

PYROLYSIS-GAS CHROMATOGRAPHY BY DIRECT
INJECTION OF SOLUTIONS

by
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To my wife Virginia, whose help made
this possible, and my children Patricia,
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I. INTRODUCTION

Gas chromatography is widely used as an analytical tool for the quantitative estimation and qualitative identification of a wide range of organic and inorganic mixtures. While the separating power and the sensitivity of detection of gas chromatography make it an extremely useful technique it is limited to use with compounds which have vapor pressures of at least a few millimeters of mercury at approximately 400°C. Another limitation of this technique is that extensive calibration may be necessary when qualitative identifications are attempted. This limitation exists because under any given conditions it is possible for more than one compound to have the identical retention volume on a certain column.

Direct combinations of various techniques with gas chromatography have been used to extend its usefulness to nonvolatile and thermally unstable compounds as well as to provide additional information, as to the structure of the compounds, which is useful in making qualitative identifications.

Pyrolysis of nonvolatile or thermally unstable compounds can produce volatile products, which may be

used as a quantitative measure of the amount originally present as well as to provide pertinent information as to the structure of the original substance. The chromatogram of the pyrolysis products, which will be referred to as a pyrogram, can also be used for qualitative identification in the same manner as a mass spectra. Many compounds which are difficult to identify qualitatively using gas chromatography would produce very different pyrograms, thus eliminating much of the calibration now necessary.

Other techniques used to obtain species more easily chromatographed are catalytic conversions and chemical reactions just prior to injection into a gas chromatograph. Catalytic conversion has been used to provide the parent hydrocarbon by reducing all multiple bonds and other functional groups. These parent hydrocarbons are often easier to identify using standards. The esterification of acids to give their more volatile esters has also been used to extend the usefulness of gas chromatography.

Thus the effectiveness of gas chromatography could be greatly enhanced if new approaches were available to provide, in a simple and quantitative manner, species amenable to gas chromatography from substances otherwise difficult to analyze. Gas chromatography could be used to provide a

wealth of information as to the original structure of these compounds if the proper combination of techniques can be found.

This dissertation is concerned with the combined use of pyrolysis and gas chromatography both as a means of analysis and as an approach for obtaining detailed information as to the structure of certain molecules.

The direct combination of pyrolysis and gas chromatography consists of an arrangement which allows the sample to be pyrolyzed in the inert carrier gas stream with the products being carried directly onto the chromatographic column to be separated. This technique will be referred to as pyrolysis-gas chromatography (P-GC).

The experimental parameters which control the mechanism of the decomposition of molecules and the products formed in a stream of inert carrier gas have not been well characterized. A pyrolysis apparatus has been designed and constructed to study these parameters. The effects of sample size, method of sample introduction, temperature, carrier gas pressure and flow rate, as well as the effects of various carrier gases were studied.

A new approach to pyrolysis-gas chromatography by direct injection of solutions has been developed and

shown to provide a much greater insight of what is occurring in the pyrolysis of compounds in a moving carrier gas stream. This technique was compared under nearly identical conditions with the more commonly used boat technique of pyrolysis.

A method is presented for determining the alkylbenzene sulfonate (ABS) detergents directly in aqueous solution. This method differentiates between the straight and branched alkyl groups much simpler than any of the methods presently used. Studies were made of the conditions for the pyrolysis-gas chromatographic analysis of certain amino acids which show that results obtained in this manner compare favorably with the techniques now used.

The approach was extended to the determination of the number and kind of organic chelating agents bound to metal atoms. This offers a simple and direct approach for further research in this area. The stability of some common organic solvents under such pyrolysis conditions were also studied.

II. HISTORICAL

Introduction

The phenomenal growth in the use of gas chromatography, as an analytical tool, since its invention by Martin and James (1) precludes the presentation of a complete resume of the literature. A number of books are available on gas chromatography; however, the books by Purnell (2) and Dal Nogare and Juvet (3) provide an excellent coverage of the present theories and practice of gas chromatography.

The combination of pyrolysis and gas chromatography has been developed to the point of having a distinctive literature. The literature, up to 1963, relative to a combination of the two techniques, pyrolysis and gas chromatography, has been conveniently compiled. The American Instrument Company, Inc. (4) has published a bibliography of pyrolysis-gas chromatography papers which includes both an author index and a subject index up to 1962. McKenney (5) published a bibliography covering 1960-1963, which is indexed for apparatus and technique, review articles, and various classes of compounds. Another convenient source of references is the section

on pyrolysis-gas chromatography in Signeur's, "Guide to Gas Chromatography Literature" (6).

There are two basically different ways of combining the two techniques of pyrolysis and gas chromatography. Gas chromatography is often used to analyze the products obtained from a conventional pyrolysis carried out in a static system. In this case the volatile products of the pyrolysis are trapped and then a sample of the mixture subjected to a normal chromatographic analysis. This sort of combination of pyrolysis with gas chromatography is referred to as the indirect combination of the techniques. In the direct combination of pyrolysis with gas chromatography the degradation takes place in a moving carrier gas stream and the fragments are carried directly onto the chromatographic column. This technique shall be referred to as pyrolysis-gas chromatography.

Perry (7) has reviewed the literature of the direct combination of pyrolysis with gas chromatography separately from the indirect method. The literature of these two approaches will be discussed separately.

Pyrolysis Used Indirectly with Gas
Chromatography

The earliest work of the application of pyrolysis in indirect combination with gas chromatography was done by Davidson, et al. (8) in 1954. They pyrolyzed certain natural and synthetic rubbers, and collected the pyrolysate in a cold trap and then subjected the pyrolysate to gas chromatographic analysis. The results of this study were characteristic "fingerprint" chromatograms by which the parent polymers could be identified. From a qualitative viewpoint the use of gas chromatography in the identification of nonvolatile materials was established; however, from a quantitative standpoint, this system left much to be desired. Pyrolysis in a static system caused a complex mixture to be formed due to the many secondary reactions which occurred. Use of a flow system for pyrolysis simplified the products but left many sampling problems.

Pyrolysis Used Directly with Gas

Chromatography

Original approach

Radell and Strutz (9) took the next logical step and connected the pyrolysis unit directly to the chromatograph. This accomplished several significant improvements: (1) small samples could be used without concern about collection efficiencies, and (2) the pyrolysis could take place in a moving stream of carrier gas thus providing a simpler mixture of products.

The apparatus used by Radell and Strutz consisted of a by-pass inlet system, similar to a conventional gas sampling device, with an indirectly heated metal sample loop. The solid sample was placed in the sample loop and attached to the inlet system of the chromatograph. The carrier gas was then diverted through the sample loop and the loop brought to the desired temperature by means of a small electric furnace in which the loop was encased. As the temperature was increased the pyrolysis occurred allowing the product to be swept onto the chromatographic column.

Although representing a breakthrough in the direct application of pyrolysis with gas chromatography, this

system had several serious limitations. The time required to reach the pyrolysis temperature was too long, causing a complex decomposition due to different fragments being formed at various temperatures. Such an apparatus was limited also, to substances of very low volatility due again to the long heating times.

Following the work of Radell and Strutz, pyrolysis apparatus has developed in two basic directions. In the first, a metal filament, which is heated directly by electric current is used, and in the second case a reaction chamber, heated indirectly by an electric furnace is employed.

Pyrolysis-gas chromatography with a filament

Janak (10) pioneered the work done with metal filaments. The technique he used was to dissolve the samples in a volatile solvent, coat a platinum spiral with the solution, and evaporate the solvent. The spiral was then placed in the carrier gas stream and current applied to reach the desired temperature. This approach gave a simpler pyrogram, in that the probability of secondary reactions was greatly decreased by the more rapid removal of the initial pyrolysis products from the bulk of the sample. However, the effects of sample size,

heating time, and filament history were found to be the controlling factors in obtaining reproducible data.

Janak (11) studied the decomposition products of some barbituates, protein derivatives, and other materials which were not sufficiently volatile for direct analysis by gas chromatography.

The limitations of this approach still remained in:

- (1) irreproducibility of sample size and the increase in secondary reaction due to the thickness of the coating,
- (2) lack of quantitative measurement of the initial sample or the amount or characteristics of the residue left on the wire,
- (3) the catalytic effect the glowing wire may have on the nature of the decomposition products by secondary reactions, and
- (4) that a mixture in solution cannot be sampled accurately using the coating technique, due to preferential adsorption of certain compounds in the mixture.

Lehmann and Bauer (12) applied the filament technique to the analysis of polymers. Using samples of poly(methylmethacrylate) and polystyrene they found that "fingerprint" pyrograms could be obtained but that the irreproducibility of the sample size made quantitative measurement questionable at best.

Jennings and Dimick (13) and others (14,15,16) found that the filament coating technique was useful for obtaining "fingerprint" pyrograms of a number of materials especially polymers.

A second mode of operation was chosen by Nelson and Kirk (17) in attempting to better reproduce their sample size. They placed the sample in a platinum cup, into which the sample could be weighed and this was heated as a flash filament.

Pyrolysis-gas chromatography with a filament and boat

Using a similar approach Ettre and Varadi (18) employed a micro coil into which they placed a small quartz combustion boat containing a weighed amount of sample. This approach eliminates many of the problems (unknown sample size, catalytic effect) associated with the filament technique but introduces a new problem. The time required to reach the desired pyrolysis temperature is extremely long. The boat, being of considerably greater mass than the filament, slows the heating rate of the pyrolysis and reaches the final temperature only after a finite period of time depending on its composition and size. The total time for the sample to reach the

expected pyrolysis temperature varies between 20 and 40 seconds. This means that the sample itself passes through a wide range of temperature before the final pyrolysis temperature is reached. Therefore, the composition of the products represents the pyrolysis up to a certain temperature rather than at a certain temperature. The pyrogram obtained under these conditions generally is more complex and often provides misleading information, as to the original structure of the molecules. This is due to the products of the low temperature pyrolysis reacting with the bulk of the sample during the course of heating.

Contributing to the complexity of the pyrograms from this method is the fact that most filament pyrolysis units do not allow high carrier gas flow rates thus allowing the primary products to remain too long in contact with the heated parts of the pyrolysis zone, causing further decomposition which provides a more complex pyrogram.

The exact measurement of the pyrolysis temperature is a problem common to all filament pyrolysis units. In many cases the temperature is only estimated by visually observing the color of the glowing wire.

Although careful control of the parameters mentioned has produced certain reproducible data the results may be

misleading due to the possible catalytic effects of the filament and the temperature range through which pyrolysis occurs.

Pyrolysis-gas chromatography with a furnace

Various designs have been employed using a relatively high mass pyrolysis furnace for heating the sample. Hewitt and Whitman (19) used a pyrolysis tube packed with glass wool and diatomeaceous earth, placed in an electric furnace, to study decomposition of polymers. The solid samples were introduced into the heated chamber by means of a glass capillary.

Smith, et al. (20) used a similarly packed pyrolysis tube for the study of the decompositions of some arylethylcarbonates.

Legate and Burnham (21) identified the alkyl groups in metal dialkyl dithiophosphates using a stainless steel pyrolysis tube packed with glass wool and heated by an electric furnace. The sample was introduced as a liquid, by a microsyringe.

Ettre and Varadi (22) reported a pyrolysis device which consisted of a furnace with a quartz pyrolysis tube. The samples are placed in microboats which are then magnetically propelled into the heated area. This

approach offered a means of more instantaneous heating, better temperature control, and a way to determine more easily the amount of residue remaining. However, the pyrograms obtained still showed a dependence on pyrolysis temperature and carrier gas flow rate.

Hudy (23) designed a system similar to that of Ettre and Varadi (22) and studied the decomposition of polyethylene and polypropylene. He also used the system at lower temperatures ca. 350° as a "solvent stripper" when analyzing solid samples.

Luce, et al. (24) described a stainless steel system with an Inconel pyrolysis tube which was directly heated by passing currents of the order of 100 amperes. The samples were placed in microboats and positioned in the heated zone by a plunger. Their results with various polymers were comparable to those of Ettre and Varadi (22).

Keulemans and Perry (25) have shown that the pyrolysis fragments of a wide range of hydrocarbons are simply related to the parent molecule and can be used in a manner similar to mass spectroscopy to ascertain structures of hydrocarbons. This work was done using an indirectly heated stainless steel tube, which was

coiled through a ceramic block. The sample is injected by hypodermic syringe in the conventional manner.

Dhont (26) used a similar system to obtain correlations for the pyrolysis products of aliphatic alcohols.

Pyrolysis-gas chromatography is to be used for the investigation of organic material on the surface of the moon. A drilling device will deliver crushed rock samples to a pyrolysis furnace and the possible organic products will be analyzed on a three-column analytical chromatograph. Certain amino acids have been determined using this system (27).

In summary, the furnace or reactor type pyrolysis units have the following advantages: (1) the heat-up time is almost instantaneous, (2) the temperature can be held constant and measured simply and accurately with thermocouples, (3) residence time in the heated zone can be estimated and varied by varying the flow rate as well as the length of the heated zone, and (4) samples can be handled either as a liquid or as a solid.

The limitations still existing are those of sample size dependence and a pyrolysis temperature dependence. These two effects are caused by the problem of secondary reactions occurring when the entire sample is not brought

to temperature instantaneously. The larger the sample size the greater the probability of reaction. Also, the larger sample requires more heat for fast pyrolysis and, therefore, the higher the temperature must be.

Present Methods of Detergent Analysis

A definite need exists for a technique which will differentiate between the various alkyl groups found in commercial alkylbenzene sulfonate products. The biodegradability of these molecules has been shown to depend on the degree of branching in the alkyl groups.

Spectroscopic measurements have long been used as the standard means of analyzing synthetic detergents. These methods are given in "Standard Methods for the Examination of Water and Wastewater" (28). Smith (29) and McGuire, et al. (30) serve as good beginning references to the vast number of papers on this particular problem.

The monograph by Longman and Hilton (31) gives exact procedures for the analysis of all types of nonsoap detergents.

The methods based on the U.V. spectra of the alkylbenzene-sulfonates are based on the absorption of the benzene chromophore and cannot distinguish between the

many alkyl groups attached to the benzene ring in commercial detergents. The I.R. methods require an extreme amount of interpretation of spectra to determine the structure of the alkyl groups and are also used only to determine the total amount of benzene sulfonate present. Both approaches require an extraction step from water into a suitable organic solvent.

III. EXPERIMENTAL

Development of Pyrolysis Unit

The pyrolysis-gas chromatographic apparatus developed and used in this study is shown schematically in Figure 1.

Furnace

A microcombustion furnace model 5676A, Arthur H. Thomas Company, Philadelphia, Pennsylvania, was used to heat the pyrolysis tube and is shown in Figure 2. This furnace was chosen because it provided a large hot mass, relative to the sample, causing the material to be pyrolyzed in approximately 0.5 second to the desired temperature.

The electric current to the furnace was regulated by means of a variable transformer or by a Tempcometer Input Controller, Thermo Electric Manufacturing Company, Dubuque, Iowa. Satisfactory results were obtained using either system of controlling the current.

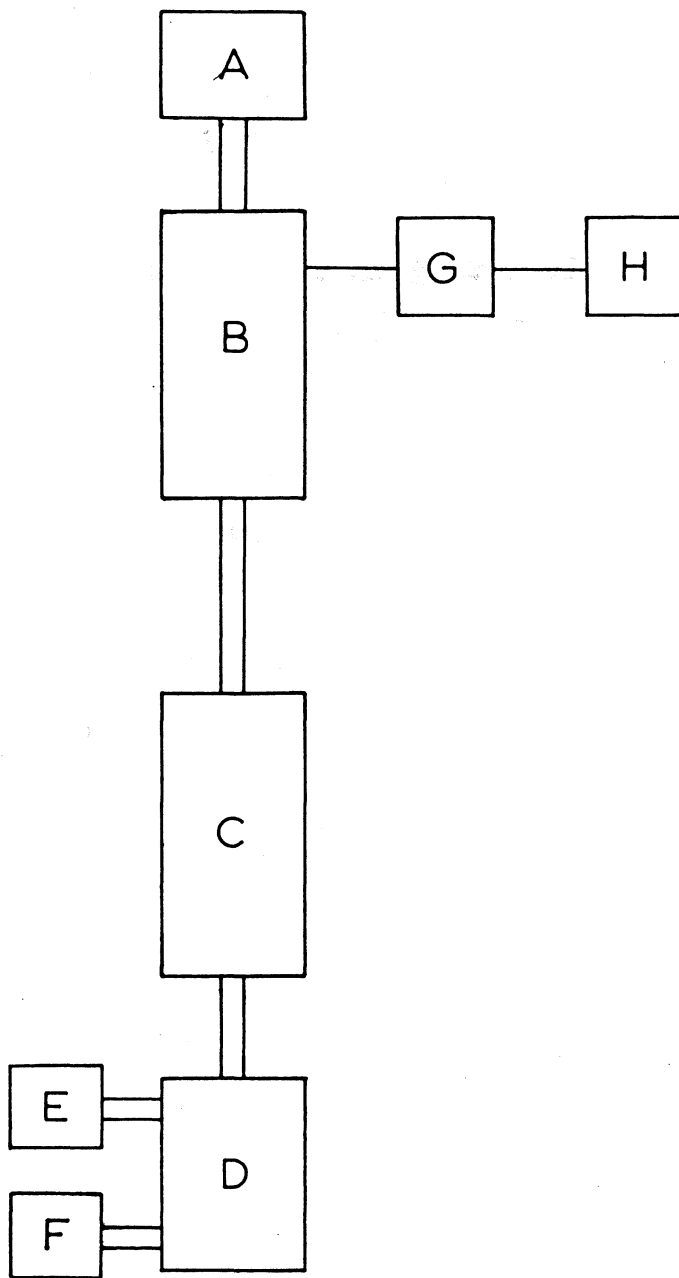
Temperature

Temperature measurements were made using Chromel-Alumel thermocouples, 36 gauge, obtained from Omega Engineering, Inc., Springdale, Connecticut, and a Leeds

Explanation of Figure 1

Block diagram of P-GC apparatus

- A. Carrier gas supply
- B. Pyrolysis furnace
- C. Chromatographic column
- D. Detector
- E. Hydrogen supply
- F. Oxygen supply
- G. Transformer
- H. 115 V a.c. line

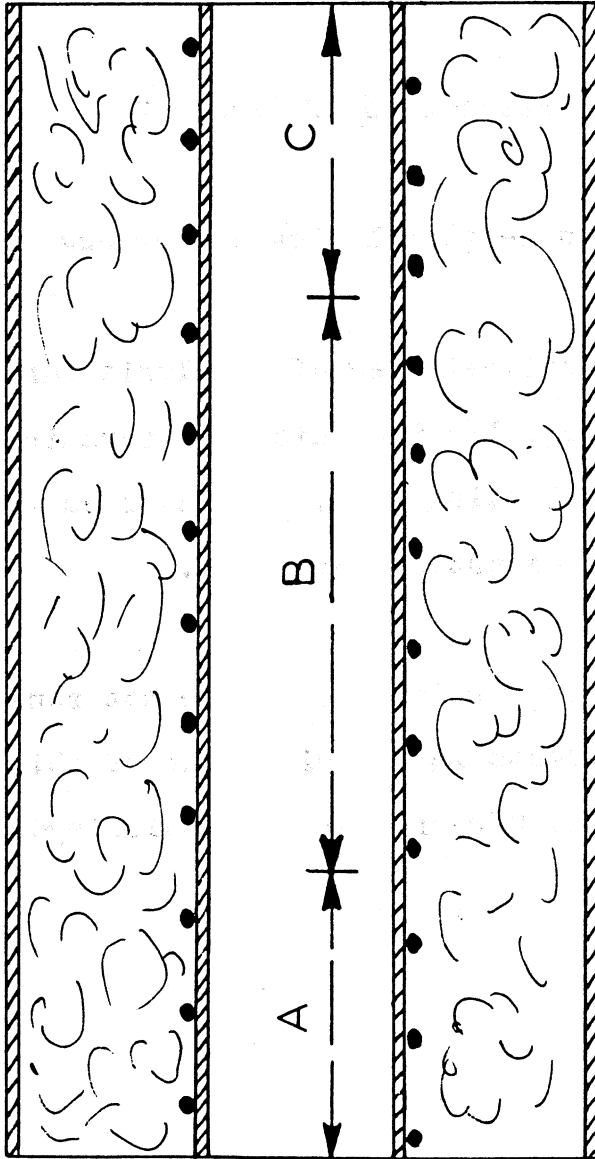


Explanation of Figure 2

Cross sectional view of furnace

Cross sectional view of pyrolysis furnace showing the 4 inch long, 1/2 inch diameter ceramic tube wound with nichrome heating wire. The hatched areas represent the asbestos insulation.

The center portion, B, is the hot zone and the thermocouple rests in the mid-point of this 2 inch section. A and C represent the cooler ends of the furnace.



and Northrup model II Potentiometer. An ice bath was used as reference and the temperature was taken from a calibration table furnished by Omega Engineering, Inc. The temperatures were measured to the nearest degree.

The thermocouple was placed in the center of the furnace so that the bead was in an indentation in the pyrolysis tube and gave direct and accurate pyrolysis temperatures.

Pyrolysis Tubes

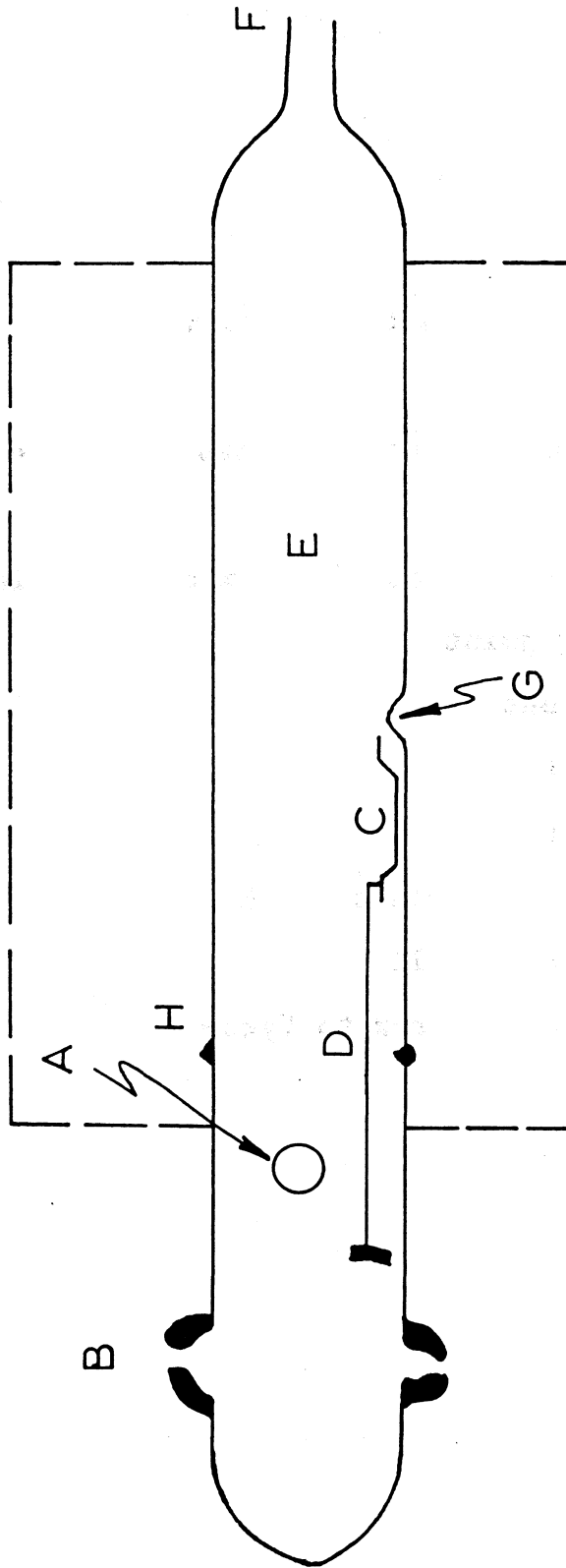
The design of the pyrolysis tubes was dictated by a desire to be able to compare the pyrolysis carried out in a small sample boat, to the pyrolysis occurring upon direct injection of a solution of the sample under the same conditions.

The temperatures used in these studies required that the hot zone, i.e., the portion of the tube within the furnace, be made of quartz or Vycor glass. The original tubes used a graded seal of Vycor to Pyrex, as shown in Figure 3, so that modifications would more easily be made on the inlet system by working with the Pyrex. Figure 3 shows a cross-sectional view of a pyrolysis tube used for studying the "boat" technique. The system is opened at the "o"-ring joint and the boat containing the sample is

Explanation of Figure 3

Pyrolysis tube for boat technique

- A. Carrier gas inlet, 2 in. x 6 mm. tubing
- B. "O" ring joint
- C. Sample boat
- D. Metal push rod
- E. Pyrolysis tube
- F. Connects to chromatograph
- G. Thermocouple well
- H. Graded seal--Pyrex to Vycor



placed in the cool front section of the pyrolysis tube. The push rod is then attached, the system closed, and the pressure drop across the column allowed to be re-established. When the baseline of the chromatographic recorder is stabilized the boat is propelled into the heated area by means of a magnet.

The samples were weighed and pyrolyzed in a micro platinum or ceramic boat about $5/16 \times 1/8 \times 3/16$ inch. All boats were obtained from Fisher Scientific Company, Silver Spring, Maryland.

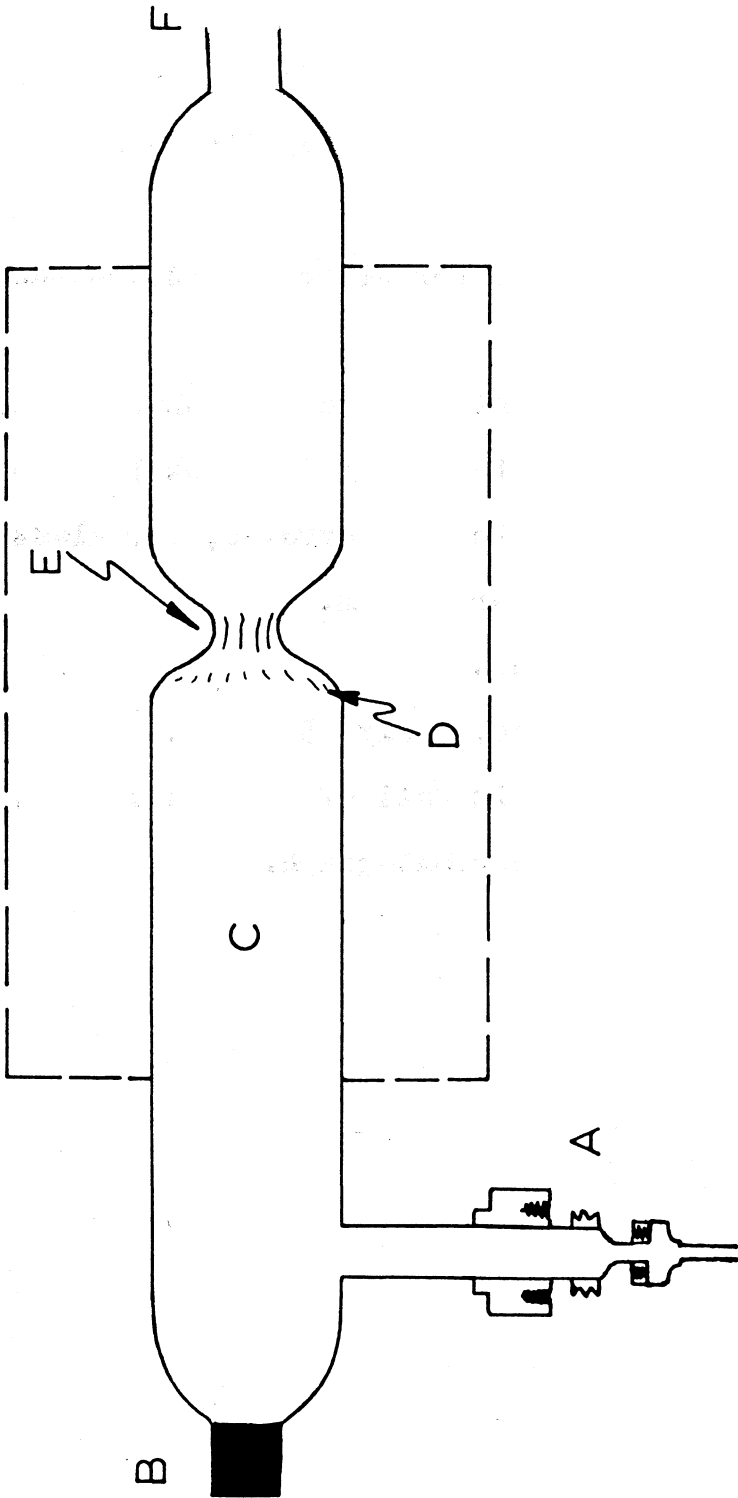
Another inlet system, in which the carrier gas was brought into the pyrolysis tube at the end of the pyrolysis tube rather than at the side, performed with equally good results; however, with this system the sample handling was found to be awkward.

A pyrolysis tube which would allow for using both sample boats and direct injection of solutions with a syringe was found to be impractical when constructed with glass, due to the length necessitated by a glass-to-metal joint. However, the tube shown in Figure 4, allows the sample to be conveniently introduced with a microsyringe under conditions similar to the boat technique and is easily interchanged with the tube used for the "boat" technique.

Explanation of Figure 4

Pyrolysis tube for direct injection technique

- A. Carrier gas inlet--2" 6 mm. tubing attached to 1/8" S.S. tubing using Swagelok 1/4" to 1/8" reducer with Teflon ferrules, for glass seal.
- B. Silicone rubber septum.
- C. Pyrolysis tube.
- D. Platinum gauze, 4 ply, 50 mesh.
- E. Indentations in wall of pyrolysis tube.
- F. Connects to chromatograph.



The silicone rubber septums used with this system are 3/8-inch thick and have a diameter of 0.16-inch. However, for ease of injection the thickness was reduced 1/8-inch by cutting the back of the septum. The septums were supplied by Applied Science, Inc., State College, Pennsylvania.

The dimensions on the external portion of the pyrolysis tube used for direct injection with a micro-syringe proved to be more critical than for the "boat" technique, in that the needle must be able to deposit the sample directly in the hot zone to insure complete pyrolysis of the sample. Attempts to construct a metal inlet system, by means of a glass-to-metal seal, so that the rubber septum could be held in place by a 1/2-inch nut, allowing higher pressures to be used, was found to require too long a needle, ca. 6 inches, for convenient injection.

With the apparatus shown in Figure 4, a 10 syringe equipped with a 3 inch needle allowed the sample to be deposited directly into the hot zone.

Initial work with injections into the pyrolysis tubes showed that a significant amount of the aerosol formed as the sample was forced from the needle was being blown

through the hot zone by the carrier gas. In order to insure sufficient conduction of heat to cause pyrolysis of the total sample, the sides of the pyrolysis tube were indented at the center of the hot zone and a piece of 50 gauge platinum wire, one square inch in area, was folded twice and placed in the center of the tube against the indentations. This arrangement provided sufficient surface area and heat conduction for reproducible pyrolysis.

All of the pyrolysis tubes were attached to the gas chromatograph by placing the tip of the tube through a silicone rubber septum, 3/8-inch in diameter, which had been punctured by a No. 1 cork borer, and held by a 1/2-inch nut furnished with the instrument.

Syringes

All syringes used in this study were supplied by Hamilton Company, Inc., Whittier, California. Syringes with capacities of 10, 50, and 100 microliters and needles 2, 3, 4, 6, and 8 inches in length were used.

Gas chromatographs

Several instruments were utilized in this study to take advantage of the unique differences in the flame ionization and the thermal conductivity detector. The flame ionization

detector was chosen in preference to the thermal conductivity, for use in the analysis of the pyrolysis products for two reasons. First, a smaller sample size could be employed with the flame detector due to its higher inherent sensitivity. The smaller samples were believed to be advantageous in pyrolysis studies, giving more rapid and uniform breakdown. Second, the fact that the flame detector does not respond to water eliminates the problem of a large solvent peak when dealing with aqueous solutions.

The thermal conductivity detector was used to determine the retention time of the water under the same conditions that the pyrolysis products were analyzed. This was done in order to ascertain the effects, if any, which the presence of the water had on the response of the organic compounds passing through the flame detector at the same time. Analysis of the carbon dioxide produced in the pyrolysis of certain amino acids was also possible with the thermal conductivity detector.

Linear programming of the column oven temperature was used and found to be beneficial for two reasons. First, the products from pyrolysis generally differ widely in volatility and isothermal separation of all the products is difficult. Second, the large dead volume of the

pyrolysis unit would, under isothermal conditions, cause a large broadening of the chromatographic peaks. The effect of the relatively cold column, which the products initially see, is to concentrate them and produce sharp, narrow peaks.

The gas chromatographs used were: (1) Aerograph model A-600C, a single column instrument with a flame ionization detector; (2) Aerograph model 204, a dual column instrument with dual flame ionization detectors and linear temperature programming (both of these instruments are made by Wilkens Instrument and Research, Inc., Walnut Creek, California); and (3) a single column instrument with a thermal conductivity detector, which was constructed in this laboratory and is shown schematically in Figure 5.

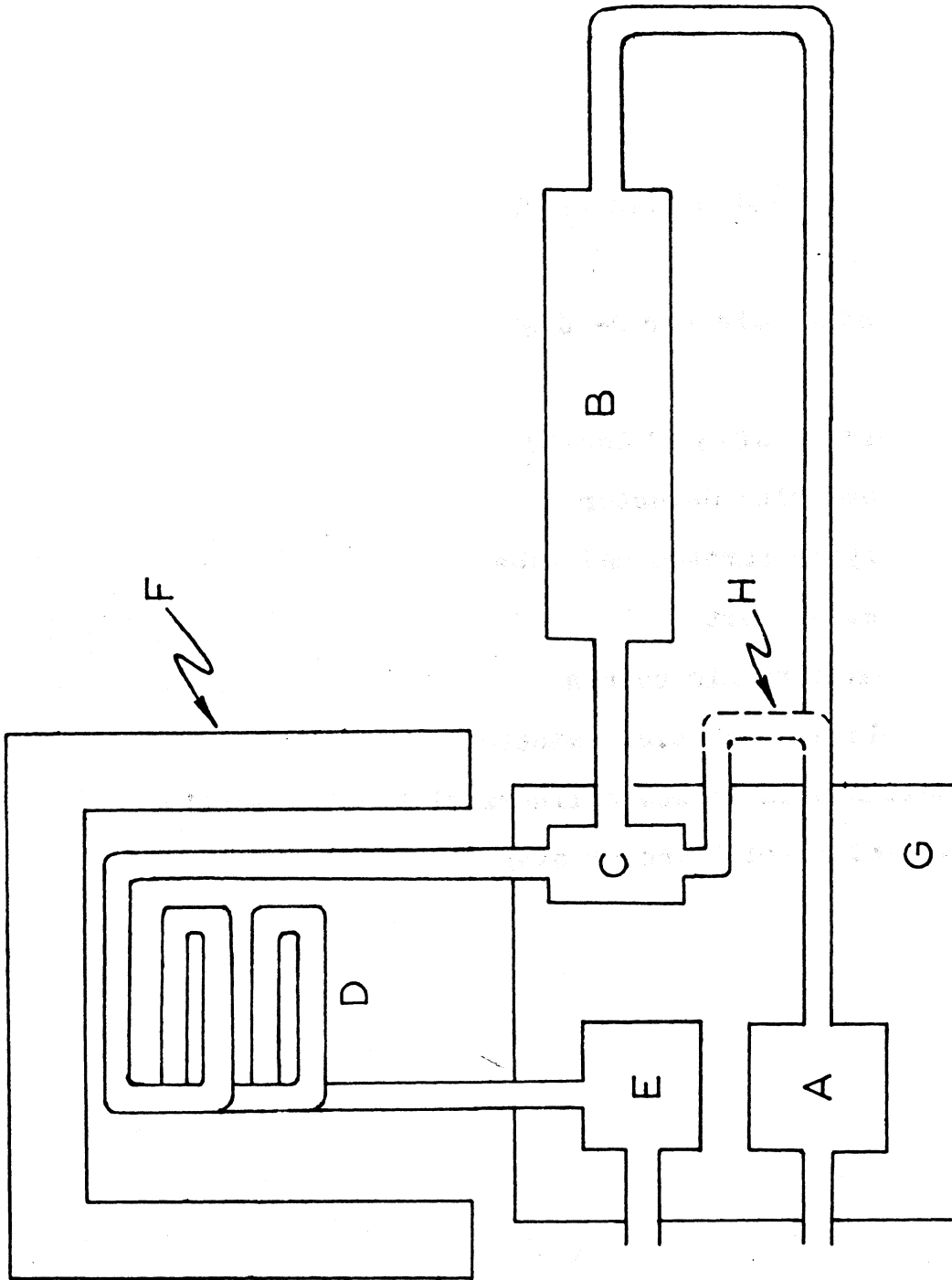
Recorders

The chromatographic measurements obtained during this study were recorded with a 1/2-second, 1-millivolt, full scale Servo-Riter recorder made by Texas Instruments, Inc., Houston, Texas, and a 1-second, 10-millivolt, full scale potentiometric recorder made by Heath Company, Benton Harbor, Michigan.

Explanation of Figure 5

Flow schematic for P-GC with T.C. detector

- A. Reference side of CowMac Model 9134II thermal conductivity detector
- B. Pyrolysis furnace and tube
- C. Injection port
- D. Chromatographic column
- E. Sample side of t.c. detector
- F. Column oven Glasco cylindrical heating mantle
- G. Detector and injector oven



Columns

The columns used with the flame ionization detectors were 1/8-inch o.d., aluminum or stainless steel coiled columns. Those used in the model 204, were coiled with a diameter of approximately 8 inches. The columns used with the model A-600C, had a coil diameter of approximately 3 inches. The columns used with the thermal conductivity detector were 1/4-inch o.d., copper tubing with a coil diameter of about 4 inches.

Two methods were used in preparing the column packings used in this work. Both methods call for making a slurry of the liquid phase and solid support in methylene chloride. The first method for removing the solvent was to evaporate it under vacuum while stirring the slurry by means of a Morton flask attached to a Roto-Vac evaporator. The slightly damp packing was then dried in an oven at about 110°C.

The second approach was to filter the slurry by gravity in a Buechner funnel, and then dry the packing in an oven at about 110°C. This approach produced the more efficiently coated support although the actual percentage of liquid phase on the solid support was found to be much less.

The reason for the difference in per cent liquid phase and the difference in efficiency apparently arises from the fact that when the solvent is evaporated, especially if it is evaporated rapidly the liquid phase is deposited in an uneven fashion on the solid support. In the case of the filtering, the liquid phase absorbed on the solid support in the slurry is a very even coating and the excess is then washed away. The actual amount of liquid phase remaining was then determined by weighing both the prepared packing and the residue remaining after evaporating the filtrate.

Carrier gases

The carrier gases, argon, helium, hydrogen, and nitrogen used in this work were obtained from the Air Reduction Company. In each case the gas pressure was regulated with a two stage pressure regulator, with the second stage set at 50 psi. The column inlet pressure was controlled by a differential flow controller and needle valve which maintained a constant flow rate when the column temperature was being programmed. The flow rate was measured with a soap bubble flowmeter with the movement of the bubble being timed with a stopwatch to within 0.2

second for approximately a 20 second period. The outlet pressure was taken as atmospheric pressure.

Chemicals

The compounds studied in this work along with certain compounds used for chromatographic identification are listed in Table I.

Commercial dodecylbenzenesulfonic acid (DDBSA) is actually a mixture of alkylbenzenesulfonic acids with alkyl groups of varying lengths. These alkyl groups, usually C_{10} , C_{11} , C_{12} , C_{13} , C_{14} , have on the average 12 carbons.

Solid phases used were diatomaceous earths Chromsorb W and Chromsorb P from Johns-Manville, Inc., New York, New York, and Gas Chrom Z, a product of Applied Science, Inc., State College, Pennsylvania. All of the above supports were silanized, i.e., the hydroxyl groups on the surface had been reacted with hexamethyldisilazane to produce a more inert substrate (32).

Substances used as liquid phases are listed in Table II, along with a pertinent description of each.

Quantitative measurements

The method used for measuring the peak areas recorded in this work was that described by Cremer and Miller (2). The area under a symmetrical curve is easily

TABLE I

Table of Chemicals

Sodium dodecylbenzene sulfonate (branched alkyl groups)	Chem-Supply, Inc. Avondale, Pennsylvania
Sodium toluene sulfonate	Same
Sodium dodecylsulfate	Same
Triethanol ammonium dodecylbenzene sulfonate	Same
Sodium dodecylbenzene sulfonate	Conoco Petrochemicals Ponca City, Oklahoma
1-nonene	Aldrich Chemical Co. Milwaukee, Wisconsin
1-decene	Same
1-undecene	Same
1-dodecene	Same
1-tridecene	Same
Primary amines	PolyScience Corporation Evanston, Illinois
Metal acetylacetonates	Mackenzie Chemical Co. New York, New York
Benzene	Reagent grade
Toluene	Same
Ethylbenzene	Same
Propylbenzene	Same

TABLE II

Table of Liquid Phases

Liquid Phase	Description
Apiezon L	Long chain unsaturated hydrocarbon Aver. M. W. 405 Temp. limit 300°C
Carbowax 20M	Polyethylene glycol polymer Aver. M. W. 20,000 Temp. limit 250°C
Ditridecylphthalate	Ester M. W. 350 Temp. limit 200°C
Armeen SO	Mixture of long chain primary amines Mean M. W. 264 Temp. limit 100°C
THEED	Tetrahydroxyethylene-diamine M. W. 280 Temp. limit 125°C

described by the equation: Area = height x width at half height. The weight per cent composition of the products was determined by normalization of the areas (A) of all of the n products seen. The per cent of a given substance i is then given by the equation,

$$\% i = [A_i / (A_i + \dots + A_n)] \times 100 .$$

The response of the hydrogen flame ionization detector is proportional to the carbon content of each sample as shown by Omkiehong (2). The observed response (peak area) was therefore corrected for the differences in carbon content by using the C-factor originated by Omkiehong, where:

$$\text{C-factor} = \frac{\text{molecular weight}}{\text{number of carbon atoms} \times 12} .$$

Multiplication of the observed peak area by the corresponding C-factor and normalization of the corrected peak areas gives a fairly good relation between peak area and weight per cent composition.

IV. RESULTS AND DISCUSSION

Pyrolysis of Solid Samples

The pyrolysis-gas chromatography of the alkylbenzene sulfonates was first approached by pyrolyzing solid samples in small combustion boats. The effects of the various experimental parameters were investigated after choosing a standard sample, dodecylbenzene sulfonate, and establishing the approximate conditions for pyrolysis and subsequent separation of the volatile products.

Establishing a standard

The determination of the basic operating parameters for the pyrolysis of detergents was done using the boat and furnace technique.

A sample of commercial sodium dodecylbenzene sulfonate (DDBSNa) obtained from Atlantic Refinery Company (New York, New York), was chosen as the standard material to which the pyrolysis of other detergents would be compared. The DDBSNa was chosen because it is representative of the type of detergents which are most commonly found in polluted water.

Samples were taken directly from the large sample (one pound) furnished by the maker. Subsequent samples were recrystallized from acetone to purify the commercial material. The samples used were approximately 0.5 mg. and were weighed directly into the boat.

The chromatographic column to be used for analysis of the pyrolysis products and the conditions under which it was operated were chosen by prior injection of suspected products, such as benzene, toluene, 1-dodecene, and biphenyl.

Figure 6 shows a pyrogram obtained under the conditions described on the adjacent table. These results were used as a reference point to compare and study the effects of the various operating parameters.

Effects of experimental parameters

Effect of pyrolysis temperature

The temperature of the pyrolysis tube was raised stepwise in increments of approximately 50°C from 400°C to 700°C, in order to determine a temperature at which the pyrolysis produced well defined and qualitatively reproducible peaks. It was found that at approximately 680°C, the resulting peaks were reproducible in number as well as in retention volume.

Explanation of Figure 6

Pyrogram of 0.2 mg. DDBSNa in ceramic combustion boat

Pyrolysis at 680°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (HMDS)

Temperatures:

Column 40-200°C

Detector 250°C

Injector 220°C

Gas flows:

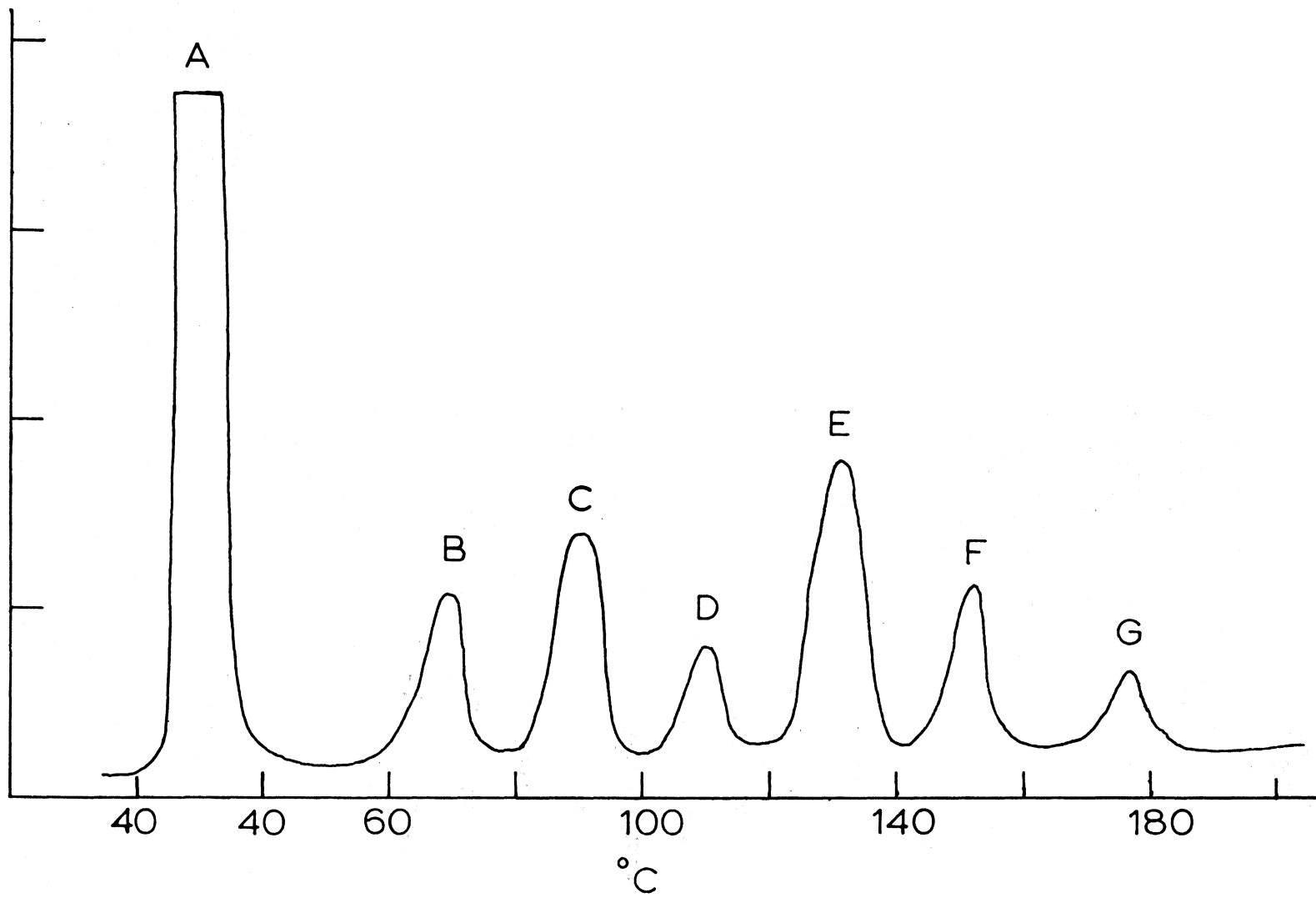
Carrier 30 ml/min He

Hydrogen 30 ml/min

Air 300 ml/min

Program rate 7.5°/min

RECORDER RESPONSE



The operating temperature was defined as the temperature at which a reproducible number of products were seen. A study was made to determine more carefully the effect of the temperature. The starting temperature was 500°C, since no pyrolysis was noted below this temperature. The temperature was increased stepwise by increments of 25°C to 625°C and from 625°C to 715°C by increments of 10°C.

The initial pyrograms at 500°C showed only the broad ill defined peaks normally associated with sample decomposition. This slow decomposition made any attempt to chromatographically identify the products impractical since in many cases more than one "peak" is caused by the same compound being given off at various stages in the slow decomposition. The residue remaining in the sample boat had a charred appearance and retained the shape of the original sample. Reweighing the sample boat showed that the residue represented approximately 75 per cent of the original sample weight.

Raising the temperature to 625°C did little to change the appearance of the pyrograms but the amount of residue remaining in the boat decreased slightly and appeared to become more and more charred. This change in the residue

will be explained in more detail later in the discussion of a possible mechanism.

Significant pyrolysis of the total sample began to occur at approximately 625°C; however, the chromatographic peaks were still broad and not satisfactory for analysis. Increasing the temperature from 625°C to 680°C, produced pyrograms with increasingly sharper and more clearly defined peaks; however, the relative ratios of the peak areas were not reproducible.

Further increases in the temperature to a maximum of approximately 720°C did not affect significantly the number of products seen or their chromatographic behavior. The reproducibility of the relative ratios of the peak areas was not improved.

The amount of residue remaining in the boats decreased only slightly through the range of 650°C to 720°C. There was no significant change in the appearance of the residue through this temperature range.

From this study it was concluded that the pyrolysis was affected not so much by the temperature above 625°C as it was by the amount of heat made available to the sample and the rate at which this heat was supplied. The broad temperature range through which the pyrolysis

products do not change in number or character points to the fact that certain bonds in the molecule are significantly weaker than the rest.

The temperature chosen for use in studying the other operating parameters was 680°C. This temperature represents approximately the midpoint of the pyrolysis range studied and produced sufficient heat for very rapid pyrolysis.

Determination of whether or not the pyrolysis occurred rapidly enough was accomplished by propelling the boat into the heated zone and withdrawing it immediately (i.e., the operation consisted of one smooth action of sliding the boat in and then out). The time involved was approximately two seconds overall with the boat being in the hot zone an estimated 0.5 second. The pyrogram obtained was compared to one produced when the boat was allowed to remain in the furnace for approximately five minutes, which showed no significant differences in the volatile products or the residue. Since the two pyrograms showed no significant differences it was concluded that the total pyrolysis was occurring in two seconds or less.

Effect of flow rate

The rate of flow of the carrier gas through the pyrolysis tube during the pyrolysis was studied in order to determine if the rate at which the initial products were removed from the heated zone had any effect on the number or relative ratio of the final products. The possibility of any secondary reaction, such as dimerization of initial products, should be reduced by a fast flow of carrier gas.

As mentioned previously the flow rate and other chromatographic conditions had been set to obtain optimum separation of the products. The effect of the flow of carrier gas through the pyrolysis tube at the time of pyrolysis was studied by setting the flow at a given rate, pyrolyzing the sample, and then returning the flow to the normal rate for the optimum chromatographic separation. These changes were accomplished by means of the needle valve and associated rotameter attached to the chromatograph.

The pyrolysis flow was varied from 0 ml/min (i.e., carrier flow was halted during the time the boat was injected) to 80 ml/min. With the carrier gas off at the time of pyrolysis, the residue in the boat was abnormally

large and the pyrogram showed the presence of higher molecular weight species which had not been seen before.

Increasing the flow rate to 30 ml/min caused the higher molecular weight products to disappear. Continued increase of the flow rate to 80 ml/min did not affect the pyrograms further. The relative amount of residue to sample size decreased from 0 ml/min to 30 ml/min and remained essentially constant from 30 ml/min to 80 ml/min.

Effect of sample size

The possibility of secondary reactions leading to larger products because of the relative availability of reacting species led to the study of the effects of changing the sample size.

The effects on the pyrogram caused by changing the sample size were found to be dependent on two factors: first, the mass of the sample and second, on the shape or volume of the sample.

The major problem, therefore, is to reproduce the condition and size of the sample rather than just the weight of the sample. The alkylbenzene sulfonates (ABS), as sold commercially and after recrystallization from acetone, are very hygroscopic and unless great care is

taken to keep it dry, the ABS crystals form flakes of varying size rather than small regular crystals. These flakes were dried in an oven at approximately 120°C for 24 hours, the resulting cake ground to obtain finely divided particles. However, even in a desiccator containing Drierite, the finely divided particles did tend to form a paste, if left for more than two hours. Therefore, the samples were stored in an oven until just before they were weighed and pyrolyzed. The sample size was varied from approximately 0.2 mg. to 2 mg. and the effect is shown in Table III.

A pattern is noticed both in the pyrogram and in the amount of residue remaining. With an increase in sample size the pyrogram shows an increase in the latter peaks relative to the first two. The amount of residue also increased with the increase in sample size.

Sufficient aqueous solution of the ABS, was placed in the sample boat and allowed to evaporate, to leave approximately 0.1 mg. of ABS. Pyrolysis of the thin film of ABS coated on the boat gave a bare minimum of residue and was the most reproducible sample in terms of peak areas.

Explanation of Table III

Variation due to sample size using boat technique.

- A. Benzene
- B. Toluene
- C. Unidentified (1-alkene) pyrolysis product
- D. Same
- E. Same
- F. Same

TABLE III

	0.21 mg.	0.47 mg.	1.12 mg.	1.85 mg.
A.	1321	2512	5431	8212
B.	832	1564	3342	4891
C.	878	1723	3817	6361
D.	532	1071	2352	3799
E.	327	629	1390	2287
F.	582	1171	2869	4621

The explanation for these results is that as the sample is heated the initial products react with each other and the unpyrolyzed bulk of the sample to form the more thermally stable residue. These initial products are probably free radical in nature. If the sample is sufficiently densely packed the probability is greater that such secondary reactions will occur before the products can be swept away in the carrier stream. The increase in the relative ratio of the later peaks to the first two products can be seen as the probable polymerization of the aromatic portion of the molecule which these two peaks represent. This possibility will be more fully discussed in the section on product identification and mechanism of decomposition.

Effect of sample boat

A study was made to determine if the sample boat used contributed in any manner to the decomposition pattern. Duplicate samples were run in three different ceramic boats for comparison of their pyrograms, and equally importantly, to compare their residues. No significant variation was seen which could not be accounted for by the slight differences in sample size. Each of these three boats was then cleaned by heating to a red heat in

an oxygen-propane flame and duplicate samples were repeated at least three times. There was no apparent effects of the sample boat's history under these conditions. All subsequent boats were cleaned in this manner just prior to use.

The difference in the thermal conductivity of a platinum boat as well as possible catalytic effects of the metal surface were of interest. Although the thermal conductivity of platinum is significantly greater than that of the ceramic material the amount and nature of the residue was not changed. The pyrograms obtained using the platinum boats showed no significant changes in the relative ratio of the products or any new products which would suggest any catalytic effects.

Effect of carrier gas

The flow rate of the carrier gas would be expected to determine the rate at which the primary pyrolysis intermediates are removed from the bulk of the sample. The less time these initial intermediates spend in relatively close contact with each other and with the bulk of the sample the smaller the probability of secondary reactions occurring. The possibility of reaction between

the initial pyrolysis intermediates with various carrier gases at these elevated temperatures was also of interest.

No new products nor any significant changes in the relative ratios of the peaks were noticed with any of the carrier gases used under the normal conditions of pyrolysis. The gases used in this study were hydrogen, helium, nitrogen, and argon.

Effect of programmed temperature gas chromatography

Linear programming of the column oven temperature is extremely useful in pyrolysis-gas chromatography for two reasons. First, the products formed in a pyrolysis often differ widely in boiling point and the choice of an isothermal temperature which will allow the separation in a reasonable length of time is difficult. Second, the relatively cold column, at the beginning of an analysis, serves to trap the products allowing the programmed temperature to bring them off in sharp, narrow peaks. This is especially advantageous due to the large amount of dead volume of the pyrolysis unit.

All of the pyrograms, therefore, show the temperature at which the products are eluted rather than the retention volume. Slight differences in the starting time of the pyrolysis with respect to injection or in the rate of

temperature programming, have a large effect on the retention volume; however, they have little effect on the temperature of elution.

Summary

The experimental parameters affecting the pyrolysis-gas chromatography of solid samples of ABS have been investigated by using the boat technique. The optimum conditions found in this study provide reproducible pyrograms from a qualitative point of view, i.e., the same products were seen each time. However, the relative ratios of the peak areas of these products were found to depend on several of the experimental parameters. The parameter affecting the results most seriously was the size and/or condition of the sample. The results showed that the occurrence of secondary reactions was largely dependent on the immediate concentration of the primary pyrolysis intermediates. These secondary reactions caused the formation of a thermally stable residue. Raising the temperature of the pyrolysis and increasing the flow rate of the carrier gas had little effect on removing these initial intermediates rapidly enough to prevent the formation of a residue.

Since the relative concentration of the initial pyrolysis intermediates appeared to be the cause of the

secondary reactions it was decided to study the pyrolysis-gas chromatography of solutions of the ABS. The solvent would be expected to provide a means for obtaining a much smaller sample in which the concentration of the initial pyrolysis intermediates would also be much smaller at any given point during the pyrolysis.

Pyrolysis of Solutions

Solutions in boats

With the pyrolysis pattern of the ABS established using the more conventional "boat" technique for pyrolyzing solid samples, a study was conducted to determine the feasibility of pyrolyzing aqueous solutions of these detergents.

The problem of solution pyrolysis which needed to be removed were apparent from the start and were two-fold: first, the effects, if any, of the solvent on the products or their relative ratio and, second, the effects of the solvent on the chromatographic analysis of the products.

As stated previously, the hydrogen flame ionization detector was chosen because of its lack of response to water. The elution time of the water on the columns used

for analysis was determined using the thermal conductivity instrument described earlier (see Apparatus). Under the conditions found to be optimum for analysis of the products of the ABS detergents, the water was eluted along with the 1-alkenes, as shown in Figure 7.

No detrimental effects were noted in the column performance when the water was present. The increase in the response of the flame detector when water is present in the effluent shown by Sternberg, et al. (1), was within the experimental error of the analysis.

The pyrolysis of the aqueous solutions in boats showed no change in the products or their relative ratios, from that seen with the solid samples. The results obtained with the boat, however, were not reproducible for several reasons. The most significant difference noted was the complete lack of the residue which had always been found when pyrolyzing the solid samples. Introduction of the boat by means of the magnet is much more difficult with the solution than the solid and spillage is a hazard. The time during which the boat is left in the cool part of the pyrolysis tube prior to injection becomes important since the water has a relatively high vapor pressure and is easily evaporated in the carrier stream, and thereby

Explanation of Figure 7

Pyrogram showing retention temperature of water

Pyrogram of ABS using flame ionization detector with the water peak as seen with a thermal conductivity detector superimposed and shown by the dotted line.

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (HMDS)

Temperatures:

Column 40-200°C

Detector 250°C

Injector 220°C

Gas flows:

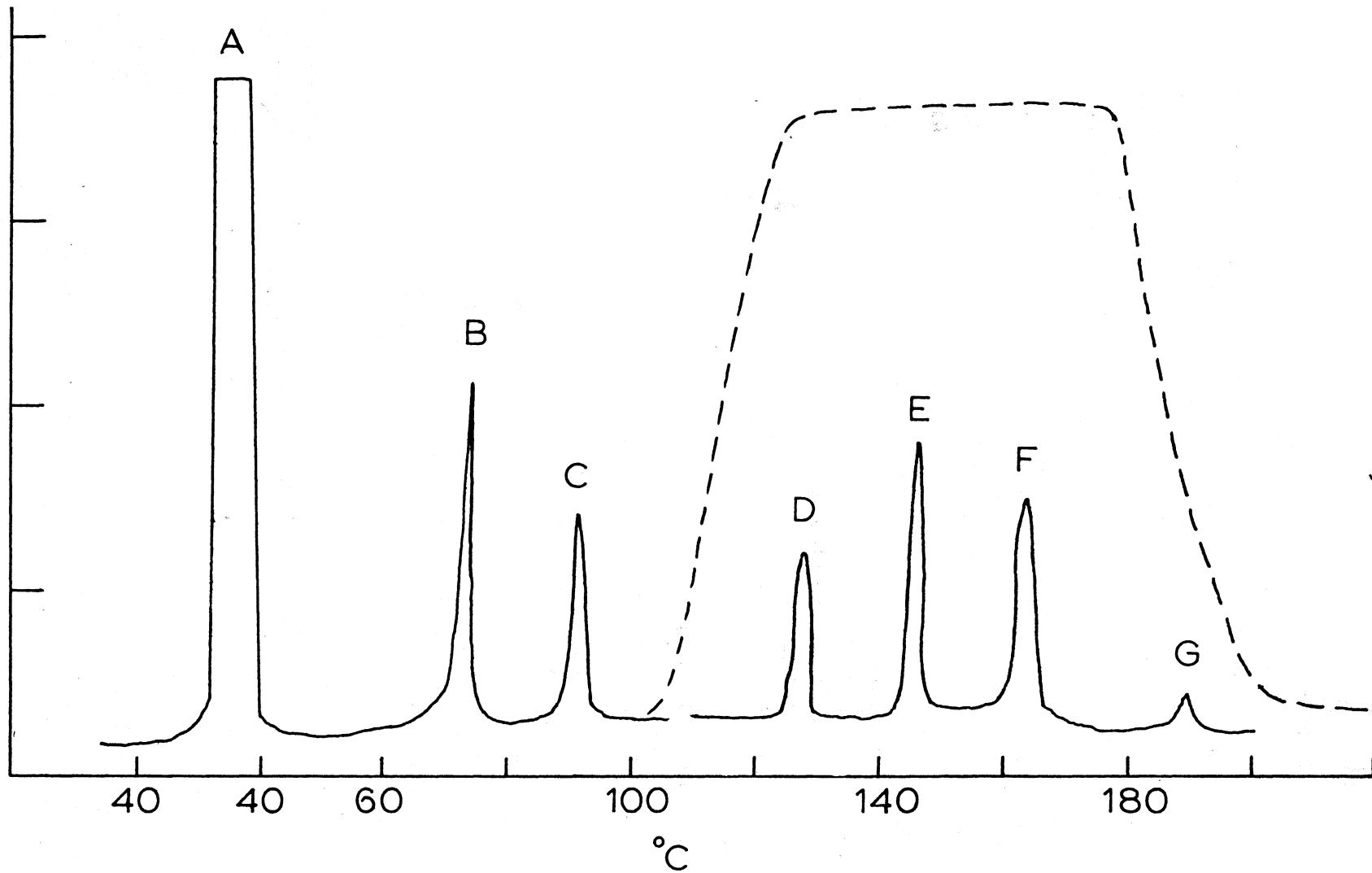
Carrier 30 ml/min He

Hydrogen 30 ml/min

Air 300 ml/min

Program rate 7.5°/min

RECORDER RESPONSE



providing a solid sample. The instantaneous heating of the solution also causes the sample to "bump," forcing some of the material outside of the heated zone without an opportunity for pyrolysis to take place.

The pyrolysis of solutions of ABS using the sample boats was found to be extremely inconvenient and hard to handle. However, the presence of the solvent did allow the pyrolysis to take place without forming a residue which had been found with all of the solid samples. The solvent apparently served to keep the initial pyrolysis intermediates separated sufficiently so as reactions between them could not take place. With these results in mind it was apparent that what was needed was a reproducible and simple means of introducing the solutions into the pyrolysis unit.

Direct injection of solutions

Due to the inadequacies of the boat system for handling solutions an attempt was made to develop a system for P-GC by direct injection of solutions using a microsyringe. The sample leaves the microsyringe as an aerosol, which has a high initial rate of vaporization (34). If the sample were to be placed directly

into the heated zone the pyrolysis should take place almost instantaneously. The sample concentration would also be very small at any point in the heated zone thus allowing the pyrolysis to take place with a minimum probability of secondary reactions occurring.

The effects of the operating parameters studied for the "boat" technique were investigated with respect to the direct injection along with the new parameters such as length of needle and the thermal conductivity of the carrier gas.

Effect of pyrolysis temperature

An investigation of the effect of the pyrolysis temperature on the samples injected directly into the furnace was carried out to establish the temperature dependence of the injection technique. The temperature range through which the pyrolysis produced well defined peaks was roughly the same, 650°C to 720°C, found for the solid samples pyrolyzed in the boats.

However, it is not the temperature which is the true measure of the effectiveness of the pyrolysis but rather the amount of heat and the ability of the system to conduct this heat to the sample. In this case, a significant amount of the sample, which was forced from the syringe as an

aerosol, was being carried past the heated zone by the moving gas stream without receiving sufficient heat.

Several attempts were made to design a system which would supply the heat necessary without at the same time lengthening the heated zone and therefore the amount of time that the molecules remained in this zone.

The most efficient system found was the insertion of a platinum gauge as shown in Figure 4 . The thermal conductivity of the platinum was great enough to transfer the heat necessary to cause pyrolysis of the total sample. By folding the platinum screen twice on itself, there were four layers of wire which prevented any of the sample spray from being blown through the heated zone without contacting a hot surface.

To insure maximum pyrolysis the sides of the pyrolysis tube were indented at the center of the hot zone. The indentations also served to hold the platinum screen in place.

Using this system it was found that the temperature was not a critical parameter above some minimum temperature required to furnish sufficient energy to break the bonds involved. This lack of temperature dependence is explained by the extremely small amount of material

involved at any given point in the hot zone. As stated previously, the sample leaves the syringe as an aerosol, so that each ABS molecule is surrounded by an atmosphere of helium and water. As long as there is sufficient heat transferred to this molecule before it is blown through the hot zone, pyrolysis will occur with no secondary reactions due to the rate of heating.

Effect of sample size

The effects of sample size in terms of the amount of material to be pyrolyzed must be separated from the limitations due to the amount of solvent which may be injected.

The injection of a sample into a furnace at 680°C causes a sudden increase in the pressure which if great enough can cause a portion of the sample to be blown back into the cooler section of the pyrolysis tube and lost in terms of the analysis. The movement against the carrier gas stream was noted by the cloud of superheated steam which could be seen drifting as far back as the septum. The amount of products seen by the chromatographic detector also decreased noticeably. Washing of the pyrolysis tube also showed the presence of unpyrolyzed detergent when large samples were injected.

Sample volumes ranging from 0.1 μl to 100 μl were studied in this work. The pressure blowback was too large for any volume greater than 20 μl . The most reproducible samples were between 2 and 10 μl .

Concentrations of the detergents were compared from 5 $\mu\text{g}/\mu\text{l}$ to 250 $\mu\text{g}/\mu\text{l}$ with no concentration dependence noted. Since the samples can be made up in higher concentrations and then diluted to a concentration convenient for use with a given gas chromatography column and detector, there is no single optimum concentration.

Effect of sample placement

The size of the sample, as stated, was not critical; however, the placement, i.e., the point at which the needle deposited the sample, was very important. It was necessary to inject the sample directly into the hot zone for two reasons. First, the nonvolatile detergent molecules, unless carried forward by the force of the injection as part of the spray or aerosol were deposited on a cool section of the tube and were not pyrolyzed. Second, the pressure surge forced a portion of the sample backward prior to pyrolysis, as mentioned. To prevent this the

sample was placed well into the hot zone, so that pyrolysis occurred before the sample was blown back.

In the apparatus used in this work, it was found that a 3 inch needle would place the sample directly into the heated zone.

Effect of flow rate

The flow rate, which controls the residence time of the molecules in the heated zone was studied through the same range, 0 to 100 ml/min, as had been studied for the boat technique.

With pyrolysis occurring while the carrier stream was cut off, the results showed the same lack of reproducibility as seen with the boat under similar conditions. Also some residue was found under these conditions.

No effects were seen with changing the flow rate from as low as 15 ml/min up to 100 ml/min. The lack of any change in the pyrograms caused by changing the flow rate, can also be attributed to the extremely dilute sample undergoing pyrolysis. The secondary reactions, which occur with the boat technique due to the slow removal of the initial products of the pyrolysis from the rest of the sample, are not as probable. The reduction in secondary reactions is due to the fact that each

molecule has an inert atmosphere of helium or water surrounding it.

Effect of carrier gas

As in the case of the boat technique, no effect was found in changing carrier gases beside changing the flow rate to obtain the most efficient separation on the column being used.

Summary

The technique of pyrolysis-gas chromatography by direct injection of solutions has been shown to have several distinct advantages over the more commonly used boat technique. Very small samples are handled more conveniently by dilution of a concentrated solution to the proper range and then using a microsyringe for placing the sample directly into the pyrolysis furnace.

Use of the small sample has been shown to eliminate the effects of heating rate, sample size, and flow rate, seen when the boat technique was used. This is accomplished by essentially removing all possibility of secondary reactions occurring, thereby providing the simplest possible pyrogram for a given compound.

The reproducibility gained by use of this new approach along with the lack of secondary products seen enables pyrolysis-gas chromatography to be used to obtain

quantitative information as to the original structure of the molecule. Since no secondary products are formed the amount of a given product observed can be used to measure directly the amount of a given species in the mixture. The next section on the identification of the pyrolysis products of the ABS system will show the advantage of being able to measure the amount of a given compound in a complex mixture and also what information can be gained about the original structure.

Product Identification

Pyrograms such as those shown of the ABS can be used for either qualitative or quantitative identification without any attempt to identify the pyrolysis products. However, a greater understanding of the process by which the decomposition takes place and the effect the various experimental parameters have on the system is possible if an analysis of the products is carried out. Also much can be learned concerning the original structure of the substance undergoing pyrolysis if the pyrolysis fragments are identified.

The structures of the type molecules used in this portion of the study are shown in Figure 8. The branching

shown in these models is not meant to represent the actual structure but rather only to serve as an example.

From considerations of the bond strengths and correlations drawn from other data on thermal degradation, the most likely bonds to be broken would be the Ar-S bond, the Ar-C bond, and the C-C bond α to the aromatic ring (shown in Figure 8) (35). Both the phenyl radical and the benzyl radical which would be formed by the breaking of either the α carbon or β carbon bond have been shown to be stable (36). The α hydrogens are the most labile in the proposed structure and the decomposition is probably initiated by the removal of a hydrogen radical followed by the rupture of either the α or β carbon bond. The long chain radicals generally form the 1-alkenes (36).

The formation of a radical whether the phenyl, benzyl, or more highly substituted benzene would be influenced by the structure of the alkyl group. The straight chain substance shown in Figure 9(a) would be expected to give both phenyl and benzyl radicals while structure (b) has a possibility of forming the ethylbenzene radical as well as the phenyl radical. The structure in 9(c) might be expected to favor formation of the benzyl radical due

Explanation of Figure 8

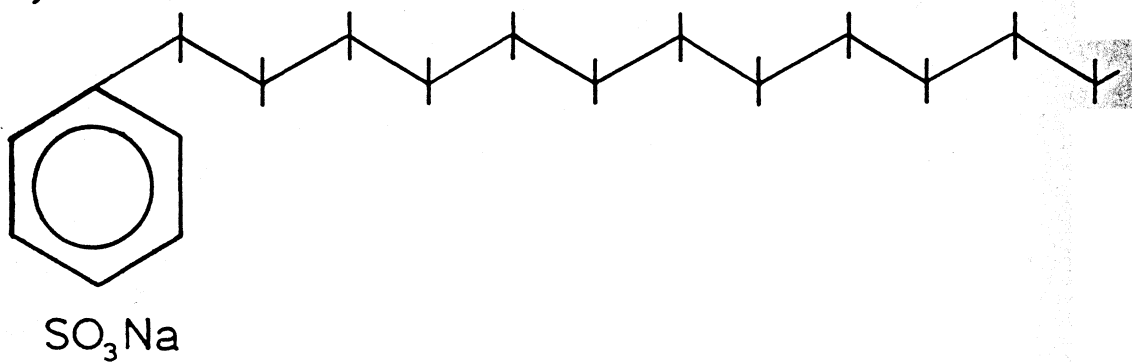
Structures of ABS systems

- (a) ABS with straight side chain. Probable products would be benzene, toluene, 1-dodecene, and 1-undecene.

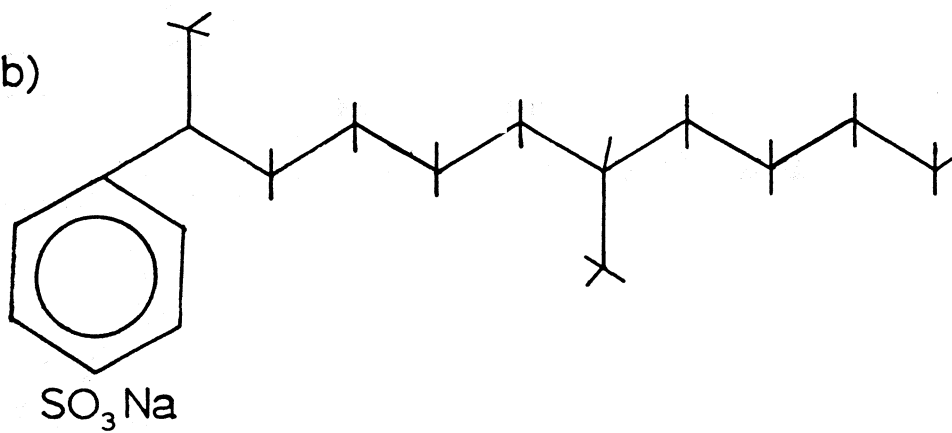
- (b) ABS with branched side chain. Probable products would be benzene, ethyl benzene, and 1-alkenes.

- (c) ABS with branched side chain. Probable products would be benzene, toluene, and 1-alkenes.

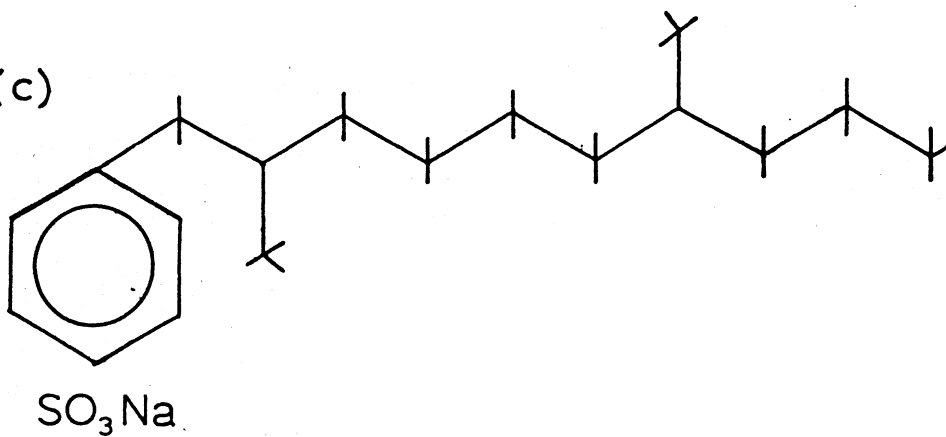
(a)



(b)



(c)



to a possible inductive effect of the methyl group on the α carbon.

The carbon to sulfur bond is known to break from the common reaction of thermal desulfurization of sulfonated aromatics to give back the nonsulfonated aromatic compound (36). Based on the above reasoning, the suspected products of the pyrolysis of the alkylbenzene sulfonates were benzene, lightly substituted benzenes, and the C₉ to C₁₃ 1-alkenes.

The $\cdot\text{SO}_3\text{Na}$ portion of the molecule cannot be directly accounted for since the number of possible products is large and the amount of residue is extremely small. The sulfur could go off as the volatile SO_2 or SO_3 ; however, if these products did not react with the column packing the flame still would not see it.

Samples of benzene, toluene, ethyl benzene, n-propyl, and isopropyl benzene were run under identical chromatographic conditions to establish their retention temperatures. Also considered were benzene sulfonic acid, a possible product if only one end of the molecule were attacked and biphenyl, a very probable product of a secondary reaction. The straight chain 1-alkenes were also used to establish the identity of some of the alkyl groups.

The pyrograms of all of the dodecylbenzene sulfonates pyrolyzed showed seven major peaks. Pyrograms of the straight and branched chain ABS are shown in Figures 9 and 10. The first peak was found to be due for the most part to the pressure surge caused by the vaporization of the sample. Injection of 1 ml. of air would give a response, though the flame ionization detector does not respond to either O_2 or N_2 , thus giving credence to the assumption of this being a pressure or flow rate phenomenon.

The second and third peaks were found to correspond to benzene and toluene, respectively. No substituted benzenes other than the toluene were seen.

In the case of the straight chain dodecylbenzene sulfonate, the last four peaks were shown chromatographically to correspond to the C_9 , C_{10} , C_{11} , and C_{12} 1-alkenes.

Figure 11 shows a plot of carbon number, for a series of 1-alkenes versus the temperature at which they were eluted on a programmed run. The circles represent samples of knowns and the square data points are from a pyrogram of the DDBSNa with straight chain alkyl groups. The dotted lines show the retention temperatures of the products of

Explanation of Figure 9

Pyrogram of DDBSNa (straight side chain)

Pyrolysis at 680°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (DMCS)

Temperatures:

Gas flows:

Column 40-200°C

Carrier 30 ml/min He

Detector 250°C

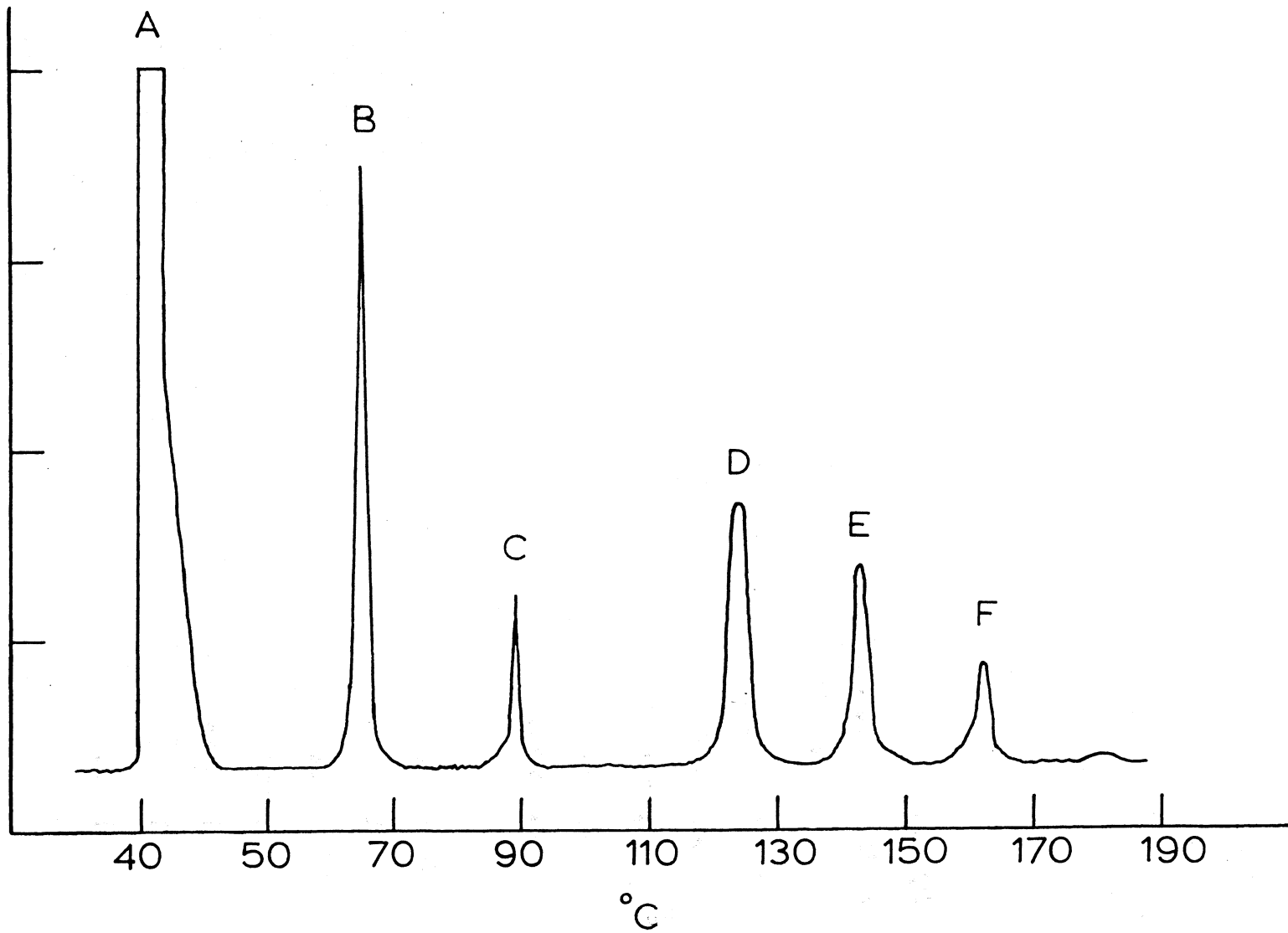
Hydrogen 30 ml/min

Injector 220°C

Program rate 7.5°/min

- A. Pressure peak
- B. Benzene
- C. Toluene
- D. 1-nonene
- E. 1-decene
- F. 1-undecene
- G. 1-dodecene

RECORDER RESPONSE



Explanation of Figure 10

Pyrogram of DDBSNa (branched side chain)

Pyrolysis at 680°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (DMCS)

Temperatures:

Gas flows:

Column 40-200°C

Carrier 30 ml/min He

Detector 250°C

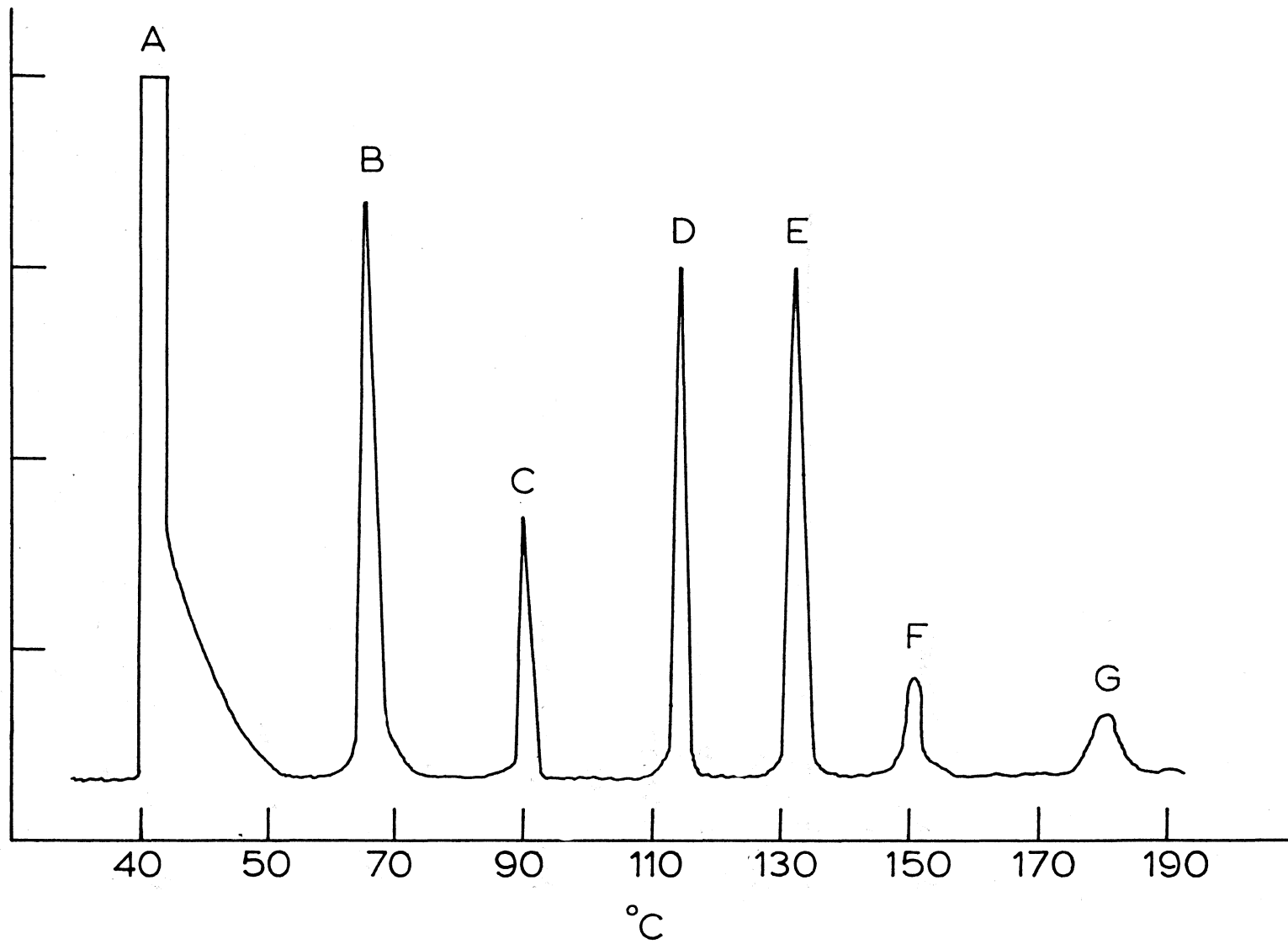
Hydrogen 30 ml/min

Injector 220°C

Program rate 7.5°/min

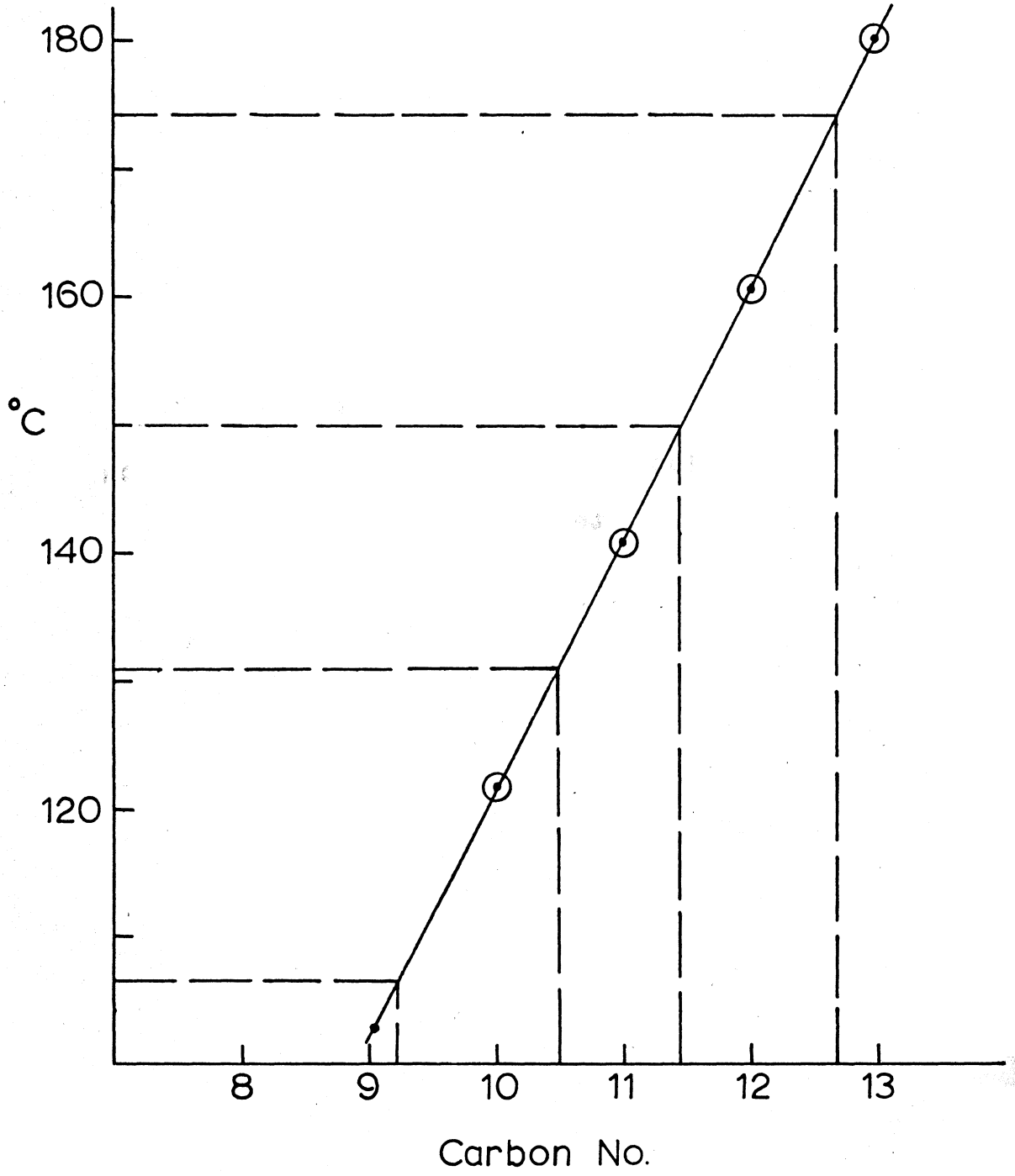
- A. Pressure peak
- B. Benzene
- C. Toluene
- D. Branched 1-alkenes
- E. Same
- F. Same
- G. Same

RECORDER RESPONSE



Explanation of Figure 11

Plot of carbon number versus retention
temperature of 1-alkenes



the pyrolysis of a sample with branched alkyl groups extrapolated to give an apparent carbon number. The decrease in the apparent carbon number corresponds well with the decrease in boiling point caused by branching in a molecule, pointing to the probability that these are the branched side chains.

A thin, white crust was formed on the inside of the pyrolysis tube by the injection of twenty to twenty-five 2 samples of aqueous sample. More injections caused the crust to grow even thicker. An x-ray diffraction analysis of a sample of the crust showed only quartz as being present. The crust is apparently caused by the reaction of the inorganic residue with the quartz pyrolysis tube. This condition showed no effect on the pyrolysis products.

A mechanism can be postulated which would have for the final products NaOH and SO₃. The dissolution and recrystallization of quartz by a strong base at elevated temperatures is known (34).

The SO₃ was not seen by the flame ionization detector; however, it is highly probable that the SO₃ would react with, and remain on, the column.

The increase in the relative ratios of the 1-alkene peaks with respect to the benzene and toluene peaks seen in the study of the sample size effect using the solid samples, can be rationalized as the polymerization of the aromatic radicals found in the pyrolysis. The residue in the boat was probably a thermally stable polymer (tar) formed by the reaction of the initial phenyl and benzyl radicals formed.

Analysis of Alkylbenzene Sulfonates

The pyrolysis-gas chromatography of the alkylbenzene sulfonates has been demonstrated as a means of determining the amount of branching in the alkyl groups. It can also be used as a means of determining the amount of detergent present.

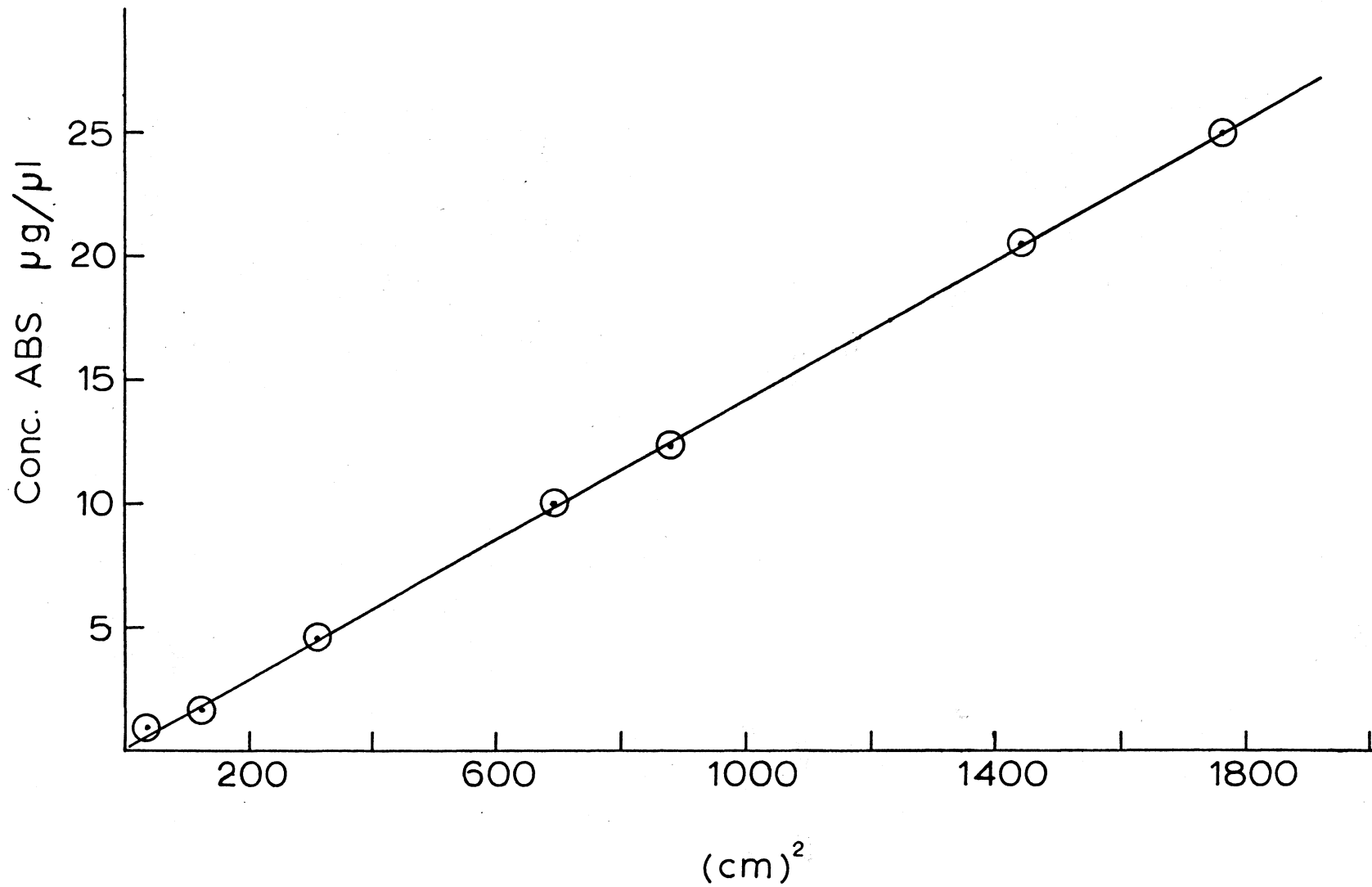
If the particular type of detergent being measured is known, any of the five major products may be used to make a calibration curve. If the total amount of ABS is needed, both the benzene and toluene peaks must be used. Figure 12 shows a calibration curve using the benzene peak for the analysis of a sample of ABS.

The detection limit was found to be 200 ppm. The reproducibility of the peak areas was better than 2 per cent as shown in Table IV.

Explanation of Figure 12

Calibration curve for DDBSNa

Plot of the area of the benzene peak versus the concentration of the alkylbenzene sulfonate in aqueous solution.



Explanation of Table IV

Shows the peak area measured for 10 samples
of 2 μ l injections of 25 μ g/ μ l of DDESNa (branched).

- A. Benzene
- B. Toluene
- C. Unidentified (1-alkene) products
- D. Same
- E. Same
- F. Same

TABLE IV

Reproducibility of Peak Areas of DDBSNa

	1756	1018	956	572	361	720
	1790	1001	972	570	354	709
	1756	1010	978	563	350	725
	1735	1036	924	549	341	740
	1780	1030	956	580	379	744
	1741	1025	948	563	353	721
	1761	1005	962	560	335	711
	1768	1008	977	575	364	715
	1739	1011	975	570	357	707
	1730	1030	935	548	349	723
Ave.	1755	1017	956	566	349	721
Ave. Dev.	15.6	10.4	15.5	8.3	8.8	9.1
% Ave. Dev.	0.89	1.00	1.62	1.43	2.52	1.26

A sensitivity limit of 200 ppm. of the ABS in water does not allow for direct analysis of polluted water. The pollution of water in the order of 1 ppm. is of great interest and in order to obtain an analysis it will be necessary to concentrate the sample used.

Samples were taken from the New River, the Roanoke River, and the James River by placing a sample bottle (500 ml.) in slow moving water which might be expected to contain some pollution. No concentration of ABS of 200 ppm. or better was found in any of the raw water samples.

Sufficient commercial ABS was then dissolved in the raw water samples to give concentrations of approximately 250 ppm. The pyrograms of these samples showed no extraneous peaks and the reproducibility was equal to that with the distilled water. Since the detection limit of the technique is not low enough to be used directly these samples were allowed to evaporate slowly to increase the concentration of possible interferences. Aliquots were analyzed as the concentration was changed by factors of 2, 10, 50, and 100. Only in the case of the James River samples were any interferences noted. These extraneous peaks occurred after concentration was

increased 100-fold and appeared with the same retention time as the 1-alkenes. The New River and the Roanoke River were found to be extremely clean with respect to organic material.

Figures 13, 14, and 15 show pyrograms of other detergents pyrolyzed by direct injection of aqueous solutions. These are used to demonstrate the applicability of the technique to systems other than the dodecylbenzene sulfonates. Under the conditions described the reproducibility of these systems was equal to that of the DDBSNa.

No product identification was attempted for these compounds; however, the pyrograms can still be used both as a qualitative "fingerprint" or for the construction of a calibration curve for quantitative analysis.

It should be noted that all of the work shown here was done with commercial grade detergents. If pure compounds of the C_9 , C_{10} , etc., substituted benzenes, both linear and branched, were available the contribution of each to the pyrogram of the mixture could be determined much more accurately. The synthesis of the compounds was not attempted.

Explanation of Figure 13

Pyrogram of Sodium dodecylsulfate

Pyrolysis at 700°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (HMDS)

Temperatures:

Column 40-200°C

Gas flows:

Detector 250°C

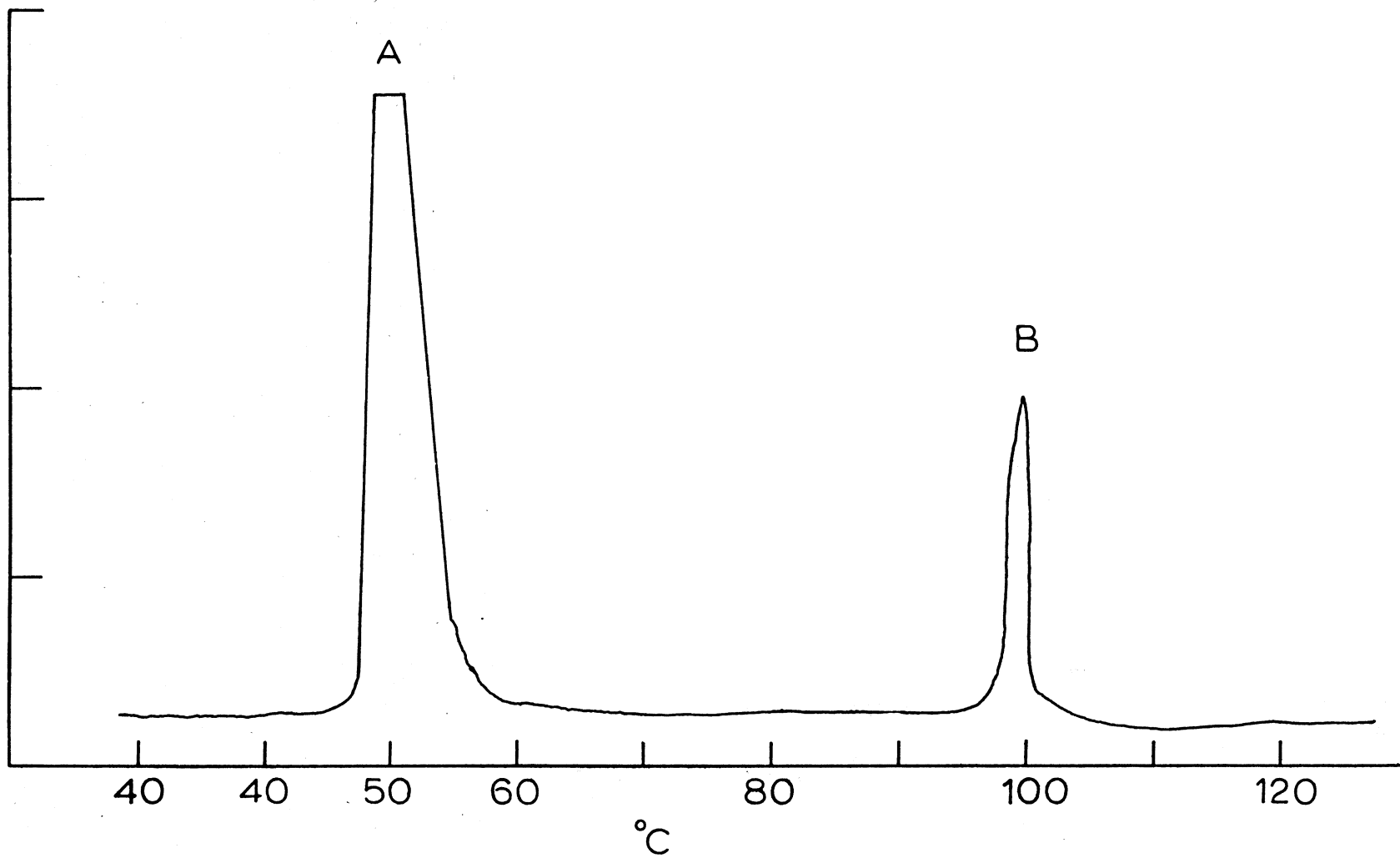
Carrier 30 ml/min He

Injector 220°C

Hydrogen 30 ml/min

Program rate 7.5°/min

RECORDER RESPONSE



Explanation of Figure 14

Pyrogram of Sodium toluene sulfonate

Pyrolysis at 700°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (HMDS)

Temperatures:

Gas flows:

Column 40-200°C

Carrier 30 ml/min He

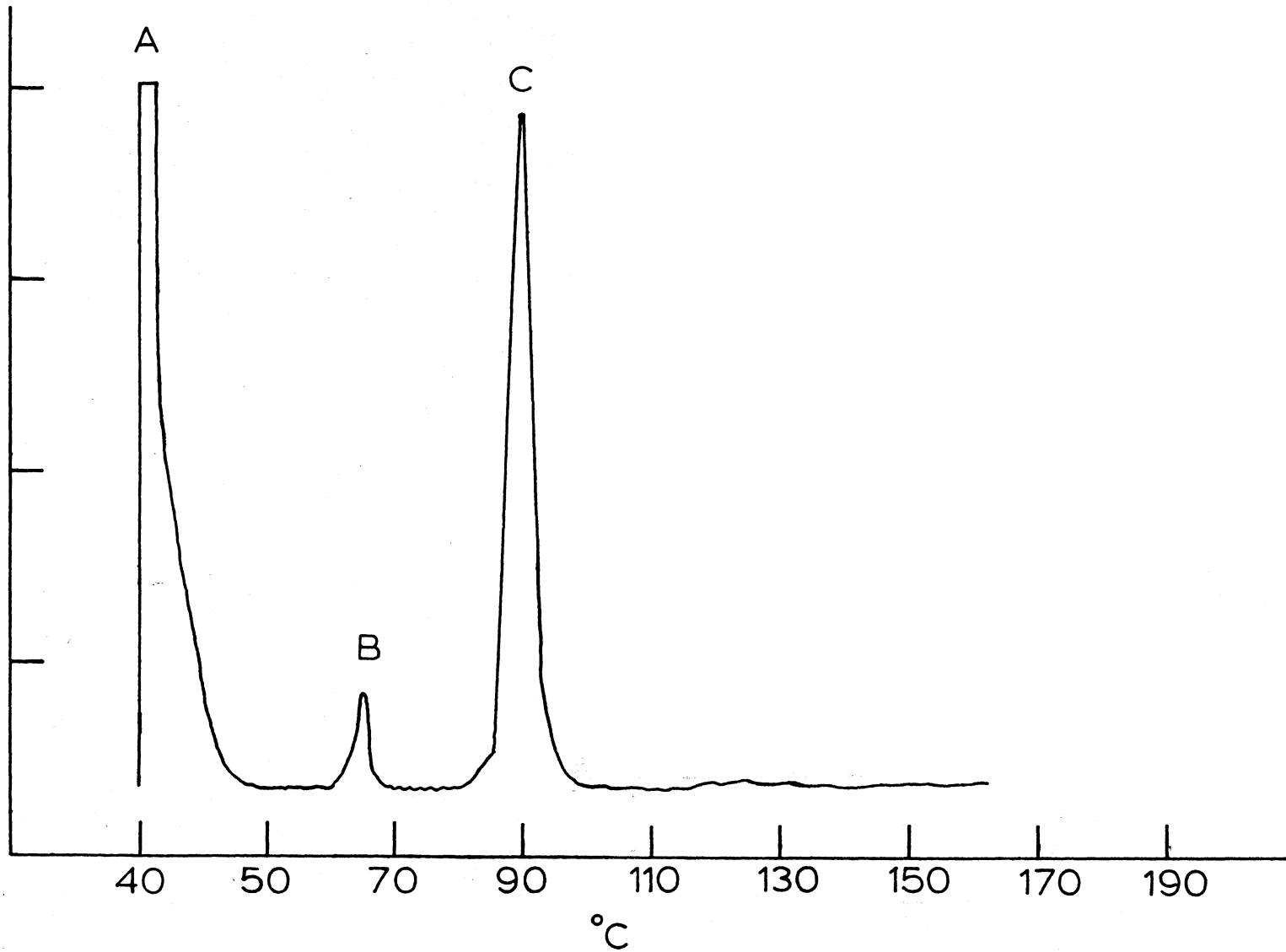
Detector 250°C

Hydrogen 30 ml/min

Injector 220°C

Program rate 7.5°/min

RECORDER RESPONSE



Explanation of Figure 15

Pyrogram of Triethanolammonium dodecylbenzene sulfonates

Pyrolysis at 700°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (HMDS)

Temperatures:

Gas flows:

Column 40-200°C

Carrier 30 ml/min He

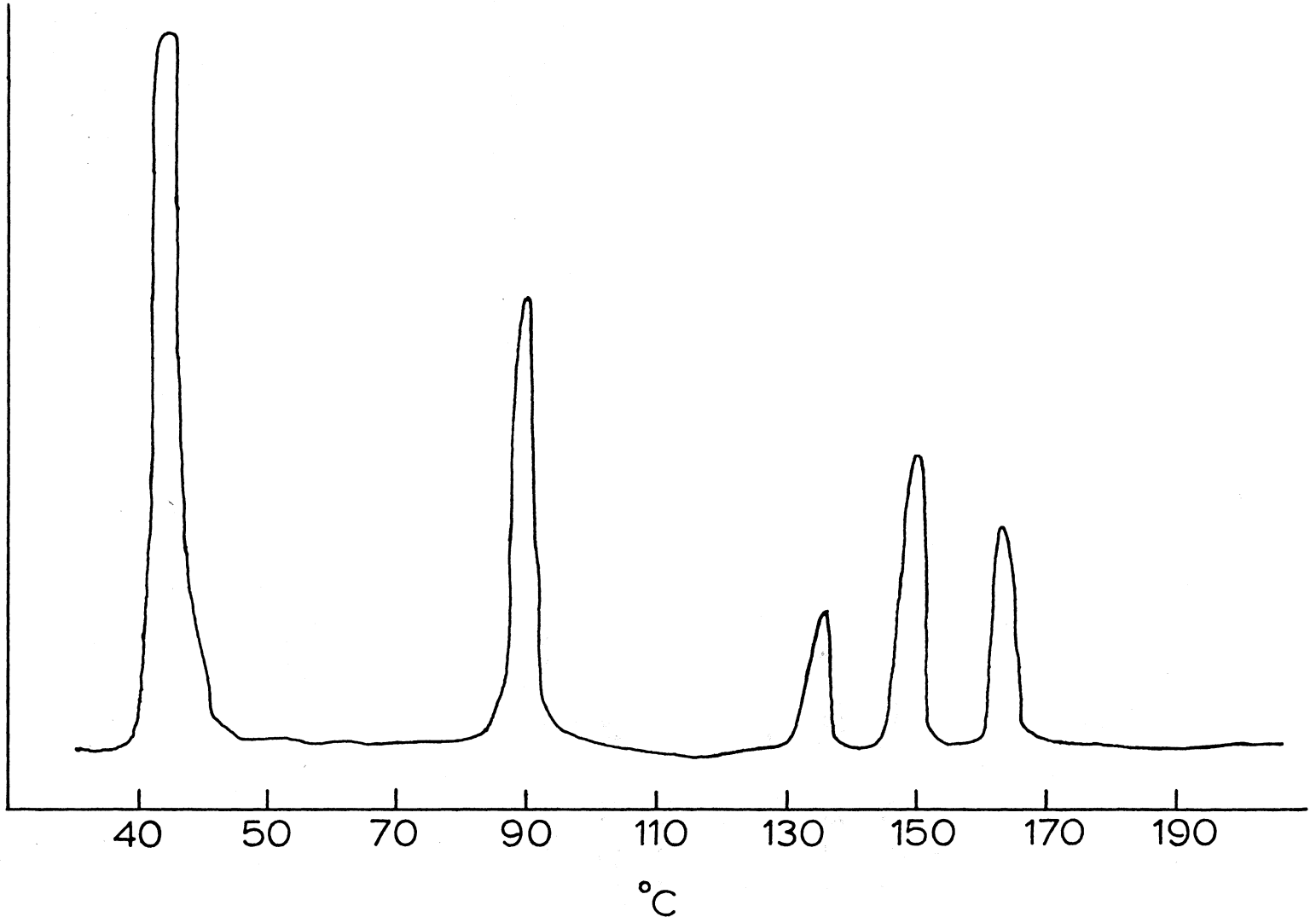
Detector 250°C

Hydrogen 30 ml/min

Injector 220°C

Program rate 7.5°/min

RECORDER RESPONSE



Solvent Stability Study

The work shown thus far has applied only to aqueous solutions. The reasons are: (1) water is extremely stable with respect to heat and (2) the detergents used in this study are most commonly found in aqueous solution.

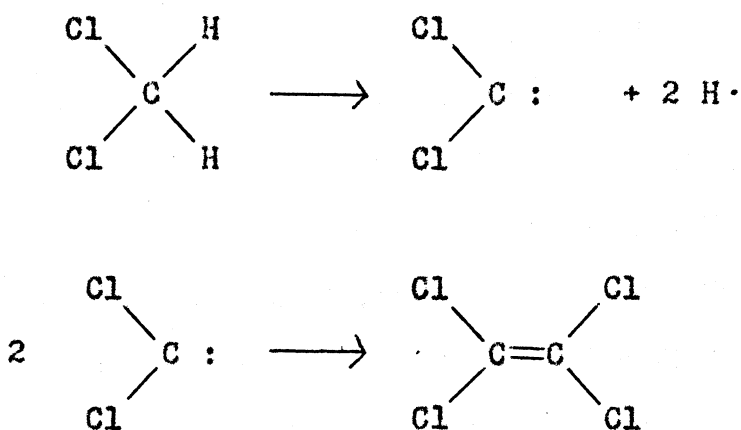
It was of interest to find out what other common solvents might be useful for pyrolysis of solutions. The main requirements are that the solvent be inert with respect to the actual pyrolysis and that the solvent peak does not interfere with the chromatographic analysis.

The following solvents were injected into the pyrolysis unit in an attempt to determine their thermal stability: methylene chloride, chloroform, carbon tetrachloride, methanol, ethanol, and acetone.

Chlorinated solvents

Methylene chloride CH_2Cl_2 , was injected into the pyrolysis unit in 2 μl samples at 25° intervals from 400°C to 600°C. Evidence of decomposition was noted by the appearance of new chromatographic peaks and by a residue first shown in the portion of the pyrolysis tube between the furnace and the gas chromatograph.

No sign of decomposition was noted until the temperature reached 550°C. The major product seen above this temperature was identified chromatographically as tetrachloroethene and is shown in Figure 16. The probable reaction for the formation of this compound is:



The dichlorocarbene is known to be stable at high temperatures (38).

This was probably not the only product of the decomposition but was the only product seen under the chromatographic conditions used. Hydrogen is a very probable product but cannot be detected by the flame detector. Other evidence of reaction was also noted by the residue left in the pyrolysis tube.

Explanation of Figure 16

Pyrogram of CH_2Cl_2 2 μl

Pyrolysis at 550°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (MeS)

Temperatures:

Column 40-100°C

Detector 250°C

Injector 220°C

Gas flows:

Carrier 30 ml/min

Hydrogen 30 ml/min

Air 300 ml/min

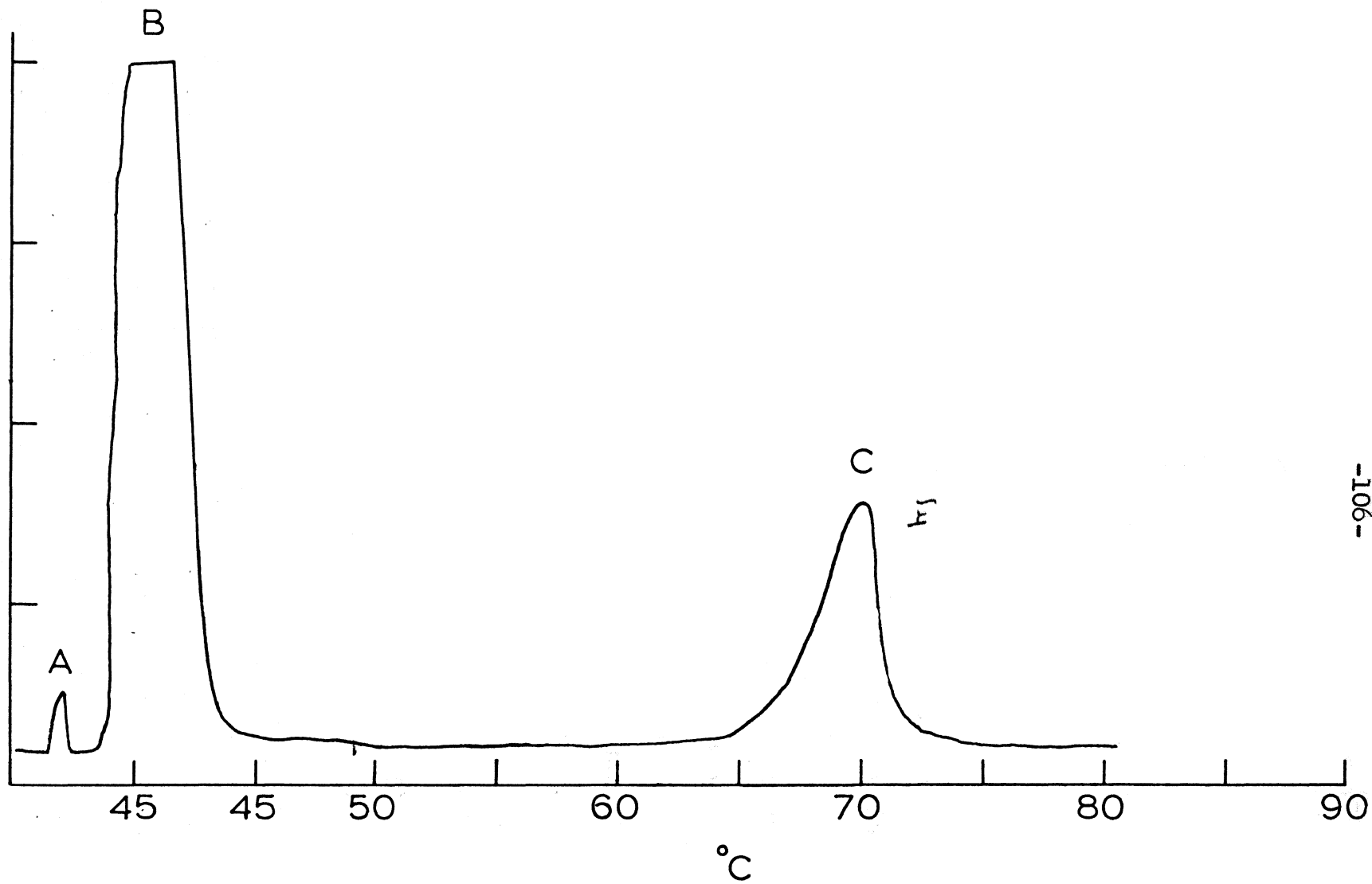
Program Rate 6°/min

A. Pressure peak

B. CH_2Cl_2

C. $\text{Cl}_2\text{C} - \text{CCl}_2$

RECORDER RESPONSE



Further increases in the temperature showed no new products but the residue coated the entire tube above 580°C.

Chloroform was studied under identical conditions. Initial decomposition was seen at ca. 520°C, with further increases in temperature showing an increase in the two major products up to 500°C, at which temperature the residue coated the entire tube.

The two major products seen and identified chromatographically were tetrachloroethene and tetrachloroethane. These products are shown in Figure 17. The probable reactions leading to these compounds are shown.

Explanation of Figure 17

Pyrogram of CHCl_3 2 μl

Pyrolysis at 520°C

Column 10' $1/8''$ S.S. 10% Apiezon L 60/80 Chrom W (MeS)

Temperatures:

Gas flows:

Column $40-100^\circ\text{C}$

Carrier 30 ml/min

Detector 250°C

Hydrogen 30 ml/min

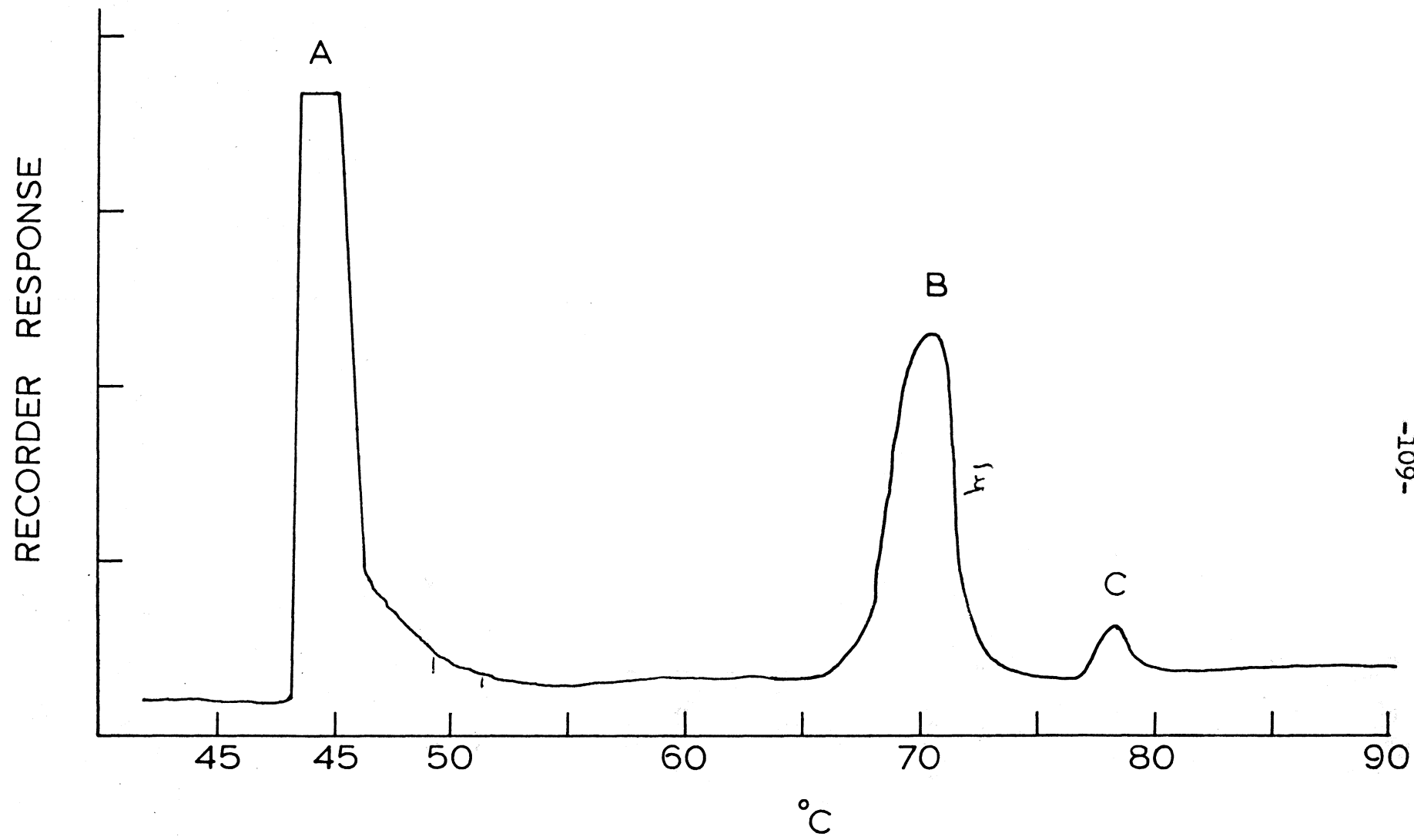
Injector 220°C

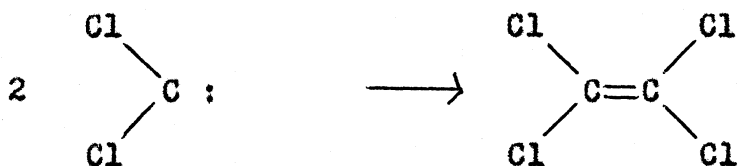
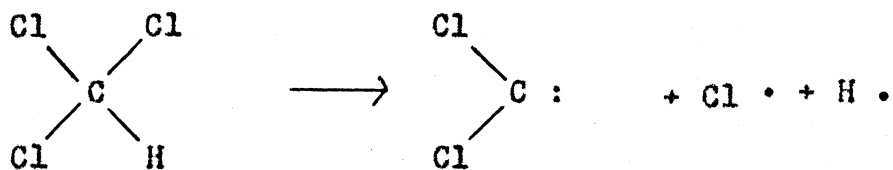
Program rate $6^\circ/\text{min}$

A. CHCl_3

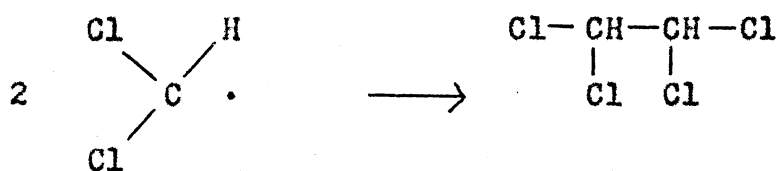
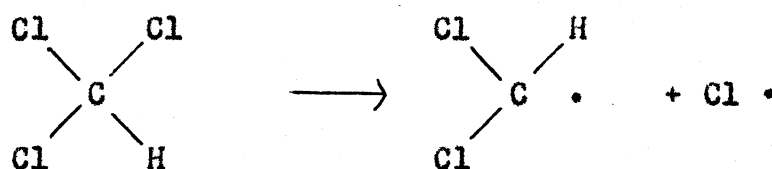
B. $\text{Cl}_2\text{C} - \text{CCl}_3$

C. $\text{Cl}_2\text{DH} - \text{CHCl}_2$





and

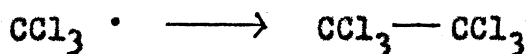
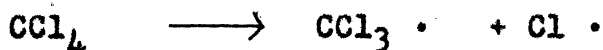


As can be seen from the above equations the other probable products would be H₂, Cl₂, and HCl (38). The H₂ cannot be detected by the flame detector whereas the Cl₂ and HCl very probably reacted with the liquid phase on the column or the column itself.

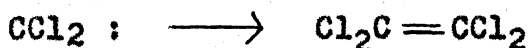
Carbon tetrachloride also yielded two major products at temperatures between 550°C and 700°C. These compounds

were shown by gas chromatography to be tetrachloroethene and hexachloroethane, in Figure 18.

Formation of these compounds is postulated below.



and



Again Cl_2 is a very probable product but was not seen.

The results of this study of the chlorinated solvents opens up many potential uses for pyrolysis gas chromatography. There is an opportunity to investigate the gas phase reactions of such molecules in an extremely easy to operate system which allows for fast product analysis. A strong possibility exists for being able to pyrolyze a compound around 450°C, have it react with the solvent, thus labeling the initial pyrolysis product. This could prove very useful in mechanism studies. The advantage the chlorinated solvents offer is that, although the

Explanation of Figure 18

Pyrogram of CCl_4 2 μl

Pyrolysis at 520°C

Column 10' 1/8" S.S. 10% Apiezon L 60/80 Chrom W (MeS)

Temperatures:

Gas flows:

Column 40-100°C

Carrier 30 ml/min

Detector 250°C

Hydrogen 30 ml/min

Injector 220°C

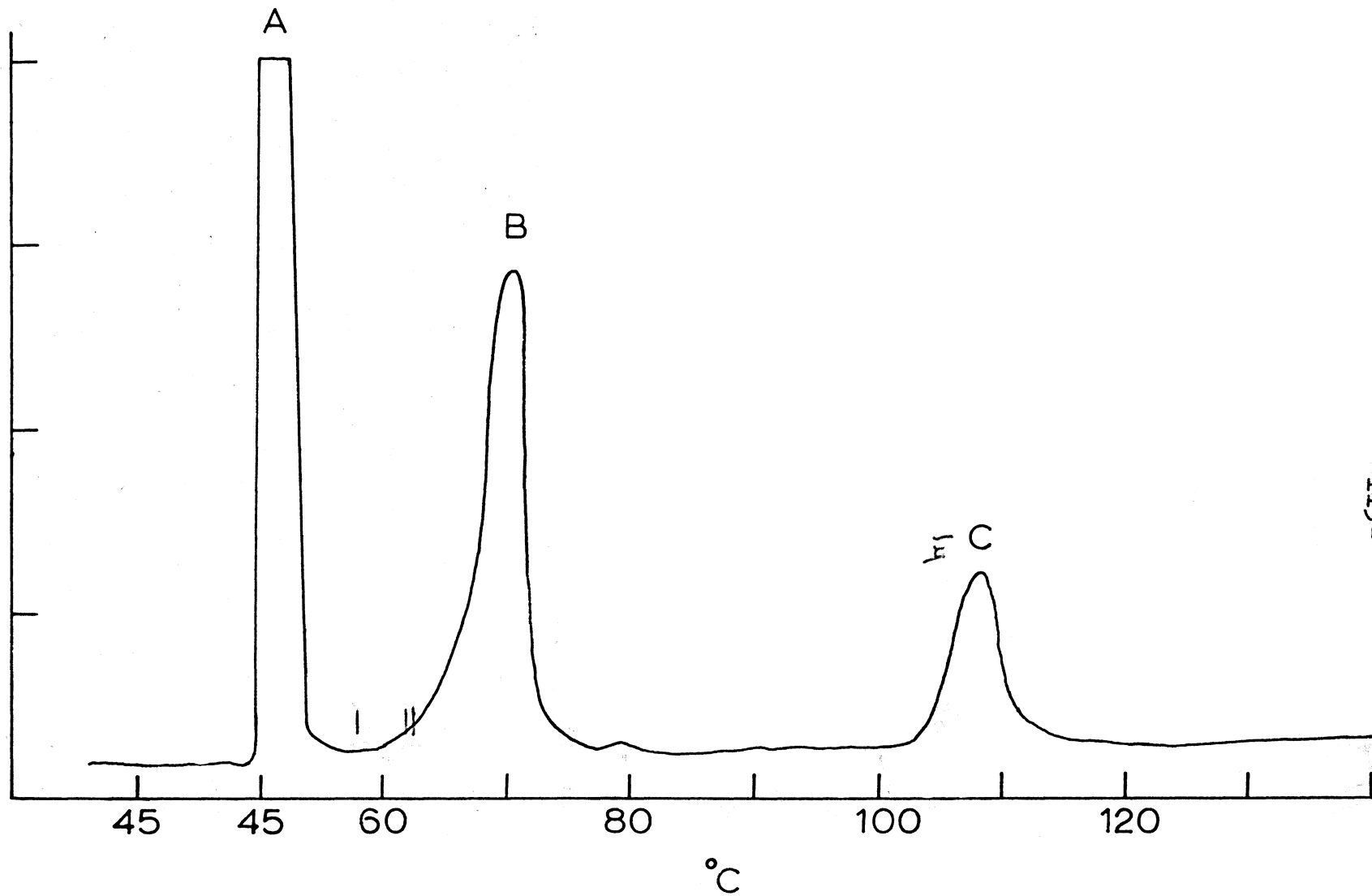
Program rate 6°/min

A. CCl_4

B. $\text{Cl}_2\text{C}=\text{CCl}_2$

C. $\text{Cl}_3\text{C}-\text{CCl}_3$

RECORDER RESPONSE



pyrogram resulting might be complicated, the chlorinated products are easily determined by use of an electron capture detector, which is an extremely sensitive and selective detector for halogenated compounds. The use of programmed temperature and a valving system such as is available in the Beckman GC-4, would allow the large solvent peak to be by-passed from the electron capture detector, so it would not swamp the detector electronics.

Oxygenated solvents

The oxygen containing solvents, methanol, ethanol, and acetone were subjected to the same temperature study as the chlorinated solvents discussed above.

Methanol showed no noticeable reaction until a pyrolysis temperature of 525°C was reached. The products obtained were light gases as would be expected and no attempt was made to specifically determine them. The point of interest was only to see at what temperature (under these conditions) methanol began to decompose. While the same possibilities for studying the reactions of the initial products of a pyrolysis exist, there is not the convenience of a selective detector for the products, as exists with the chlorinated solvents.

Ethanol was found also to decompose at around 530°C. From the work reported by Barnard (39) using a static system, the main product is expected to be CH_3CHO . Acetaldehyde was shown to be present; however, no further work was attempted.

Acetone was found to decompose above 515°C, giving a complex pyrogram of many light products. Again, the only point of interest was the temperatures at which the solvent began to decompose.

The study of these solvents shows the limitations of temperature placed on the direct injection of solutions in organic solvents into a pyrolysis unit. This temperature limitation could be reduced greatly by the use of various freons, which are known to be thermally stable above 800°C (40). The freons offer a wide range of polarity as well as stability due to the fluorine in the molecule.

It should be noted, however, that in all cases mentioned the limit of thermal stability has been defined as the point at which, the decomposition products of the molecules are first seen under the conditions described. The temperature at which a radical formed by the pyrolysis of a sample molecule would attack and react with the solvent would depend on the specific radical formed.

Systems Other than Detergents

Several systems other than the detergents previously discussed were investigated for the possible application of the technique of pyrolysis-gas chromatography by direct injection of solutions. Two of these systems were the amino acids and certain metal chelate compounds. Pyrolysis-gas chromatography was shown in both cases to offer a method of obtaining qualitative information as to the structure of the compounds as well as potentially a means of quantitative measurements.

Amino acids

The amino acids are another class of compounds which are not volatile enough to be analyzed conveniently by direct gas chromatography. The standard method for analysis of these compounds is the ion exchange separation followed by titration, first published by Moore and Stein (41). This method is much slower and more cumbersome than would be the gas chromatographic separation and detecting of the pyrolysis products, provided that this could be done with sufficient reproducibility.

Several workers have applied the technique of pyrolysis-gas chromatography to certain amino acids (42,43).

The problems are two-fold: (1) to find a pyrolysis system which gives a simple pyrogram of each acid, preferably only two compounds such as decarboxylation to give CO_2 and the amine, and (2) it would be necessary to find the proper chromatographic column and conditions to effect a separation of all of the products formed by the pyrolysis of a complex mixture.

In this study, the problems of producing a simple pyrogram of certain amino acids was undertaken.

Figure 19 shows the pyrogram obtained with a mixture of glycine and alanine in 80 per cent ethanol-20 per cent water solution injected with the pyrolysis furnace at 350°C . A comparison of the boat technique versus the direct injection of solution technique demonstrated the greater reproducibility of the latter system.

Only two significant peaks were noted in this pyrogram and were assumed to represent methyl and ethyl amine as these are the most probable products to occur at the low temperature pyrolysis. The amine would result from the decarboxylation of the amino acids. No peaks were seen which would represent reaction of the solvent, ethanol, with the products.

Explanation of Figure 19

Pyrogram of alanine and glycine in
Ethanol-water solution

Pyrolysis at 350°C

Column 6' 1/8" S.S. 10% THEED on 60/80 Gas Chrom Z

Temperatures:

Gas flows:

Column 60°C

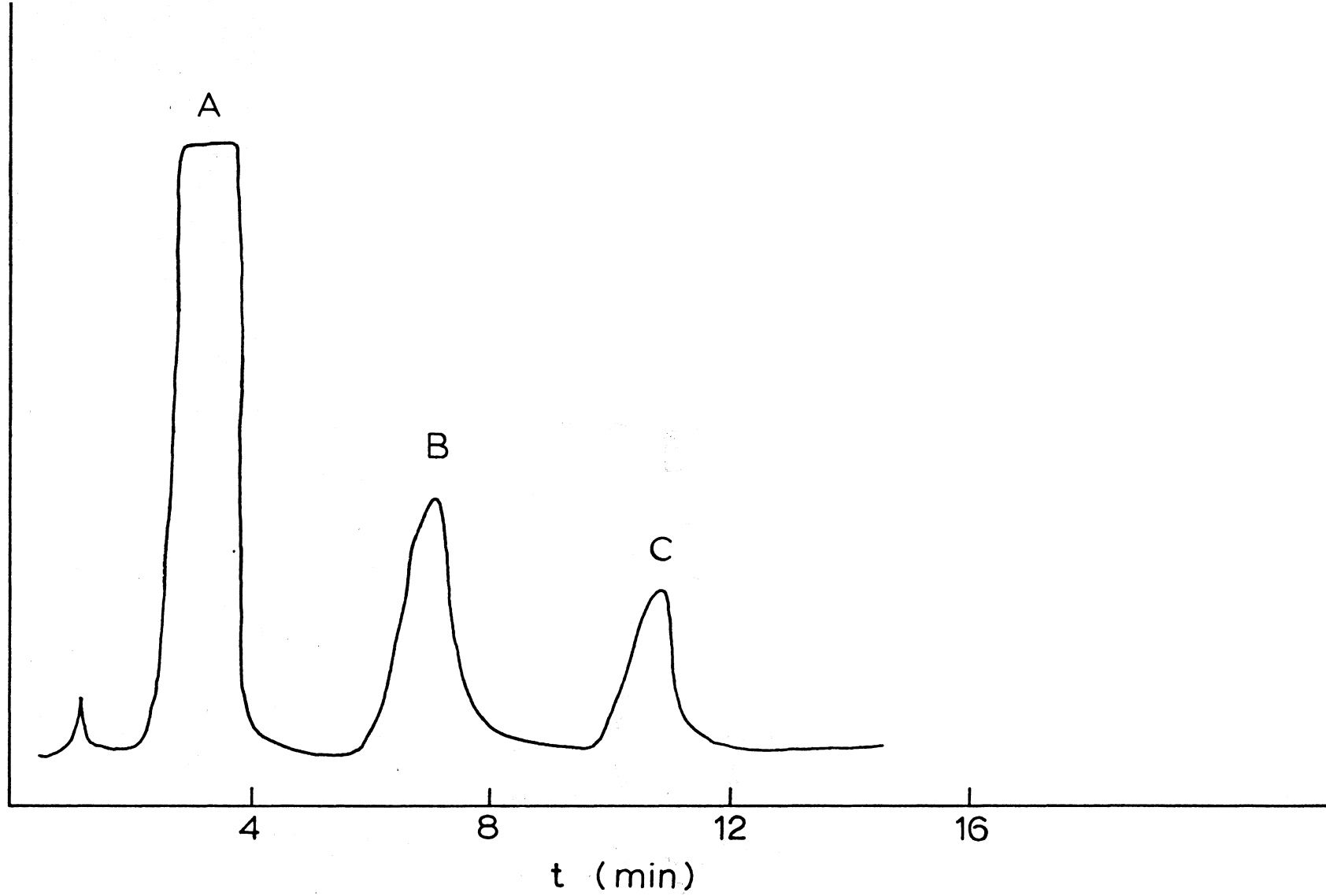
Carrier 30 ml/min He

Detector 250°C

Hydrogen 30 ml/min

Injector 220°C

RECORDER RESPONSE



The hydrogen flame ionization detector was used since, as stated previously, this allows use of a much smaller sample; however, a more concentrated mixture was run using the thermal conductivity detector in order to check for the presence of the CO_2 which does not respond in the hydrogen flame. This also provided an opportunity to observe the water peak. Figure 19 shows the pyrogram obtained. The first peak was shown to correspond to carbon dioxide.

An attempt was made to use the CO_2 peak as a means to determine the composition of a mixture of two acids. If the total weight of the sample were known only the carbon dioxide peak area would be necessary for determining the per cent composition of the two acids. However, the concentrations of the acids necessary to obtain sufficient response from the thermal conductivity detector, ca. $250 \mu\text{g}/\mu\text{l}$ proved to be too large to be of much use.

The technique of pyrolysis-gas chromatography by direct injection of solutions as shown here offers a means of determining which amino acids are present provided that the resulting amines can be separated. The work necessary to determine the column and conditions necessary for the separation of all the common amino acids has not been

done. However, for simple mixtures of these compounds this technique offers a fast and simple means of determining the composition.

Metal acetylacetonates

The metal acetylacetonates offer another area in which pyrolysis-gas chromatography may be used to obtain certain information as to the structure of the molecules. Brandt and Heveran (44) first showed the possibility of determining volatile metal chelates by gas chromatography. Since then much work has been done in this area by other workers (45,46). While pyrolysis-gas chromatography does not offer a means of separating a mixture of metal chelates, since the expected product would be the chelate itself, the technique does provide a means for determining the structure of the chelate. The number of chelating molecules attached to each metal atom is generally determined spectrophotometrically. This technique does not allow for showing easily which chelates are attached, if there is more than one chelating agent present.

Figures 20 and 21 show the results of a preliminary study using copper II and chromium III acetylacetonates.

Explanation of Figure 20

Pyrogram of 2 μ l Cr(III)(ACAC)₃ in CHCl₃

Pyrolysis at 400°C

Column 10' 1/8" S.S. 5% ditridecylphthalate 80/100
Gas Chrom Z

Temperatures

Gas flows:

Column 85°C

Carrier 30 ml/min H₂

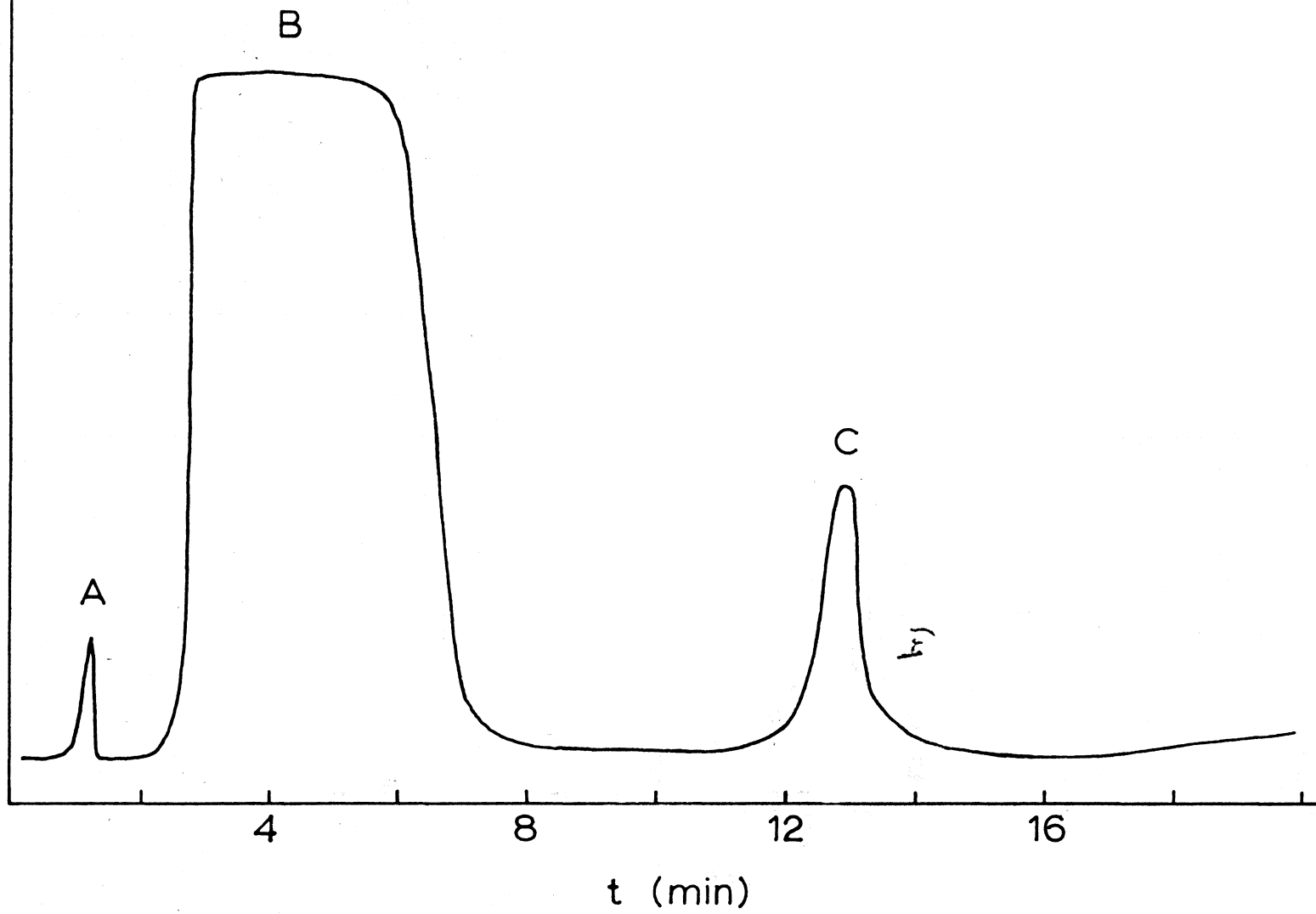
Detector 200°C

Air 300 ml/min

Injector 210°C

- A. Pressure peak
- B. Acetylacetone
- C. Cr(III)(ACAC)₃

RECORDER RESPONSE



Explanation of Figure 21

Pyrogram of 2 μ l $\text{CuII}(\text{ACAC})_2$ in CHCl_3

Pyrolysis at 400°C

Column 10' 1/8" S.S. 5% ditridecylphthalate 80/100
Gas Chrom Z

Temperatures:

Gas flows:

Column 85°C

Carrier 30 ml/min H_2

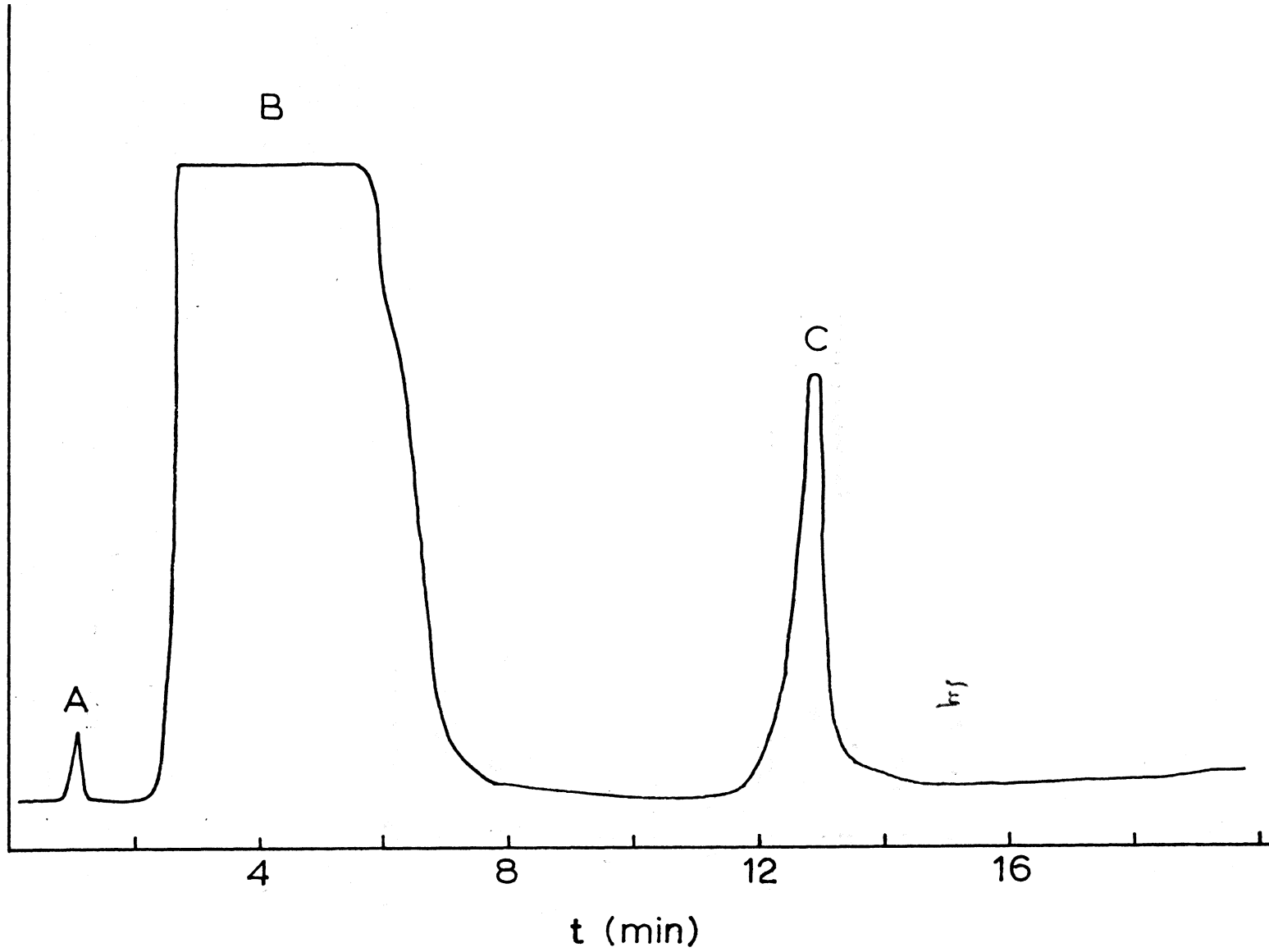
Detector 200°C

Air 300 ml/min

Injector 210°C

- A. Pressure peak
- B. Acetylacetone
- C. $\text{Cu}(\text{II})(\text{ACAC})_2$

RECORDER RESPONSE



In both cases the only major pyrolysis product was shown chromatographically to be the acetylacetone.

With equimolar concentrations of the metals the areas of the acetylacetone peaks were in the ratio of 3 to 2 for the CrIII and CuII.

This technique should prove extremely useful for determining the structures of mixed chelate systems such as amine adducts of the metal acetylacetonates and other chelating agents.

V. CONCLUSIONS

The experimental parameters controlling the rate and mechanism of the decomposition of compounds and the products formed in a moving carrier gas stream have been investigated. The size of the sample and the rate at which it is brought to a pyrolysis temperature were found to be the most significant factors.

A new technique was developed for the pyrolysis-gas chromatography of solutions by direct injection. This technique was shown to be more reproducible than the more commonly used boat technique. By injecting the dilute solution directly into the pyrolysis furnace it is possible to use a much smaller sample than in the case of the solid sample in a boat. More importantly the solvent serves to isolate the sample molecules from each other sufficiently that presumably an essentially unimolecular decomposition takes place giving the simplest possible pyrogram. This simple pyrogram provides more accurate information as to the original structure of the compound.

The alkylbenzene sulfonates were used to compare the direct injection approach to the boat approach. A method was worked out for analyzing the ABS detergents in solution.

This method offers a means of differentiating between the straight and branched chain alkyl groups more easily than the present I.R. method. The limit of the sensitivity of the method is 200 ppm. with a relative reproducibility of the various product peak areas being better than 2 per cent. The most promising point of the ABS work is that it offers a means of determining the biodegradability of a given detergent in as much as this biodegradability depends on the degree of branching. Examples of detergent molecules other than the ABS were pyrolyzed to show the usefulness of the P-GC by direct injection of solutions.

While most of the work was done in aqueous solutions an attempt was made to determine the stability of some of the common organic solvents in such a pyrolysis system. The common chlorinated solvents, methylene chloride, chloroform, and carbon tetrachloride were shown to be stable up to 500°C. The oxygenated solvents methanol, ethanol, and acetone also began to show decomposition products around 500°C.

Mixtures of amino acids in ethanol-water solutions were also pyrolyzed using the system developed. The products were carbon dioxide and the primary amines. This offers a means of analyzing for the amino acids

directly in solution. The usefulness of the technique in determining the structure of organic chelates attached to metal atoms is also described.

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ABSTRACT

The experimental parameters controlling the rate and mechanism of the decomposition of compounds and the products formed, in a moving carrier gas stream were investigated. The parameters studied included the effects of pyrolysis temperature, sample size, sample weight, flow rate of the carrier gas, the the method of introducing the sample into the pyrolysis unit.

An apparatus for pyrolysis-gas chromatography, using the commonly used boat and furnace technique, was developed. Commercial grade sodium dodecylbenzene sulfonate was chosen for a model compound. The optimum conditions for the pyrolysis-gas chromatographic analysis of this material were established by the careful study of the experimental parameters.

The most serious limitations to this method of pyrolysis-gas chromatography appeared to be the strong dependence on the sample size and the dependence on pyrolysis temperature, i.e., on the rate at which the sample was brought to the pyrolysis temperature. As the size of the sample was increased the amount of residue in the boat also increased. Also, although the majority of

the sample was pyrolyzed at 580°C the amount of residue would decrease as the temperature was raised to a maximum of 710°C. A certain amount of residue always remained in the boat. The residue can be explained as the product of secondary reactions occurring between the initial pyrolysis intermediates (free radicals) and the unpyrolyzed portion of the sample.

In an attempt to eliminate these effects of secondary reactions a new technique of pyrolysis-gas chromatography by direct injection of solutions was developed. By handling the samples in dilute solution it was shown that a much smaller sample could be pyrolyzed such that the probability of secondary reactions was greatly reduced. Also the very small samples allow an apparent instantaneous heating of the samples to a given pyrolysis temperature. This approach offers a means of obtaining the simplest possible products from the pyrolysis of a compound, therefore offering a more accurate insight into the mechanism of the pyrolysis. These products then offer a means of establishing the structure of the original compound.

Using this technique a method was developed for analyzing aqueous solutions containing the alkylbenzene

sulfonates. This method provides not only a measure of the total detergent present but also differentiates between the various alkyl groups found in the commercial products. The alkyl groups form the 1-alkenes which can be easily identified chromatographically. The conditions for this analysis along with curves showing the products obtained from the pyrolysis of samples with both straight and branched alkyl groups are given.

While the majority of the work done here was with aqueous solutions an attempt was made to determine the stability of some of the common organic solvents under such pyrolysis conditions. Those solvents studied were methylene chloride, chloroform, carbon tetrachloride, methanol, ethanol, and acetone. All of these solvents were found to be stable up to 500°C; however, at temperatures greater than this the decomposition of the solvents limits their use.

The technique of pyrolysis-gas chromatography by direct injection of solutions was also applied to certain amino acids in ethanol-water solutions. The results were again much more accurate than those found with the boat technique.

This technique was also shown to be useful in determining the structure of organic chelates bound to metal atoms. Solutions of copper II and chromium III acetylacetonates in chloroform were pyrolyzed and the product identified as acetylacetone. This offers a means of determining both the number and type of chelates bound to a given metal atom.