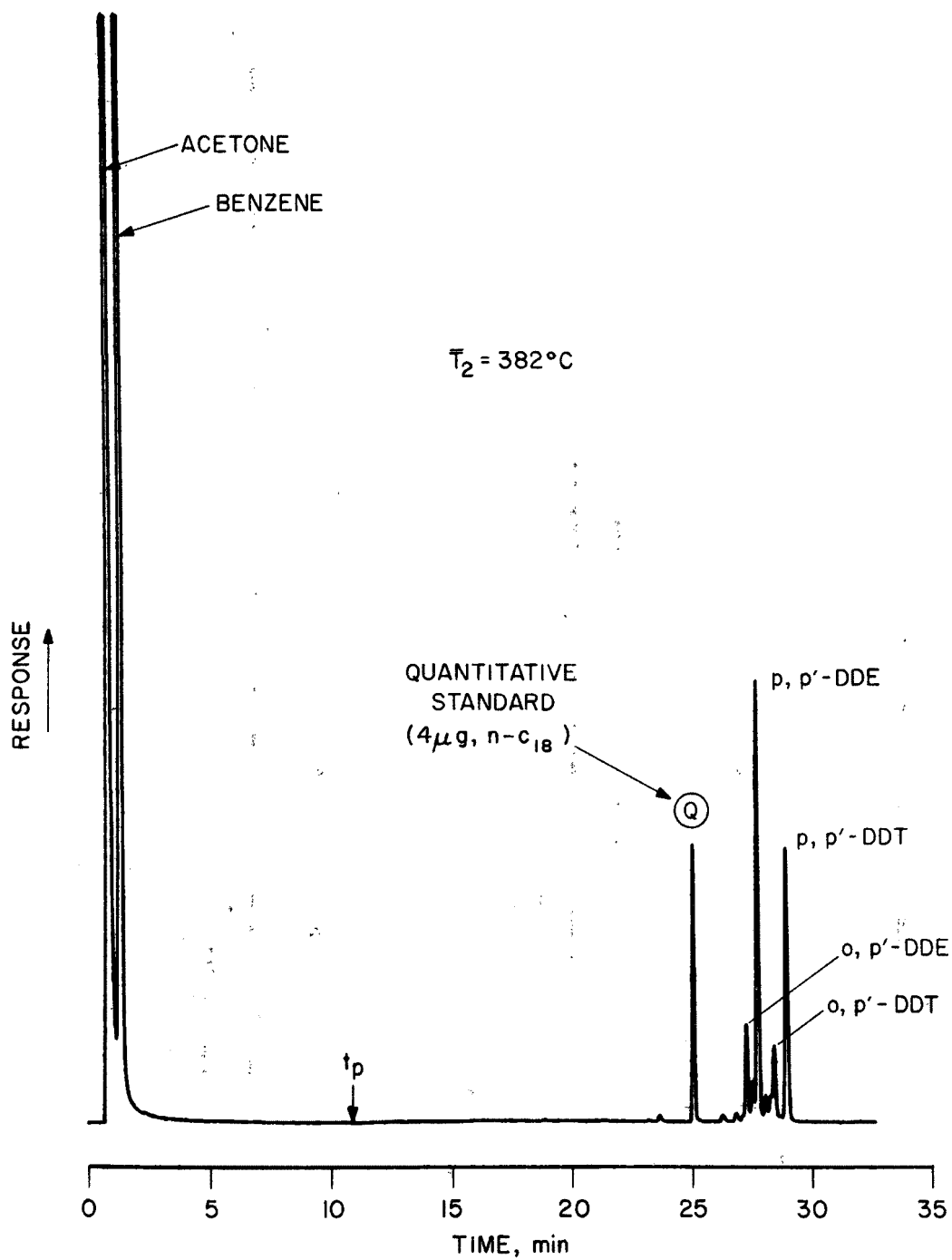
Figure 15.   Chromatogram of Thermally Stressed Mirex.

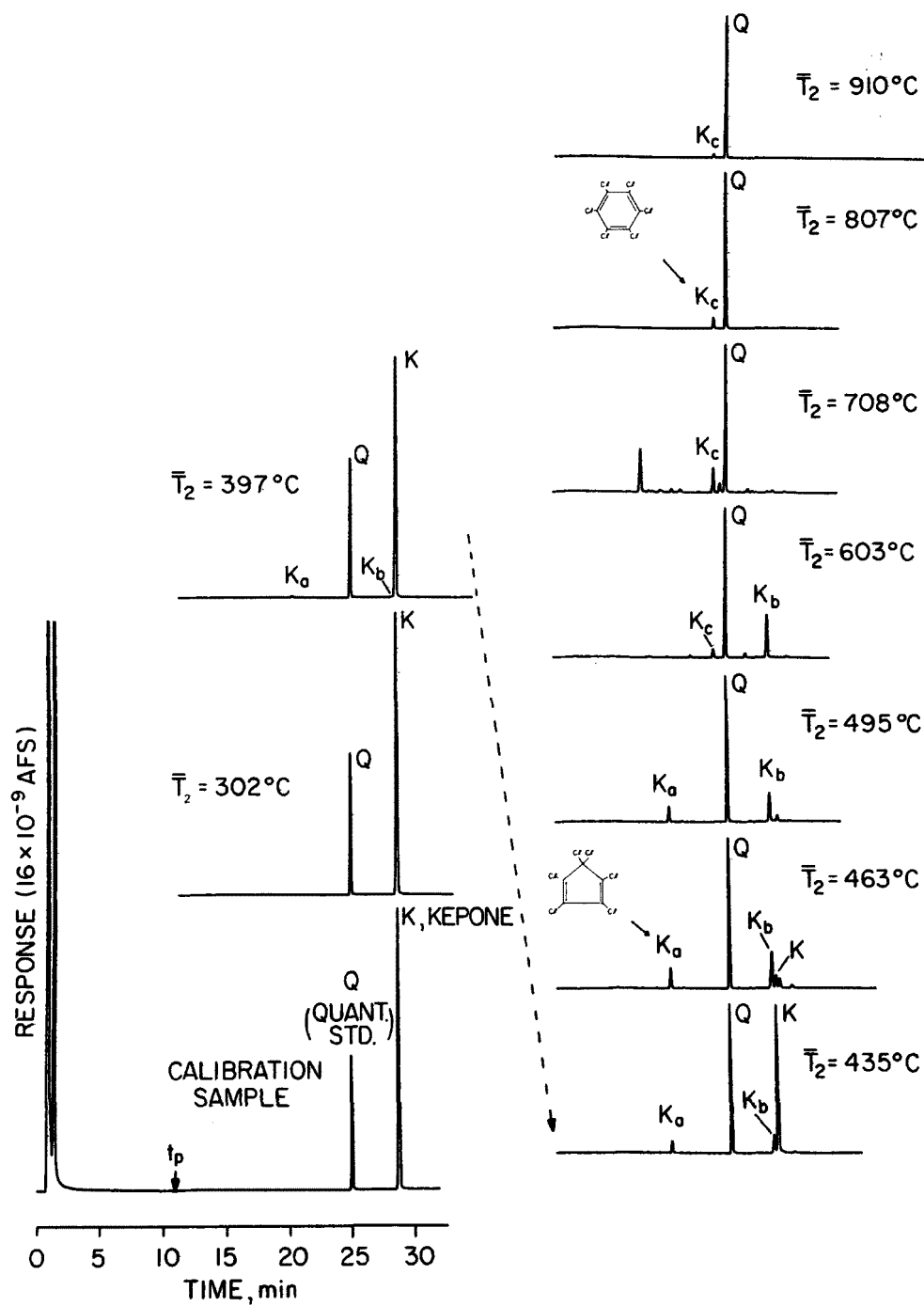Figure 16. Chromatogram of Thermally Stressed DDT.

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Figure 17.   Series of Chromatograms from Thermally Stressed Kepone.

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TABLE I

High Temperature Exposures and Corresponding Analytical Data

Average Furnace Temperature--$\bar{T}_2$ (°C)	Calculated Mean Residence Time--t_r (sec)	Gas Chromatographic Peak Height (cm)			
		K, Kepone	K_a	K_b	K_c
23*	----	11.2	----	----	----
302	0.93	11.5	----	----	----
397	0.99	9.9	0.05	0.05	----
435	0.94	5.8	0.5	0.75	----
463	0.93	0.5	0.85	1.5	----
495	1.10	BGML**	0.65	1.2	BGML
603	0.99	----	0.05	1.75	0.40
708	0.91	----	----	0.05	1.10
807	0.92	----	----	----	0.45
910	0.94	----	----	----	0.15
		M, Mirex	M_a	M_b	M_c
23*	----	8.5	----	----	----
274	0.94	7.7	----	----	----
409	0.94	7.9	----	----	----
504	0.92	7.9	0.05	----	----
599	0.92	5.2	----	0.40	0.10
703	0.93	BGML	0.25	----	0.45
804	0.97	----	----	----	0.30
897	0.97	----	----	----	0.15
		p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE
23*	----	19.3	4.5	0.30	0.05
289	0.93	15.4	3.7	1.2	0.25
382	1.01	5.7	1.6	9.1	2.0
521	1.07	BGML	----	16.1	3.5
612	0.90	----	----	15.2	3.1
704	0.93	----	----	5.5	0.90
810	0.94	----	----	0.05	----
906	0.91	----	----	----	----

* Sample was not passed through quartz tube furnace.
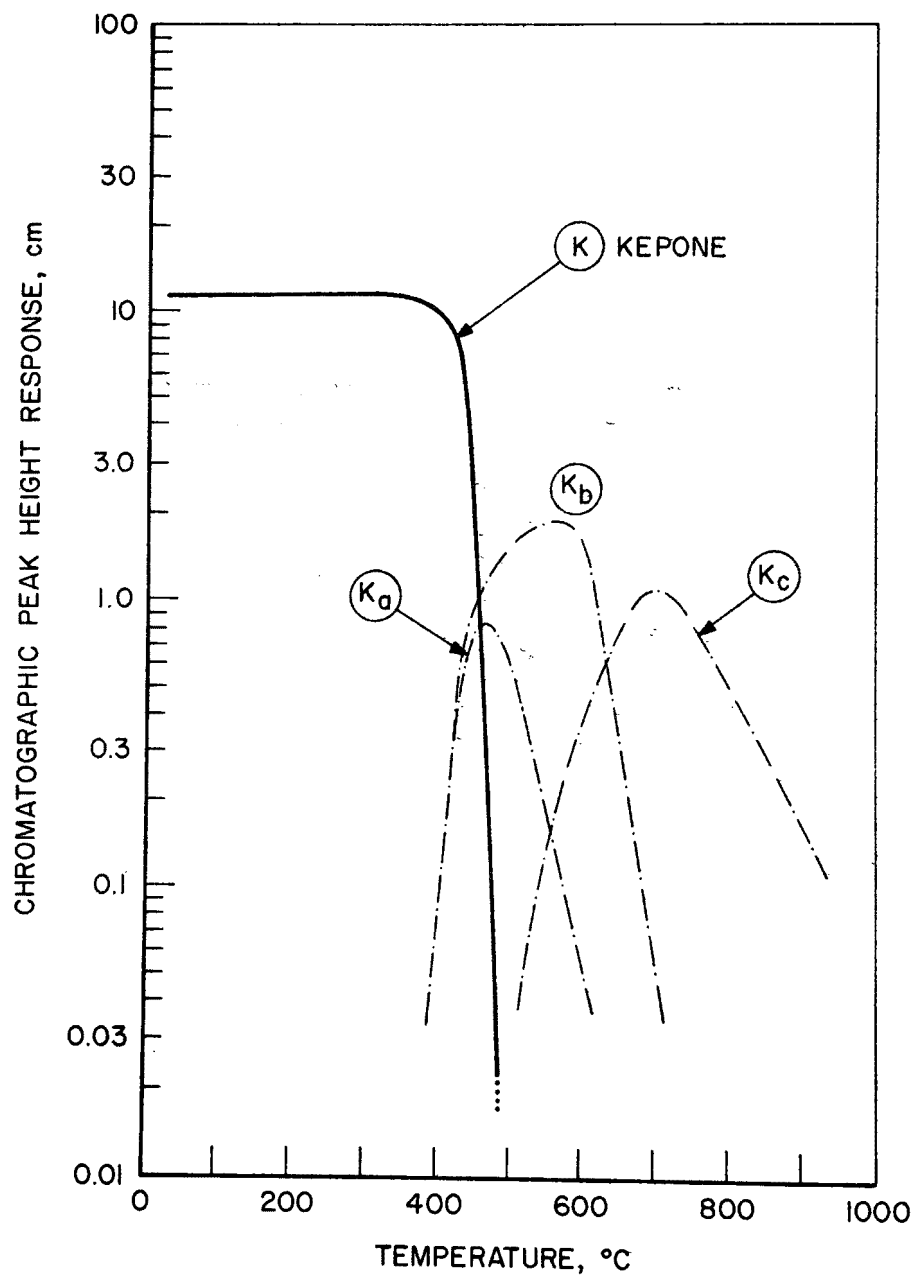** BGML denotes "below graphical measurement level".
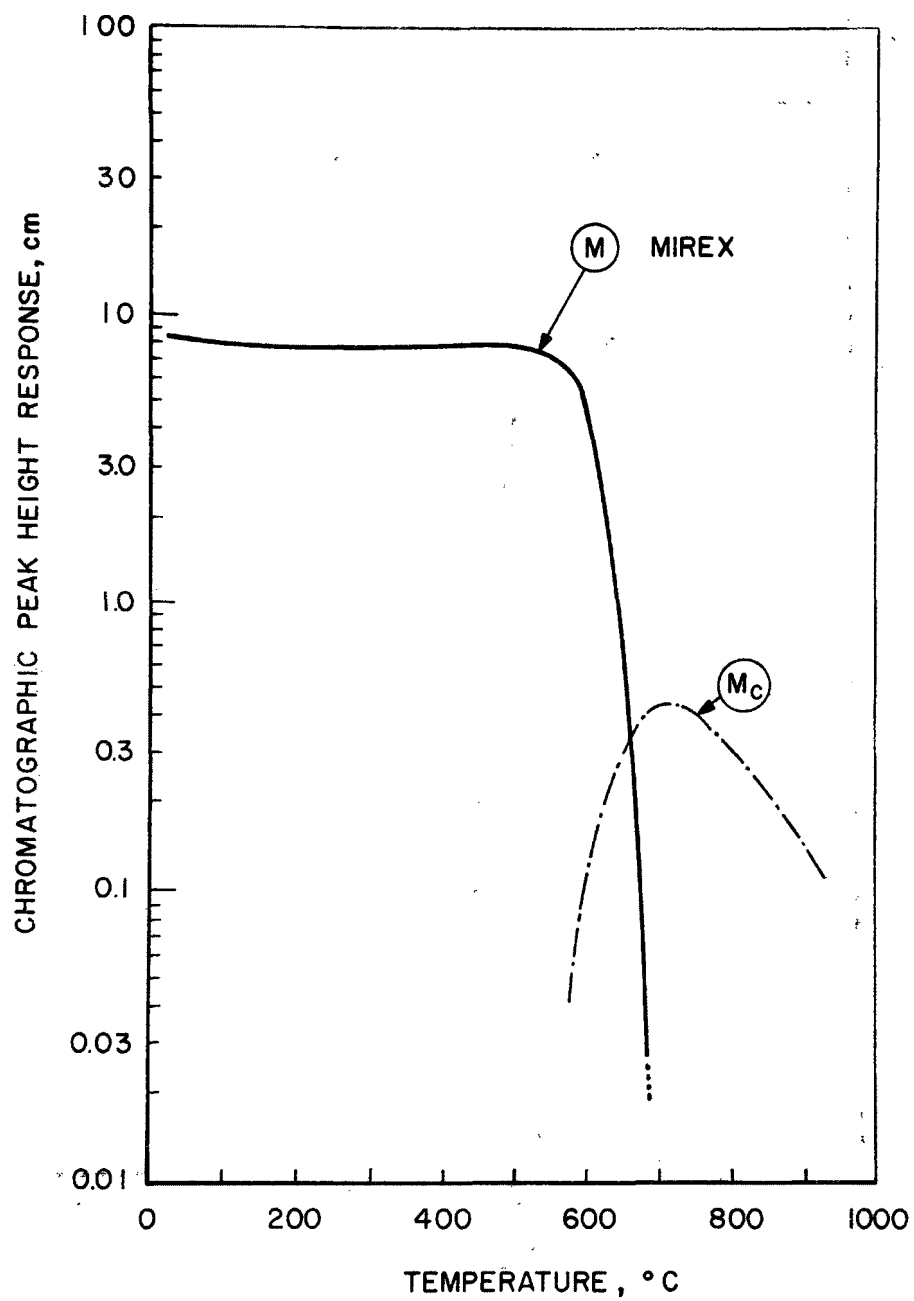
Figure 18. Thermal Destruction Plot for Kepone.

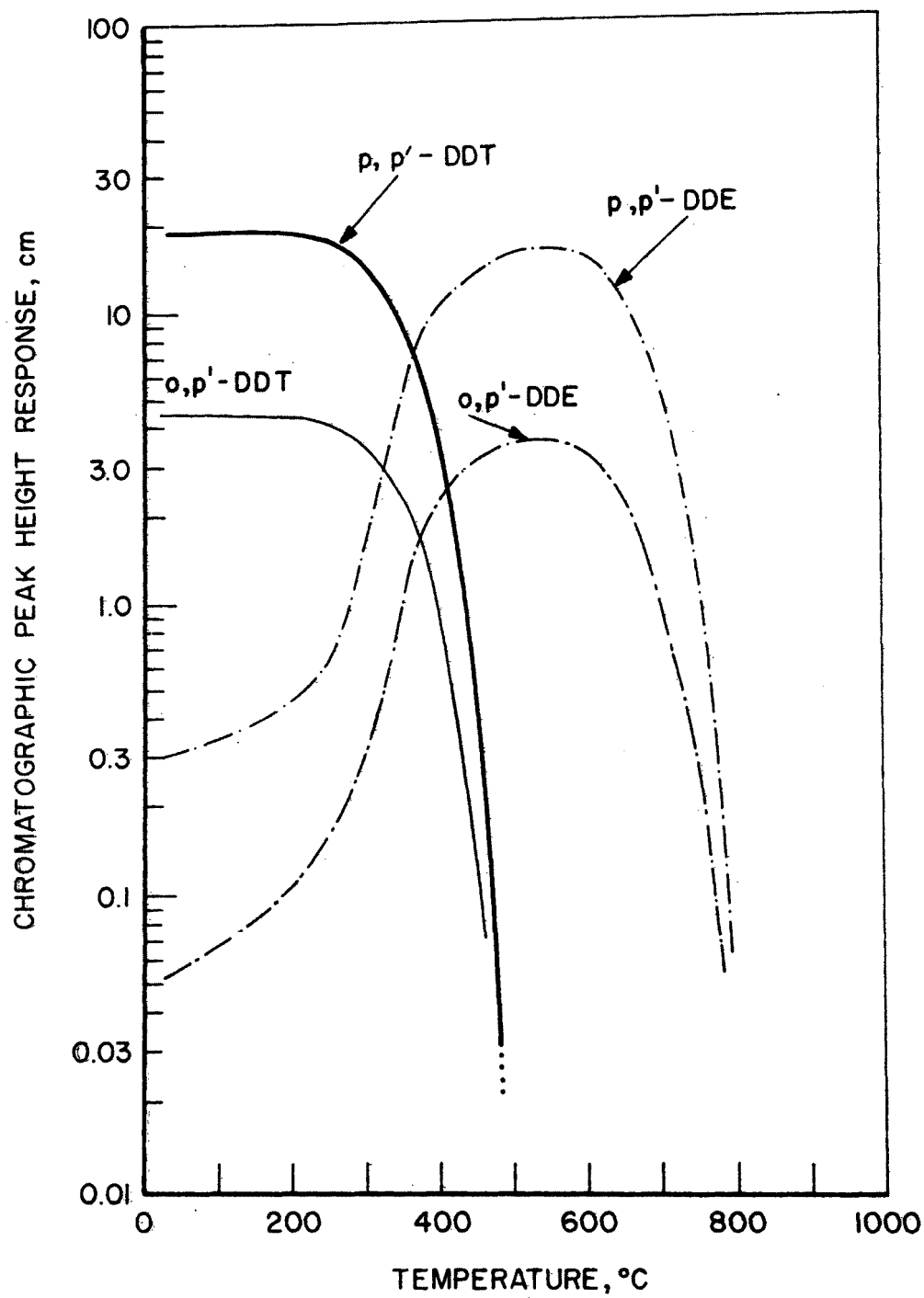Figure 19. Thermal Destruction Plot for Mirex.
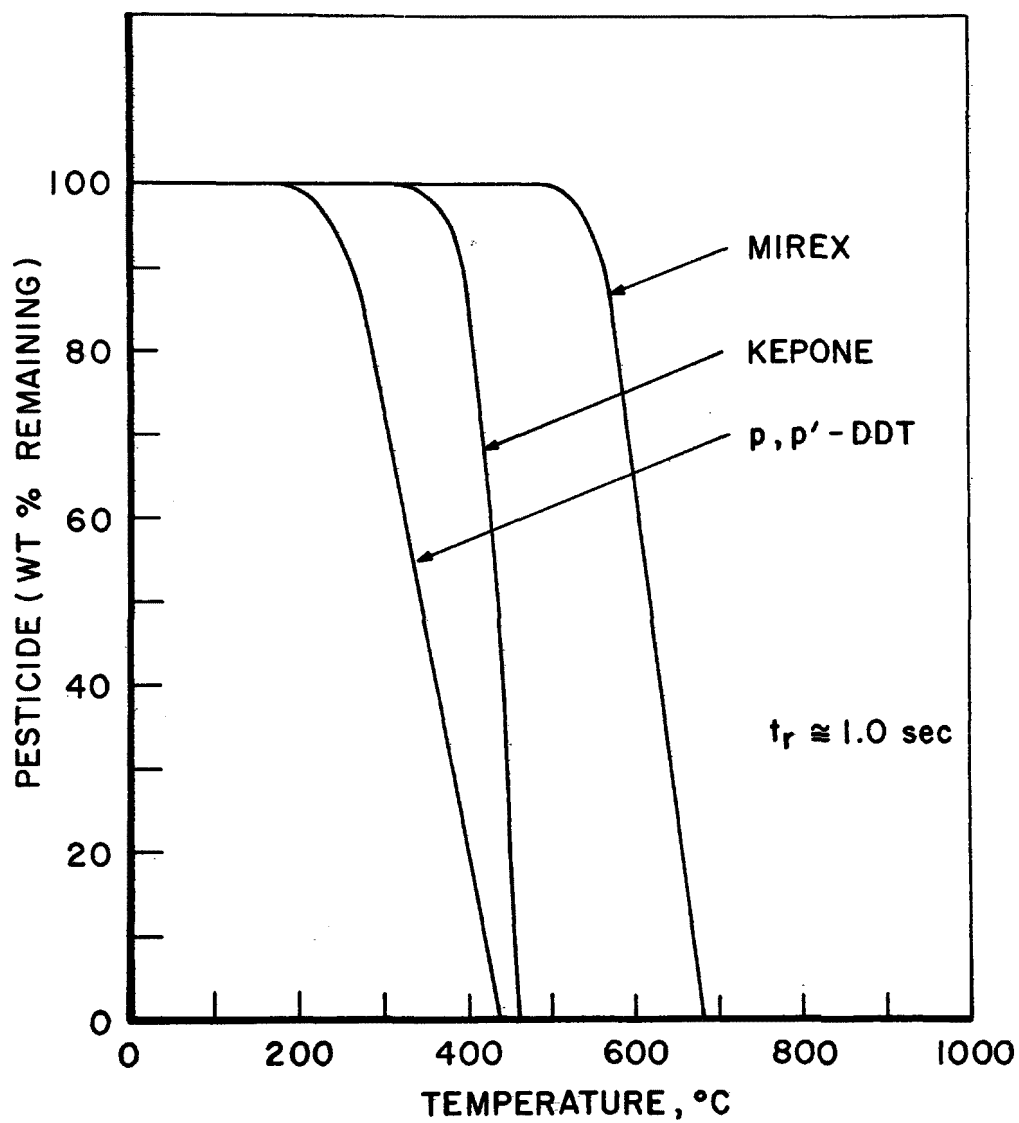
Figure 20. Thermal Destruction Plot for DDT.

Figure 21. Comparison of Thermal Destruction of the Three Pesticides.

600° to 700°C. Also, upon re-inspection of the series of Kepone GC traces (Figure 17), it is noticed that in the 700°C region, a large variety of decomposition products are present. In order to confirm this complex high-temperature behavior, Kepone was re-examined at 705°C and the previous results were verified. The significance of the 700°C behavior of both Kepone and Mirex will be dealt with later.

Additional high-temperature destruction tests were conducted with Kepone, Mirex, and DDT samples at 900°C. The effluents from these tests were passed through charcoal (previously cleaned with carbon disulfide) which was then chemically desorbed with a mixture of acetone (44 vol%), benzene (44 vol%), and carbon disulfide (12 vol%). The results of these 900°C examinations are presented in Table II, along with the analytical conditions.

The chromatographic peaks designated K_c and M_c were determined to be the same compound, as they showed exact retention properties on two, quite different GC columns. Further investigation with pure reference standards identified K_c and M_c as being hexachlorobenzene (C_6Cl_6). Another set of peaks, K_a and M_b, were also determined to be the same compound, and then subsequently identified as hexachlorocyclopentadiene (C_5Cl_6). It is interesting to note that these two decomposition products are formed at different temperatures, i.e., hexachlorocyclopentadiene is formed at 400°C to 600°C, while hexachlorobenzene is present in the 500° to 900°C effluents.

Differential Thermal Analysis

Each of these pesticides was subjected to a differential thermal analysis while in air using a DuPont 900 DTA instrument. The test conditions and resulting DTA tracings are presented in Figure 22. It is important to note that each of these pesticides shows no thermal reactivity above 600°C. This is reasonable, as one would not expect any endotherms or exotherms

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TABLE II

ECD ANALYSIS OF 900°C EFFLUENT

Sample	Pesticide Extracted From Effluent Trap	Pesticide Destruction (%)	Other Trapped Products
Kepone, 40 µg	138 pg	>99.9995	~200 ng Hexachlorobenzene
Mirex, 40 µg	543 pg	>99.998	~400 ng Hexachlorobenzene
DDT, 40 µg	None Detected	>99.9998	Only Trace Quantities

$$\text{Pesticide Destruction, } \% = 100 \left[1 - \left(\frac{\text{wt, trap extract}}{\text{wt, input sample}} \right) \right]$$

GAS CHROMATOGRAPHIC CONDITIONS

Instrument __Varian 2440__

Analyst __W. Rubey__

Date __March 10, 1976__

Column:

　　tubing material __Pyrex__

　　tubing length __2.0__ meters

　　tubing bore __3.0__ mm

Stationary Phase __1.5% OV-17 + 1.95% QF-1__

　　weight __noted__

Support __Gas Chrom Q__

　　mesh __80/100__

Carrier Gas __Nitrogen__

　　inlet pres __2.0__ abs atm

　　linear velocity __8__ cm/sec

　　outlet flow __20__ ml/min

Chart Advance __1.27__ cm/min

Read Out __1.0__ mv full scale

Sample __Residue in Solvent__

　　size __2.0 µl__

Detector __ECD, ^{3}H--Sc__

　　range __10^{-10}__

　　attenuation __16__

Gas Flows, ml/min

　　hydrogen __---__

　　air __--__

　　split ratio __---__

Temperatures, °C

　　detector __275__

　　injector __240__

　　column:

　　　　initial __220__

　　　　final __220__

　　　　progam rate __0__ °C/min

Sample Solvent __Acetone + Benzene + CS$_2$__

　　concentration __99+__ % solvent

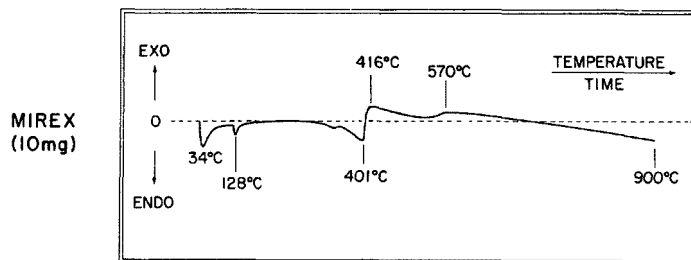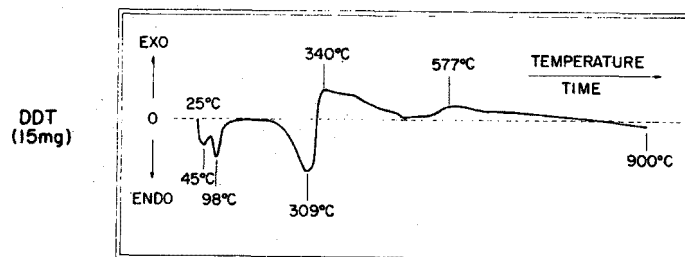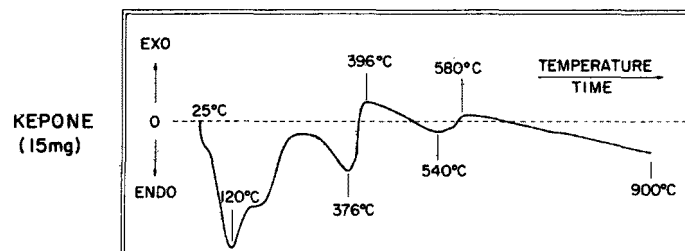| DTA CONDITIONS	
Instrument	duPont Model 900
Reference	Alumina
Crucibles	Platinum
Thermocouples	Platinum vs Platinum + 13% Rhodium
Atmosphere	Dried Air
Temperature Program	Ambient to 900°C at 20°C/min

KEPONE
(15mg)

DDT
(15mg)

MIREX
(10mg)

Figure 22. DTA Tracings of the Three Pesticides.

occurring for pure, organic pesticides at the higher temperatures. However, it is observed that thermal reactions are occurring at temperatures in excess of those found in the TG examinations. The explanation for this difference is that the TG analyses were performed in a 60 ml/min flow of purging air, while the escape of volatiles, or decomposition products, in the DTA was mainly by diffusion into a moving air stream.

Earlier DTA data [22] for various pesticides reported high temperature regions of thermal activity; however, such behavior has to be associated with inorganic impurities, or incorporated clays, fillers, etc.

Effect of Pesticide Residence Time

The thermal breakdown of Kepone is pronounced in the 420° to $440^{\circ}C$ region. Consequently, this temperature region was selected for an experimental evaluation of the effect of residence time on the destruction of Kepone. Accordingly, three separate tests were conducted with 40 μg samples of Kepone at a carefully controlled $\overline{T}_2$ of $433^{\circ}C$. The first test was conducted with a residence time, t_r, of 1.79 sec. The t_r for the second test was 1.04 sec, while for the third test, t_r was 0.23 sec. These different residence times were obtained by appropriately adjusting the air flow control valve of the quartz tube apparatus. Figure 23 shows each of the chromatograms which were obtained from the captured effluents. From these GC data, the concentrations of emerging Kepone were plotted versus residence time, as shown in Figure 24. Thus, it is evident from this logarithmic plot that residence time is a strong factor in the destruction of Kepone at $433^{\circ}C$.
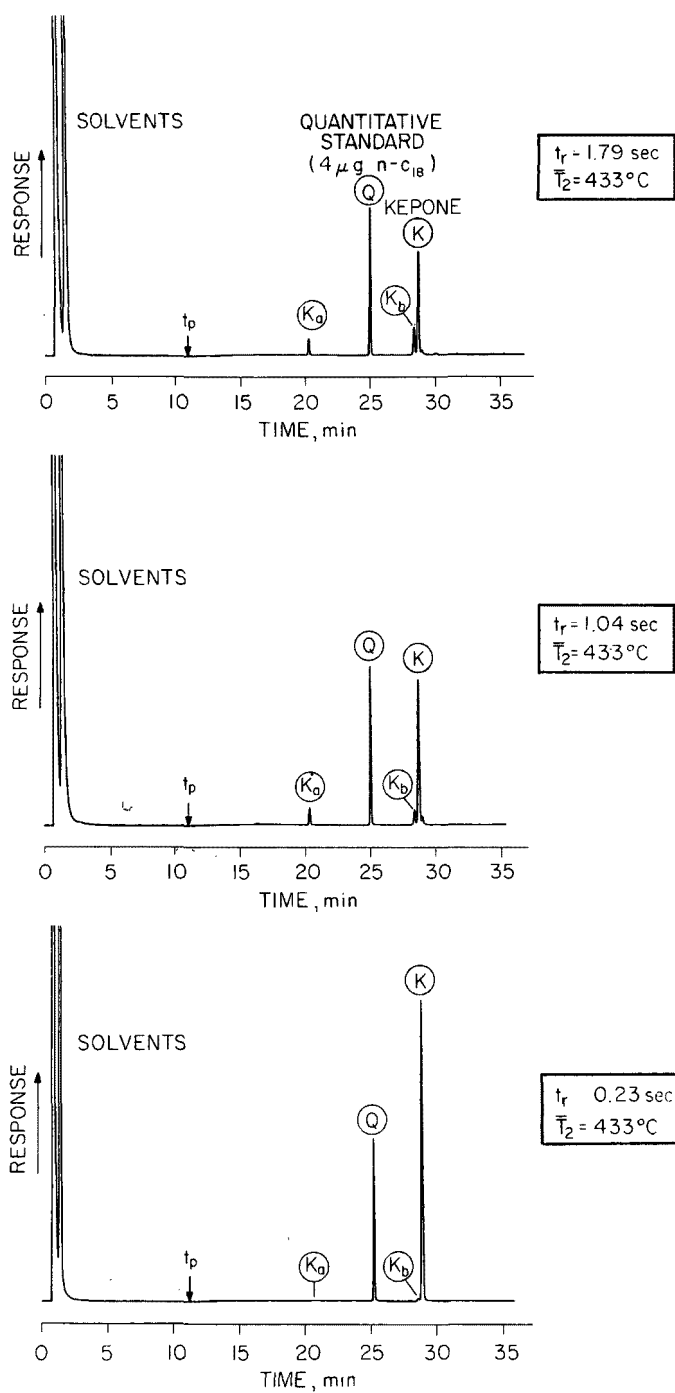
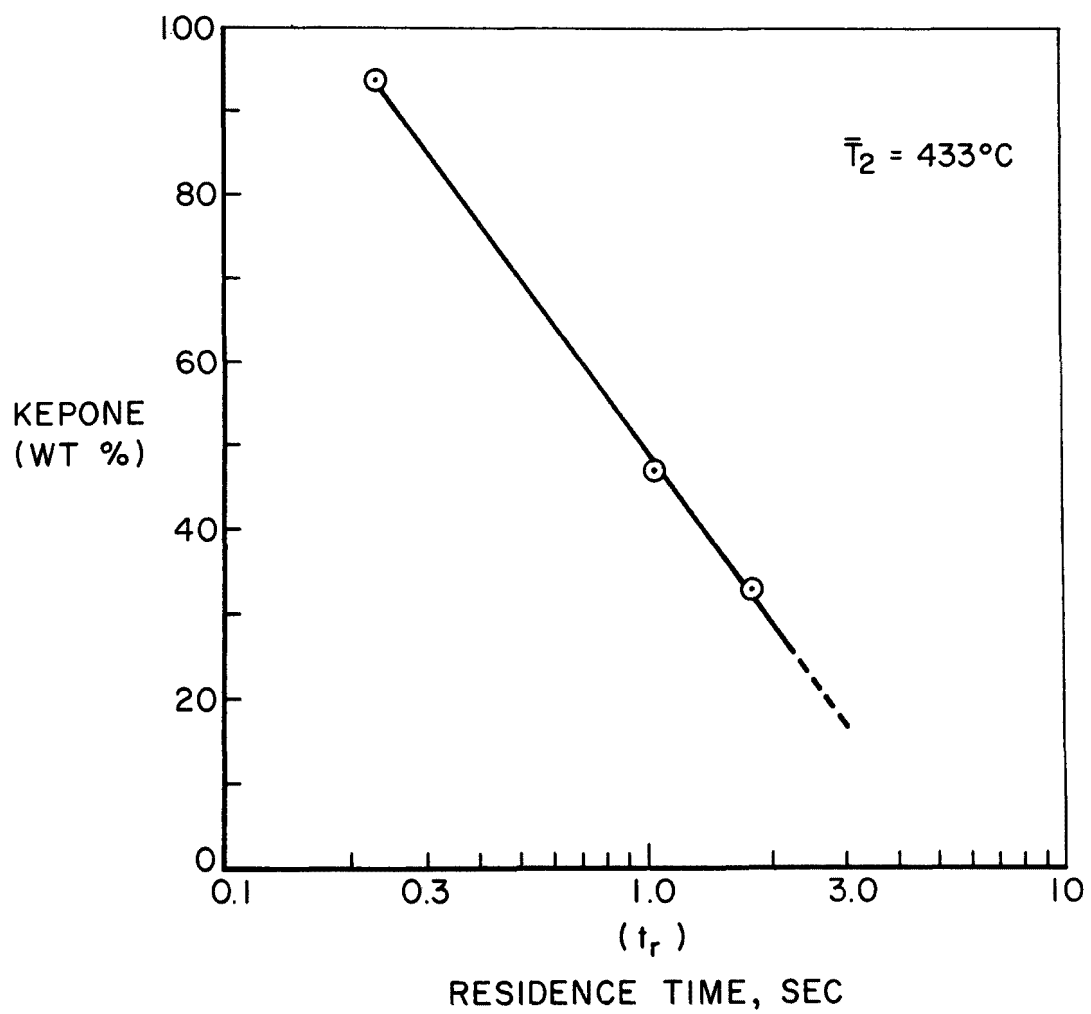Figure 23.   Chromatograms Showing Kepone Levels.

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Figure 24.   Effect of Residence Time on Thermal Destruction of Kepone.

Destruction of Kepone

From the presented experimental data, it is observed that Kepone can be vaporized in flowing air at temperatures ranging from approximately 200° to 300°C. It is also observed from the series of chromatograms in Figure 17, that this temperature range is not destructive to the Kepone molecule. However, when Kepone is subjected to temperatures above 350°C, decomposition does occur as is evidenced by the rapid drop in the Kepone concentration shown in Figure 18. Eaton et al [23] have suggested that this lower thermal stability of Kepone relative to the chemically similar Mirex is due to the presence of Kepone's carbonyl group. Also, from the series of chromatograms shown in Figure 17, it is seen that the thermal degradation of Kepone at exposure temperatures less than 600°C is markedly different from that which occurs when Kepone vapor is instantaneously subjected to a temperature greater than 600°C. For example, peak K_a, which was identified as hexachlorocyclopentadiene, was formed at temperatures below 500°C; however, it was not found above 600°C. Conversely, K_c, which was determined to be hexachlorobenzene, was observed only in the products of tests conducted above 600°C.

From the experimental data presented in Figure 24, the effect of residence time on the destruction of Kepone vapor is indeed a strong factor, at least in the 433°C region. Further work is required to determine the effect of Kepone residence time at other exposure temperatures.

When Kepone vapor (in an excess of flowing air) is subjected to a 900°C environment for approximately one second, it is observed that essentially only hexachlorobenzene is found in the effluent. And, at this temperature, hexachlorobenzene is only present in trace levels as indicated in Table II. From results to date, it would appear that this molecule has considerable thermal stability. However, the residence time of hexachlorobenzene at

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900°C has <u>not</u> been established in this study, as one does not know at what point in the Kepone travel through the quartz tube that hexachlorobenzene was formed. To determine the high-temperature destruction properties of hexachlorobenzene, samples of the pure material would have to be deposited at the inlet of the quartz tube and evaluated in the same manner as were the three pesticides.

Destruction of Mirex

The thermal destruction of Mirex has been studied by numerous investigators [24-32]. Thus, a considerable body of information already exists on the thermal behavior of this compound.

From the information obtained in the experimental work, it was found that Mirex could be vaporized into a flowing air stream at temperatures as low as 230°C. From the data presented in Figure 19, it is observed that Mirex decomposes in the 600° to 700°C region. It is also observed from this same figure, that the decomposition product M_c follows approximately the same contour as K_c in the Kepone examination. In fact, both of these decomposition products have been identified as being the same compound, hexachlorobenzene. Further study of the evolved products revealed that another compound was common to the decomposition products of Kepone and Mirex, and is designated as chromatographic peaks K_a and M_b. This component, hexachlorocyclopentadiene, was discussed earlier with regards to Kepone where it was found only in the tests conducted below 500°C. In the Mirex work, however, it was observed only in the 600°C testing.

The destruction of Mirex at 900°C is similar to that of Kepone. However, the degree of destruction for Mirex is just slightly less than that found for Kepone.

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Destruction of DDT

DDT has probably been subjected to more thermal decomposition testing than any other pesticide. Also, the behavior of DDT in the environment has been subjected to numerous studies.

In this experimental work with DDT, it was found that p, p'-DDT starts to thermally decompose at much lower temperatures than Kepone or Mirex (see Figures 20 and 21). The data presented in Figure 20 shows the conversion of the DDT molecules to their respective DDE products. This thermal conversion seemingly follows the same degradation path as the metabolic conversion which occurs over a long period of time in soil and water. From the data presented in Figure 20, it would appear that this is a quantitative conversion from p, p'-DDT to p, p'-DDE and o, p'-DDT to o, p'-DDE. Also, the thermal testing of DDT at 900°C (see Table II) indicated a complete destruction of DDT and DDE compounds.

It is interesting to note that apparently DDE is much more thermally stable than DDT. It has also been reported [33] that DDE is considerably more toxic to phytoplankton than DDT. Thus, for adequate thermal disposal of DDT, one must be certain that there is both sufficient temperature and residence time necessary to destroy not only the parent molecules, but also their toxic decomposition products.

Appendix I.
Error Analysis of Mean Residence Time Distribution.

Earlier, equation (V. 6) described the mean residence time of a substance as it passed through a high-temperature quartz tube. This residence time equation,

$$t_r = \left(\frac{\pi r^2 L}{F_o}\right)\left(\frac{T_o}{\overline{T}_2}\right)\left(1 + \frac{p_d}{p_o}\right) , \qquad (A.I.1)$$

contains many variables, some of which have a pronounced effect on t_r and are difficult to measure.

Upon investigation, it is found that fused quartz has a very small coefficient of expansion (approximately 0.59×10^{-6}). Therefore, for a given tube, the radius r and the length L can be assumed temperature invariant. Thus, the effective volume of a specific quartz tube, i.e.,

$$V_t = \pi r^2 L , \qquad (A.I.2)$$

remains essentially constant.

Further, the laboratory temperature T_o and pressure p_o can be easily and accurately measured. However, the outlet ambient flow rate F_o, the average oven temperature $\overline{T}_2$, and the system differential pressure p_d require special measurement equipment.

The maximum change in t_r which can be attributed to an addition of errors in F_o, $\overline{T}_2$, and p_d can be expressed as

$$\Delta t_r = \left|\left(\frac{\partial t_r}{\partial F_o}\right)\Delta F_o\right| + \left|\left(\frac{\partial t_r}{\partial \overline{T}_2}\right)\Delta \overline{T}_2\right| + \left|\left(\frac{\partial t_r}{\partial p_d}\right)\Delta p_d\right| . \qquad (A.I.3)$$

From equations (A.I.1) and (A.I.2), we find

$$\frac{\partial t_r}{\partial F_o} = -\left(\frac{V_t T_o}{F_o^2 \bar{T}_2}\right)\left(1 + \frac{P_d}{P_o}\right) , \qquad (A.I.4)$$

$$\frac{\partial t_r}{\partial \bar{T}_2} = -\left(\frac{V_t T_o}{F_o}\right)\left(\frac{1}{\bar{T}_2}\right)^2\left(1 + \frac{P_d}{P_o}\right) , \qquad (A.I.5)$$

$$\frac{\partial t_r}{\partial P_d} = \frac{V_t T_o}{F_o \bar{T}_2 P_o} . \qquad (A.I.6)$$

Now the maximum errors typically associated with the selected measurement methods are

$$\Delta F_o = F_o \times 10^{-2} \text{ cm}^3 \text{sec}^{-1}$$

$$\Delta \bar{T}_2 = 5\,°K$$

$$\Delta P_d = 5 \times 10^{-3} \text{ atm}$$

Next, an example case is presented where

$$t_r = 1.0 \text{ sec}$$

$$F_o = 1.235 \text{ cm}^3 \text{sec}^{-1}$$

$$T_o = 296\,°K$$

$$\bar{T}_2 = 873\,°K$$

$$P_o = 0.974 \text{ atm}$$

$$P_d = 0.2 \text{ atm}$$

$$V_t = 3.021 \text{ cm}^3$$

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By substituting into equation (A. I. 3) the data for this case and the typical measurement errors, the worst condition is found to be

$$\Delta t_r = \left| \Delta t_{r(flow)} \right| + \left| \Delta t_{r(temperature)} \right| + \left| \Delta t_{r(pressure)} \right|$$

$$\Delta t_r = 0.00999 + 0.00575 + 0.00426$$

Thus,

$$\frac{\Delta t_r}{t_r} = 0.020$$

or, the maximum relative error in t_r is 2.0%.

With this instrumentation, the flow measurement possesses about twice the effective error in t_r as the temperature or pressure measurement. Also, upon further examination, it is observed that $\Delta t_r / t_r$ is essentially unaffected by the broad temperature range and the various residence times.

Consequently, this error analysis shows that the individual measurement errors encountered in determining t_r are small and in the same domain.

Appendix II.
Pesticide Residence Time Distribution.

The longitudinal dispersion of a gas as it passes through an open cylindrical tube has been thoroughly studied [34, 35]. Consequently, in the absence of a retentive or interactive wall surface, the variation in transport of like molecules can be expressed by

$$H \equiv \frac{d(\sigma_x)^2}{dx} = \frac{2D_g}{\bar{v}} + \frac{\bar{v}r^2}{24D_g} \ ,$$

(A. II. 1)

where H is the height equivalent to a theoretical plate (as commonly utilized in chromatography), σ_x is the distribution standard deviation in distance units, x is distance, D_g is the intermolecular diffusion coefficient, $\bar{v}$ is the average linear velocity of the gas, and r is the radius of the open cylindrical tube.

From equation (A. II. 1) we can write

$$(\sigma_x)^2 = \int_o^{x=L} \left(\frac{2D_g}{\bar{v}} \right) dx + \int_o^{x=L} \left(\frac{\bar{v}r^2}{24D_g} \right) dx \ ,$$

(A. II. 2)

and, at distance x = L

$$(\sigma_x)^2 = \frac{2D_g L}{\bar{v}} + \frac{\bar{v}r^2 L}{24D_g} \ .$$

(A. II. 3)

Now, for like pesticide molecules that are randomly entering and passing through a narrow bore tube, the variation in residence time can be represented by a Gaussian distribution with a time-based independent variable. Thus, it is necessary to convert σ_x to a time-based sigma value. This is readily accomplished as

$$(\sigma_x)^2 = (\sigma_t)^2 (\bar{v})^2 \ .$$

(A. II. 4)

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Equation (A. II. 3) can now be rewritten as

$$(\sigma_t)^2 = \frac{2D_g L}{(\bar{v})^3} + \frac{r^2 L}{24\bar{v}D_g} \ ,$$

(A. II. 5)

or

$$\sigma_t = \sqrt{\frac{2D_g L}{(\bar{v})^3} + \frac{r^2 L}{24\bar{v}D_g}} \ .$$

(A. II. 6)

The intermolecular diffusion coefficient has been equated by Reid and Sherwood [36] as

$$D_g = D_{1,2} = \left(\frac{b}{Pd^2}\right) T^{\frac{3}{2}} \sqrt{\frac{M_1 + M_2}{M_1 M_2}} \ ,$$

(A. II. 7)

where P is pressure, T is temperature, d is distance between the molecular centroids, M_1 and M_2 are the respective molecular weights, and b is a constant.

Due to the absence of high-temperature diffusion data for pesticides in air, it was necessary to select a model compound for which D_g data did exist. Calculated D_g data could then be obtained with the use of equation (A. II. 7) for the entire range of pesticides.

The selected model compound was naphthalene. This substance is low enough in molecular weight that D_g data are available, e. g., D_g for naphthalene in air = 0.0611 $cm^2 sec^{-1}$ at 298°K and 1.0 atm [36], and it is a common household pesticide. Also, naphthalene is structurally similar to other fused-ring pesticide compounds, e. g., aldrin, carbaryl, dichlone, dieldrin, endrin, and the halowaxes.

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Next, from the diffusion expression, i.e., equation (A.II.7), it is observed that

$$\frac{\partial D_g}{\partial T} = \frac{3b}{2Pd^2} \sqrt{\frac{T(M_1+M_2)}{M_1 M_2}} \quad . \qquad \text{(A.II.8)}$$

Therefore, even with fixed values of P, r, L, and residence time, σ_t will continue to vary with temperature and M_2 (the molecular weight of the pesticide).

To clarify this situation, residence time distribution data, as represented by σ_t, have been calculated and plotted for the specific case where pesticide molecules experience a 1.0 sec residence time while passing through a tube 84 cm in length by 0.8 mm inside diameter with an internal pressure of 1.2 atmospheres. These calculated σ_t data which are presented in Figure 25a encompass the temperature range of 298°K to 900°K, and the molecular weight range of 128 (naphthalene) to 546 (mirex).

Another graph was prepared, again from calculated data, where σ_t was plotted versus residence time for naphthalene at 700°K and 1.2 atmospheres. This information is presented in Figure 25b.

From information contained in Figures 25a and 25b, a number of conclusions can be drawn. First, from Figure 25a, it is observed that molecular scatter, or variation in residence time, is small. As an example, it is seen that at 700°K the residence time for 95% of the naphthalene molecules would fall within $1.0 \pm 2\,\sigma_t$ seconds, that is, between 0.96 and 1.04 seconds. Secondly, it is observed from this same figure that the molecular weight of the vaporized pesticide has only a small effect on σ_t. This is evidenced by narrowness of molecular weight band. Thirdly, it is observed that molecular scatter is strongly dependent upon temperature. In fact, although the
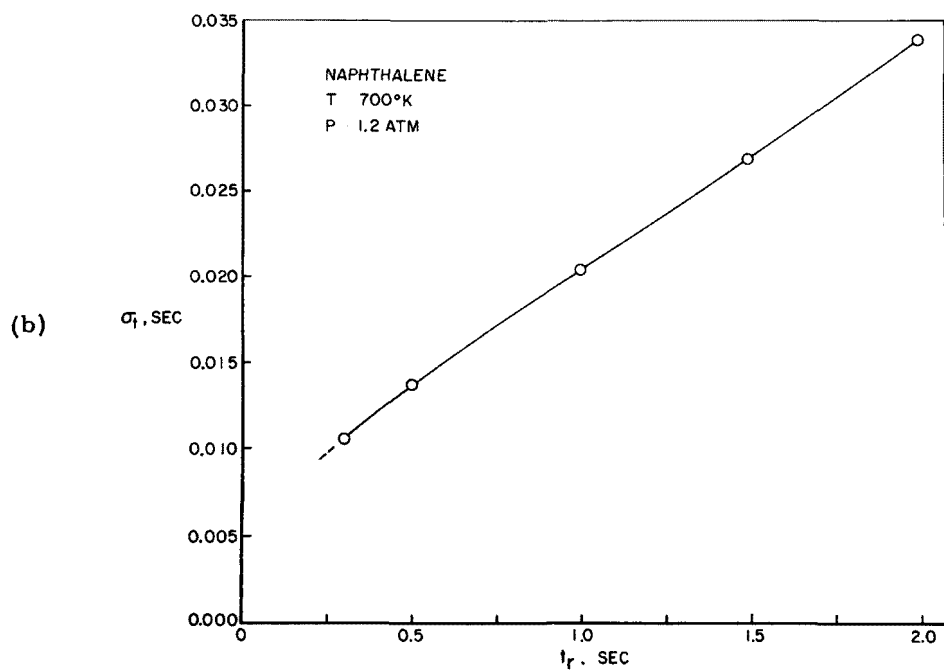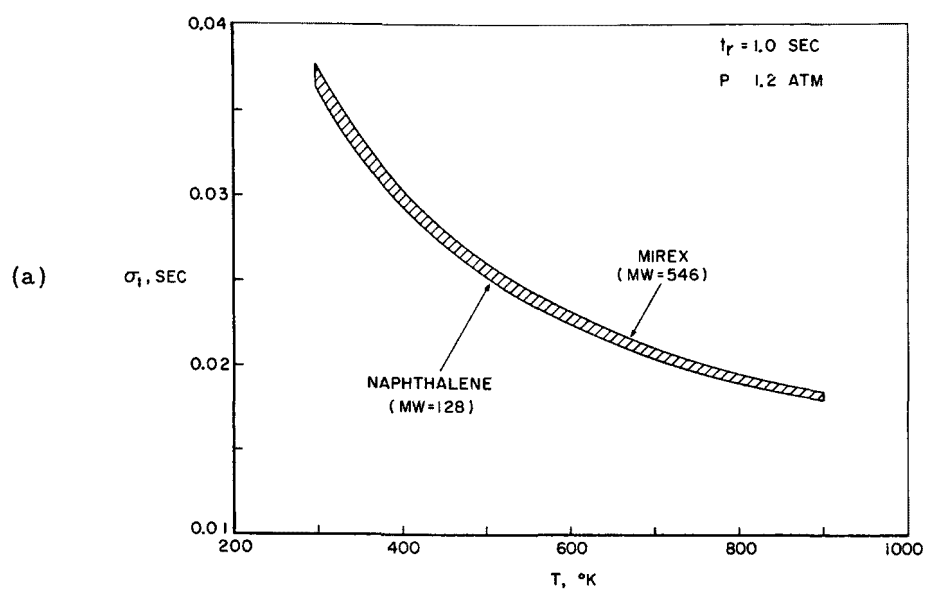
(a)

(b)

Figure 25. Residence Time Distribution Data.
    (a) Effect of Temperature and Molecular Weight
    (b) Effect of Residence Time

intermolecular diffusion coefficient increases with temperature, the pesti-
cide residence time distribution, as represented by σ_t, decreases with
temperature.

Figure 25b shows the variation of σ_t with t_r for naphthalene. Upon further
investigation it is determined that the term $4\sigma_t/t_r$ varies only by a factor of
two over the residence time range of 0.3 to 2.0 seconds. Thus, the relative
change in σ_t with t_r is tolerable.

Lastly, it is important to note that σ_t is strongly dependent upon the tube
radius r. It is seen from equation (A. II. 6) that as r increases, the residence
time distribution broadens. Thus, for a small variation in pesticide trans-
port time, a quartz tube with a narrow bore is required.

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-76-299	2.	3. RECIPIENT'S ACCESSION▸NO.	
4. TITLE AND SUBTITLE LABORATORY EVALUATION OF HIGH-TEMPERATURE DESTRUCTION OF KEPONE AND RELATED PESTICIDES		5. REPORT DATE December 1976 issuing date	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) D. S. Duvall W. A. Rubey		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Dayton Research Institute 300 College Park Avenue Dayton, Ohio 45469		10. PROGRAM ELEMENT NO. 1DC618 SOS# 6, Task 03	
		11. CONTRACT/GRANT NO. R-803540-01-0	
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory - Cin., OH Office of Research and Development U. S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED	
		14. SPONSORING AGENCY CODE EPA/600/14	

15. SUPPLEMENTARY NOTES

Richard A. Carnes (Project Officer) 513/684-7871

16. ABSTRACT

Thermal destruction testing was conducted with three pesticides: Kepone, Mirex, and DDT. A specialized laboratory technique incorporating a two-stage quartz system was developed. It is important to note that in this system the pesticide was first converted to the gas phase, then exposed to the high-temperature destruction conditions. Critical parameters of temperature and residence time were accurately measured. Both the Kepone and DDT molecules, at a residence time of ∿1 second, were essentially destroyed at 500°C; however, Mirex, at the same residence time, required 700°C for destruction.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Pesticides Research Detoxification Temperature Degradation Recombination Reactions	Retention Time Excess Air	13B

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 70
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

☆USGPO: 1977 — 757-056/5480 Region 5-11