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LIQUID-LIQUID CHROMATOGRAPHY FRACTIONATION OF ORGANIC COMPOUNDS IN COMPLEX MIXTURES: APPLICATION TO AUTOMOBILE EXHAUST

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Liquid-liquid chromatography fractionation of organic compounds in complex mixtures: Application to automobile exhaust

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TABLE OF CONTENTS

LIST OF ABBREVIATIONS AND ACRONYMS

ALF	aldehyde fraction
A.P.I.	American Petroleum Institute
AVE	average
BAF	base fraction
CIMS	chemical ionization mass spectrometry
DMSO	dimethyl sulfoxide
DNP	2,4-dinitrophenylhydrazine
EtOH	ethanol
FIA	fluorescent indicator adsorption
FID	flame ionization detector
FT-IR	Fourier transform infrared spectrometry
GC	gas chromatography
GC/FT-IR	gas chromatography/ Fourier transform infrared spectrometry
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
HOAc	acetic acid
HPLC	high performance liquid chromatography
I.C.	ion current
in.	inches
IPA	isopropyl alcohol
KEF	ketone fraction
LC/MS	liquid chromatography/mass spectrometry
LLC	liquid-liquid chromatography
MeOH	methanol
MS/MS	mass spectrometry/mass spectrometry
m/z	mass-to-charge ratio
NPF	nonpolar fraction
PAH	polynuclear aromatic hydrocarbon
POF	polar fraction
ppb	parts per billion
ppm	parts per million

p.s.i.	pounds per square inch
R.I.	retention index
R.T.	retention time
SAF	strong acid fraction
subst.	substituted
temp.	temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TOT	total
UV	ultraviolet

INTRODUCTION

During the past decade, considerable progress has been made in the analysis of organic compounds in complex mixtures. In the early 1970s, Americans began to have a great concern for the environment and its effect on human health. As a result, scientists began to study anthropogenic indignities to the environment in more detail than ever before. Environmental samples, especially those containing organic compounds, can be very complex. Air and water samples can contain thousands of organic compounds at a wide range of concentrations, and a considerable amount of analytical skill is usually required to identify and quantify those compounds.

Gas chromatography/mass spectrometry, (GC/MS), is the most widely used technique for the analysis of organic compounds in complex mixtures. Before the advent of GC/MS, it was impractical to consider a complete qualitative analysis on an organic mixture of twenty or more compounds (1). With the development of high resolution gas chromatography and computerized data systems to accumulate and manipulate mass spectral data, GC/MS now provides the ultimate tool for the general analysis of trace organic compounds in complex mixtures (2).

GC/MS has several advantages, including high sensitivity and high selectivity. Structural information is obtained from the mass spectral data, and with the use of a computer, it is possible to match sample spectra with those of known standards. The computer also aids in the storage of mass spectral data for future use. In addition to supplying

qualitative information, GC/MS also provides quantitative data (2).

GC/MS does have some disadvantages. One of the major disadvantages is that the technique requires relatively expensive instrumentation. Some of the problems with the technique include those resulting from limitations of gas chromatography and mass spectrometry as individual techniques. For example, it is often difficult to distinguish between chemical isomers using mass spectrometry because of the similarity of the spectra (2). Another problem with mass spectral analysis is that in most cases, the compound entering the mass spectrometer must be fairly pure in order to obtain an accurate mass spectrum. The requirement of a pure compound places a great demand on the gas chromatographic separation using GC/MS, especially when complex mixtures are analyzed. Great technological advances have been made with respect to columns for gas chromatography, especially in the development of glass capillary columns and the highly-rated fused silica columns (3). However, even with the best columns available, it is often impossible to separate all of the components of complex mixtures such as those obtained from petroleum and coal liquids.

Because GC/MS cannot always provide all of the information needed to characterize a sample completely, other analytical techniques are often used to give additional data. One technique which has been used since the early stages in development of chromatographic methods involves the use of subtractive columns (4). These columns remove various types of compounds by a physical or chemical interaction in the gas phase (5). When used in conjunction with gas chromatography, subtractive

columns can provide qualitative information. Mercury, silver, and palladium salts have been used to remove unsaturated hydrocarbons from gas streams (4,6-12). Materials such as N,N-bis(2-cyanoethyl)-formamide, 1,2,3-tris(2-cyanoethyl)propane, and various other cyano-substituted liquid phases used in gas chromatography, have been used in combination with other subtractive columns to separate aromatics, olefins, and paraffins (13-19). Subtractive columns have also been developed for amines (20-23), acids (24-26), alcohols (24,27,28), and carbonyl compounds (6,24,27,29-31).

Another technique used to obtain qualitative information involves the chemical conversion of compounds in solution. With this technique, various chemical reagents are used to convert certain types of compounds into derivatives which can either be removed or analyzed along with the other compounds in the solution. One of the most common chemical conversions involves the derivatization of carbonyl compounds with hydrazine reagents (32-47). Other derivatizations include the bromination (48,49) and nitrosation (50) of olefins, and the formation of acetals from aldehydes (5). The separation of olefins from cycloparaffins by chemical conversion is especially important in mass spectral analysis because the two types of compounds have similar mass spectra.

Selective gas chromatography detectors have been used to provide qualitative and quantitative information (5,51,52). Compounds containing sulfur or phosphorus can be measured with flame photometric detectors (53-59). The electrolytic conductivity detector can also be used to analyze sulfur compounds (60). Electron capture detectors can be used

to measure polynuclear aromatic hydrocarbons (PAH's) and compounds containing electronegative functionalities (55,59,61,62). Other selective detectors include nitrogen detectors (55,63,64), photoionization detectors (10 electron-volt lamp) (65), and ultraviolet gas cell detectors (66,67).

Specialized mass spectrometric techniques can provide qualitative and quantitative information. High resolution mass spectrometry is useful in determining accurate molecular weights of various compounds (68-70). Chemical ionization mass spectrometry, (CIMS), can also provide molecular weight information (71-75). Chemical ionization mass spectra result from ion/molecule reactions that occur between a low-pressure sample gas and the primary ions of a high-pressure reactant gas such as methane. Both gases are introduced into the ion chamber of the mass spectrometer where the gases are bombarded by an electron beam. Because of the low abundance of the sample, virtually all primary ionization due to electron bombardment occurs with the reactant gas. The ionized reactant gas then undergoes ion/molecule reactions with itself to form a steady-state plasma which in turn ionizes the sample molecules (1). Because it yields fairly simple mass spectra, CIMS can often be used to analyze mixtures of organic compounds without having to separate the individual components by a chromatographic method. However, CIMS would not be very useful in determining the structures of the various components of a mixture.

In some cases it is possible to analyze mixtures directly using electron impact ionization. For example, aromatic compounds can be determined in the presence of aliphatic hydrocarbons by using a low ionizing voltage ($\leq$12 electron-volts) (76,77). The analysis is made

possible by the fact that the ionization potentials of aromatic compounds are usually 2-4 electron-volts below those of aliphatic compounds.

Another technique used in mass spectrometry to analyze classes of organic compounds is single ion monitoring (2,78-80). Many classes of compounds have characteristic fragmentation patterns in mass spectrometry. Because of this, it is often possible to measure a class of compounds by monitoring an ion (or group of ions) with a mass-to-charge ratio (m/z) which is indicative of that class of compounds. For example, m/z 85 is usually chosen to monitor alkanes. Phthalates usually have a strong signal at m/z 149, and methyl esters have a characteristic ion at m/z 74. PAH's can be measured by monitoring the molecular ions.

During the past few years, a technique which uses two mass spectrometers has been developed. This technique, known as mass spectrometry/mass spectrometry (MS/MS), appears to be promising for the analysis of complex hydrocarbon mixtures (81,82). The first mass spectrometer is used to separate sample ions. One of those ions is then focused into a region where metastable decompositions, or those induced by a collisional activation gas, yield fragment ions whose mass-to-charge ratios and abundance values are measured by the second mass spectrometer. The mass spectrum obtained is characteristic of the parent ion.

Another technique which has been developed recently involves the combination of a Fourier transform infrared spectrometer (FT-IR) with a gas chromatograph (GC/FT-IR) (83-85). GC/FT-IR is very useful in providing information which is complementary to that obtained with GC/MS analysis. For example, isomers which usually cannot be

distinguished by mass spectrometry can often be distinguished by infrared spectrometry. Computerized identification systems have been developed to aid in the interpretation of the infrared spectra (86,87). Unfortunately, it is still difficult to identify unknowns because of the lack of vapor-phase infrared spectra of known compounds (85).

Techniques which probably allow for the maximum characterization of a given sample involve the use of fractionation (88). Various chromatographic methods have been used to separate complex mixtures. Such methods have been used for a long time. In fact, the early history of the fractionation of crude petroleum samples predates by several years the independent development of chromatography by Tswett in 1906 (89).

Most of the early development of fractionation methods was associated with the petroleum industry. One of the first methods for fractionating hydrocarbons involved the use of a distillation apparatus developed by Podbielniak (90). The distillation column used in the apparatus was made from a long pyrex tube having a diameter of 3.8mm. A coil of wire was wound around the inside wall of the tube to provide a large surface area for vapors to condense.

In 1927 the American Petroleum Institute began a study (A.P.I. Research Project #6), the purpose of which was to develop methods to separate, identify, and quantify the constituents of petroleum. The study lasted until the late 1960s, and it led to the development of liquid-solid, liquid-liquid, and gas-liquid chromatographic methods. One of the important methods developed during the 1950s was called the

Fluorescent Indicator Adsorption (FIA) analysis. The FIA method was used to separate gasoline-range mixtures into saturates, olefins, and aromatics. The sample and a mixture of fluorescent dyes were placed on the top of a silica gel column and were eluted with isopropyl alcohol. The mixture of dyes made the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light (89).

Several different types of liquid-solid chromatographic methods have been used to fractionate complex mixtures of organic compounds. These types include adsorption chromatography, gel permeation chromatography (GPC), ion-exchange chromatography, and coordination chromatography. The most widely used adsorption materials are silica gel, alumina, Florisil (see Appendix), and charcoal. These materials are used to separate organic compounds on the basis of polarity. GPC, on the other hand, is used to separate compounds on the basis of molecular size. Commercially available GPC materials include Styragel (see Appendix), Poragel (see Appendix), and Bio-Beads (see Appendix). Another popular material for liquid-solid chromatography is Sephadex LH-20 (see Appendix). Sephadex can be used to separate compounds on the basis of molecular size and/or polarity. Ion-exchange resins can be used to separate acids or bases from neutral compounds. Coordination materials separate specific types of compounds by complexation. Examples of compounds which have been separated by complexation include olefins, PAH's, and neutral nitrogen compounds (91).

Liquid-liquid chromatography (LLC), or solvent partitioning, is also widely used to fractionate complex mixtures. This method separates

compounds in an organic solvent on the basis of solubility in another liquid phase (usually aqueous). Acids and bases can be separated by controlling the pH of the aqueous phase. Other types of compounds can be separated by converting them to water-soluble derivatives with a chemical reagent. Some compounds can also be separated by partitioning between two organic solvents. The most common method using two organic solvents involves the separation of PAH's from aliphatic materials.

LLC methods have several disadvantages. It is often necessary to remove the organic solvent prior to analysis. Such concentration steps can result in losses of volatile compounds (92). Emulsions can cause problems in LLC methods. Another problem with liquid-liquid methods is that they require a great amount of sample manipulation, and this can lead to losses of compounds and to chemical alterations of compounds (93). Compounds can also be introduced into the sample if the solvents and reagents used are not pure.

Liquid-solid methods have many of the same problems which the liquid-liquid methods have. In addition, irreversible adsorption can occur in liquid-solid methods (92). In reality no fractionation method is totally free of problems. In a paper published in 1968, Snyder and Buell (94) stated that little attention had been given in the past to the evaluation and optimization of fractionation procedures. In 1978 Garrison et al. (95) expressed a similar opinion. Also in 1978, Bursey et al. (93) stated that the literature provided little data regarding the problems of alteration of samples during solvent partitioning methods. They also stated that a considerable amount of work needed to

be done to "precisely define the percent recoveries of specific chemical classes utilizing solvent partitioning schemes in combination with other analytical operations."

The purpose of this research effort was to provide more information about the feasibility of liquid-liquid chromatographic methods for fractionating organic compounds in complex mixtures. A liquid-liquid fractionation method based upon well-known chemical reactions has been developed. Organic compounds, representing several chemical classes, were used to determine how much material would be lost during the fractionation and to determine how well the various compound types could be separated from each other. The problems with blanks and formation of artifacts were also examined. The advantages of using the liquid-liquid fractionation method as a pre-separation method for GC/MS were shown for the analysis of real samples, including gasoline, diesel fuel, and exhaust from internal combustion engines using those fuels.

FRACTIONATION OF ORGANIC COMPOUNDS IN COMPLEX MIXTURES

Evaluation of Fractionation Methods

Numerous methods for fractionating organic compounds in complex mixtures have been proposed. These methods make use of a wide variety of chromatographic techniques, including adsorption, partition, size-exclusion, and ion-exchange (96). Chromatographic methods used to fractionate mixtures include liquid-liquid extraction, column chromatography, thin layer chromatography, and paper chromatography (97). Fractionation methods have been used to study specific classes of compounds in a wide variety of samples. For example, methods have been developed to isolate PAH's in particulate matter (98), cigarette smoke (99), and environmental samples (100). The optimum conditions for separating the compounds of interest depend upon the nature of those compounds and upon the sample matrix. It is very unlikely that a fractionation method would yield good results with all types of samples. While it may not be possible to develop an ideal fractionation method, it is helpful to examine the characteristics which such a method would have.

Quantitative recovery

In an ideal fractionation method, the sample components should be recovered completely. Components of a sample are often present in trace amounts; a significant loss of such components during the fractionation step would make their detection and identification difficult, if not impossible. A complete recovery of sample components would obviate

the need for internal standards, such as isotope-labeled compounds, during the fractionation, and thus, would greatly simplify the quantification procedure.

Reproducible results

A fractionation method must be reproducible if accurate quantitative data are to be obtained. Two aliquots of a sample should provide the same results. An ideal fractionation method would give reproducible results irrespective of the sample matrix.

Simplification of mixture

One of the major reasons for fractionating a mixture is to make the identification and quantification of sample components less difficult. Samples containing a large number of components are often difficult to analyze directly by instrumental techniques. A fractionation method can subdivide a sample into fractions which are analyzed more easily by the use of the instrumental techniques. In an ideal fractionation method, all of the sample components would be separated completely from each other.

Chemical information

In addition to simplifying a mixture, a fractionation method should provide information about the components of the mixture. Liquid chromatography methods making use of adsorption materials can often provide information about the polarity of the sample components. Size-exclusion chromatography can provide information about the molecular size of sample components. A knowledge of the molecular size of sample

components is helpful in determining whether they can be analyzed by gas chromatography. Chromatographic methods which separate compounds on the basis of the interaction of functional groups with various reagents can supply information about the chemical classes of compounds in samples. In general, information about the chemical class of a particular compound is more useful than information about its polarity or molecular size. This is especially important when fractionation is used as a pre-separation method for GC/MS. For example, the knowledge that a compound is an aldehyde would probably eliminate more possibilities of the compound's identity on the basis of mass spectral data than would knowledge of the compound's size or polarity.

Introduction of impurities

A fractionation method should not introduce impurities into a sample. The introduction of impurities into a sample could make it more difficult to identify the sample components and could cause problems with quantification. Impurities are especially troublesome when they are present at concentrations approaching those of the sample components. Fractionation methods which have several separation steps in sequence are often troublesome because impurities introduced into the sample during each fractionation step can accumulate in the process of the fractionation. Solvents, reagents, and chromatographic columns should be purified before use. Because of the possibility of the introduction of impurities into a sample, a blank should be fractionated along with the sample.

Alteration of sample

Sample components should not be altered during the fractionation. The alteration of sample components is usually a more serious problem than is the introduction of impurities. In samples containing many components, it is often difficult to know when alterations have occurred. Therefore, it is important that fractionation methods be tested very thoroughly with known compounds to determine the likelihood of sample alteration.

Solute concentrations

The ideal fractionation method would be applicable for samples having components with a wide range of concentrations. Components of "real" samples are rarely present at the same concentration. In fact, it is not uncommon for sample components to be present at concentrations which differ by several orders of magnitude. The analysis of trace components in the presence of major components can be very difficult. Fractionation can often simplify mixtures enough so that the analysis of trace components is possible. Fractionation methods should be equally suitable for compounds at parts-per-billion (ppb) levels as well as for those present at percent levels.

Number of steps

The number of fractionation steps should be kept to a minimum. The best separation scheme is that which provides the necessary detail of information in the least number of fractions (101). Sample component losses, sample alterations, and impurity introductions are more likely

to occur when several fractionation steps are used. There is a trade-off between minimizing the number of fractionation steps and maximizing the amount of information obtained about the sample. It is usually desirable to maximize the analytical separation method, such as gas chromatography, so that fewer fractionation steps are needed (102).

Cost

The cost of fractionating a sample is usually not very important, especially when expensive identification methods, such as GC/MS, are used. However, the cost is important when deciding between two fractionation methods which both give acceptable results. In such a case it is desirable to use the less expensive method.

Review of Related Work

One of the most widely used fractionation methods involves the separation of acids, bases, and neutral compounds using liquid-liquid chromatography. Acids and bases have been separated from coal-derived asphaltenes by passing dry HCl gas through a toluene solution of the asphaltenes (103,104). The basic components precipitate, while the acidic components stay in solution. Fentiman separated acids and phenols from other compounds in marihuana smoke condensate by dissolving the sample in methylene chloride, extracting with saturated $NaHCO_3$ solution, and extracting with 0.1N sodium hydroxide solution (72). Hruza et al. used a solution of $NaHCO_3$ to separate acids from an ether solution of hickory wood smoke (105). Ishiguro et al. used 10% sodium hydroxide solution and 5% sulfuric acid to extract acids and bases, respectively,

from an ether solution of tobacco smoke (63,106,107). The phenols were then separated from the acids by saturating the sodium hydroxide solution with carbon dioxide and extracting with ether. The phenols could also be separated after the acids by extracting the sample with 5% $NaHCO_3$ solution, then with a solution of sodium hydroxide. Jones et al. separated marihuana smoke condensate into acids, bases, and neutral compounds by extraction of a CH_2Cl_2-acetone solution of the smoke with 10% HCl and 5% NaOH solution (108). Phenols were separated from acids by adding $NaHCO_3$ to the acidified sodium hydroxide extract and extracting with ether. Maskarinee et al. and Kornreich et al. used similar methods to analyze acids in marihuana smoke and phenols in wood smoke, respectively (109,110). Acid-base-neutral methods have also been used to analyze organic compounds in air samples (111), nitrogen compounds in coal liquids (112), and polynuclear aza compounds in automobile exhaust (113).

Chemical reagents can be used to separate various classes of organic compounds. In liquid-liquid partitioning, compounds can often be extracted by converting them to water-soluble derivatives. For example, many aldehydes and methyl ketones can be separated from other types of compounds by a reaction with bisulfite ions (114,115). The aldehydes and methyl ketones react to form bisulfite addition products which are water soluble. The bisulfite reaction is actually an equilibrium which is more favorable for aldehydes than for ketones:

$$RCH + NaHSO_3 \rightleftharpoons R-\underset{\displaystyle OSO_2^{\ominus}\ Na^{\oplus}}{\overset{\displaystyle OH}{\overset{|}{C}}}-H \qquad [1]$$

After being extracted into an aqueous phase, the bisulfite addition products can be hydrolyzed with acid or base to regenerate the original compounds.

A chemical reagent which has often been used to isolate ketosteroids is (carboxymethyl)trimethylammonium chloride hydrazide, more commonly known as Girard's Reagent T (46,47,116). Girard's Reagent T reacts with carbonyl compounds to form water-soluble hydrazones:

$$RC(=O)R_1 + H_2NNHC(=O)CH_2\overset{\oplus}{N}(CH_3)_3\ Cl^{\ominus} = RC(=NNHC(=O)CH_2\overset{\oplus}{N}(CH_3)_3\ Cl^{\ominus})R_1 + H_2O \quad [2]$$

The Girard T hydrazones are commonly formed in 10% acetic acid in either ethanol or methanol using a large excess of the reagent as a 5-10% solution. The solution is then refluxed for 20-30 minutes. Solutions of the Girard T hydrazones are stable in nearly neutral solution (pH 6.5-7), but are readily hydrolyzed in acid medium. After reacting the carbonyl compounds with Girard's Reagent T, the cooled solution is titrated with aqueous NaOH to neutralize about 90% of the acetic acid, using bromothymol blue as an indicator if necessary. The solution is then diluted with water to give a 10-20% aqueous solution and is extracted several times with a nonhydroxylic solvent to remove the noncarbonyl compounds. The carbonyl compounds are usually regenerated by acidifying the aqueous solution and extracting with an organic solvent. However, some carbonyl compounds will decompose during the hydrolysis. For example, Teitelbaum found that citral, a mixture of geranial and neral, would decompose to form p-cymene during the acid hydrolysis of the Girard T hydrazones (117). He suggested using

an excess amount of formaldehyde to regenerate carbonyl compounds. Also, he used a cation-exchange resin as an acid catalyst instead of acetic acid. The resin could be removed easily by filtration. Gadbois et al. used formaldehyde to regenerate carbonyl compounds from the Girard T hydrazones (118), and later, they developed a method for generating the formaldehyde from methylolphthalimide (119). Stenlake and Williams did a study of the Girard T reaction in different solvents (45). They found that many Girard T hydrazones could be formed from aldehydes in ethanol, while other less-reactive carbonyl compounds required 10% acetic acid in ethanol. Osman and Barson did a study of the reaction of farnesyl acetone with Girard's Reagent T and found that some of the hydrazone formed was hydrolyzed during the extraction of noncarbonyl compounds (39). They suggested using dimethyl sulfoxide (DMSO) as a solvent instead of ethanol. The noncarbonyl compounds could be extracted from the DMSO solution with hexane. The carbonyl compounds were recovered by adding water to the DMSO solution, heating, and extracting with hexane. Gaddis et al. found that the Girard T reaction in ethanol or methanol gave a high blank (35). They attributed part of the blank to an impurity in the Girard's Reagent T, but the major part was found to be caused by a reaction of the reagent with the primary alcohols used as solvents. t-Butyl alcohol was proposed as a better solvent.

Several different liquid chromatographic materials have been used to fractionate organic compounds in complex mixtures. The most popular material is silica gel. By eluting a sample on the top of a silica

gel column with solvents of increasing polarity, it is possible to separate the sample components into fractions of increasing polarity. In 1955 Rosen and Middleton developed a method for fractionating petroleum refinery wastes in water (120). Using silica gel, they separated mixtures into aliphatic, aromatic, and polar fractions by eluting with isooctane, benzene, and chloroform-methanol (1:1), respectively. Lao et al. used the procedure to isolate PAH's from airborne pollutants (121). Boyer and Laitenin used silica gel to separate organic materials in automobile exhaust into six fractions (122). The eluents they used were pentane, pentane-ether (1:1), ether-acetone (1:1), and acetone-methanol (1:1). Jones et al. used silica gel to separate mixtures into eight fractions (123). The eluents which they used and the types of compounds found in each fraction are listed in Table 1. Bertsch et al. separated the materials in coal-derived fluids into nonpolar and polar fractions with a silica gel column and hexane and benzene as eluents (124). Ciacco et al. used 5% benzene in hexane, chloroform, isopropyl alcohol, methanol, acetone, and hot acetone to fractionate organic materials obtained from particulate matter (125). Severson et al. fractionated tobacco extracts on a silica gel column with hexane, benzene-hexane (1:3), and benzene-ether (3:1) as eluents (126). Silica gel fractionation methods have been used to isolate alkanes from high-boiling hydrocarbon mixtures (127) and PAH's from soot samples (128). In addition, silica gel has been used to fractionate the organic compounds in diesel exhaust (129-132).

Another chromatographic adsorbent which is frequently used to

Table 1. Silica gel fractionation of Jones

Fraction Number	Eluent	Compounds Eluted
1	Petroleum Ether	Aliphatic Hydrocarbons
2	20% Methylene Chloride in Petroleum Ether	Aromatic Hydrocarbons, PAH's Polychlorinated Biphenyls, and Halides
3	50% Methylene Chloride in Petroleum Ether	Esters, Ethers, Nitro Compounds, and Epoxides
4	Methylene Chloride	Phenols, Esters, Ketones, Aldehydes, and Phthalates
5	5% Methanol in Methylene Chloride	Phenols, Alcohols, Phthalates, and Amines
6	20% Methanol in Methylene Chloride	Amides, Sulfonates, Aliphatic Acids, and Carboxylic Acid Salts
7	50% Methanol in Methylene Chloride	Sulfonates, Sulfoxides, and Sulfonic Acids
8	Methanol	Sulfonic Acids

fractionate complex mixtures is alumina. Sawicki et al. used pentane with increasing concentrations of ether to elute compounds in particulate matter extracts from a column of alumina (133). Karasek et al. used a similar procedure to fractionate organic compounds obtained from diesel exhaust particulates (134). Brown et al. used cyclohexane, cyclohexane-benzene (4:1), benzene, and benzene-methanol (1:1) as eluents in the alumina fractionation of automobile exhaust, gasoline, and crankcase oil (135). Sorrell and Reding used alumina to isolate PAH's obtained from water samples (136). They used pentane, 25% methylene chloride

in pentane, 50% methylene chloride in pentane, 75% methylene chloride in pentane, and methylene chloride as eluents. Zdrojewski et al. (137) and Cleary (138) used alumina to separate PAH's obtained from particulate matter. Spears et al. (139) and McPherson et al. (48) used alumina to isolate alkanes from cigarette smoke and airborne particulates, respectively. They removed unsaturated compounds using alumina after the compounds were brominated. They separated branched alkanes from the normal alkanes by using molecular sieves. Hoffman and Rathkamp used a column of alumina to isolate nitrobenzenes from other compounds in cigarette smoke (140). Wilmhurst used alumina fractionation and gas chromatography to analyze PAH's in mixtures (141).

Silica gel adsorption and alumina adsorption techniques are often combined in factionation methods. Snyder developed a method for separating petroleum into saturates, monoaromatics, diaromatics and aliphatic monosulfides, polyaromatics and polyfuctional sulfides, and oxygen and nitrogen compounds on alumina (142). He then combined the method with silica gel fractionation to separate petroleum into many more fractions (143-145). Grimmer and Hildebrandt used silica gel fractionation, paper chromatography, and alumina fractionation to analyze PAH's in foodstuffs (146). Popl et al. (147) and Moore et al. (148) combined silica gel and alumina fractionation methods to analyze PAH's in white petroleum products and in airborne pollutants, respectively. In most cases, PAH's are separated from other compounds on the silica gel column, while the individual PAH's are separated on the alumina column. Alumina usually has a better selectivity for

Table 2. Florisil fractionation of Kissinger

Fraction Number	Eluent	Compounds Eluted
1	2% Methylene Chloride in Petroleum Ether	Aliphatic Hydrocarbons, Aromatic Hydrocarbons, and Halides
2	60% Methylene Chloride in Petroleum Ether	Nitro Compounds, Carbonyl Compounds, Esters, Nitriles, Phenols, and Amines
3	2% Acetonitrile - 60% Methylene Chloride in Petroleum Ether	Carbonyl Compounds, Phthalates, Alcohols, Amines, Nitriles, and Polyfunctional Compounds

unsaturated compounds than does silica gel (149).

Florisil, a strongly acidic coprecipitate of silica and magnesia, has been used to fractionate organic compounds in mixtures. After it is deactivated with water, Florisil is intermediate between silica and alumina in its behavior (91). Eisner et al. used Florisil to fractionate materials in butter, margarine, olive oil, and vegetable oil (150-153). They used hexane and various hexane-ether combinations to elute the sample compounds. Kissinger developed a Florisil method for fractionating organic pollutants in drinking water. Table 2 lists the eluents used and the compound types found in the three fractions. Kissinger tested the method by fractionating model compounds dissolved in petroleum ether (at concentrations ranging from 10 parts per million (ppm) to 1 part per thousand). With most compounds, he obtained recoveries between 80% and 120%. He attributed large deviations in the results to chromatogram peak height measurements, upon which the

the recovery data were based, and upon problems with measuring solution volumes. One compound which Kissinger had difficulty eluting from the Florisil column was tributyl phosphate. Florisil has also been used to isolate PAH's in crude oils (154) and to fractionate grapefruit oils (155).

Ion-exchange resins have been used to fractionate complex mixtures. Boduszynski et al. used anion-exchange and cation-exchange resins to separate asphaltenes into acids, bases, and neutrals (156). Ellington et al. separated acids from a tobacco extract by using an anion-exchange resin (157). The neutral compounds were eluted from the resin with chloroform-methanol (1:1), and the acids were recovered by eluting with 25% formic acid in acetone. McKay et al. used a cation-exchange resin to separate bases from petroleum distillates (158).

Size-exclusion chromatography has been used to fractionate mixtures on the basis of molecular size. Size-exclusion methods were originally used to fractionate large molecules such as polymers, but with improvements in the quality of size-exclusion materials, it is now possible to separate smaller molecules. Kirkland has used silica microspheres to fractionate small molecules (159). The most useful fractionation range with the silica microspheres was molecular weights of 100 to 10,000. Kirkland and Antle have also used silica microspheres which were modified with trimethylsilane (160).

Most of the size-exclusion methods reported in the literature involve fractionations on polymeric materials. The technique which makes use of such materials is usually referred to as gel permeation chromatography (GPC). GPC is usually a good technique for separating

materials which do not exhibit sufficient differences in solubility, polarity, adsorption, or ionic characteristics essential for most other liquid chromatographic methods (161,162). Krishen and Tucker reported that GPC separations, using tetrahydrofuran as the eluent, could separate materials in the molecular weight range of 100 to 2000 in less than thirty minutes (162). A difference of one carbon atom was sufficient for satisfactory resolution of components in the low molecular weight range. One of the most widely used GPC materials is a copolymer of styrene and divinylbenzene. Nakae and Muto used the copolymer to separate alkylbenzenes and alkylbenzoates (163). They found that the elution of compounds followed the order of increasing alkyl chain length. Popl et al. used a styrene-divinylbenzene gel to separate PAH's (164). They found that adsorption effects were a factor in the separation. Hausler et al. used a styrene-divinylbenzene gel to fractionate coal liquids (165). They found that a large number of compounds, especially N-alkylated anilines, exhibited a non-size-exclusion mechanism of separation. Two of the commercially available styrene-divinylbenzene gels which have been used to fractionate a wide variety of samples are micro-Styragel (166,167) and Bio-Beads (168,169) (see Appendix for manufacturers).

One of the more versatile materials which has been used to fractionate mixtures is Sephadex LH-20 (see Appendix for manufacturer). Sephadex LH-20 is prepared by hydroxypropylation of Sephadex G-25, a bead-formed, dextran gel (170). The dextran chains are cross-linked to give a three-dimensional polysaccharide network. The hydroxypropyl groups

are attached by ether linkages to glucose units of the dextran chains. Sephadex LH-20 can be used under different conditions to separate materials on the basis of partition, adsorption, and gel filtration mechanisms. Jones et al. Used Sephadex LH-20 to fractionate crude oils derived from shale and coal (171). Their procedure involved the use of the gel in three different modes: 1) lipophilic-hydrophilic partitioning using the gel swollen with methanol-water and eluted with hexane, 2) molecular size separation using the gel swollen with tetrahydrofuran (THF) and eluted with THF, and 3) aliphatic-aromatic separation using the gel swollen with isopropyl alcohol (IPA) and eluted with IPA. Klimisch used Sepahdex LH-20 to fractionate cigarette smoke condensate (172). Sephadex LH-20 was used by Gjessing and Lee to fractionate organic matter in natural waters (173). Gladen (174) and Lee et al. (175) used Sephadex LH-20 to isolate PAH's in automobile exhaust and in airborne particulate extracts, respectively.

Gel permeation chromatography has often been used in combination with other separation methods. Cogswell et al. (176) and McKay and Latham (177) used GPC and ion-exchange methods to analyze acids in petroleum. In addition, McKay and Latham used GPC, ion-exchange, and thin layer chromatographic methods to analyze PAH's in petroleum distillates (178). Giger and Schaffner used GPC and silica gel chromatography to separate PAH's in environmental samples (179). Wakeham et al. used the method to analyze PAH's in lake sediments (77). Cukor et al. used silica gel chromatography and GPC to fractionate organic compounds extracted from particulate matter (180). Popl et al. combined

GPC and alumina chromatography with high performance liquid chromatography (HPLC) in the analysis of 3,4-benzpyrene in tars and petroleum (181).

Some types of compounds can be separated from other types by a technique known as coordination chromatography. The most widely used type of coordination chromatography involves the separation of unsaturated compounds by complexation with certain transition metal ions. Lam and Grushka treated silica gel with sodium aluminate to give a polyanionic surface which could readily exchange its counter ions for silver ions (182). They used the silver-loaded silica gel to separate unsaturated compounds, including geometric isomers. Ozcinder and Hammers (183) and Ghosh et al. (184) separated unsaturated fatty acid esters on silica gel impregnated with silver nitrate. Heath et al. packed HPLC columns with $AgNO_3$-coated silica, and used them to separate geometric isomers (185). Vivilecchia et al. impregnated a commercially available HPLC packing with silver ions, and they used it to separate polynuclear aza-heterocyclic compounds (186). They found that the column was reactive toward certain classes of compounds, including aldehydes, acids, carbazoles, indoles, and phenols. Prasad et al. coated TLC plates with silver salts and used them to separate olefins (187). Kunzru and Frei used silica gel impregnated with cadmium ions to separate aromatic amine isomers (188). They found that mercaptans, which elute from plain silica gel, reacted irreversibly with the impregnated cadmium ions. Ion-exchange resins can be used as supports for transition metal ions. Ion-exchange resins in the Ag^{+}, Ni^{+2}, Zn^{+2}, and Cd^{+2} forms show different selectivities with unsaturated hydrocarbons depending upon their nature,

degree of substitution, and pi-bonding abilities (189). Schofield and Mounts treated a macroreticular arylsulfonic acid resin with silver ions, and used it to separate unsaturated fatty acid esters (190). Warthen used a cation-exchange resin in the silver ion form to purify geometric isomers used as insect attractants (191). Other materials used in coordination chromatography include Fe(III) on clay for complexing nitrogen compounds (192), anion-exchange resins in the bisulfite form for separating aldehydes and ketones (193), and 2,4,7-trinitro-9-fluorenone for complexing PAH's (194,195).

Some classes of compounds can be fractionated by partitioning between two immiscible organic solvents. In 1960, Hoffmann and Wynder developed a method for separating aromatic hydrocarbons from aliphatic hydrocarbons (196). They used a two-step partitioning scheme: 1) polar materials were extracted from a cyclohexane solution with methanol-water (4:1) and 2) the aromatic materials were extracted from the cyclohexane solution with nitromethane. The aliphatic compounds stay in the cyclohexane. The method of Hoffmann and Wynder has been used frequently in the analysis of PAH's (64, 197-201). Davis et al. developed a method for separating aromatic compounds from aliphatic compounds which involved partitioning between hexane and acetonitrile (62,202,203). Hoffmann and Rathkamp used a hexane-acetonitrile partitioning method to analyze 1-alkylindoles in cigarette smoke (204). In addition, they developed a partitioning method using hexane and dimethylformamide-water (4:1) (205). They used the method to analyze fluorenes in cigarette smoke. Lijinsky et al. used dimethyl sulfoxide (DMSO) to extract PAH's from an isooctane

solution of petroleum wax (61). Griest et al. extracted PAH's from cyclohexane with DMSO, and they recovered the PAH's by diluting the DMSO solution with a saturated aqueous solution of calcium chloride and extracting with cyclohexane (206). Kaschani and Reiter (207) and Radecki et al. (208) used cyclohexane-DMSO partitioning to isolate PAH's from vehicle exhaust condensate and from liquid smoke preparations, respectively. Natusch and Tomkins did a study of DMSO extractions of PAH's from various nonpolar hydrocarbons (209). They found that DMSO extractions of PAH's from hexane were more efficient than those from cyclohexane, n-heptane, isooctane, and n-pentane. Because it gave extraction efficiencies close to those with hexane, and because of its greater volatility, n-pentane was selected as the optimum solvent for extracting with DMSO. By using the n-pentane-DMSO partitioning method, Natusch and Tomkins were able to separate mixtures into three fractions: 1) aliphatic hydrocarbons, 2) alcohols, phenols, and low molecular weight aliphatic and aromatic acids, and 3) PAH's, phthalates, aromatic bases, and high molecular weight aliphatic acids. The aliphatic hydrocarbons were not extracted into DMSO. PAH's, phthalates, etc. could be back-extracted from the DMSO after the addition of two volumes of water. Alcohols, phenols, and other highly-polar materials could not be back-extracted from the DMSO solution. The partition efficiencies of PAH's are governed by the extent of the interaction of the sulfur atoms in the DMSO with the pi electron systems of the PAH's. Hydrogen-bonding of the oxygen atoms in the DMSO becomes important when compounds with hydroxyl groups are present.

Thin layer chromatography (TLC) has been used to fractionate complex mixtures. The sample is spotted on a plate coated with a suitable adsorbent. The plate is then placed in a vertical position in a special developing chamber. Solvent in the bottom of the chamber moves up the plate and displaces the sample components. Compounds with different polarity characteristics move up the plate at different rates, and thus, the compounds are separated. TLC is a simple method for fractionating mixtures. One of the major advantages of the technique is that the separated sample components can be extracted from the TLC plate with a small volume of solvent, and no concentration steps are required for the next analysis step (210). TLC has been used frequently in the analysis of PAH's. Most PAH's fluoresce under ultraviolet light, and therefore, the compounds can be detected easily on TLC plates. Sawicki et al. used TLC to analyze PAH's in atmospheric pollutants (211). They studied separations of PAH's on alumina, cellulose, and cellulose-acetate TLC plates. Pierce and Katz used alumina TLC plates to isolate PAH's from atmospheric aerosols (212). The plates were developed with pentane-ether (19:1). They found that recoveries of PAH's from the alumina plates were in the range of 94% to 98%. By combining a group separation on alumina with a separation on acetylated cellulose, they were able to separate isomeric PAH's (213). Kohler and Eichhoff separated PAH's on a plate coated with a mixture of alumina and cellulose acetate (214,215). Kushnir et al. used a combined silica-cellulose TLC plate to fractionate phenols (216). Brocco et al. used silica gel to separate PAH's from other compounds in atmospheric dust (217). The

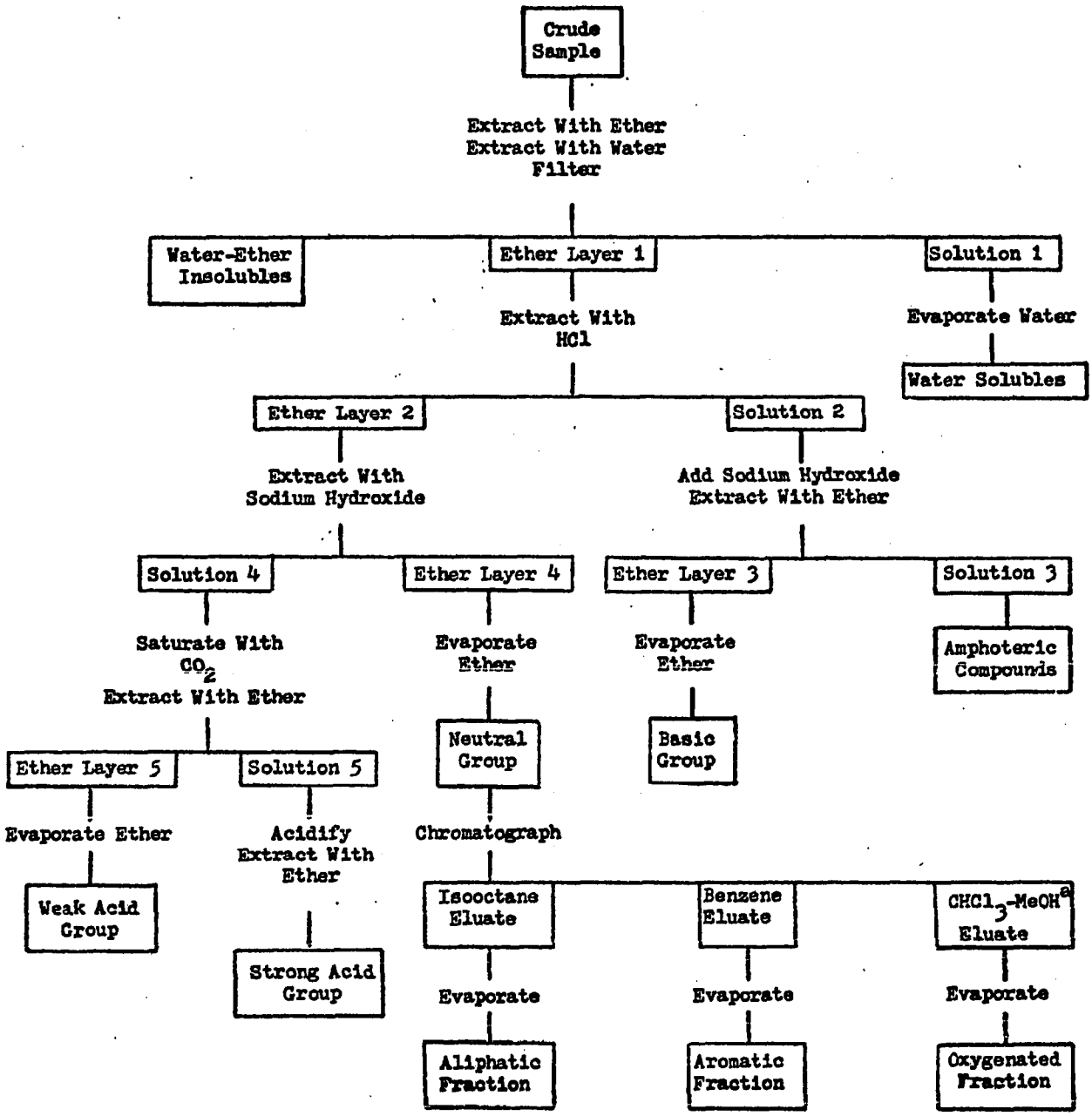
silica TLC plate was developed with cyclohexane-benzene (2:3). Dong et al. used the method to analyze PAH's in extracts from particulate matter (218). Nielsen used silica gel TLC to analyze PAH's in automobile exhaust (219). He developed the silica TLC plate with hexane, and then with toluene-cyclohexane (1:1). The hexane development kept the TLC plate from being overloaded when the sample contained high levels of nonpolar materials. Zoccolillo et al. used silica gel TLC to isolate PAH's in particulate matter extracts (220). They used hexane-benzene (1:1) as the developing solvent. Biermoth found that a mixture of PAH's could be separated into groups according to the number and arrangement of the aromatic rings by repeated development with isooctane on alumina TLC plates (221). Other thin layer chromatographic methods which have been reported in the literature include the analyses of PAH's in cigarette smoke condensate (222), liquid smoke flavors (223), air (224-226), bituminous materials (227), and automobile exhaust (228-230), and the analyses of alkanes in atmospheric dust samples (231) and in cigarette smoke condensate (232). TLC is used frequently to fractionate mixtures prior to analysis by gas chromatography. Janak used the combination in the reverse order (233). He collected fractions from a gas chromatograph by moving a TLC plate past the outlet of the gas chromatographic column.

High performance liquid chromatography (HPLC) has been used to fractionate mixtures of organic compounds. Dark et al. used HPLC to fractionate coal liquids (234,235). The combination of liquid chromatography and mass spectrometry (LC/MS) was used to characterize the

sample components. Dark and McFadden (235) used a commercially available HPLC column containing an adsorbent with an amine functionality to separate coal liquids into saturate, aromatic, and polar materials. Stevenson developed an HPLC method for separating petroleum fuels into saturates, monoaromatics, and diaromatics (236). Suatoni et al. used HPLC to separate gasoline-range hydrocarbon mixtures into saturates, olefins, and aromatics (237). They used a low-polarity perfluorocarbon mobile phase and a small-particle silica column to achieve the fractionation. Later, Suatoni and Garber developed an HPLC method for separating petroleum fractions into saturates, monoolefins, diolefins, and aromatics (238). They used two small-particle silica columns, and used hexane as the mobile phase. Suatoni and Swab developed HPLC methods for separating hydrocarbon mixtures into saturates, aromatics, polar compounds, and hexane-insoluble compounds (239,240). They used silica gel columns to separate the saturate, aromatic, and polar compounds.

The combination of acid-base-neutral fractionation and liquid chromatography on silica gel has been used frequently in the analysis of complex mixtures. In 1958, Tabor et al. used liquid-liquid chromatography to separate organic particulate matter into water-soluble, basic, strongly acidic, weakly acidic, neutral, and water-ether insoluble fractions (241). The neutral fraction was separated into aliphatic, aromatic, and oxygenated fractions by silica gel chromatography. Hauser and Pattison used Tabor's method to isolate the aliphatic materials in extracts of particulate matter (242). In 1962,

Hueper et al. used a fractionation method based upon the method of Tabor et al. (243). A schematic diagram of the fractionation method is shown in Figure 1. Bases are extracted from the sample with HCl. The acids are extracted with a solution of sodium hydroxide. The weak acids are separated from the strong acids by saturating the NaOH extract with carbon dioxide and extracting with ether. The neutral materials are chromatographed on silica gel, using isooctane, benzene, and chloroform-methanol as eluents. Cautreels and Van Cauwenberghe used a method based upon that of Hueper et al. to fractionate organic materials in airborne particulate matter (78,79). Schmeltz et al. fractionated the neutral fraction of cigarette smoke condensate on silica gel, using hexane-benzene (19:1) and hexane-benzene (1:1) as eluents (244). Vitorovic and Saban developed a method for fractionating shale bitumen (245). They separated the bitumen into acidic, basic, and neutral compounds. The neutral compounds were chromatographed on silica gel with petroleum ether, benzene, and methanol. The aliphatic materials, found in the petroleum ether fraction, were separated into normal and branched alkanes by chromatographing on molecular sieves. Walters et al. developed a method for fractionating cigarette smoke condensate (246). The condensate, in ether, was extracted with 1M aqueous NaOH and with 0.2M HCl in order to separate the mixture into acidic, basic, and neutral compounds. The neutral materials were fractionated on silica gel with petroleum ether, 25% benzene-petroleum ether, benzene, ether, and methanol. The compounds in the benzene eluate were dissolved in cyclohexane. The PAH's were extracted from the cyclohexane with DMSO.

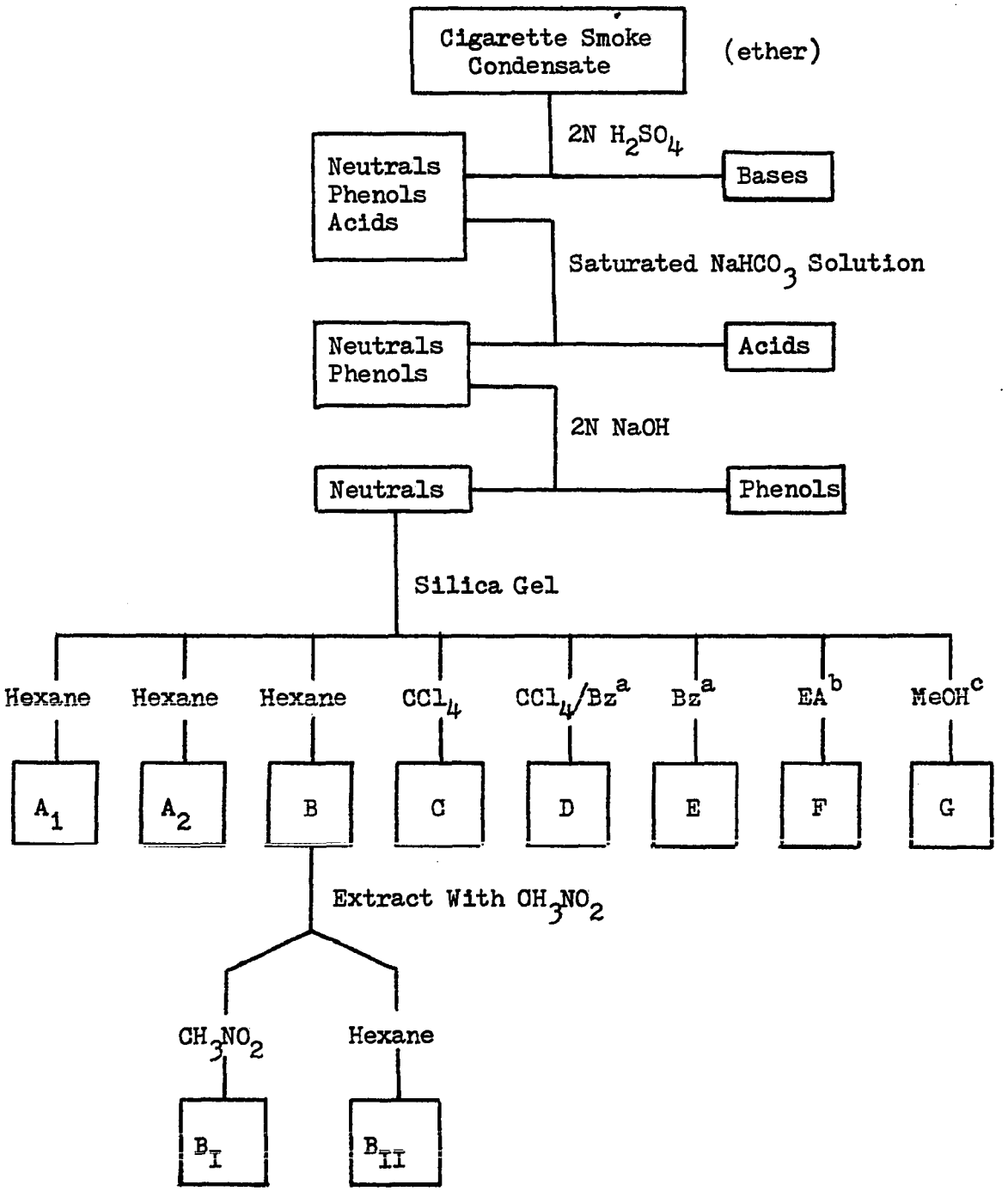


[a]Methanol.

Figure 1. Fractionation method of Hueper

The PAH's were recovered by adding water to the DMSO solution and extracting with a nonpolar solvent. The PAH's were separated by gel permeation chromatography. Several modifications of the method were made during other studies of tobacco smoke (247-250). Kettenes-van den Bosch and Salemink developed a method for fractionating marihuana smoke condensate (251). The condensate was dissolved in ether and was extracted with saturated aqueous sodium carbonate, 2N potassium hydroxide, and 1N hydrochloric acid to isolate acids, phenols, bases, and neutrals. The neutrals were chromatographed on silica gel with hexane, hexane-benzene (3:1), benzene, diethyl ether, and methanol. Brunnenmann and Hoffmann combined acid-base-neutral fractionation, silica gel chromatography, and hexane-nitromethane partitioning to isolate PAH's from air samples (252). A schematic diagram of their method is shown in Figure 2. Erickson et al. and Carugo and Rossi combined acid-base-neutral fractionation with silica gel chromatography for the analysis of diesel exhaust (253), and cigarette smoke (254), respectively.

Florisil has been used in combination with acid-base-neutral methods for fractionating complex mixtures. Bell et al. used Florisil to fractionate neutral compounds in cigarette smoke condensate (255). They used hexane, hexane-benzene (8:1), benzene-ether (4:1), and methanol to elute the neutrals from the Florisil column. The hexane-benzene eluate was fractionated further by solvent partitioning, additional separations on Florisil, and chromatography on alumina. Rubin et al. (256) combined the Florisil fractionation of Bell et al. with the



[a]Benzene.

[b]Ethyl Acetate.

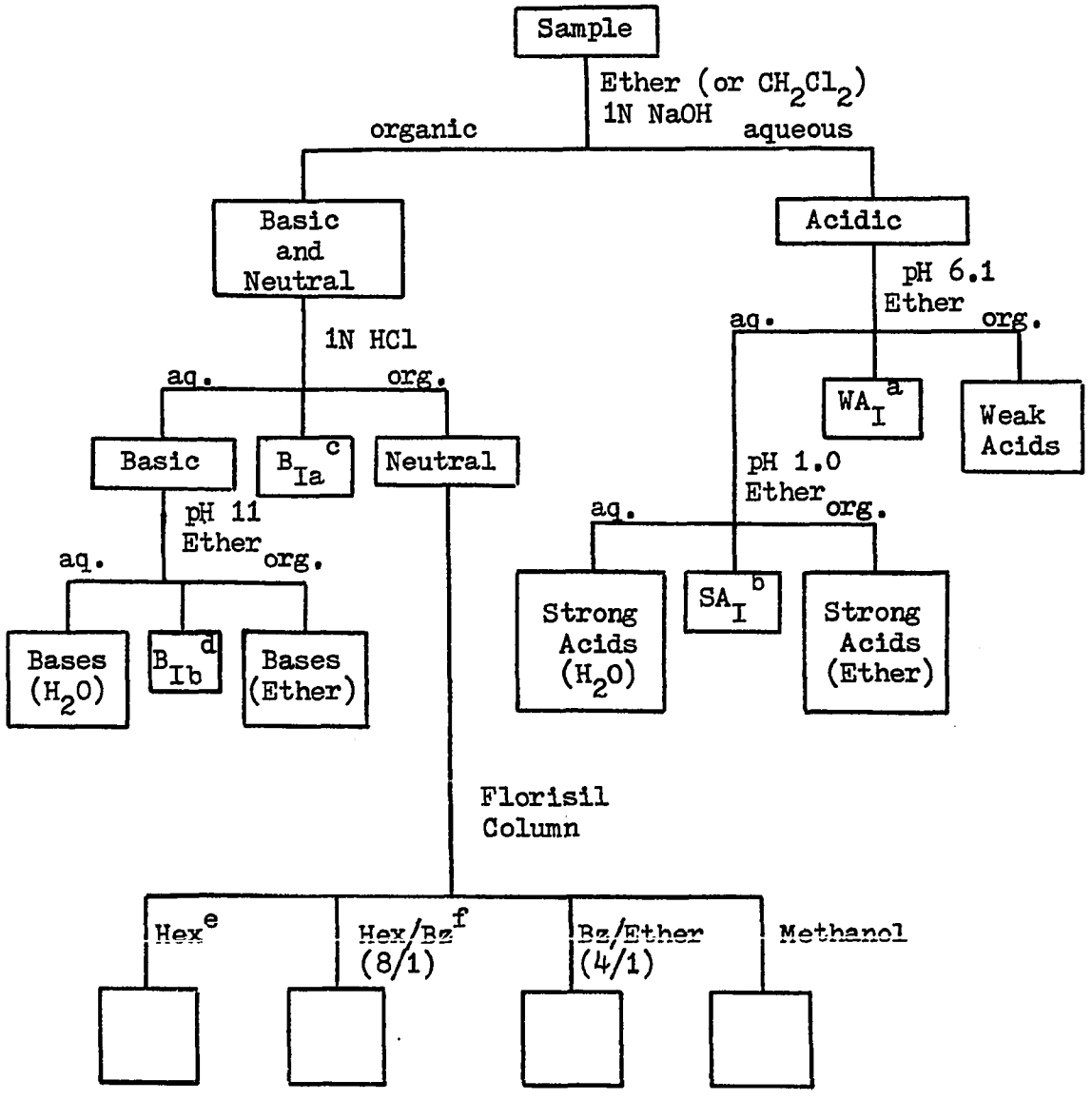
[c]Methanol.

Figure 2. Fractionation method of Brunnenmann and Hoffmann

acid-base-neutral fractionation of Swain et al. (257) in their analysis of synthetic crude oils. A schematic diagram of Rubin's method is shown is Figure 3. Hoffmann and Wynder combined acid-base-neutral fractionation, the Florisil fractionation of Bell et al., and solvent-partitioning between hexane and nitromethane in their analysis of cigarette smoke condensate (258). Haq et al. used acid-base-neutral fractionation and chromatography on Florisil to isolate nitrogen-heterocyclics in marihuana smoke condensate (259).

Combined chromatographic methods have often been used to fractionate petroleum. The American Petroleum Institute Research Project 60 group developed a separation scheme which combined ion-exchange chromatography, coordination chromatography, silica gel chromatography, and, in some cases, alumina chromatography (260-266). A diagram of the separation scheme, which is a combination of the methods of Haines et al. (260) and Jewell et al. (265), is shown in Figure 4. Acids are removed from the sample with an anion-exchange resin. The bases are removed with a cation-exchange resin. The neutral nitrogen compounds are removed by complexation with ferric chloride. The neutral compounds are separated into saturates and aromatics by using silica gel (method of Jewell et al.) or into saturates, monoaromatics, diaromatics, and polyaromatics by using silica gel and alumina (method of Haines et al.). A combination of base extraction, ion-exchange, and silica chromatography were used by Seifert and Howells in a study of the acids and phenols in crude oil (267).

Novotny et al. developed a liquid-liquid method for fractionating



[a]Weak Acid Insolubles.

[b]Strong Acid Insolubles.

[c]Base Insolubles Fraction "a".

[d]Base Insolubles Fraction "b".

[e]Hexane.

[f]Benzene.

Figure 3. Fractionation method used by Rubin

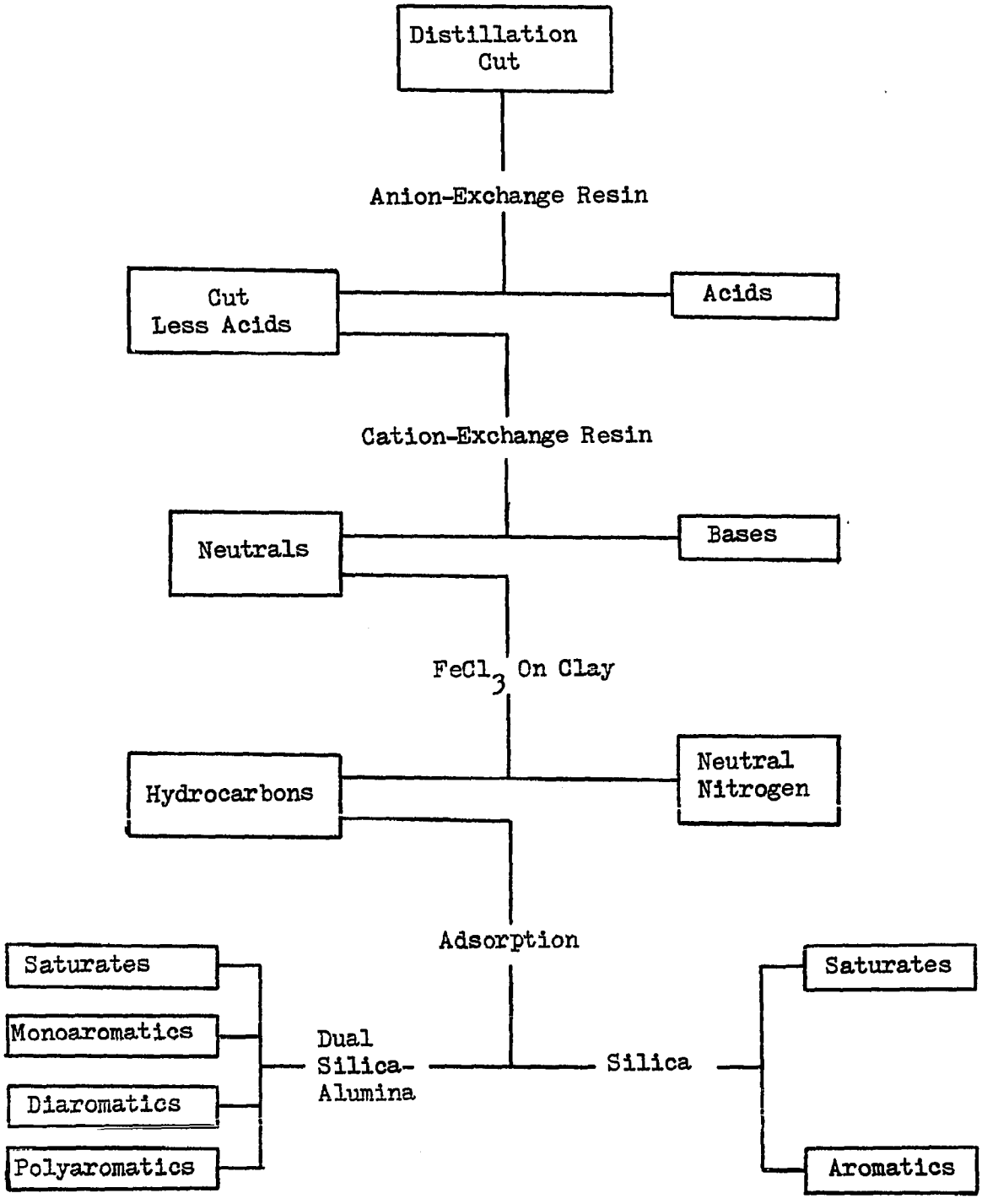


Figure 4. American Petroleum Institute Project 60 - Fractionation methods of Haines and Jewell

complex mixtures into acids, bases, neutral aliphatics, and neutral aromatics (268). They used the liquid-liquid fractionation in combination with fractionation on Sephadex LH-20 to analyze PAH's in airborne particulate matter. The liquid-liquid portion of Novotny's method is shown in Figure 5. Acids were extracted from the sample with 1M sodium hydroxide. Bases were extracted with 0.2M hydrochloric acid. The neutral compounds were separated into aliphatics and aromatics by cyclohexane-nitromethane partitioning. Lee et al. (269) and Janini et al. (270) used the method of Novotny et al. in the analysis of tobacco smoke. Klimisch and Stadler used hexane-nitromethane partitioning and chromatography on Sephadex LH-20 in their analysis of cigarette smoke condensate (271).

Fujimaki et al. developed a liquid-liquid fractionation method (272). They combined acid-base-neutral fractionation with a Girard Reagent T separation of carbonyl compounds from noncarbonyl compounds. Bases were extracted from the sample solution with 5% hydrochloric acid. The acids were extracted with 5% aqueous sodium bicarbonate, and the phenols were extracted with 5% aqueous sodium hydroxide. The carbonyl compounds were separated from the other neutral compounds by using Wheeler's method (46) (see page 16). The method, a schematic diagram of which is shown in Figure 6, was used in the analysis of wood smoke. The noncarbonyl fraction of the sample was fractionated further on silica gel with hexane, various hexane-ether combinations, and methanol eluents (273).

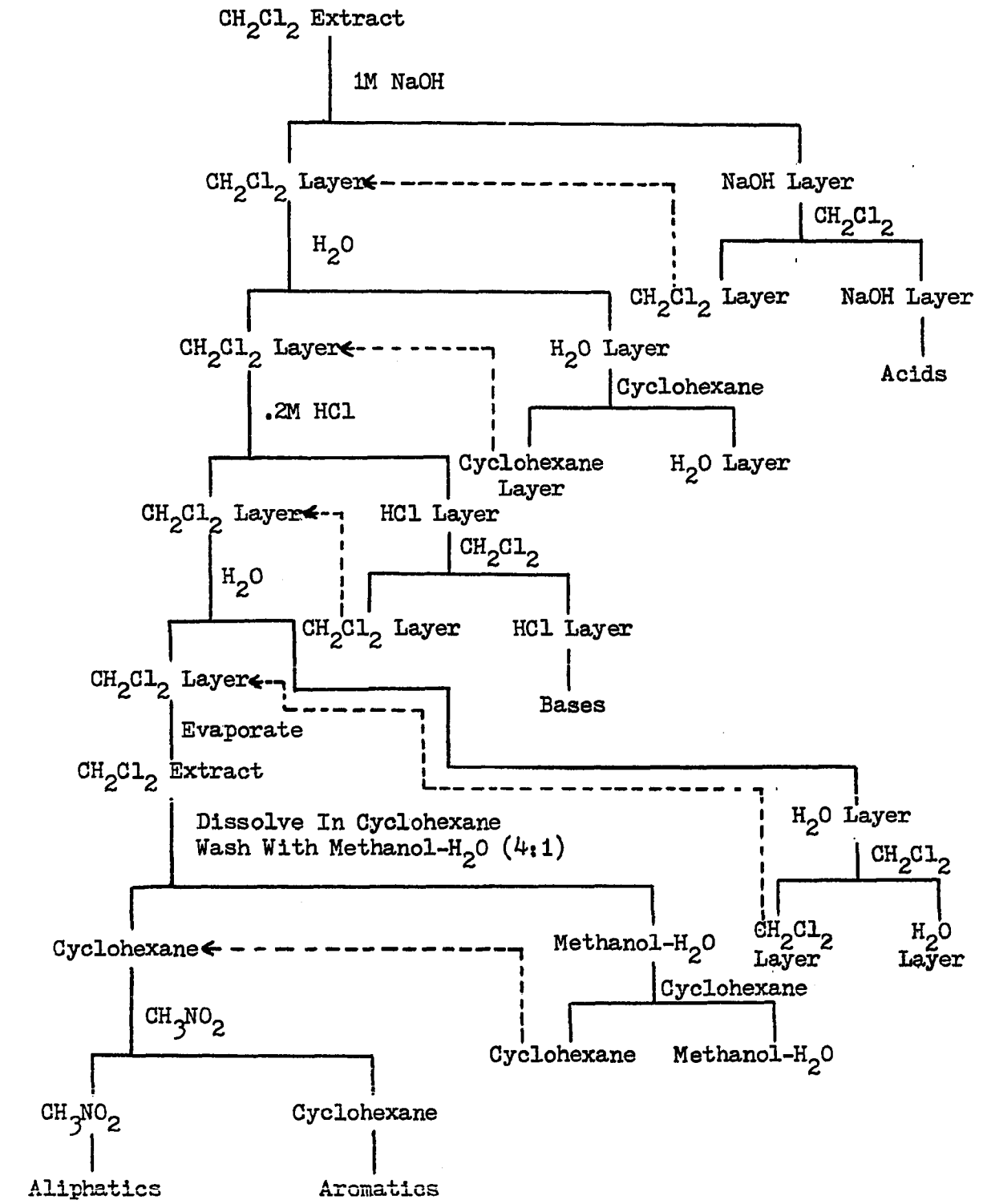


Figure 5. Fractionation method of Novotny

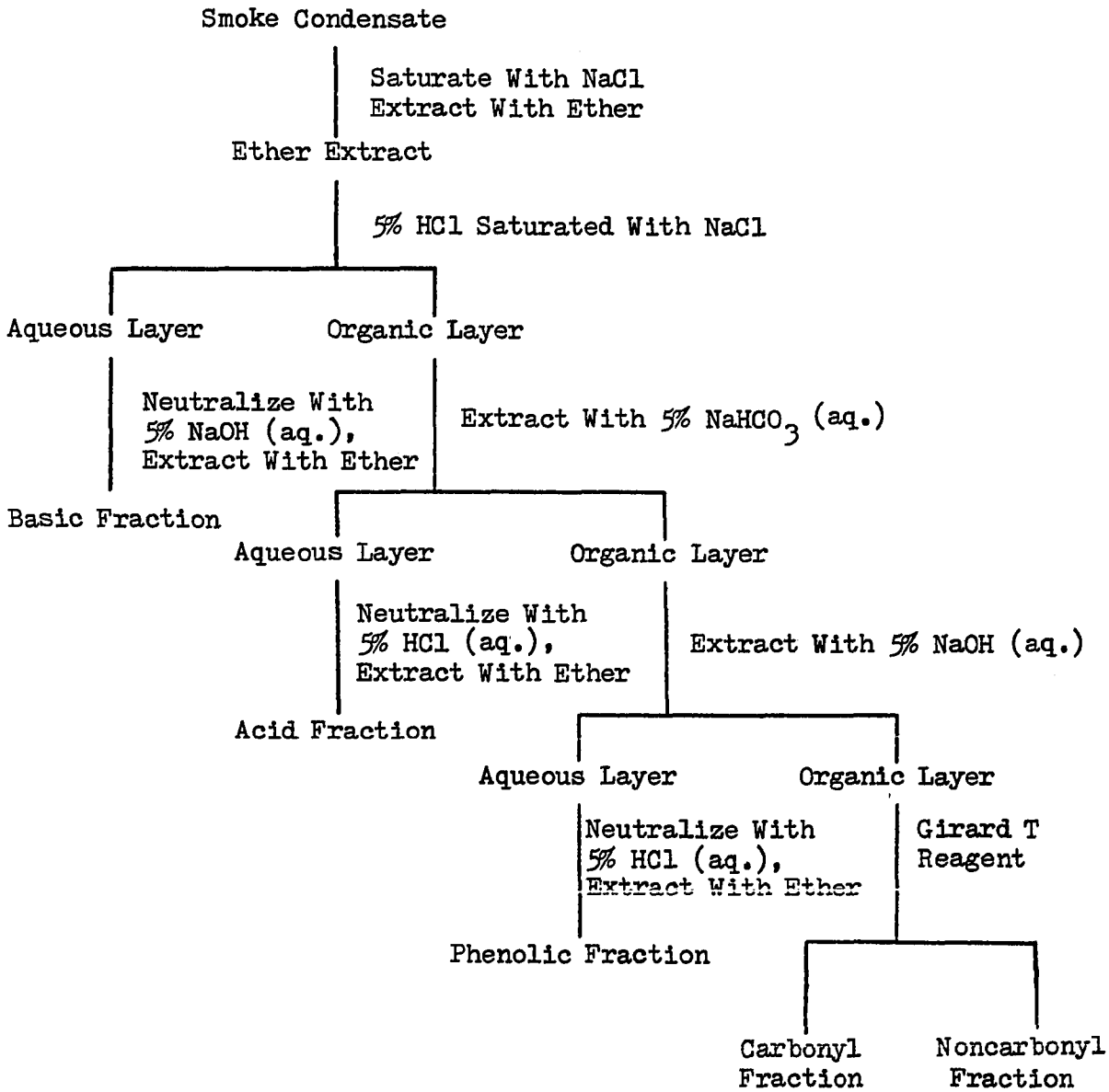


Figure 6. Fractionation method of Fujimaki

Experimental

Apparatus and reagents

Gas chromatography A Varian model 1200 gas chromatograph, equipped with a linear temperature programmer and a flame ionization detector (FID), and a Tracor model 560 gas chromatograph, equipped with a linear temperature programmer, dual columns (one packed column and one capillary column), and dual FIDs, were used for this work. Identifications of sample components were done using a Varian model 1200 gas chromatograph interfaced to a DuPont model 21-490 mass spectrometer and using a Finnigan model 4000 GC/MS instrument with an INCOS data system. All of the capillary column separations with mass spectral identification of the effluents were done using the Finnigan instrument.

Solution concentrators Kuderna-Danish evaporative concentrators (274), as modified by Junk et al. (275) were used to reduce the volumes of solutions before gas chromatographic analysis. The concentrators, equipped with three-cavity Snyder columns, were heated in a water bath at a temperature 25-30 degrees higher than the boiling point of the solvent to be removed. When the solution volumes reached about 0.5 ml, the concentrators were removed from the water bath and sprayed with acetone. In most cases, the solution volumes were adjusted to be 1.0 ml by adding the appropriate amount of solvent.

Solvents Benzene, nitromethane, and diethyl ether were obtained from Fisher Scientific Company, Fair Lawn, New Jersey. The benzene contained small amounts of toluene and xylenes, but they did not

interfere with the analysis of standards. The nitromethane contained many trace impurities, most of which could be removed by extraction with pentane (see results and discussion section). The diethyl ether was distilled to remove the anti-oxidant additive.

Cyclohexane, dimethyl sulfoxide (DMSO), methanol, methylene chloride, and pentane were "distilled-in-glass" grade obtained from Burdick and Jackson Laboratories, Inc., Muskegon, Michigan. The methylene chloride and pentane were redistilled using a three-cavity Snyder column. One bottle of methanol contained some trace impurities, which could be removed by a combination of extraction and distillation (see results and discussion section for details). The DMSO contained several sulfur compounds which were difficult to remove (see results and discussion section). The cyclohexane was used as received.

"Nanograde" hexane was obtained from Mallinckrodt, Inc., Saint Louis, Missouri.

Specially purified water was obtained by passing distilled water through a column of Amberlite MB-3 monobed ion-exchange resin (Rohm and Haas, Philadelphia, Pennsylvania), distilling over alkaline permanganate, and doubly-distilling in a quartz still.

Reagents Sodium hydroxide, potassium hydroxide, sodium bisulfite, magnesium sulfate, sodium chloride, sodium carbonate, adsorption alumina, and molecular sieves were obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Hydrochloric acid and sodium sulfate were obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Acetic acid was obtained from Matheson, Coleman, and Bell Manufacturing

Chemists, Norwood, Ohio. Amberlite IRC-50 ion-exchange resin was obtained from Mallinckrodt, Inc., Saint Louis, Missouri. Girard's Reagent T was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Brom Thymol Blue indicator was obtained from Wilkens-Anderson Company, Chicago, Illinois. Methelute, a methylating reagent, was obtained from Pierce Chemical Company, Rockford, Illinois. Boron trifluoride - methanol methylating reagent was obtained from Supelco, Inc., Bellefonte, Pennsylvania. Organic chemicals used as standards were obtained from Chem Service, Inc., West Chester, Pennsylvania; Aldrich Chemical Company, Milwaukee, Wisconsin; Eastman-Kodak Company, Rochester, New York; Pfalz and Bauer, Inc., Stamford, Connecticut; and Tridom Chemical, Inc., Hauppauge, New York.

Fractionation method

Background The fractionation method evaluated in this work was based on the fractionation method of Fujimaki et al. (272) (see Figure 6) and the DMSO-pentane partitioning method of Natusch and Tomkins (209) (see p. 27). A schematic diagram of the acid-base-neutral fractionation is shown in Figure 7. A schematic diagram of the fractionation of neutral compounds is shown in Figure 8. The fractionation method was altered several times during the course of this research effort. Initially, nitromethane was used instead of DMSO during the polar-non-polar fractionation, and sodium bicarbonate was used instead of sodium carbonate during the extraction of strong acids. The schematic diagrams in Figures 7 and 8 outline the fractionation method in its final form. In addition, the procedure in the next section is given in its final form.

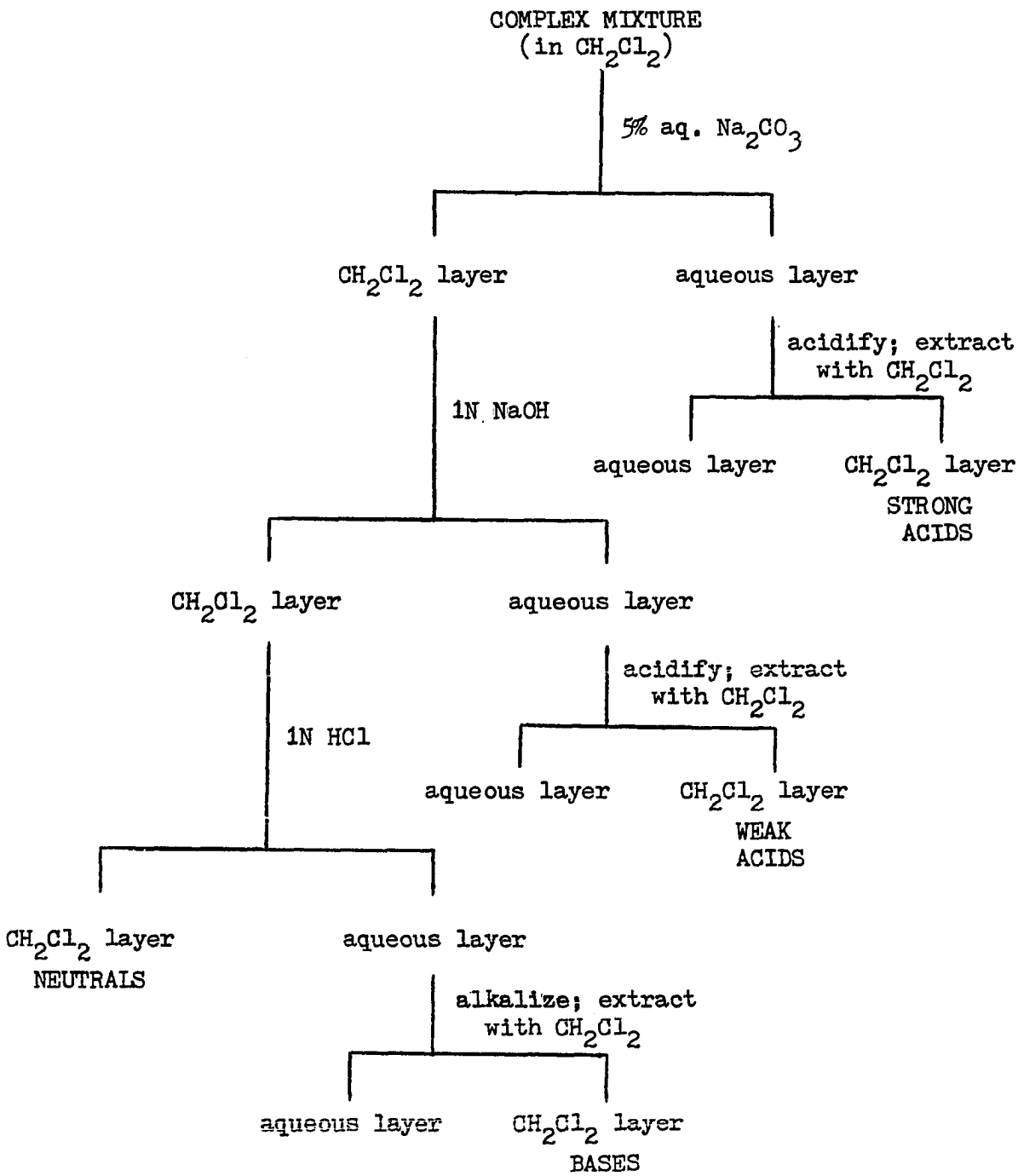


Figure 7. Acid-base-neutral fractionation scheme flow chart

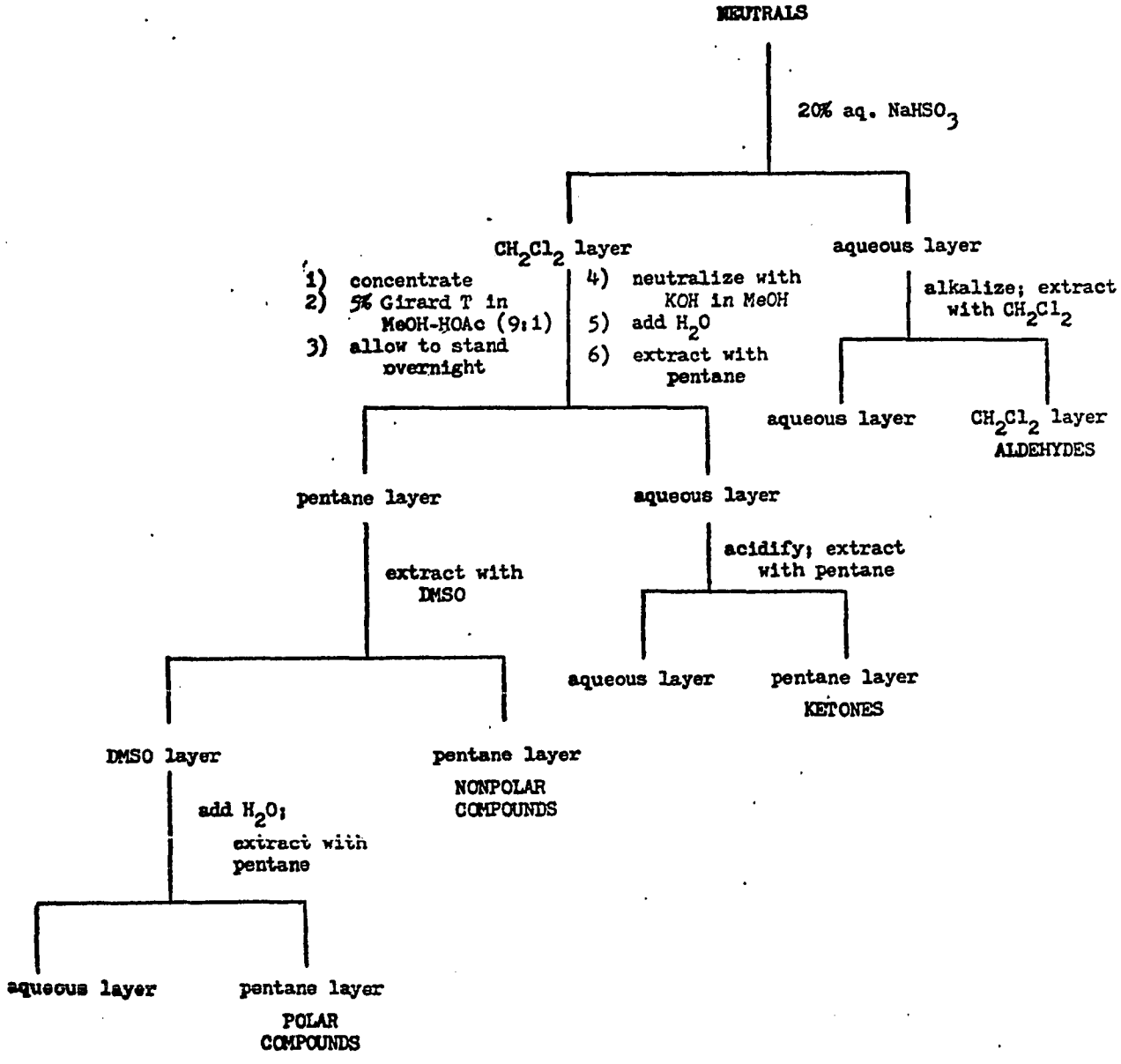


Figure 8. Neutrals fractionation scheme flow chart

Fractionation procedure Place 30 ml of a methylene chloride solution of the sample to be fractionated in a 125 ml separatory funnel, (#1), (ideally, the concentration of each sample component should be at least 10 ppm). Place 30 ml of methylene chloride in another separatory funnel, (#B1), and use it as a blank. The blank should be fractionated along with the sample.

Extract the sample with 30 ml of 5% aqueous sodium carbonate. Drain most of the organic layer, solution #1, into separatory funnel #2. Stop the transfer when approximately one milliliter of the organic layer remains in separatory funnel #1. Add a few milliliters of methylene chloride to separatory funnel #1, and tap the side of the funnel to get most of the methylene chloride to settle to the bottom of the funnel (do not shake the funnel as would be done during an extraction). Drain the rest of the organic layer into separatory funnel #2. Acidify the aqueous phase carefully with 35 ml of 1 N hydrochloric acid. Extract the acidified solution with 20 ml of methylene chloride (be careful when shaking the separatory funnel - carbon dioxide is evolved). Drain the organic layer into separatory funnel #3. Extract the acidified aqueous layer again with a 10 ml volume of methylene chloride, then combine the two extracts. Dry the CH_2Cl_2 solution with anhydrous magnesium sulfate. Remove the magnesium sulfate by filtering the dried solution through a fritted glass funnel. Concentrate this solution to 1.0 ml using a Kuderna-Danish concentrator. Transfer the concentrated solution to a micro reaction vial. Use 1 ml of benzene to rinse the boiling flask. Add 0.5 to 1.0 ml of BF_3-methanol (14% w/v) to the vial. Heat the capped vial in a water

bath at 80 °C for about five minutes, then add 2 ml of 20% aqueous sodium chloride to decompose the excess BF_3. Allow the aqueous and organic layers to separate, then analyze the organic layer (the upper layer) by gas chromatography.

Extract solution #1 with 30 ml of 1 N sodium hydroxide. Drain the organic layer, solution #2, into separatory funnel #4. Extract the aqueous layer again with 5 ml of methylene chloride. Drain the organic layer into separatory funnel #4. Acidify the aqueous layer with 35 ml of 1 N hydrochloric acid. Extract the acidified solution with 20 ml of methylene chloride. Drain the organic layer into separatory funnel #5. Extract the aqueous layer again with 10 ml of methylene chloride. Combine the two extracts. Dry the CH_2Cl_2 solution with anhydrous magnesium sulfate. Filter this dried solution and concentrate it to 1.0 ml. Analyze the solution by gas chromatography.

Extract solution #2 with 30 ml of 1 N hydrochloric acid. Drain the organic layer, solution #3, into separatory funnel #6. Extract the aqueous phase again with 5 ml of methylene chloride. Drain the organic layer into separatory funnel #6. Alkalize the aqueous phase with 35 ml of 1 N NaOH. Extract the alkalized solution with 20 ml of methylene chloride. Drain the organic layer into separatory funnel #7. Extract the aqueous phase again with 10 ml of methylene chloride. Combine the two extracts. Dry the CH_2Cl_2 solution with anhydrous magnesium sulfate. Filter the solution and concentrate it to 1.0 ml. Analyze the solution by gas chromatography.

Wash solution #3, the neutral fraction, with 5 ml of 20% aqueous

sodium chloride. Drain the organic layer into separatory funnel #8. Dry this CH_2Cl_2 solution with anhydrous magnesium sulfate. Filter the solution and concentrate it to 1.0 ml. Analyze the solution by gas chromatography.

Using 30 ml of methylene chloride, transfer the neutral fraction to separatory funnel #9. Extract the solution two times with 20 ml volumes of 20% aqueous sodium bisulfite. Wash the organic layer, solution #4, with 10 ml of 20% aqueous NaCl. Dry the organic solution with anhydrous magnesium sulfate. Filter the solution and concentrate it to 1.0 ml.

Combine the bisulfite extracts. Wash the solution with 5 ml of methylene chloride. Add 20 ml of 4 N NaOH to the aqueous solution. Extract with 20 ml of methylene chloride. Drain the organic layer into separatory funnel #10. Extract the aqueous layer again with 10 ml of methylene chloride. Combine the two extracts. Dry the solution with anhydrous magnesium sulfate. Filter the organic solution and concentrate it to 1.0 ml. Analyze the solution by gas chromatography.

Pipette 10.0 ml of 5% Girard's Reagent T in acetic acid-methanol (1:9) into the flask containing solution #4. Pipette 10.0 ml of the Girard's Reagent T solution into another flask, and use the solution as a titration blank. Allow the solutions to stand overnight.

Using the titration blank, determine how much methanolic KOH (saturated solution) is needed to reach the brom thymol blue endpoint. Add the same amount of base to the sample. Transfer the sample solution to separatory funnel #11. Use 50 ml of purified water to rinse the flask. Extract the solution with 30 ml of n-pentane. Drain the aqueous

layer into separatory funnel #12. Wash the pentane layer, solution #5, two times with 10 ml volumes of 20% aqueous sodium chloride. Using 5 ml of pentane, transfer solution #5 to separatory funnel #13. Dry the solution with anhydrous magnesium sulfate. Filter the solution and concentrate it to 1.0 ml.

Acidify the aqueous phase with 10 ml of 8 N HCl. Extract the solution with 30 ml of pentane. Wash the pentane solution with 10 ml of 5% aqueous sodium bicarbonate. Wash the solution a second time with 10 ml of 20% aqueous sodium chloride. Using 5 ml of pentane, transfer the pentane solution to separatory funnel #14. Dry the solution with anhydrous magnesium sulfate. Filter the solution and concentrate it to 1.0 ml. Analyze the solution by gas chromatography.

Using 4 ml of pentane, transfer solution #5 to a 60 ml separatory funnel, (#15). Extract the solution three times with 5 ml volumes of DMSO. Wash the pentane solution two times with 10 ml volumes of 20% aqueous sodium chloride. Using 10 ml of pentane, transfer the pentane solution to separatory funnel #16. Dry this solution with anhydrous magnesium sulfate. Filter the solution and concentrate it to 1.0 ml. Analyze the solution by gas chromatography.

Slowly add 30 ml of purified water to the combined DMSO extracts. Extract the solution with 30 ml of pentane. Wash the pentane solution two times with 10 ml volumes of purified water. Using 5 ml of pentane, transfer the pentane solution to separatory funnel #17. Dry this solution with anhydrous magnesium sulfate. Filter the solution and concentrate it to 1.0 ml. Analyze the solution by gas chromatography.

Recovery studies

Acid-base-neutral fractionation Model compounds were used to test the fractionation procedure. Compounds representing the following chemical classes were used: alkanes, PAH's, ketones, aldehydes, esters, alcohols, halides, carboxylic acids, phenols and amines. Mixtures of compounds representing the chemical classes were fractionated separately, e.g. ketones were fractionated separately from aldehydes. The concentration of each component of the mixtures was usually between 10 ppm and 40 ppm during the fractionation.

The strong acid, weak acid, base, and neutral recoveries were determined for the mixtures. The fractionation procedure which was used differed slightly from the one given on pages 46-48. The aqueous extracts were washed with 10 ml of methylene chloride instead of 5 ml. The 10 ml wash solutions were added to the original organic extracts. The organic extracts were washed with 20 ml of purified water (in the procedure given on pp. 46-48, only the neutral fraction was washed; and it was washed with 20% aqueous NaCl). A 5% solution of sodium bicarbonate in water was tested in addition to the 5% aqueous sodium carbonate during the analysis of phenols and carboxylic acids. The carboxylic acids were not derivatized with BF_3-methanol. An "on-column" methylating agent was used to convert the acids to methyl esters in the injection port of the gas chromatograph. Five microliters of Methelute, a commercially available reagent (phenyltrimethylammonium hydroxide in methanol, 14% w/v), were mixed with a 10 microliter aliquot of the acid fraction (which had been concentrated to 1.0 ml). One microliter

of the solution was injected into a gas chromatograph with its injection port at 270 °C.

The compounds were analyzed by gas chromatography with packed columns. The following stationary phases were used: OV-17 (see Appendix) for esters, ketones, aldehydes, alcohols, phenols, and acid esters; Dexsil 300 (see Appendix) for alkanes, halides, and PAH's; and 2% KOH-10% Carbowax 20M (see Appendix) for amines. The percent recovery of each compound was determined by comparing its gas chromatogram peak height, relative to an internal standard, before and after fractionation. Three standards were made for each mixture by pipetting 1.0 ml volumes of the mixture into three vials and adding 45 microliters of an appropriate internal standard solution to each vial. In most cases, six sample determinations were made by pipetting 1.0 ml aliquots of the mixture into separatory funnels containing 29 ml of methylene chloride, fractionating the solutions, concentrating the fractions to 1.0 ml, adding 45 microliters of internal standard solution, and analyzing by gas chromatography.

Aldehyde fractionation Aldehyde standards were used to test the bisulfite extraction part of the fractionation procedure. Mixtures of aldehydes in methylene chloride, pentane, and diethyl ether were extracted with 20% aqueous sodium bisulfite using the applicable portion of the fractionation procedure given on page 48. Percent recoveries for the compounds in the aldehyde fraction and in the "nonaldehyde" fraction (the organic solution left after the extraction with bisulfite) were determined by the same method given in the previous

section. Some of the aldehyde samples were chromatographed on an OV-17 column, and the other samples were chromatographed on a Carbowax 20M column.

A mixture of ketones in ether was extracted with 20% aqueous sodium bisufite using the same procedure as was used with the aldehyde mixtures. The percent recoveries of the ketones in the aldehyde and nonaldehyde fractions were determined.

Ketone fractionation The efficiency of Girard's Reagent T for extracting ketones was tested. A 30 ml volume of an ether solution of ketones was extracted two times with 20 ml volumes of 10% Girard's Reagent T in water. The ether layer was washed with 10 ml of 20% aqueous sodium chloride. The wash solution was added to the combined Girard T extracts. The Girard T solution was acidified with 10 ml of 4 N HCl and back-extracted with methylene chloride (once with 20 ml, then once with 10 ml). The ether solution and the methylene chloride solution (nonketone and ketone fractions, respectively) were dried, filtered, and concentrated. The recoveries of the ketones in both fractions were determined.

The efficiency of Girard's Reagent T in acetic acid-methanol (1:9) was tested. A comparison was made between the reactions of ketones with the reagent at room temperature and at 75 ^{o}C. One ml of a methylene chloride solution of ketones was pipetted into a separatory funnel containing 20 ml of 5% Girard's Reagent T in acetic acid-methanol (1:9). The funnel was shaken for five minutes. The acetic acid was neutralized with 4 N NaOH. After the addition of 40 ml of water, the solution was

extracted twice with methylene chloride (20 ml, then 10 ml). The extracts were combined, dried, filtered, and concentrated. Another sample was fractionated the same way, except that it was heated in a water bath at 75 °C for half an hour instead of being shaken in a separatory funnel at room temperature. The aqueous extracts from both samples were acidified with 20 ml of 4 N HCl. The solutions were extracted twice with methylene chloride (20 ml, then 10 ml). The combined methylene chloride extracts were washed with 10 ml of 5% aqueous sodium carbonate. The solutions were then dried, filtered, and concentrated. Internal standards were added to the ketone fraction solutions and the nonketone fraction solutions. The solutions were analyzed by gas chromatography.

Amberlite IRC-50 cation-exchange resin was tested as an acid catalyst for the Girard T reaction. Mixtures of ketones in methanol and in ethanol were reacted with Girard's Reagent T in the presence of the weak acid ion-exchange resin.

Formaldehyde hydrolysis of Girard T hydrazones was compared with acid hydrolysis. The formaldehyde hydrolysis was accomplished by adding an excess amount of 37% formaldehyde in water to the Girard T hydrazone solutions. The solutions were allowed to stand overnight.

A comparison was made between pentane and methylene chloride as extracting solvents in the ketone fractionation with 5% Girard's Reagent T in acetic acid-methanol (1:9). Percent recoveries were determined for ketones in the ketone fraction and in the "nonketone" fraction obtained with both solvents.

A mixture of ketones was fractionated with 5% Girard's Reagent T in acetic acid-methanol using the applicable portion of the fractionation procedure given on pp. 48-49 (except CH_2Cl_2 was used to extract the hydrolyzed ketones) (later, pentane was found to extract less CH_3COOH, so it was used in the fractionation of samples). The recoveries of the ketones in the ketone and nonketone fractions were determined by gas chromatography.

Solutions of esters, PAH's, and alcohols were extracted with 5% Girard's Reagent T in acetic acid-methanol (1:9). The recoveries of the compounds in the nonketone fractions were determined.

Polar-nonpolar fractionation A mixture of alkanes and PAH's was fractionated between pentane and nitromethane. Five ml aliquots of a pentane solution of alkanes and PAH's were extracted three times with 5 ml volumes of nitromethane. The percent of each PAH remaining in the pentane after each extraction was determined by gas chromatographic analysis. The chromatogram peak heights of the PAH's, relative to the alkanes, were determined before the nitromethane extractions and after each nitromethane extraction. The alkanes were assumed to be 100% recovered in the pentane.

Mixtures of alcohols, esters, halides, and single-ring aromatic compounds were fractionated between nitromethane and pentane. The recoveries of the compounds in the pentane layer were determined (relative to n-hexadecane). The pentane solutions were extracted three times with nitromethane using the same procedure as was used for the PAH's. The concentration of each component in the mixtures used to study the pentane-nitromethane partitioning was about 500 ppm.

A cyclohexane solution of some esters, halides, and aromatic compounds was extracted three times with nitromethane. The recoveries of the compounds in the cyclohexane layer were determined (relative to n-hexadecane) after each extraction. A cyclohexane solution of PAH's was also analyzed.

A pentane solution of PAH's was extracted three times with DMSO using the procedure used in the nitromethane partitioning. The recoveries of the PAH's in the pentane layer were determined (relative to n-hexadecane) after each extraction. A pentane solution of alcohols was also analyzed.

Qualitative fractionation of standards in a mixture A mixture of 53 compounds was used to determine how well compounds in various chemical classes could be separated from each other. A methylene chloride solution of the 53 compounds was made, and the concentration of each component was about 50 ppm. Five ml of the solution was pipetted into a separatory funnel containing 25 ml of methylene chloride. For the most part, the procedure given on pp. 46-49 was used to fractionate the mixture. However, during the ketone fractionation, 20 ml of the Girard's Reagent T solution was used instead of 10 ml; and the solution was diluted with 40 ml of water instead of 50 ml.

Quantitative fractionation of standards in a mixture A mixture of 41 neutral compounds, most of which have been found in automobile exhaust, was used to determine how much material would be lost during fractionation. Previous recovery studies gave information about losses during each section of the fractionation procedure, but did not give

recovery information for neutral compounds using the entire fractionation scheme. A methylene chloride solution of the 41 compounds was made, and the concentration of each component was about 50 ppm. One ml of the solution was pipetted into a separatory funnel containing 29 ml of methylene chloride. Thus, the concentration of each component in the mixture during the fractionation was about 1.7 ppm. The sample was fractionated according to the procedure on pp. 46-49. The recoveries of the components in each fraction were determined by gas chromatographic analysis on an SE-54 capillary column. An electronic integrator was used to determine chromatogram peak areas. Internal standards were used in the analysis. Two samples were fractionated in order to check the reproducibility of the method.

Results and Discussion

Problems with solvent blanks and with artifacts

During the course of the recovery studies, several problems with the fractionation method were discovered. Many of the solvents used during the fractionation were not pure. Because of that, impurities were introduced into the samples. In addition, it was found that some of the reactions used during the fractionation led to the formation of artifacts. These problems were studied, and attempts were made to minimize them.

Solvent blanks The solvents used during the recovery studies were methylene chloride, benzene, diethyl ether, methanol, pentane, ethanol, nitromethane, DMSO, cyclohexane, hexane, and water. The water, hexane, cyclohexane, and diethyl ether (after distillation) did not

Gas chromatographic conditions:

sample:	Burdick and Jackson methylene chloride
amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	isothermal
oven temp.:	60 °C
detector temp.:	250 °C
injector temp.:	250 °C
split ratio:	60:1
He pressure	18 p.s.i.
attenuation:	X 1
detector	FID
chart speed:	0.25 in./minute

Figure 9. Methylene chloride gas chromatogram

contain any impurities which would have interfered with the analysis of the samples. The benzene, which was used during the BF_3-methanol methylation of acids, contained some toluene and xylenes, but they did not cause any significant problems in the analysis. The methylene chloride contained cyclohexene at a concentration of about 2 ppm. A gas chromatogram of the solvent is shown in Figure 9. The cyclohexene eluted just after the methylene chloride. During the fractionation,

the concentration of the cyclohexene increased dramatically (concentration of the sample from 30 ml to 1.0 ml, alone, increases the concentration of cyclohexene by a factor of thirty). Presumably, the cyclohexene functions as a preservative in the methylene chloride. Although its concentration in the methylene chloride could be reduced by distillation, the cyclohexene could not be removed completely.

Methanol and ethanol were used as solvents during the ketone fractionation. Ethanol was used in only a couple of studies, and was not tested thoroughly for impurities. The methanol, which was chosen as the better solvent for the ketone fractionation, did have impurities in it. Methanol was used as a solvent for the Girard's Reagent T and for the KOH. During a fractionation study, it was found that the blank became significant after the extraction of ketones. The impurities in the blank were traced to both the methanolic KOH and the acetic acid-methanol (1:9) reagents which had been made several weeks prior to the analysis. A 5-ml aliquot of the methanolic KOH was diluted with 40 ml of purified water and extracted with distilled pentane. The pentane extract was analyzed by gas chromatography. The chromatogram is shown in Figure 10. Some of the impurities were found in the methanol used to make the reagent; others formed after the KOH was dissolved in the methanol. Figure 11 shows the gas chromatogram of a pentane (not distilled) extract of 20 ml of methanol in 50 ml of purified water. Most of the peaks near the solvent peak are C_6-C_8 hydrocarbons present in the pentane (Burdick and Jackson). Those compounds could be removed from the pentane by distillation. The impurities in the methanol

Figure 10. Distilled-pentane extract of 5 ml methanolic KOH and 40 ml of water

Figure 11. Pentane extract of 20 ml methanol and 50 ml of water

Figure 12. Pentane extract of 20 ml distilled methanol and 50 ml of water

Figure 13. Pentane extract of 23 ml purified methanol and 50 ml of water

Gas chromatographic conditions for Figures 10-13:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	150 °C
final hold:	0 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	35:1
He pressure:	20 p.s.i.
attenuation:	
Figure 10:	X 2
Figures 11-13:	X 4
detector:	FID
chart speed	0.25 in./minute

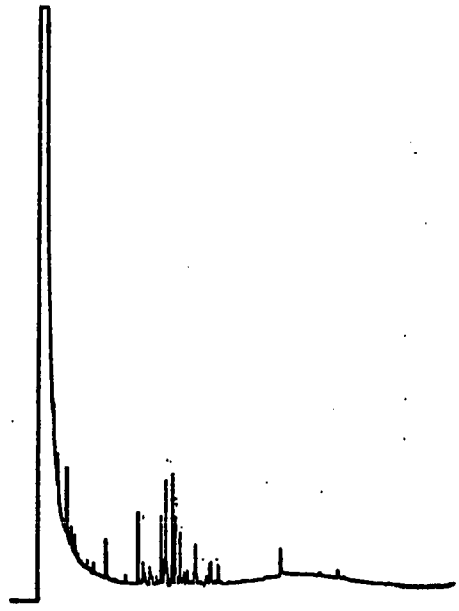


Figure 10

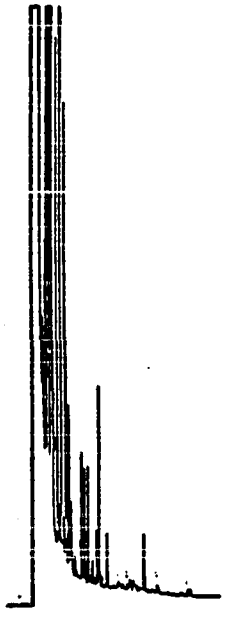


Figure 11

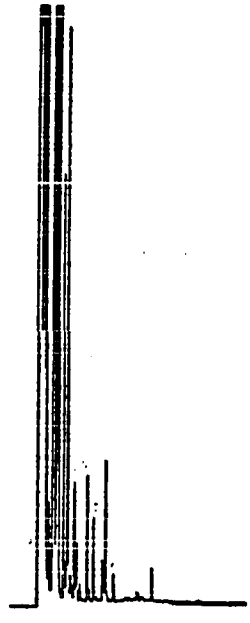


Figure 12

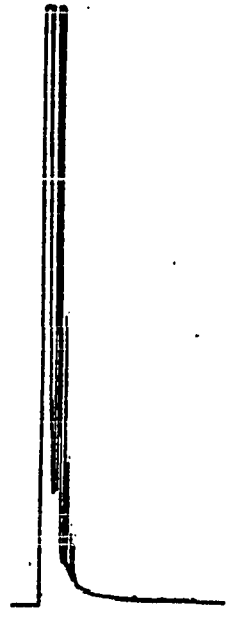


Figure 13

were difficult to remove by distillation. Figure 12 shows the gas chromatogram of a pentane (not distilled) extract of the methanol after distillation. Only one impurity was removed from the methanol as a result of the distillation. During the Girard T fractionation of ketones, the methanol impurities were extracted into the pentane layer containing the nonketone material. An attempt was made to purify the methanol by extracting it under the same conditions as were used during the fractionation of samples. The methanol was diluted with purified water and extracted with pentane. The aqueous layer was distilled to separate the methanol from the water. Figure 13 shows the gas chromatogram of the pentane extract of the purified methanol. The only significant amounts of compounds in the extract were those originally in the pentane.

The impurities which were found in the acetic acid-methanol reagent were traced to impurities in the methanol and impurities formed after the methanol was in contact with the acetic acid for several days. Figure 14 shows the chromatogram of a distilled-pentane extract of an aqueous solution of methanol which was taken from a different bottle than the one used previously. The concentrations of impurities in the methanol were lower than those in previous methanol samples. Figure 15 shows the chromatogram of an aqueous solution of acetic acid. All of the peaks in the chromatogram are from compounds in the pentane. Figure 16 shows the chromatogram of a distilled-pentane extract of the acetic acid-methanol reagent which had been made several weeks before it was analyzed. Impurities were present in the reagent

Figure 14. Distilled-pentane extract of 20 ml of methanol and 50 ml of water

Figure 15. Distilled-pentane extract of 2 ml of acetic acid and 50 ml of water

Figure 16. Distilled-pentane extract of 10 ml of the acetic acid-methanol reagent and 50 ml of water

Figure 17. Distilled-pentane extract of 9 ml of methanol, 1 ml of acetic acid, and 50 ml of water

Gas chromatographic conditions for Figures 14-17:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	160 °C
final hold:	0 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

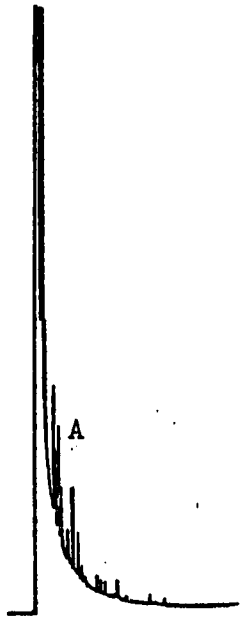


Figure 14

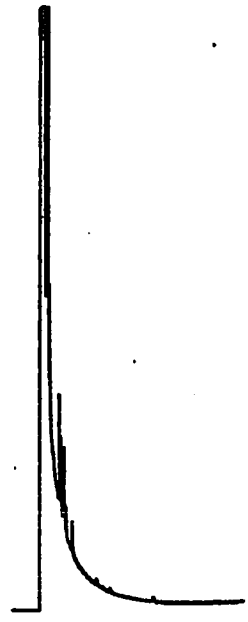


Figure 15

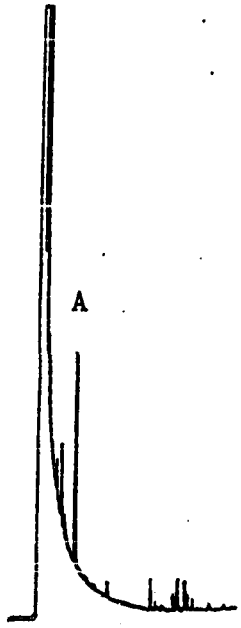


Figure 16

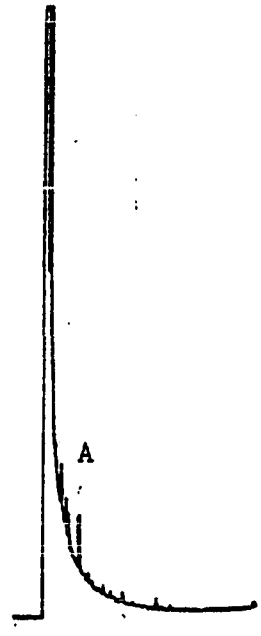


Figure 17

which were not present in the methanol or acetic acid used to make the reagent. Figure 17 shows the chromatogram of a distilled-pentane extract of a solution containing 9 ml of methanol, 1 ml acetic acid, and 50 ml of water. The peaks in the chromatogram are from compounds in the methanol and pentane. Because the acetic acid and methanol react slowly with one another to form impurities, the acetic acid-methanol reagent should be made just before use, and should not be stored for any length of time.

The major impurity in the methanol is shown as peak A in Figures 14, 16, and 17. Not only was the impurity present in the methanol, but also its concentration was increased when the methanol was mixed with acetic acid. The impurity appeared to be a methoxy compound. The mass spectrum of the compound is shown in figure 18. The mass spectral fragmentation pattern was similar to that of 1,1-dimethoxy-isobutane (molecular ion at m/z 118). Another possibility for the impurity's identity was 1,1-dimethoxyethene (molecular ion at m/z 88). A positive identification of the impurity was not obtained.

The nitromethane which was used to fractionate polar and nonpolar compounds contained several impurities. Some of the impurities could be removed by distillation. However, three of the impurities remained after the distillation. Figure 19 shows the chromatogram of a pentane extract of distilled nitromethane. Figure 20 shows the chromatogram of the pentane extract of nitromethane after it was purified by extraction with pentane followed by distillation. The purified nitromethane was used during the analysis of known compounds.

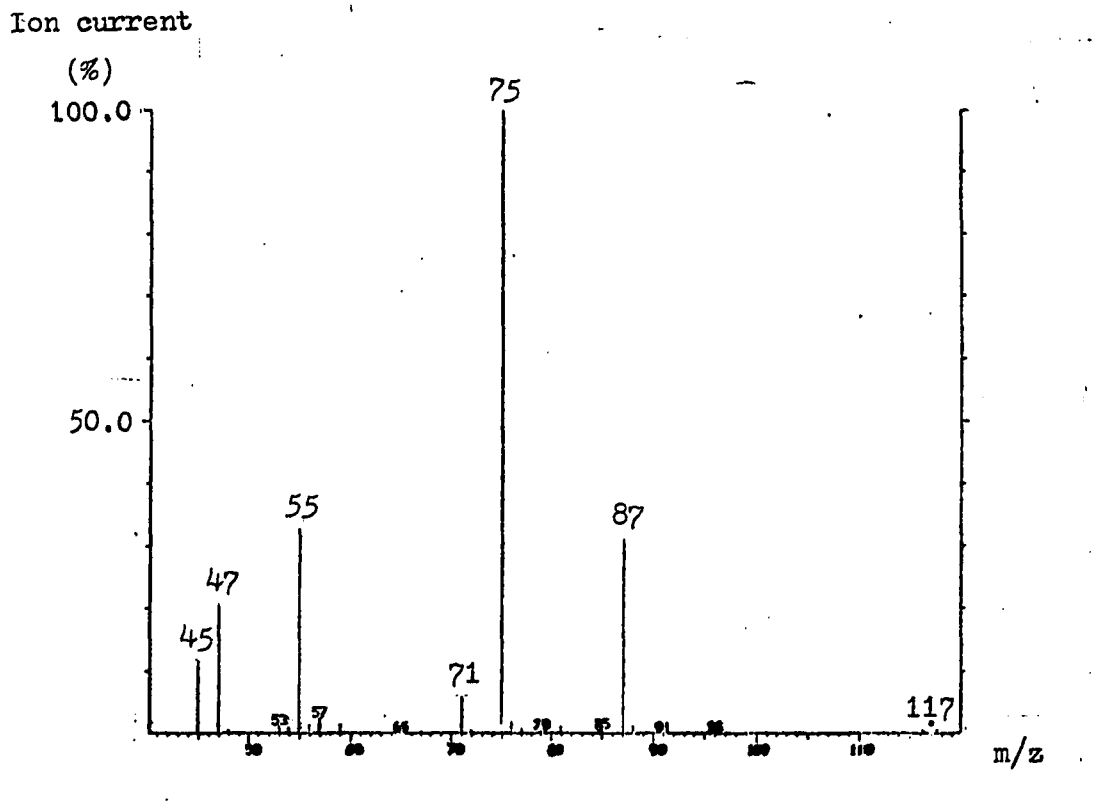


Figure 18. Mass spectrum of an impurity in methanol

The DMSO, which was also used to fractionate polar and nonpolar compounds, contained many impurities. Figure 21 shows a chromatogram of a pentane extract of DMSO. Seven major impurities and fifteen minor ones were present. Most of the impurities were sulfur compounds. The mass spectra of the 22 compounds are shown in Figure 22. The concentrations of some of the impurities in the DMSO were lowered by distilling the DMSO. The DMSO was purified further by eluting it through a column of activated alumina and was stored over molecular sieves. All of the

Figure 19. Pentane extract of doubly-distilled nitromethane

Figure 20. Pentane extract of nitromethane which had been extracted with pentane and distilled

Figure 21. Pentane extract of 15 ml of DMSO and 30 ml of water

Gas chromatographic conditions for Figures 19-21:

amount:	
Figure 19:	1 microliter
Figures 20-21:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	
Figure 19:	150 °C
Figures 20-21:	270 °C
final hold:	0 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	35:1
He pressure	20 p.s.i.
attentuation:	
Figure 19:	X 4
Figures 20-21:	X 2
detector:	FID
chart speed:	0.25 in./minute

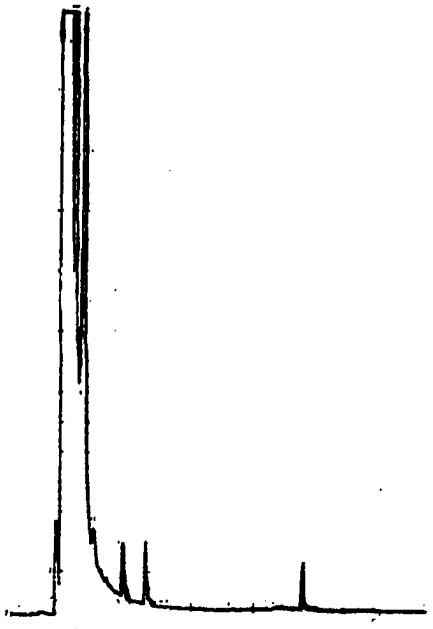


Figure 19

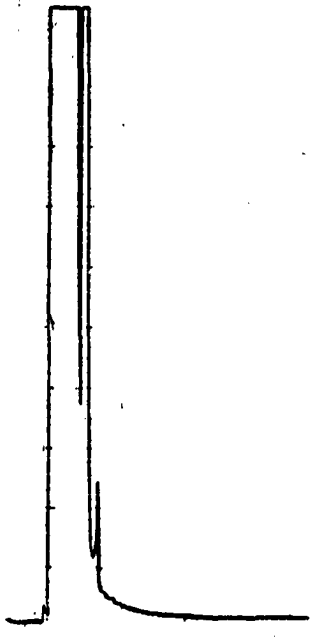


Figure 20

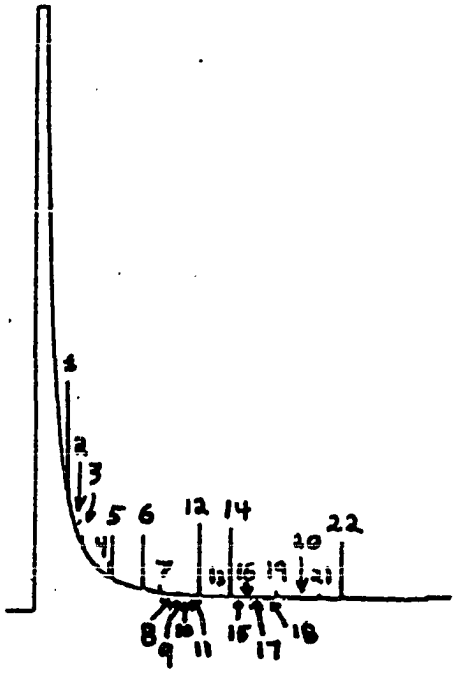


Figure 21

Figures 22. Mass spectra of impurities in dimethyl sulfoxide

Figure #	Molecular Ion	Base Peak	Compound
22a	94	94	Dimethyldisulfide
22b	106	48	$CH_3CH_2OCH_2SCH_3$?
22c	92	45	$CH_3CH_2OCH_2SH$?
22d	120	61	$CH_3SCH_2CH_2CH_2OH$??
22e	108	61	$CH_3SCH_2SCH_3$
22f	126	126	Dimethyltrisulfide

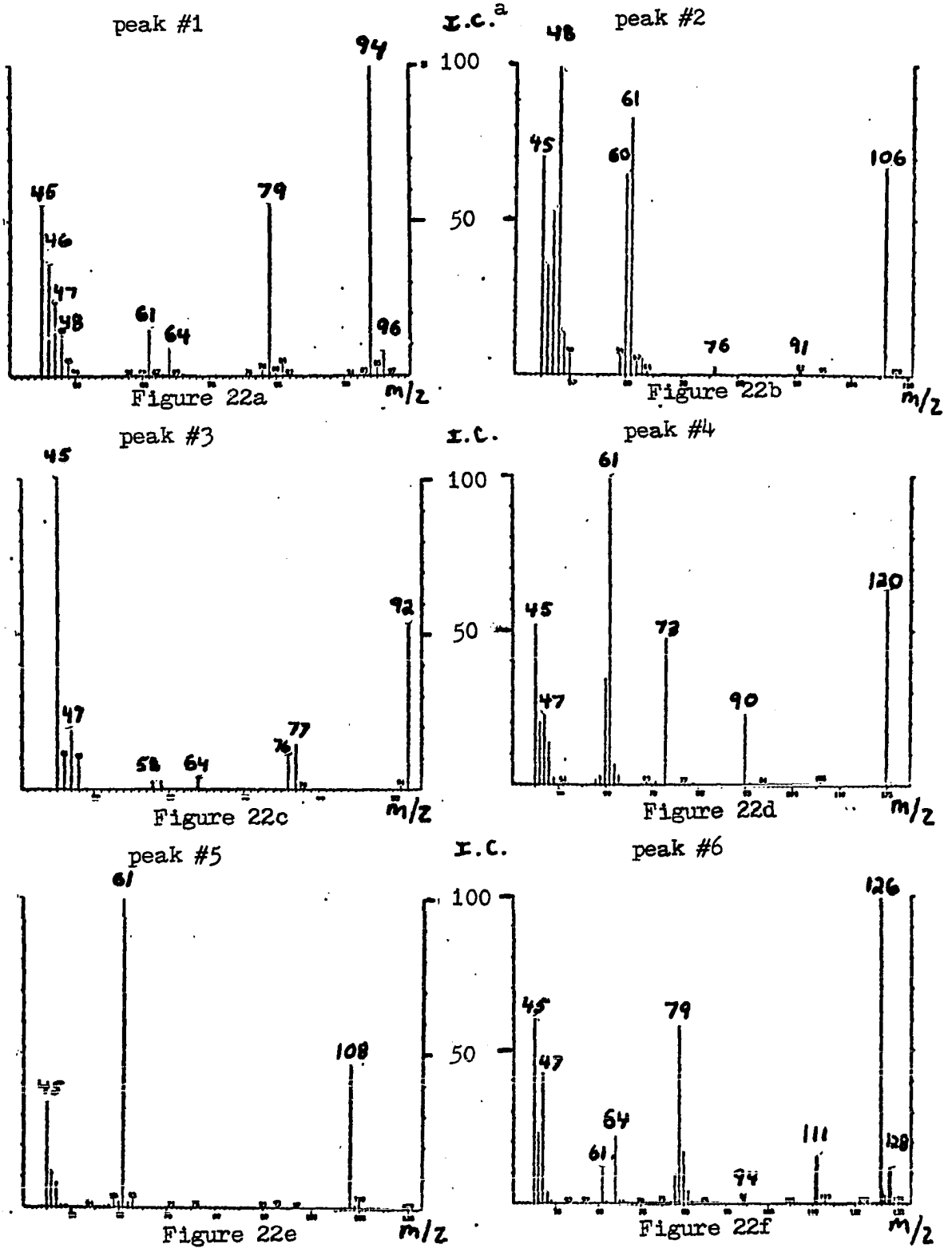


Figure 22a

Figure 22b

Figure 22c

Figure 22d

Figure 22e

Figure 22f

[a]Ion Current

Figure 22. continued

Figure #	Molecular Ion	Base Peak	Compound
22g	130	89	$C_6H_{10}OS$? $C_5H_6O_2S$?
22h	140	47	$CH_3SSCH_2SCH_3$?
22i	138	61	$CH_3SCH_2SCH_2CH_2OH$?
22j	120	61	$C_5H_{12}OS$? $C_4H_8S_2$?
22k	124?	78	unknown
22l	140	61	$CH_3SCH_2SCH_2SH$?

peak #7

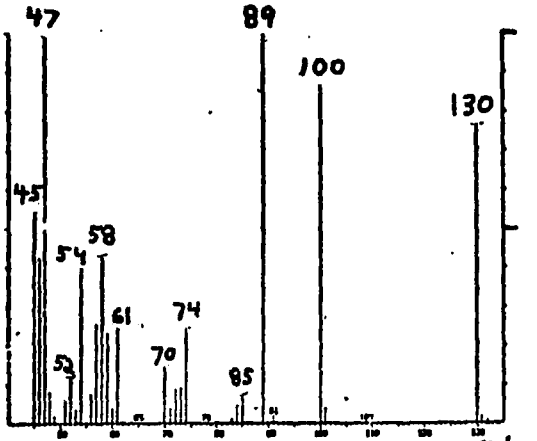


Figure 22g

I.C.

peak #8

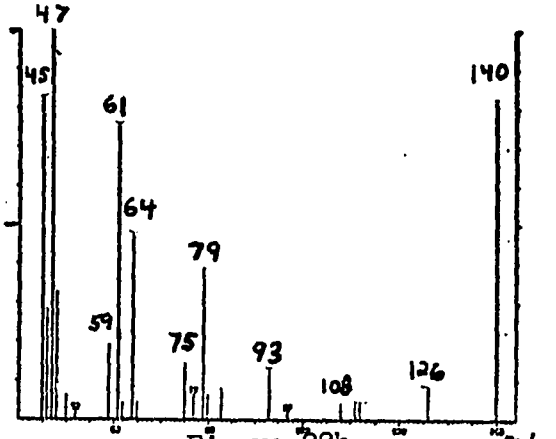


Figure 22h

peak #9

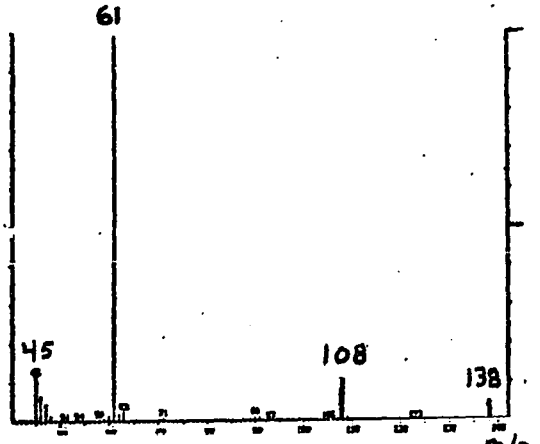


Figure 22i

I.C.

peak #10

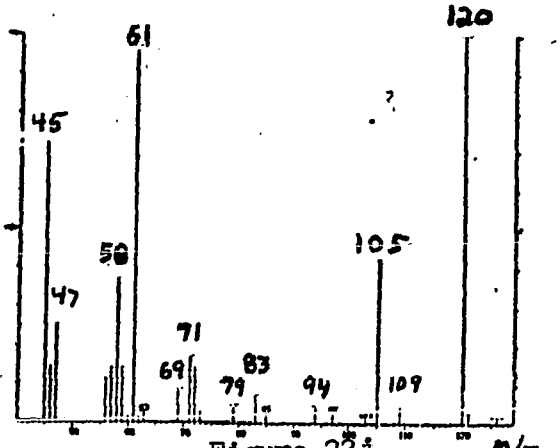


Figure 22j

peak #11

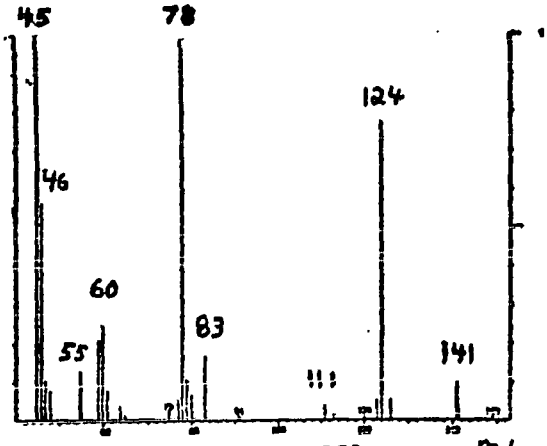


Figure 22k

I.C.

peak #12

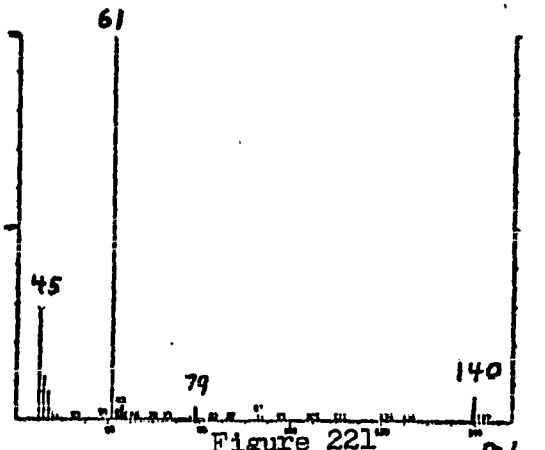


Figure 22l

Figure 22. continued

Figure #	Molecular Ion	Base Peak	Compound
22m	152	61	$CH_3SCH_2CH_2SCH_2CH_2OH$?
22n	154	107	$C_4H_{10}S_3$?
22o	?	75	unknown
22p	154	61	$(CH_3S)_3CH$
22q	?	89	unknown
22r	172?	45	unknown

peak #13

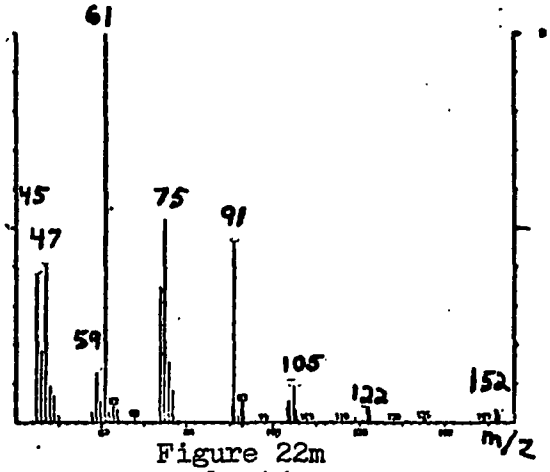
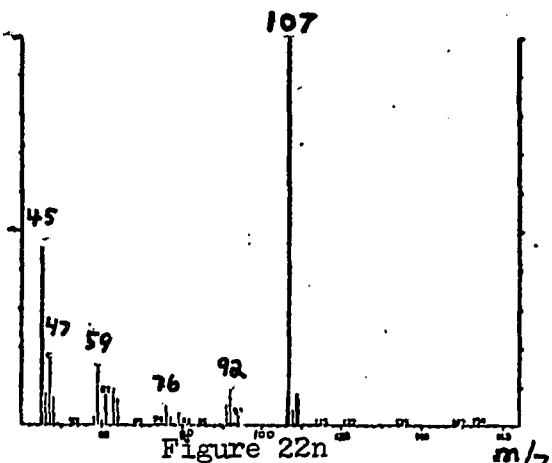


Figure 22m

I.C.



peak #14

Figure 22n

peak #15

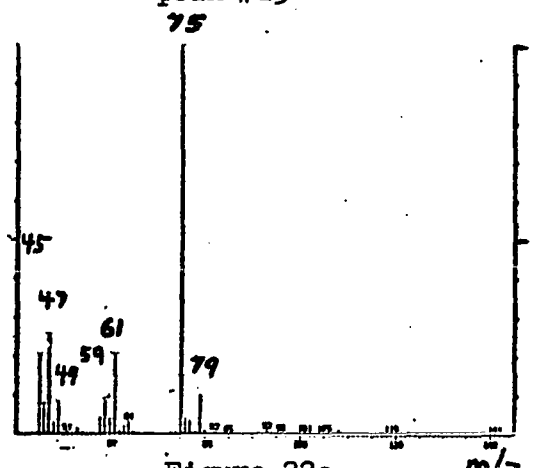
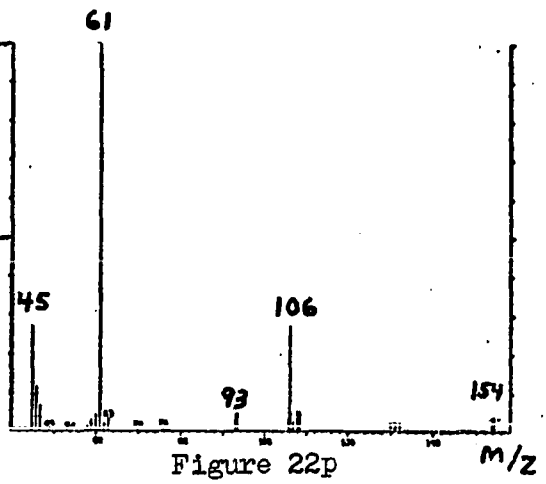


Figure 22o

I.C.



peak #16

Figure 22p

peak #17

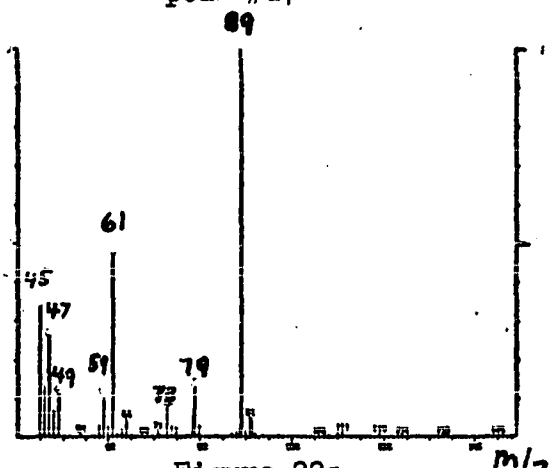
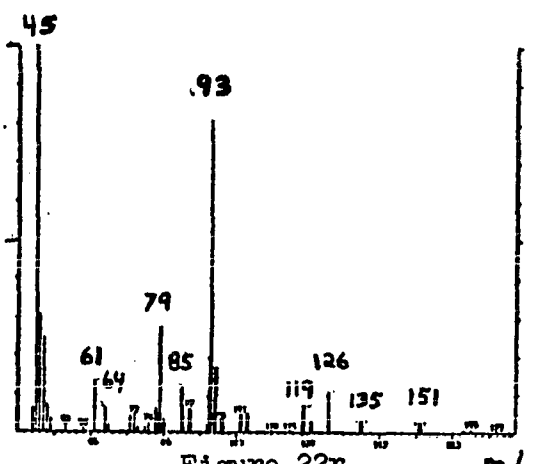


Figure 22q

I.C.



peak #18

Figure 22r

Figure 22. continued

Figure #	Molecular Ion	Base Peak	Compound
22s	172	61	$CH_3SCH_2SSSCH_3$?
22t	?	45	unknown
22u	?	61	unknown
22v	222	149	Diethylphthalate

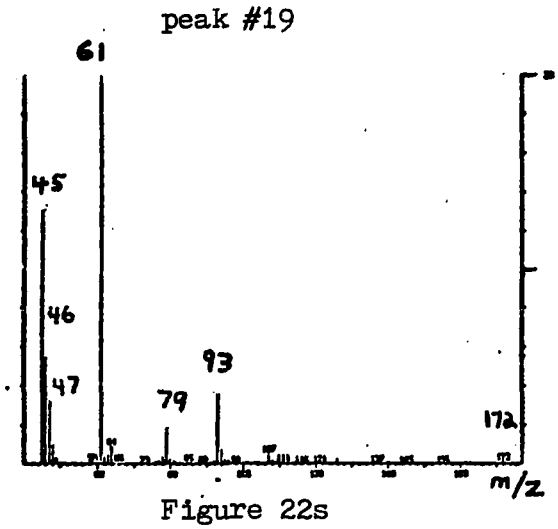


Figure 22s

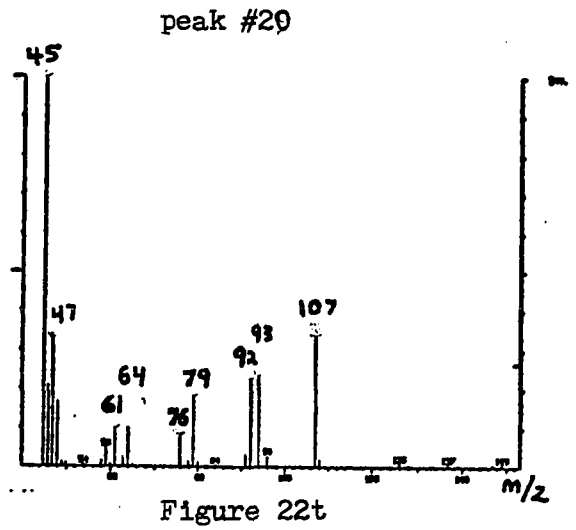


Figure 22t

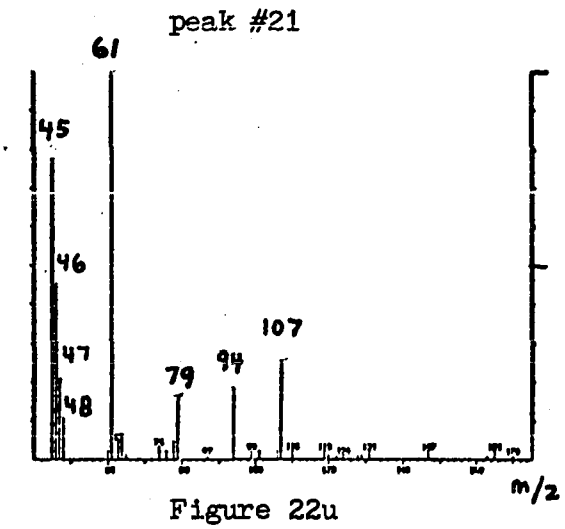


Figure 22u

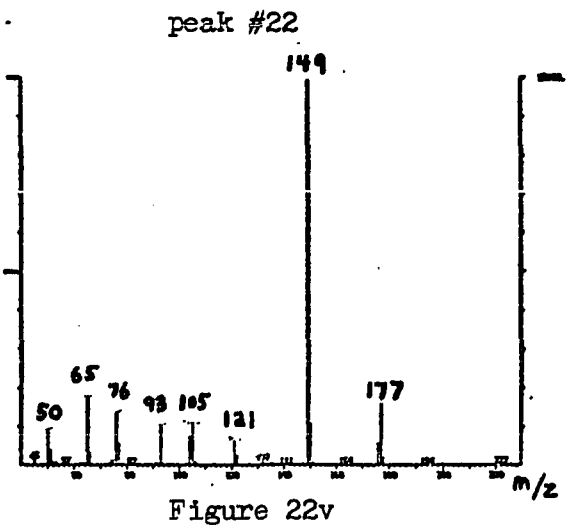


Figure 22v

impurities were not removed by the alumina.

Bisulfite decomposition of citronellal and citral During a study of the extraction of aldehydes with bisulfite, it was found that some of the aldehydes decomposed during the extraction. The aldehydes which decomposed under certain conditions were citronellal, citral (a mixture of geranial and neral), and trans cinnamaldehyde. The organic solvent used during the extraction was a factor in the decomposition of the aldehydes. Pentane, diethyl ether, and methylene chloride were tested. The decomposition of the aldehydes occurred to the greatest extent when diethyl ether was used.

A comparison was made between the bisulfite extraction of citronellal in methylene chloride and in diethyl ether. Figure 23 shows the chromatogram of a methylene chloride solution of the citronellal standard. Peak "a" corresponds to the citronellal; peak "b" is an impurity (possibly isopulegol). The structures of the two compounds are shown in Figure 26. An ether solution and a methylene chloride solution of the citronellal standard were extracted with 20% aqueous sodium bisulfite. Figure 24 shows the chromatogram of the "nonaldehyde" fraction, i.e. the organic solution after extraction with bisulfite, for the standard in ether. Figure 25 shows the chromatogram of the nonaldehyde fraction for the standard in methylene chloride. Figures 27 and 28 show the chromatograms for the "aldehyde" fractions, i.e. the solutions obtained from extracting the bisulfite extracts, for the standard in ether and methylene chloride,

Figure 23. Citronellal standard in methylene chloride

Figure 24. Nonaldehyde fraction of citronellal standard - ether

Figure 25. Nonaldehyde fraction of citronellal standard - methylene chloride

Figure 26. Structures of citronellal and decomposition products

Figure 27. Aldehyde fraction of citronellal standard - ether

Figure 28. Aldehyde fraction of citronellal standard - methylene chloride

Gas chromatographic conditions for Figures 23-25, 27, and 28:

amount:	1 microliter
column:	glass capillary, 30 meter
liquid phase:	SP-1000
mode:	temperature programmed
initial temp.:	70 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	220 °C
final hold:	0 minutes
detector temp.:	250 °C
injector temp.:	180 °C
split ratio:	50:1
He pressure:	20 p.s.i.
attenuation:	X 8
detector:	FID
chart speed:	0.25 in./minute

Peak identifications:

Peak #	M^+	Compound
a	154	citronellal
b	154	isopulegol?
1	134	a cymene?
2	136	alpha-phellandrene
3	134?	?
4	134?	?
5	136	terpinolene?
6	?	?
7	?	?
8	154?	?

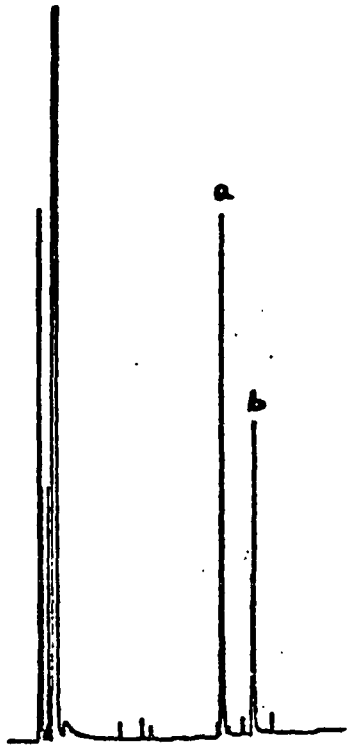


Figure 23

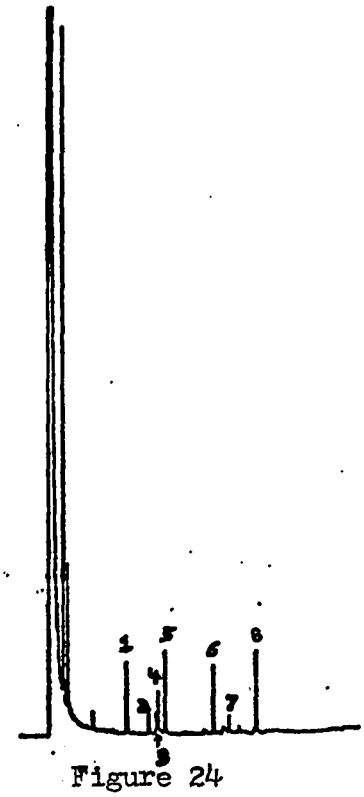


Figure 24

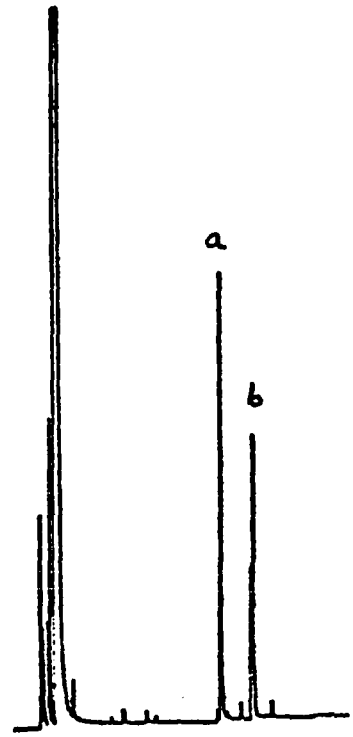


Figure 25

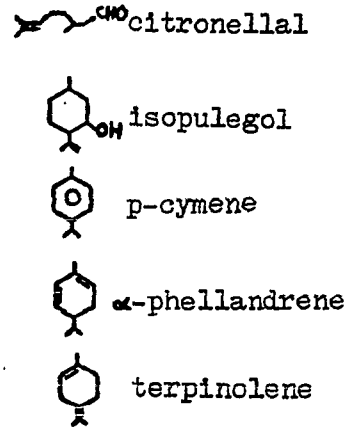


Figure 26

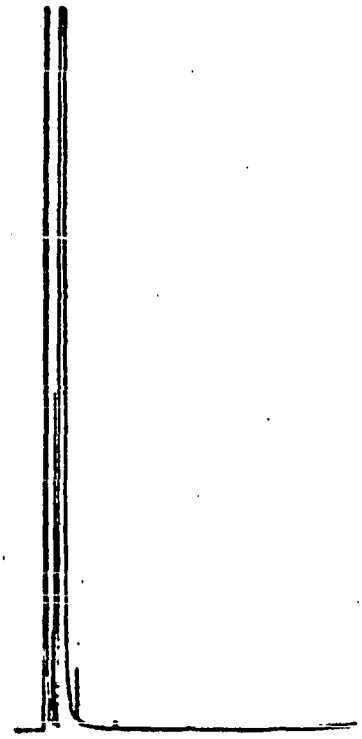


Figure 27

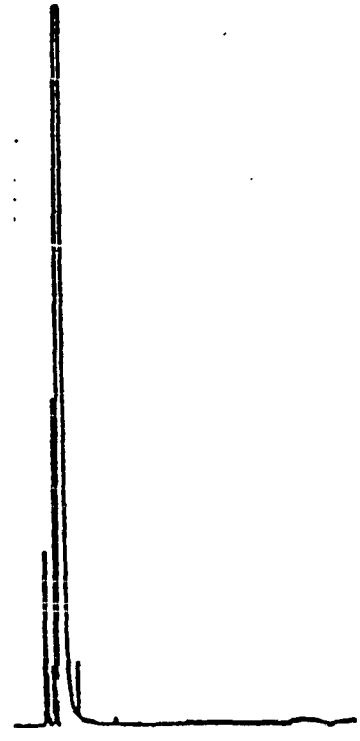


Figure 28

respectively. The citronellal standard decomposed when ether was used as the solvent. The decomposition products were found in the nonaldehyde fraction, and they appeared to be terpenes. The structures of some of the possible decomposition products are shown in Figure 26. The decomposition products, which were analyzed by GC/MS, could not be identified with certainty. The best mass spectral matches and the molecular ion mass-to-charge ratios, $M^{+\cdot}$, are shown on page 77. A possible mechanism for the formation of p-cymene is shown in Figure 29. The bisulfite ion is the source of hydrogen ions. The basic reactant, labeled "B" in the figure, can be either a sulfite ion or a water molecule.

The citronellal standard did not decompose when methylene chloride was used as the solvent during the extraction with bisulfite. The components of the standard were recovered in the nonaldehyde fraction No compounds from the citronellal standard were extracted into the bisulfite solution when either methylene chloride or ether was used as the solvent.

Diethyl ether and methylene chloride were compared as solvents for the bisulfite extraction of citral. Citral has been shown by several workers to decompose under acidic conditions and when the mixture is heated (276-279). Figure 30 shows the chromatogram of a methylene chloride solution of citral. The standard contained several impurities. The compounds in the standard were analyzed by GC/MS. The molecular ion mass-to-charge ratios, $M^{+\cdot}$, and the best matches for the compounds are listed on page 81. Figure 31 shows the

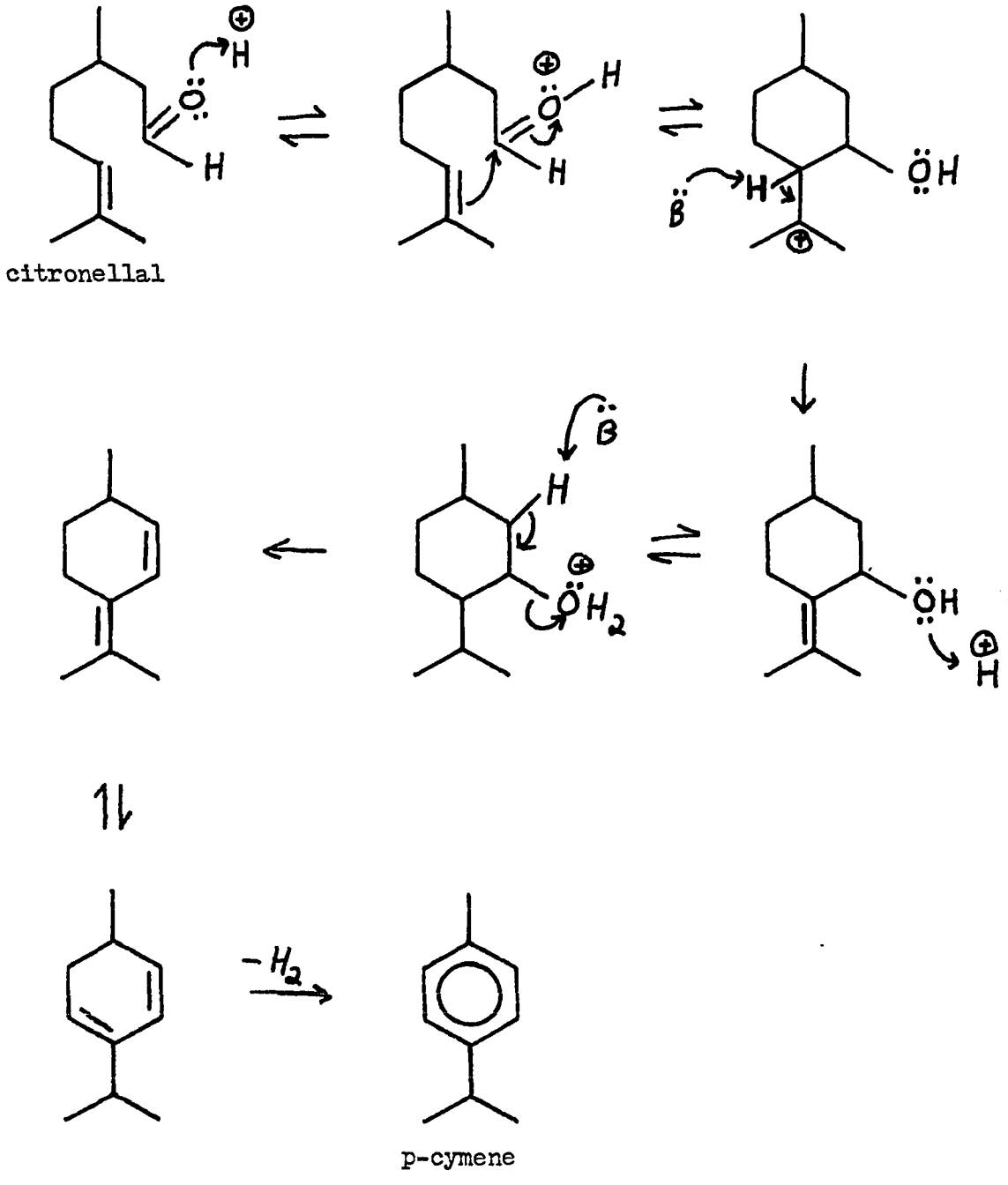


Figure 29. Possible mechanism for the formation of p-cymene from citronellal

Figure 30. Citral standard in methylene chloride

Figure 31. Nonaldehyde fraction of citral standard - ether

Figure 32. Nonaldehyde fraction of citral standard - methylene chloride

Figure 33. Structures of citral and decomposition products

Figure 34. Aldehyde fraction of citral standard - ether

Figure 35. Aldehyde fraction of citral standard - methylene chloride

Gas chromatographic conditions for Figures 30-32, 34, and 35:

amount:	1 microliter
column:	glass capillary, 30 meter
liquid phase:	SP-1000
mode:	temperature programmed
initial temp.:	70 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	220 °C
final hold:	0 minutes
detector temp.:	250 °C
injector temp.:	180 °C
split ratio:	50:1
He pressure:	20 p.s.i.
attenuation:	X 8
detector:	FID
chart speed:	0.25 in./minute

Peak identifications:

Peak #	$M^{+\cdot}$	Compound
1	136	myrcene?
2	136	limonene?
3	132	p,α-dimethylstyrene
4	134	unknown
5	134	p-cymene?
6	136	terpinolene?
7	134	a menthatriene?
8	132	a dimethyl styrene?
9	136	a menthadiene?
10	150?	unknown
11	152	geranial
12	152	neral
a	?	unknown
b	?	unknown
c	?	unknown

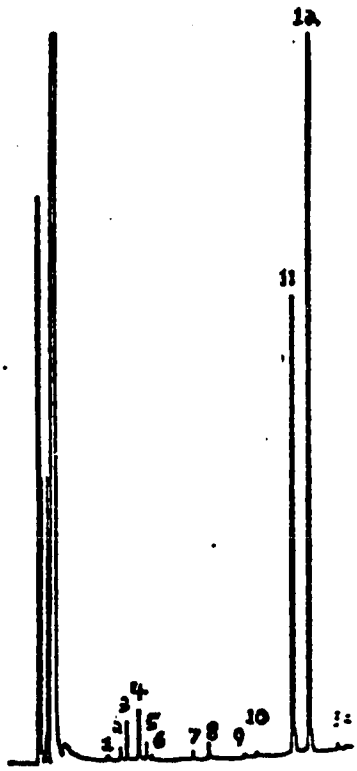


Figure 30

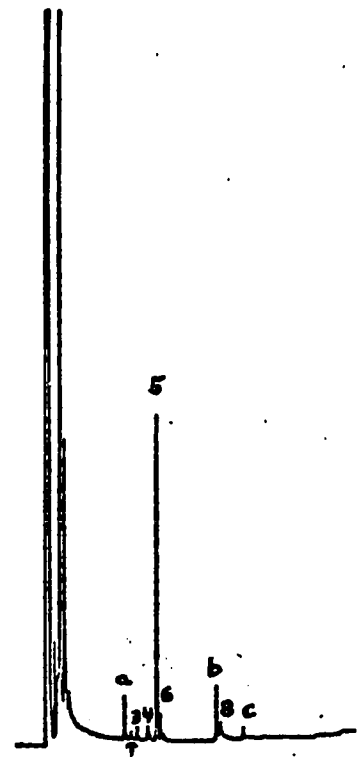


Figure 31

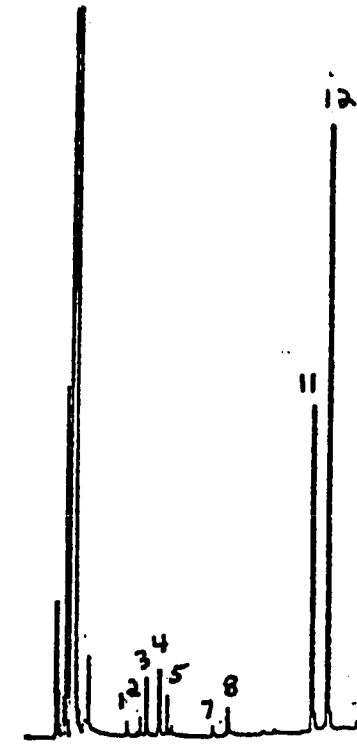


Figure 32

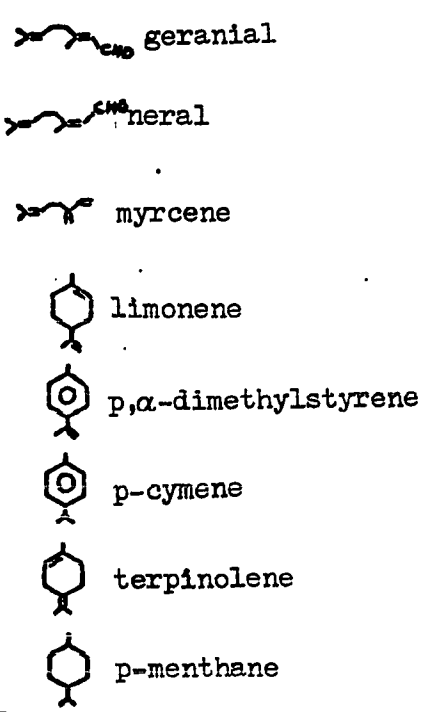


Figure 33

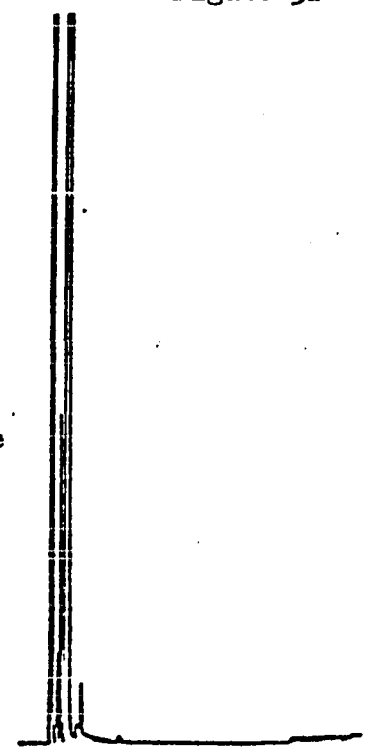


Figure 34

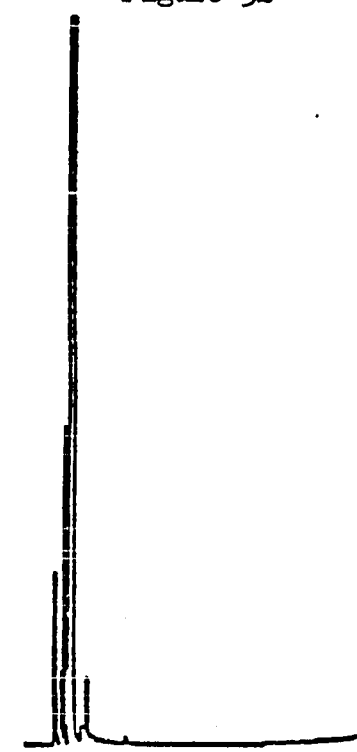


Figure 35

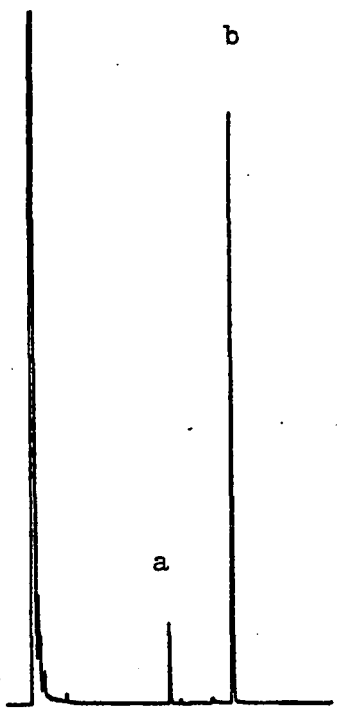
chromatogram of the nonaldehyde fraction of the citral standard in ether. The neral and geranial decomposed during the bisulfite extraction. The decomposition products were recovered in the nonaldehyde fraction. The products, which were analyzed by GC/MS, were mainly cyclic terpenes. The molecular ion mass-to-charge ratios, $M^{+\cdot}$, and the best mass spectral matches for the compounds are shown on page 81. Figure 32 shows the nonaldehyde fraction of the citral standard in methylene chloride. The neral and geranial did not decompose when methylene chloride was used as the solvent. Figure 33 shows the structures of geranial, neral, and some of the decomposition products. Figures 34 and 35 show the aldehyde fractions for the citral standard in ether and methylene chloride, respectively. No compounds were extracted into the bisulfite solution when either solvent was used.

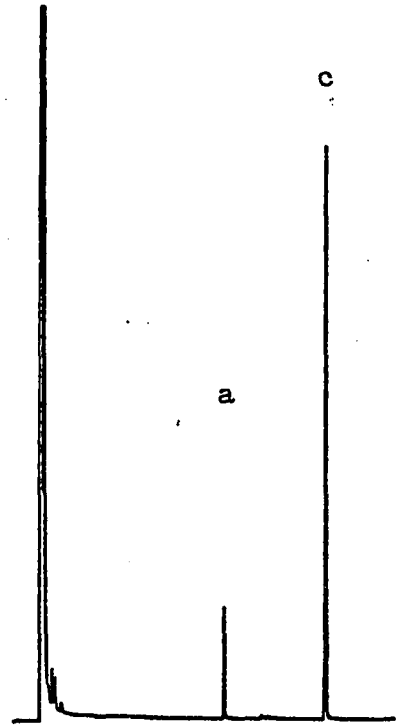
Most aldehydes could be extracted to a greater extent by bisulfite when diethyl ether was used as the solvent than when methylene chloride was used. Because of the problems relating to the decomposition of sensitive aldehydes, CH_2Cl_2 was chosen as the solvent to be used during the fractionation of samples. Many aldehydes would not be extracted completely when methylene chloride was used, and they would end up in the solution which would be extracted with the Girard's Reagent T. One of the aldehydes in the test solutions which was not extracted completely by bisulfite was hydrocinnamaldehyde.

Reaction of hydrocinnamaldehyde with methanol During the analysis of a mixture of standards, it was found that hydrocinnamaldehyde would decompose to a large extent during the fractionation of ketones with Girard's Reagent T. Most carbonyl compounds, including hydrocinnamaldehyde,

were extracted from the organic solution by the Girard's Reagent T. The carbonyl compounds were hydrolyzed with HCl and back-extracted into an organic solvent (pentane). A gas chromatographic analysis of the ketone fraction showed that much of the hydrocinnamaldehyde was converted into a compound which eluted after the original aldehyde. It was found that the hydrocinnamaldehyde reacted with methanol in the presence of HCl. A solution of hydrocinnamaldehyde was mixed with 20 ml of methanol, 40 ml of water, and 15 ml of 8 N HCl. The solution was extracted with pentane. The chromatogram of the products is shown in Figure 36. Peak "a" corresponds to the hydrocinnamaldehyde; peak "b" corresponds to the artifact. A solution of hydrocinnamaldehyde was mixed with 20 ml of ethanol, 40 ml of water, and 15 ml of 8 N HCl. The solution was extracted with pentane. The chromatogram of the products is shown in Figure 37. Peak "c" corresponds to the artifact. The artifacts from the methanol and ethanol solutions were analyzed by GC/MS. Figure 38 shows the mass spectra of the two artifacts. The methanol artifact was found to be (3-methoxy-2-propenyl)benzene. The ethanol artifact was found to be (3-ethoxy-2-propenyl)benzene. A possible mechanism for the formation of the methanol artifact is shown in Figure 39.

A study was done to determine the relationship between the concentration of the methanol in the aqueous solution and the amount of the artifact produced. One ml of a 1 part-per-thousand solution of hydrocinnamaldehyde in methylene chloride was pipetted into each of three separatory funnels, containing 5, 10, and 20 ml, respectively,





Gas chromatographic conditions:

amount:	1 microliter
column:	glass capilary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	75 °C (Fig. 36) 55 °C (Fig 37)
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	200 °C
final hold:	0 minutes
detector temp.:	270 °C
injector temp.:	250 °C
split ratio:	50:1
He pressure	20 p.s.i.
attenuation:	X 32
detector:	FID
chart speed:	0.25 in./minute

Figure 36. Chromatogram of the products from the reaction of hydrocinnamaldehyde with HCl in methanol-H_2O

Figure 37. Chromatogram of the products from the reaction of hydrocinnamaldehyde with HCl in ethanol-H_2O

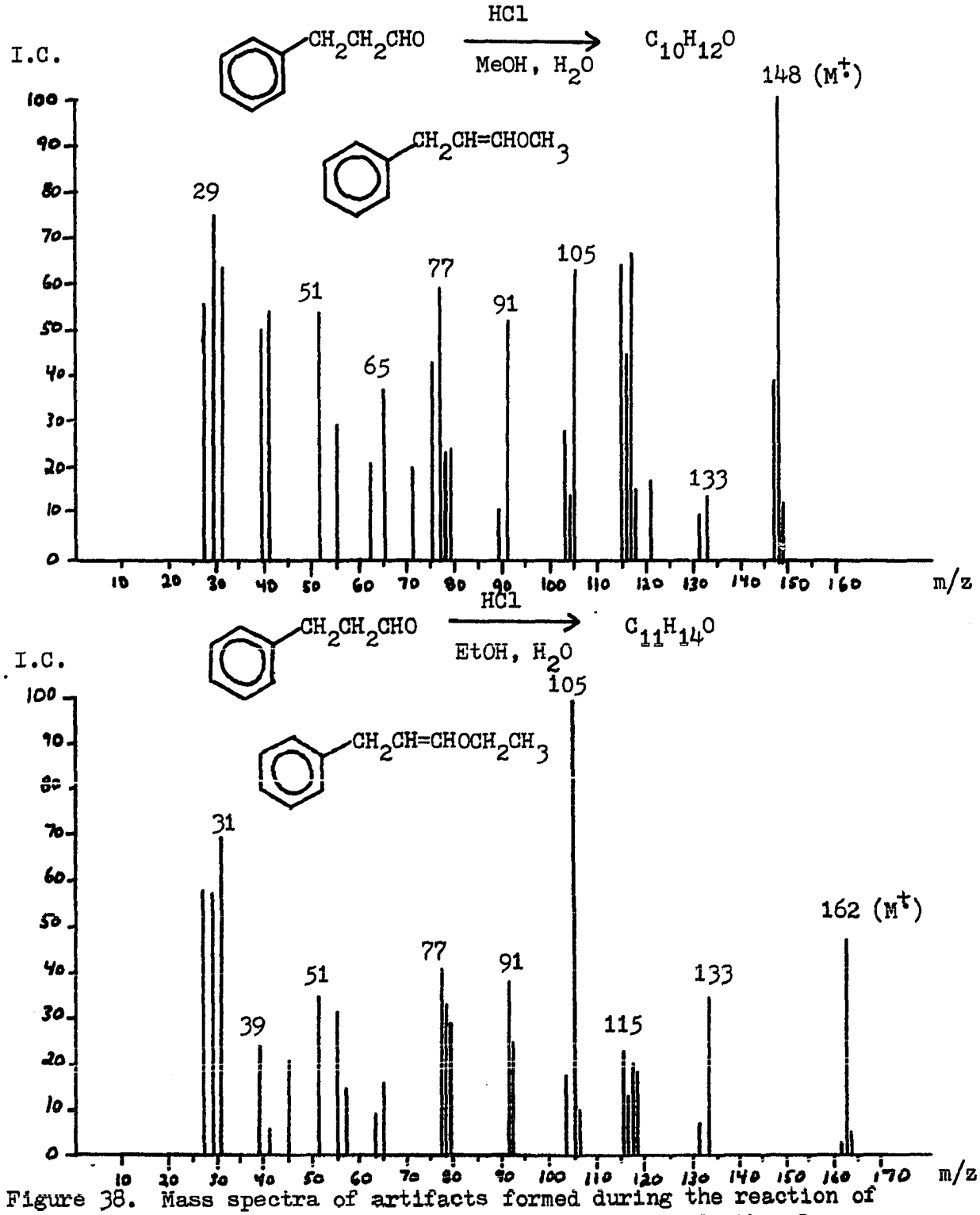


Figure 38. Mass spectra of artifacts formed during the reaction of hydrocinnamaldehyde with methanol and ethanol

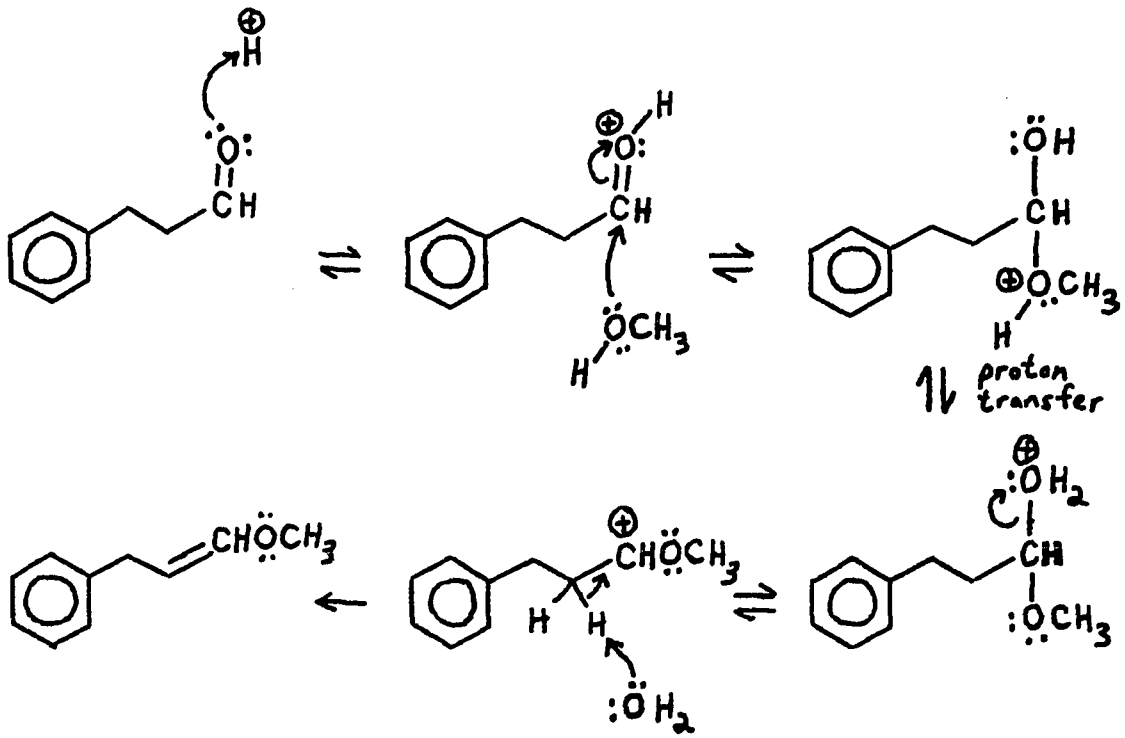


Figure 39. Possible mechanism for the formation of (3-methoxy-2-propenyl)benzene from hydrocinnamaldehyde and methanol

of methanol. Forty ml of water were added to each funnel. Five ml of 8 N HCl were added to each funnel. The solutions were extracted with 30 ml of pentane. The pentane solutions were washed with aqueous sodium carbonate and aqueous sodium chloride solutions. The pentane solutions were dried, filtered, and concentrated. The solutions were analyzed by gas chromatography. The amount of the artifact formed in each solution was determined by measuring the area of the chromatogram peak. Figure 40 shows a graph of the amount of the artifact formed as a function of the relative concentration of methanol. It can be seen that the amount of artifact formed is directly proportional to the concentration of the methanol. The amount of the artifact formed

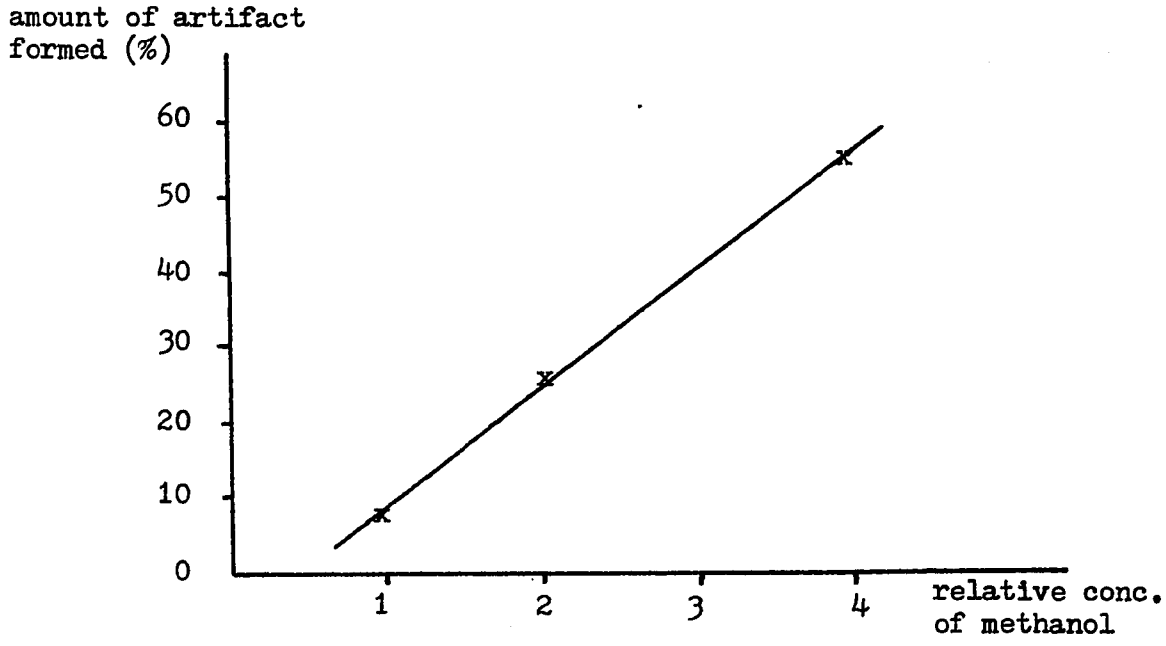


Figure 40. Graph of the amount of (3-methoxy-2-propenyl)benzene formed as a function of the concentration of methanol

can be minimized by diluting the methanol with a sufficient amount of water. The fractionation procedure was changed in order to provide for an adequate dilution of the methanol.

Recovery study results

Class separation results The recoveries of acids, phenols, and bases are listed in Table 3. The standard deviations (in most cases, for six determinations) are listed for the various compounds. The recoveries of carboxylic acids were greater than 65%. The higher molecular weight acids were recovered to a greater degree than were the lower molecular weight acids. The recoveries for phenylacetic acid and trans cinnamic acid were not very reproducible.

Table 3. Recovery study results for acids, phenols, and amines

Acids:	% Recovery	Standard Deviation
Strong Acid Fraction		
Phenylacetic Acid	67	8.2
Decanoic Acid	68	2.5
Trans Cinnamic Acid	94	6.2
Palmitic Acid	87	0.8
Stearic Acid	88	0.9
Phenols:		
2-Chlorophenol	86	3.3
m-Cresol	21	1.7
3,4-Dimethylphenol	5	0.4
2-Naphthol	10	0.2
p-Phenylphenol	0	-
Weak Acid Fraction		
Phenols:		
2-Chlorophenol	9	0.9
m-Cresol	51	4.8
3,4-Dimethylphenol	86	3.1
2-Naphthol	76	2.7
p-Phenylphenol	91	3.7
Base Fraction		
Amines:		
N,N-Dimethylaniline	92	1.2
Dicyclohexylamine	40	19.4
Aniline	82	5.9
n-Hexadecylamine	0	-
Dibenzylamine	81	5.2

The poor reproducibilities may have resulted because of the way the acids were methylated. The acids were converted to their phenyltrimethylammonium salts. The salts were pyrolyzed in the injection port of a gas chromatograph. The procedure has been described by Middleditch and Desiderio to be rapid and quantitative (280). Kralovsky and Matousek found that the yields of methyl esters depended upon the phenyltrimethylammonium hydroxide concentration and on the pyrolysis temperature (281). They found the ester yields of standards to be greater than 85%. It has been noted that the efficiency of the pyrolysis reaction depends on the rate at which the sample is injected into a gas chromatograph (282). The recoveries of phenylacetic acid and trans cinnamic acid may have been affected more by the pyrolysis conditions than were the aliphatic acids.

Eventually, the use of phenyltrimethylammonium hydroxide as a methylating agent was abandoned. The high temperature required in the gas chromatograph injection port led to the decomposition of some unsaturated acids. In addition, the reagent gave many byproducts, including aniline, N-methylaniline, and N,N-dimethylaniline, during the pyrolysis reaction. The byproducts interfered in the analysis of volatile acids. When complex mixtures were analyzed, BF_3-methanol was used as the methylating agent.

The acid recoveries shown in Table 3 were obtained using an aqueous solution of sodium carbonate. When an aqueous solution of sodium bicarbonate was used, the recoveries were much lower. The recoveries of the aromatic acids were between 30% and 55%. Less than

5% of the palmitic and stearic acids were recovered when sodium bicarbonate was used.

Phenols were recovered in both the strong acid fraction and in the weak acid fraction when sodium carbonate was used to extract strong acids. The more acidic phenols, such as 2-chlorophenol, were found in the strong acid fraction. Phenols with many alkyl groups were found mainly in the weak acid fraction. Many phenols were found in both fractions. The recoveries of the phenols were greater than 70%, and in many cases, greater than 90%. The recoveries were fairly reproducible. Because of their polarity, phenols usually do not give sharp peaks when gas chromatographed; and the quantitative analysis based on peak height measurements is less accurate as a result.

The recoveries of phenols were determined when an aqueous solution of sodium bicarbonate was used to extract strong acids. The recoveries of phenols in the weak acid fraction were greater than 85%. Although phenols end up in the strong acid fraction and the weak acid fraction when it was used, sodium carbonate was chosen as the reagent for the extraction of strong acids. The strong acids had to be derivatized before analysis, and it was desirable to isolate them in one fraction.

Problems were encountered in the fractionation of amines. The amines which were tested did not give sharp peaks when they were gas chromatographed. Dicyclohexylamine appeared to decompose during the gas chromatographic analysis. Only 40% of the dicyclohexylamine was recovered, and the results were not reproducible. N,N-dimethylaniline, aniline, and dibenzylamine were recovered in reasonably good yields,

but the latter two compounds gave results with only fair reproducibilities. n-Hexadecylamine was not recovered at all in the base fraction. When the neutral fraction was analyzed, only 5.5% of the n-hexadecylamine was recovered. When the neutral fraction was made basic, however, the recovery of the compound increased to 67%. Apparently, the n-hexadecylamine was carried into the neutral fraction as a salt. The salt would not elute through the gas chromatograph. Addition of base to the neutral fraction hydrolyzed the salt back to the amine.

The problem with the n-hexadecylamine showed what can happen when two "functional groups" in a molecule exert their influence to a comparable degree. The n-hexadecylamine can be thought of as a combination of a polar amine group and a nonpolar alkane group. The long alkane group makes the molecule soluble in an organic solvent even after the amine group is converted to the salt form. It was not expected that compounds like n-hexadecylamine would be found in real samples used to test the fractionation method, so the problem was not considered to be crucial. However, when analyzing samples suspected of containing compounds like n-hexadecylamine, appropriate steps need to be taken in order to recover such compounds.

Problems similar to those with n-hexadecylamine were encountered in the analysis of carboxylic acids. Some of the long-chain aliphatic acids would form precipitates when reacted with sodium carbonate solution. Usually the precipitates would be suspended in the aqueous layer, and would not present a problem. When the aqueous layer was washed with methylene chloride, however, some of the precipitate would become

suspended in the CH_2Cl_2 layer. The fractionation procedure on pp. 46-49 was designed to minimize the loss of the precipitate.

The recoveries of neutral compounds are shown in Table 4. The recoveries for most of the compounds were greater than 90%. In some cases, as much as 98% recoveries were obtained. Considering the large number of sample manipulation steps during the fractionation, the recoveries were considered to be phenomenal. In addition, the results were reproducible. The only neutral compound which was not recovered in greater than 80% yield was benzyl alcohol. This alcohol is soluble in water, and some of it was lost during washing steps. By using aqueous sodium chloride instead of water to wash the extracts, the recovery of benzyl alcohol was increased from 56% to 75%.

The extraction of aldehydes with bisulfite was studied. Initially, methylene chloride was used as the organic solvent. It was found that many aldehydes were not extracted very well from methylene chloride with bisulfite. Better results were obtained when diethyl ether was used. The recoveries of aldehydes from methylene chloride, pentane, and diethyl ether are shown in Table 5. The amounts of the aldehydes were measured in the aldehyde and nonaldehyde fractions. Although ether gave the best recoveries in the aldehyde fraction, it also promoted the decomposition of some of the aldehydes. Some decomposition also occurred when pentane was used as the solvent. Methylene chloride did not promote any significant amount of decomposition. Although it gave the lowest recoveries of aldehydes in the aldehyde fraction, methylene chloride was chosen as the solvent for the aldehyde fractionation because it

Table 4. Recovery study results for compounds in the neutral fraction

Amines:	% Recovery	Standard Deviation
N,N-Dimethylaniline	2	-
Dicyclohexylamine	5	-
Aniline	0	-
n-Hexadecylamine	5.5	-
	67 (alkaline soln.)	-
Dibenzylamine	7	-
Alkanes:		
n-Decane	96	2.5
n-Dodecane	97	0.9
n-Hexadecane	97	1.0
n-Octadecane	98	1.3
PAH's:		
Naphthalene	97	1.0
Fluorene	97	1.5
Anthracene	97	2.2
Fluoranthene	98	1.0
Pyrene	98	0.9
Halides:		
2,4-Dichlorotoluene	97	4.0
p-Dibromobenzene	96	3.6
1-Bromodecane	95	2.0
1-Chlorooctadecane	95	3.1
Esters:		
Ethylhexanoate	92	1.8
Methylbenzoate	94	0.8
Ethylphenylacetate	95	1.4
Methylmyristate	96	2.2
Benzylbenzoate	96	1.6
Ketones:		
2-Octanone	92	1.8
Acetophenone	92	0.9
p-Methylacetophenone	94	0.6
Benzophenone	97	1.4
Benzil	95	1.3

Table 4. continued

Aldehydes:	% Recovery	Standard Deviation
Heptanal	91	3.2
Benzaldehyde	96	2.6
Citronellal	90	2.5
Trans Cinnamaldehyde	98	2.4
Alcohols:		
2-Octanol	95	2.1
Benzyl alcohol	75	-
1-Dodecanol	96	1.7
1-Tetradecanol	98	0.8
1-Hexadecanol	98	1.8

did not promote decomposition of the aldehydes. The aldehydes which would not be extracted by bisulfite would be isolated along with the ketones by the Girard's Reagent T fractionation.

A mixture of ketones in ether was extracted with an aqueous solution of sodium bisulfite in order to determine if any of the ketones would be recovered in the aldehyde fraction. The recoveries of most of the ketones in the aldehyde fraction were less than 4%. However, some methyl ketones were extracted by bisulfite. As much as a 74% recovery in the aldehyde fraction was obtained for 2,5-hexanedione. The recovery of phenyl-2-propanone in the aldehyde fraction was about 25%.

The extraction of ketones with Girard's Reagent T was studied. When a mixture of ketones in ether was extracted with an aqueous solution of Girard's Reagent T, most of the ketones remained in the organic solution (nonketone fraction). Better results were obtained when acetic

Table 5. Recovery study results for the extraction of aldehydes with bisulfite

Aldehydes:	% in Aldehyde Fraction	% in Nonaldehyde Fraction
	-pentane-	
Heptanal	5	89
Furfural	97	0
Citronellal	0	70
Benzaldehyde	89	9
4-Methylbenzaldehyde	37	59
Geranial	0	93
Neral	0	93
Hydrocinnamaldehyde	46	41
Trans Cinnamaldehyde	12	47
	-ether-	
Heptanal	10 (2.1)[a]	87 (9.4)
Furfural	95 (3.6)	0
Citronellal	0	1
Benzaldehyde	95 (4.6)	1 (1.1)
4-Methylbenzaldehyde	57 (12)	35 (9.4)
Geranial	0	0
Neral	0	0
Hydrocinnamaldehyde	66 (9.9)	21 (3.3)
Trans Cinnamaldehyde	15 (6.4)	18 (3.4)
	-methylene chloride-	
Heptanal	7	101
Furfural	100	0
Benzaldehyde	73	28
4-Methylbenzaldehyde	17	80
Hydrocinnamaldehyde	18	73
Trans Cinnamaldehyde	3	92

[a]Standard deviation.

acid-methanol (1:9) was used as the solvent for the Girard's Reagent T. It was found that Girard's Reagent T would extract from 25% to 80% of most ketones when acetic acid-methanol was used as the solvent. Refluxing the ketones with the Girard's Reagent T in acetic acid-methanol did not offer any significant advantages over the room temperature reaction.

The acetic acid in the acetic acid-methanol solvent had to be neutralized in order to extract the nonketone materials. It was inconvenient to titrate the samples with base, so a weak acid ion-exchange resin was tested as an acid catalyst for the Girard T reaction. The recoveries of ketones were lower when the ion-exchange resin was used instead of the acetic acid in both ethanol and methanol solutions. Ethanol offered no advantages over methanol, and the Girard's Reagent T was much less soluble in the ethanol than in methanol.

The use of formaldehyde to hydrolyze Girard T hydrazones was tested. An aqueous solution (37%) of formaldehyde was mixed with a solution of Girard T hydrazones and allowed to stand overnight. The formaldehyde hydrolysis gave results which were similar to those obtained when sodium hydroxide was used to hydrolyze the hydrazones. The formaldehyde solution contained several impurities which would be extracted with the hydrolyzed ketones.

Pentane and methylene chloride were compared as solvents for extracting nonketone materials. It was found that a greater fraction of the ketones would remain in the aqueous layer when pentane was used. Because better results were obtained with pentane than with CH_2Cl_2,

Table 6. Recovery study for the extraction of ketones with Girard's Reagent T

Ketones:	% in Ketone Fraction	% in Nonketone Fraction
4-Heptanone	86 (1.9)[a]	3.6 (1.9)
3-Heptanone	83 (2.0)	5.3 (3.5)
2-Heptanone	84 (1.8)	3.1 (2.8)
Fenchone	0	96 (1.9)
2,5-Hexanedione	4	0
Isophorone	54 (7.5)	0
Acetophenone	99 (2.2)	0
Phenyl-2-propanone	97 (2.8)	0
4-Methylacetophenone	100 (2.0)	0

[a]Standard deviation.

pentane was chosen as the extracting solvent for nonketones. In addition, pentane was used as a solvent during the polar-nonpolar fractionation, so it was not necessary to dissolve the ketone materials in a different solvent before the polar-nonpolar fractionation.

An aqueous solution of sodium hydroxide had been used to neutralize the acetic acid during the ketone fractionation. It was found that some of the Girard T hydrazones would be hydrolyzed during the neutralization. The hydrazones were stable in neutral aqueous solutions, but enough water was added in the course of the neutralization to cause some hydrolysis. Methanolic KOH gave better results because it minimized the amount of water in solution during the neutralization.

Ketones were extracted with Girard's Reagent T using the procedure on pp. 48-49 as modified on page 54. The results are shown in Table 6. The recoveries are given for the ketone fraction and the nonketone

fraction. In most cases, greater than 80% recoveries were obtained for ketones in the ketone fraction. The best results were obtained with the aromatic ketones. The only compound which was not extracted at all by the Girard's Reagent T was fenchone, a bicyclic ketone. The reaction of Girard T with fenchone probably does not occur because of steric effects. 2,5-Hexanedione was extracted with the Girard's Reagent T, but only 4% of the ketone was recovered in the ketone fraction. Fortunately, the 2,5-hexanedione would be recovered in the aldehyde fraction during a complete fractionation. With the exception of isophorone, the ketone results were fairly reproducible.

Solutions of esters, PAH's, and alcohols were extracted with Girard's Reagent T in order to determine if any of the compounds would be lost during the fractionation of ketones. Most of the esters and high molecular-weight alcohols were recovered in the nonketone fraction at yields of about 95%. The lower molecular-weight alcohols were not recovered as well. Only about 80% of 2-octanol was recovered, and greater than 95% of the benzyl alcohol was lost (undoubtedly because of its water solubility). The PAH's were recovered in the nonketone fraction at yields which were essentially quantitative.

The polar-nonpolar fractionation was tested by extracting pentane solutions of PAH's, single-ring aromatic compounds, alcohols, esters, and halides with nitromethane. The amounts of the compounds remaining in the pentane solution after three extractions with nitromethane are shown in Table 7. In addition, the mass distribution ratio, D_M, is listed for each compound. The mass distribution ratios, which are

Table 7. Pentane-nitromethane fractionation results

Compound:	% Remaining in Pentane After 3 Extractions	D_M	(D_M - DMSO)
Naphthalene	1	2.2	(3.0)
Fluorene	0.4	2.4	(3.9)
Anthracene	0	3.4	(8.5)
Fluoranthene	0	3.7	(15.4)
Pyrene	0	3.0	(15.4)
Cumene	23	0.63	
Limonene	28	0.56	
t-Butylbenzene	64	0.23	
Diethylbenzene	34	0.49	
Triethylbenzene	55	0.36	
Phenylcyclohexane	37	0.41	
2-Octanol	4	1.6	(5.7)
2-Ethyl-1-hexanol	3	1.8	(8.4)
1-Decanol	9	1.1	(4.7)
Benzylalcohol	10	2	(124)[a]
2-Phenylethanol	0	18	(82)[a]
1-Tetradecanol	39	0.32	
Methylhexanoate	4	1.9	
Ethylhexanoate	9	1.2	
Methylbenzoate	2	6.5	
Benzylbenzoate	0	12	
Benzylacetate	0	8.4	
Ethylphenylacetate	2	1.9	
Butylbenzoate	43	0.27	
Methyllaurate	66	0.04	
Benzylbenzoate	0.2	6.1	
Butylphthalate	0.2	4.0	
1-Chlorohexane	34	0.41	
1-Bromohexane	37	0.36	
4-Chlorotoluene	11	0.95	
1,3-Dichlorobenzene	12	0.89	
Iodobenzene	8	1.2	
1,4-Dibromobutane	0	3.17	
2,4-Dichlorotoluene	22	0.58	
1,4-Dibromobenzene	9	1.1	
1-Bromodecane	76	0.11	
1-Chloronaphthalene	7	1.2	

[a]These alcohols could not be recovered by extracting the DMSO-water.

a measure of the efficiency of the extraction, were calculated using the following equation:

$$D_M = \frac{100}{\%\text{ remaining in pentane after one extraction}} - 1 \qquad [3]$$

Some of the mass distribution ratios are listed in Table 7 for compounds extracted with dimethyl sulfoxide (D_M - DMSO).

Most of the PAH's were removed completely from pentane after three extractions with nitromethane. The efficiency of the extraction increased with the number of aromatic rings in the PAH's. Single-ring aromatics were not extracted completely from the pentane. Benzene compounds with many aliphatic carbons were less soluble in nitromethane than were benzene compounds with fewer aliphatic carbons. Most of the alcohols were fairly soluble in nitromethane; the solubility decreased with increasing aliphatic character of the molecules. Aromatic esters were quite soluble in the nitromethane; the aliphatic esters were less soluble in the nitromethane. The nitromethane solubilities of halides depended upon the type of halide and the type of hydrocarbon to which the halides were attached. Bromine compounds were more soluble in nitromethane than were the corresponding chlorine compounds. Iodine compounds appeared to be more soluble than the corresponding bromine compounds. The presence of one halide on an aliphatic molecule increased slightly the solubility in nitromethane. In summary, the compounds with high electron densities were more soluble in nitromethane than those with low electron densities.

A mixture of esters, halides, and aromatic compounds in cyclohexane was extracted with nitromethane. In each case, the extraction by nitromethane was less efficient than when pentane was used as the nonpolar solvent. The increased fractionation efficiency and the lower boiling point made pentane a better choice as the solvent.

Dimethyl sulfoxide was compared with nitromethane during the fractionation of PAH's and alcohols. In every case, DMSO extracted a greater amount of the compounds. Compounds could be recovered from the DMSO by adding water to the solution and extracting with pentane. However, two of the alcohols which were tested could not be recovered from the DMSO solution. Because of its efficiency for extracting polar materials, DMSO was chosen as the solvent to be used during the fractionation of polar and nonpolar compounds in mixtures.

Qualitative results for a mixture of standards A mixture of 53 compounds was fractionated. The gas chromatogram of the mixture is shown in Figure 41. Not all of the components eluted through the gas chromatograph when the mixture was analyzed directly. The carboxylic acids had to be derivatized before they could be gas chromatographed (although peaks 32 and 35, which are listed as "unknown," may have been due to two of the more volatile acids). The strong acid fraction chromatogram is shown in Figure 42. The carboxylic acids were methylated with BF_3-methanol. Apparently, some of the 2-chlorophenol was methylated along with the acids (peak #52 was considered to be 2-chloroanisole). The chromatogram of the weak acids is shown in Figure 43. m-Cresol was the only phenol in the mixture which was found to have a significant

Figure 41. Chromatogram of a complex mixture of standards[a]

Figure 42. Chromatogram of the strong acid fraction of the complex mixture[a]

Figure 43. Chromatogram of the weak acid fraction of the complex mixture[a]

Figure 44. Chromatogram of the base fraction of the complex mixture[a]

Gas chromatographic conditions for Figures 41-44:

amount:	1 microliter	
column:		
Figs. 41-43:	glass capillary, 30 meter	
Fig. 44:	¼" diam. glass packed, 3 feet	
liquid phase:		
Figs. 41-43:	SE-54	
Fig. 44	10% Carbowax 20M - 2% KOH	
mode:	temperature programmed	
initial temp.:	55 °C (Figs. 41-43)	70 °C (Fig. 44)
initial hold:	2 minutes	
rate:		
Figs. 41-43:	8 degrees/minute	
Fig. 44:	10 degrees/minute	
final temp.:	270 °C (Figs. 41-43)	210 °C (Fig. 44)
final hold:	0 minutes	
detector temp.:	270 °C (Figs. 41-43)	230 °C (Fig. 44)
injector temp.:	250 °C (Figs. 41-43)	225 °C (Fig. 44)
split ratio:	50:1 (Figs. 41-43)	
He pressure:	20 p.s.i. (Figs. 41-43)	
He flow:	60 ml/min. (Fig. 44)	
attenuation:		
Figs. 41-42:	X 8	
Fig. 43:	X 16	
Fig. 44:	X 64	
detector:	FID	
chart speed:	0.25 in./minute	

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[a]See Table 8 for chromatogram peak identifications.

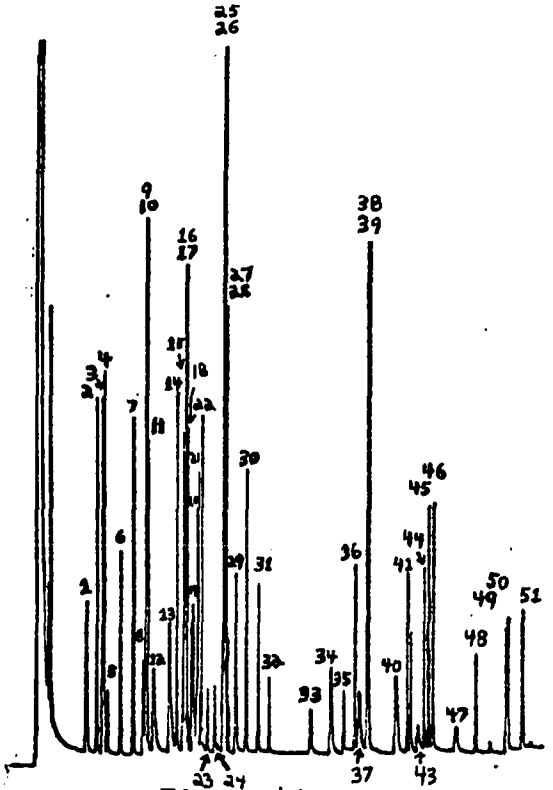

Figure 41

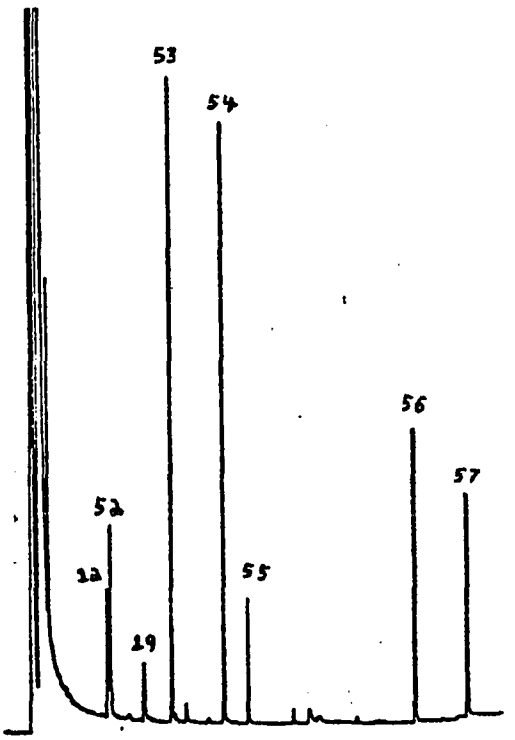

Figure 42

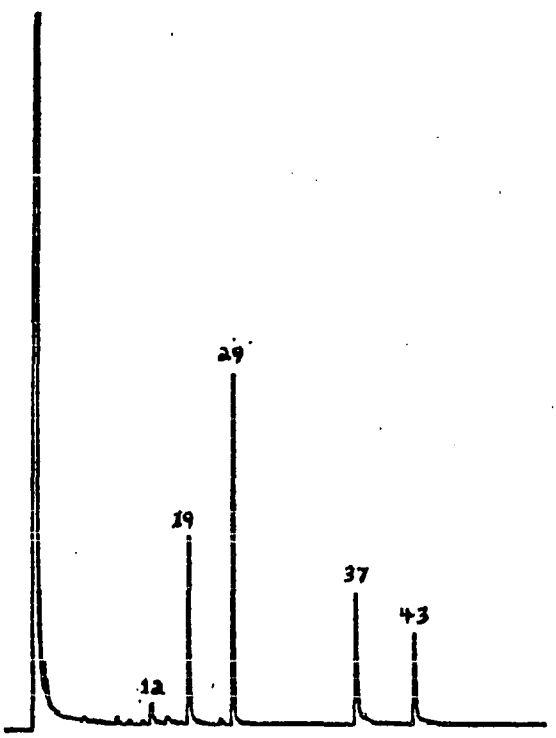

Figure 43

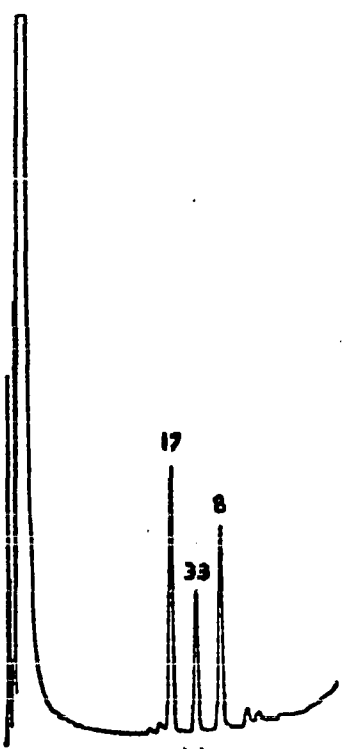

Figure 44

concentration in both acidic fractions. The chromatogram of the base fraction is shown in Figure 44. Good separations of acids, bases, and neutrals were obtained.

The chromatogram of the aldehyde fraction is shown in Figure 45. Almost all of the furfural, benzaldehyde, 2,5-hexanedione, and hydrocinnamaldehyde which were recovered, were found in the aldehyde fraction. 4-Methylbenzaldehyde was not extracted as efficiently with bisulfite as was benzaldehyde. Small amounts of methyl ketones (having only one carbonyl group) were found in the aldehyde fraction. In addition, some benzyl alcohol was also found in the aldehyde fraction.

Figure 46 shows the chromatogram for the ketone fraction. The carbonyl compounds which were not extracted by bisulfite were found in the ketone fraction. Hydrocinnamaldehyde, which was not completely removed by the bisulfite extraction, reacted with methanol to form (3-methoxy-2-propenyl)benzene (the problem with the formation of the artifact from hydrocinnamaldehyde was discovered at this point, and the basic fractionation procedure was changed in order to minimize the problem).

The chromatogram of the nonpolar fraction is shown in Figure 47. Alkanes, aliphatic esters, and aliphatic halides were recovered in the nonpolar fraction. Small amounts of fenchone and 2,4-dichlorotoluene were also found in the nonpolar fraction.

The chromatogram of the polar fraction is shown in Figure 48. The polar fraction contained PAH's, alcohols, aromatic esters, some aliphatic esters, and aromatic halides. In addition, most of the fenchone

Figure 45. Chromatogram of the aldehyde fraction of the complex mixture[a]

Figure 46. Chromatogram of the ketone fraction of the complex mixture[a]

Figure 47. Chromatogram of the nonpolar fraction of the complex mixture[a]

Figure 48. Chromatogram of the polar fraction of the complex mixture[a]

Gas chromatographic conditions for Figures 45-48:

amount:	1 microliter
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	0 minutes
detector temp.:	270 °C
injector temp.:	250 °C
split ratio:	50:1
He pressure:	20 p.s.i.
attenuation:	
Figs. 45-46:	X 16
Figs. 47-48:	X 8
detector:	FID
chart speed:	0.25 in./minute

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[a]See Table 8 for chromatogram peak identifications.

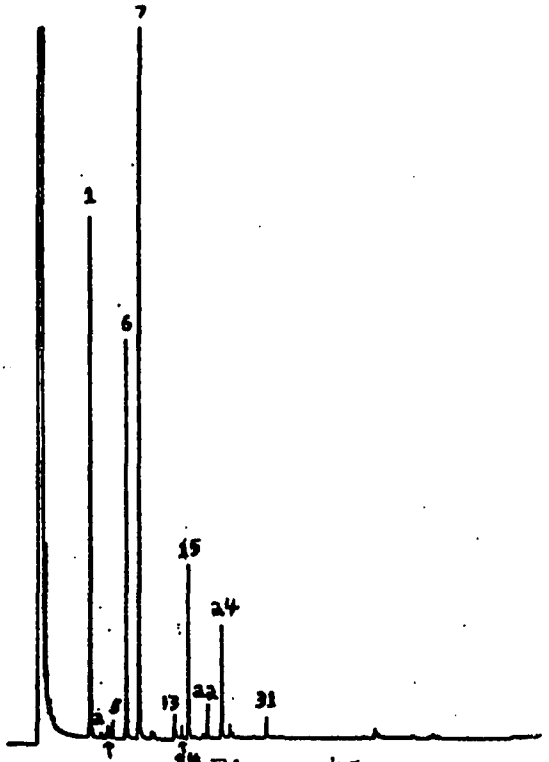


Figure 45

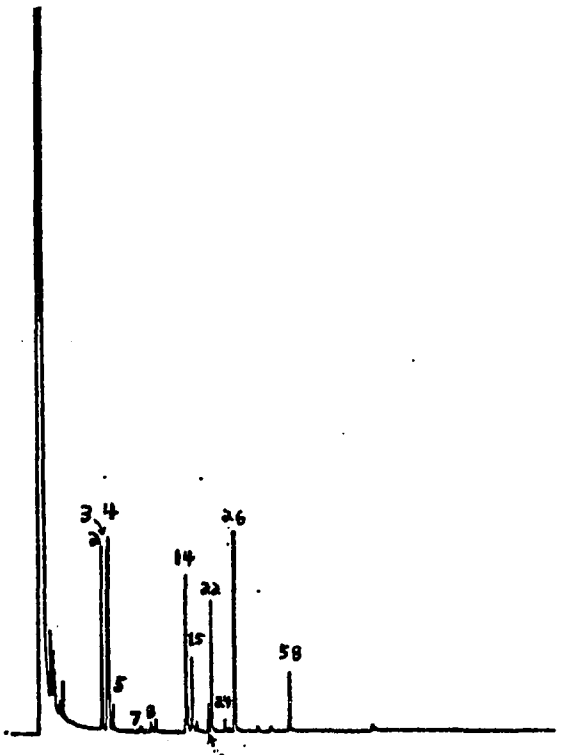


Figure 46

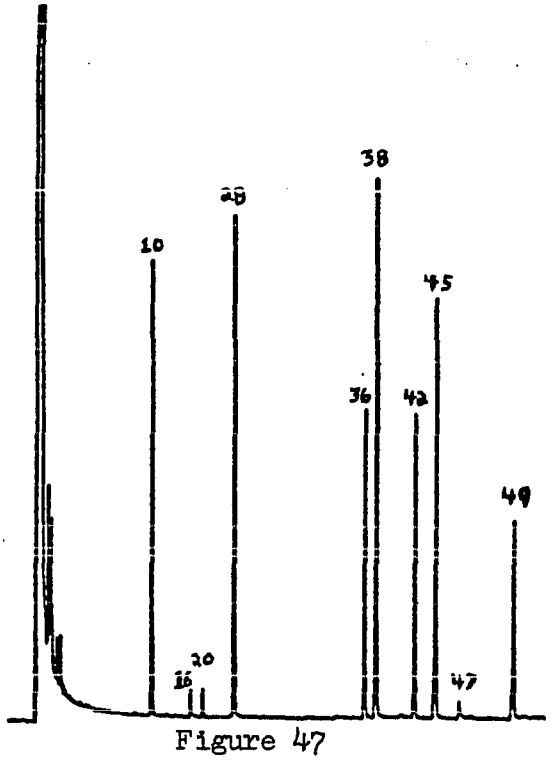


Figure 47

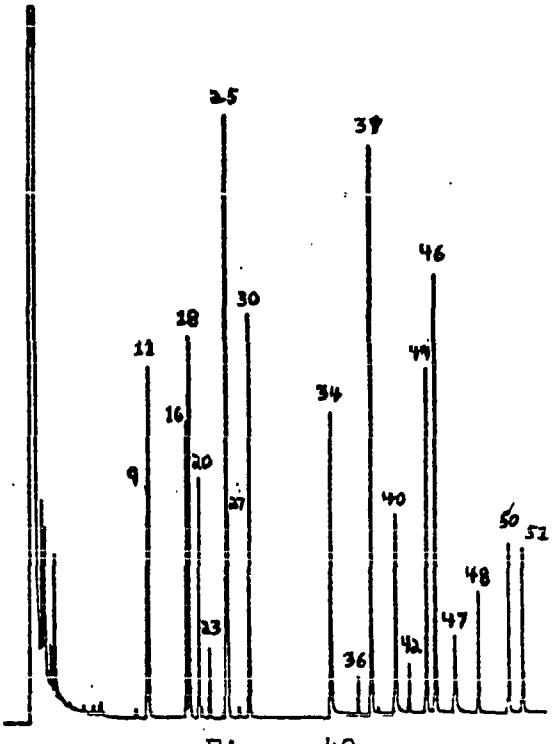


Figure 48

Table 8. Complex mixture chromatogram peaks

1.	Furfural	30.	Ethylphenylacetate
2.	4-Heptanone	31.	Trans Cinnamaldehyde
3.	3-Heptanone	32.	unknown
4.	2-Heptanone	33.	Dicyclohexylamine
5.	Heptanal	34.	1-Dodecanol
6.	2,5-Hexanedione	35.	unknown
7.	Benzaldehyde	36.	1-Bromododecane
8.	Aniline	37.	2-Naphthol
9.	Ethylhexanoate	38.	n-Hexadecane
10.	n-Decane	39.	Fluorene
11.	2-Octanol	40.	1-Tetradecanol
12.	2-Chlorophenol	41.	Dibenzylamine
13.	Benzyl alcohol	42.	Methylmyristate
14.	Acetophenone	43.	4-Phenylphenol
15.	4-Methylbenzaldehyde	44.	Benzylbenzoate
16.	Fenchone	45.	n-Octadecane
17.	N,N-Dimethylaniline	46.	Anthracene
18.	Methylbenzoate	47.	1-Hexadecanol
19.	m-Cresol	48.	Butylphthalate
20.	2,4-Dichlorotoluene	49.	1-Chlorooctadecane
21.	Isophorone	50.	Fluoranthene
22.	Phenyl-2-propanone	51.	Pyrene
23.	impurity	52.	2-Chloroanisole?
24.	Hydrocinnamaldehyde	53.	Phenylacetic acid, methyl ester
25.	Naphthalene	54.	Decanoic acid, methyl ester
26.	4-Methylacetophenone	55.	Trans Cinnamic acid, methyl ester
27.	1,4-Dibromobenzene	56.	Palmitic acid, methyl ester
28.	n-Dodecane	57.	Stearic acid, methyl ester
29.	3,4-Dimethylphenol	58.	artifact : (3-methoxy-2-propenyl)benzene

was recovered in the polar fraction.

The fractionation procedure worked well for the complex mixture of standards. For the most part, clean separations of the various compound classes were obtained. Compounds which eluted together from the gas chromatograph were separated during the fractionation. The

fractionation simplified the complex mixture to the point where it was possible to identify peaks for all of the 53 components.

Quantitative results for a mixture of standards A mixture of 41 neutral compounds was fractionated. The recoveries of the compounds in the strong acid fraction, SAF; the weak acid fraction, WAF; the base fraction, BAF; the aldehyde fraction, ALF; the ketone fraction, KEF; the nonpolar fraction, NPF; and the polar fraction, POF, were determined. The results of two determinations are given in Table 9. In addition, the total amount of each compound recovered, TOT, and the average of the two determinations, AVE, are listed.

Some of the toluene was found in every fraction except the strong acid fraction. However, most of the compound was found in the polar fraction. Almost all of the 2-cyclopentenone was lost during the fractionation, and all of the 2,4-dimethylbenzylalcohol was lost. The recoveries for most of the other compounds were between 40% and 90%. Most of the results were reproducible. Considering the fact that the concentrations of the compounds were less than 2 ppm during the fractionation, these results were considered to be quite good. As the concentration of the compounds decrease, the relative amounts of the compounds lost due to water solubility, adsorption on surfaces, and sample manipulation would be expected to increase.

The most interesting results were obtained with 1,2-benzenedicarboxylaldehyde. This compound was expected to be found in the aldehyde fraction or the ketone fraction. The compound was recovered in the weak acid fraction. Apparently the 1,2-benzenedicarboxylaldehyde

Table 9. Recovery results for a complex mixture of standards[a]

COMPOUND	% RECOVERIES SAF	WAF	BAF	ALF	KEF	NPF	POF	TOT	AVE
Toluene		1 2	0.8 0.6	1.1 0.9	2 2	5 9	50 39	60 54	57
2-Cyclopentenone					1.8 0.9			1.8 0.9	1.3
p-Xylene						9.1 17	54 43	63 60	62
o-Xylene						6.4 12	61 52	66 64	65
4-Ethyltoluene						15 25	45 34	60 59	60
Benzaldehyde				50 46	<1 <1			50 46	48
2-Ethyltoluene						12 20	51 41	63 61	62
1,2,4-Trimethylbenzene						40 22	49 40	89 62	76
n-Decane						61 63		61 63	62
1,2,3-Trimethylbenzene						10 17	56 47	66 64	65
Indan						7 12	63 56	70 68	69
Indene						0 1.6	73 70	73 72	72
Acetophenone					60 66			60 66	63
1,3-Dimethyl-4-ethylbenzene						20 28	38 29	58 57	58
4-Methylbenzaldehyde				6.4 6.2	41 28			46 34	40
n-Hendecane						64 65		64 65	64
1,2,4,5-Tetramethylbenzene						20 27	47 36	67 63	65
3-Methylacetophenone					88 89			88 89	88
Naphthalene							80 77	80 77	78
1,3,5-Triethylbenzene						45 54	30 19	75 73	74
2-Indanone					47 50			47 50	48

[a]See text for explanation of abbreviations.

Table 9. continued

COMPOUND	% RECOVERIES SAF	WAF	BAF	ALF	KEF	NPF	POF	TOT	AVE
2,4-Dimethylbenzylalcohol								0 0	0
1,2-Benzenedicarboxylaldehyde		42 45						42 45	44
2-Methylnaphthalene						0 1.7	80 79	80 81	80
2,4,6-Trimethylbenzaldehyde					73 40			73 40	56
1-Methylnaphthalene							76 76	76 76	76
Biphenyl							83 81	83 81	82
1-Ethylnaphthalene						1.7 4.0	80 76	82 80	81
1,4-Dimethylnaphthalene						2.3 4.7	79 76	81 81	81
Acenaphthylene						0 1.3	88 88	88 89	88
Acenaphthene							82 80	82 80	81
1-Naphthaldehyde				0.4 <.5	59 38			59 38	48
Dibenzofuran							75 73	75 73	74
2,3,5-Trimethylnaphthalene						2.1 5.9	76 68	78 74	76
Fluorene							79 76	79 76	78
4,4'-Dimethylbiphenyl						1.9 4.6	73 66	75 71	73
1,1-Diphenylacetone					76 75			76 75	76
9-Fluorenone					76 73			76 73	74
Phenanthrene						4.5 4.7	76 69	80 74	77
n-Octadecane						64 73		64 73	68
Benzil		1 0			18 11		31 30	50 41	46

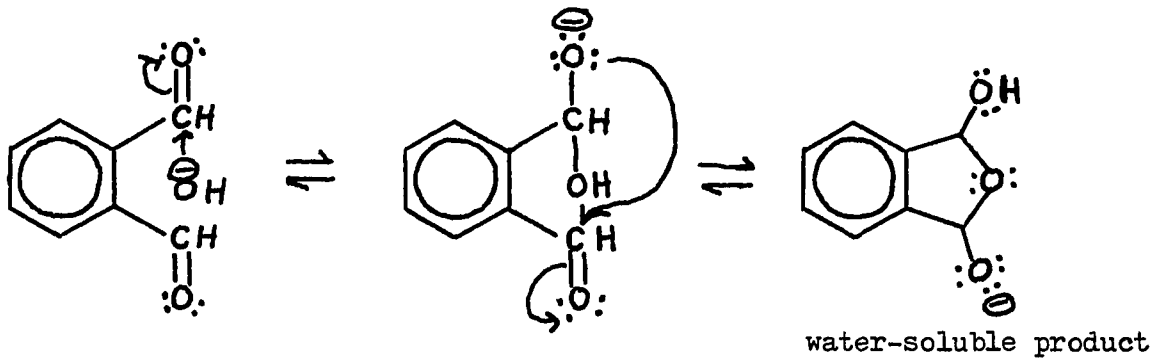


Figure 49. Possible mechanism for the formation of the water-soluble product from the reaction of 1,2-benzenedicarboxylaldehyde with sodium hydroxide

forms a water-soluble species in the presence of sodium hydroxide. A possible mechanism for the formation of the water-soluble species is shown in Figure 49. The fact that the aldehyde groups are in the "ortho" configuration makes the reaction possible. The "meta" and "para" isomers would not be expected to form a water-soluble species in the presence of hydroxide. That hypothesis was confirmed by extracting a methylene chloride solution of 1,2-benzenedicarboxylaldehyde and 1,4-benzenedicarboxylaldehyde with an aqueous solution of sodium hydroxide. Almost 80% of the ortho isomer was recovered from the sodium hydroxide solution, while about 2% of the compound was found in the methylene chloride layer. None of the para isomer was recovered from the sodium hydroxide solution, while about 94% of the compound was recovered in the methylene chloride solution.

The analysis of 1,2-benzenedicarboxylaldehyde showed that acid-

base-neutral fractionation is not always as simple as it might seem. Any compound which forms a water-soluble derivative in the presence of acid or base can be extracted into base or acid fractions, respectively. In addition, special precautions must be taken in order to recover materials which can form water-soluble derivatives with both acids and bases. For example, in order to recover an amino acid, the pH of the solution must be adjusted so that the amino acid is in its neutral form.

The results in Table 9 show that most compounds in a complex mixture can be separated into various chemical classes, even when the compounds are present at low concentrations. Although some compounds may be lost during the fractionation, most compounds can be recovered in sufficient yield to obtain good qualitative and quantitative data.

FRACTIONATION OF GASOLINE, DIESEL FUEL, AND AUTOMOBILE EXHAUST

Review of Related Work

Automobile exhaust consists of a mixture of inorganic gases, water vapor, organic compounds, and particulate matter. The organic material in the exhaust has been shown to consist of several hundred compounds, including phenols, aldehydes, ketones, alkanes, and PAH's. Because of the presence of many different types of compounds, automobile exhaust was chosen to test the liquid-liquid fractionation method developed in this work. In addition, gasoline and diesel fuel, which are complex mixtures of organic compounds, were fractionated by the same method in order to show the relationship between the fuels and the exhaust from automobiles using those fuels.

Gasoline consists of a mixture of aliphatic hydrocarbons (straight-chain, branched-chain, and cyclic), one and two-ring aromatic compounds, and, at lower concentrations, aliphatic olefins (283). Martin (16) and Stavinoha (9) used subtractor columns in combination with gas chromatography to analyze the three hydrocarbon types in gasoline. Schwende and Novotny determined aromatic compounds in the presence of other fuel components by using gas chromatography with UV detection (67). Stavinoha and Newman separated aromatic compounds from other gasoline components by using an N,N-bis(2-cyanoethyl)formamide gas chromatographic column (19). Hauser and Pattison developed a method for determining aliphatic compounds in gasoline, diesel fuel, and automobile exhaust (242). Petrovic and Vitorovic developed a gas chromatographic "fingerprinting"

method for identifying the sources of pollution from various fuels (284). An automatic gas chromatographic method for analyzing natural gas and light petroleum samples was developed by Johansen (285).

Several workers have used gas chromatography to characterize the individual components of gasoline. Dell'Acqua et al. analyzed several different brands of gasoline, and they identified 22 of the major components (286). Calvin et al. found that most of the hydrocarbons in gasoline were in the carbon number range of C_3 - C_{12} (283). They found that toluene was the most abundant single component in all of the gasolines which they analyzed. Sanders and Maynard used capillary column gas chromatography to analyze the C_3 - C_{12} hydrocarbons in gasolines (287). Their results for the composition of a typical regular-grade gasoline are shown in Table 10. DiCorcia et al. chromatographed premium-grade gasoline and naphtha samples on gas chromatographic columns packed with graphitized carbon black modified with 2,4,5,7-tetranitrofluorenone (288). They observed 196 compounds in premium-grade gasoline; 157 of the compounds were identified.

The composition of diesel fuel differs significantly from that of gasoline. Typical diesel fuels contain 50 - 85% saturated and 10 - 45% aromatic compounds (289). O'Donnell and Dravnieks analyzed #1 diesel fuel, and they found that the fuel contained 15.3% aromatics, 83% saturates, and 1.7% olefins (290). In addition, the fuel contained phenols at a concentration of 149 ppm. Elemental analysis of the fuel indicated that the concentrations of nitrogen and sulfur were 14 ppm and 0.13%, respectively. Reinhard et al. found that diesel fuel contained the

Table 10. Hydrocarbon composition of typical regular-grade gasoline

Component	Weight %	Component	Weight %
Propane	0.14	Methylcyclopentane + 3,3-dimethyl-1-pentene	1.50
Isobutane	0.30	2,2-Dimethylpentane + 2,3-dimethyl-2-butene + 2,3,3-trimethylbutene	0.20
Isobutylene + 1-butene	0.02	Benzene	1.35
n-Butane	3.93	2,4-Dimethylpentane	0.32
trans-2-butene	0.16	2,2,3-Trimethylbutane	trace
Neopentane	0.02	4,4-Dimethyl-cis-2-pentene	0.02
cis-2-butene	0.13	2,4-Dimethyl-1-pentene	trace
3-Methyl-1-butene	0.08	1-Methylcyclopentene + 2-methyl-cis-3-hexene	0.37
Isopentane	7.88	2,4-Dimethyl-2-pentene + 3-ethyl-1-pentene + 3-methyl-1-hexene	0.05
1-Pentene	0.34	2,3-Dimethyl-1-pentene	0.01
2-Methyl-1-butene	0.35	2-Methyl-trans-3-hexene + 5-methyl-1-hexene	0.05
n-Pentane	7.27	3,3-Dimethylpentane	trace
trans-2-pentene	0.52	Cyclohexane + 4-methyl-trans-2-hexene	0.36
cis-2-pentene	0.43	4-Methyl-1-hexene + 4-methyl-trans-2-hexene	0.08
2-Methyl-2-butene	1.09	3-Methyl-2-ethyl-1-butene + 5-methyl-trans-2-hexene	0.03
2,2-Dimethylbutane	0.17	Cyclohexene	0.03
Cyclopentene	0.13	2-Methylhexane + (5-methyl-cis-2-hexene)	1.25
3-Methyl-1-pentene + 4-methyl-1-pentene	0.16	2,3-Dimethylpentane + (1,1-dimethylcyclopentane) + (3,4-dimethyl-cis-2-pentene)	0.47
4-Methyl-cis-2-pentene	0.05	3-Methylhexane	1.41
2,3-Dimethyl-1-butene	0.10	1-cis-3-Dimethylcyclopentane + 2-methyl-1-hexene + 3,4-dimethyl-trans-2-pentene	0.41
Cyclopentane	0.58	1-trans-3-Dimethylcyclopentane + 1-heptene + 2-ethyl-1-pentene	0.40
2,3-Dimethylbutane	0.59		
4-Methyl-trans-2-pentene	0.30		
2-Methylpentane	3.85		
2-Methyl-1-pentene	0.22		
3-Methylpentane + (1-hexane)[a] + (2-ethyl-1-butene)	2.72		
cis-3-Hexene	0.13		
trans-3-Hexene	0.15		
3-Methylcyclopentene	0.08		
2-Methyl-2-pentene	0.32		
3-Methyl-cis-2-pentene	0.45		
n-Hexane + (4,4-dimethyl-1-pentene)	3.50		
trans-2-Hexene	0.36		
cis-2-Hexene	0.24		
3-Methyl-trans-2-pentene	0.44		
4,4-Dimethyl-trans-2-pentene	trace[b]		

[a] ( ) Designates a minor component.

[b] Less than 0.01 weight %.

Table 10. continued

Component	Weight %	Component	Weight %
3-Ethylpentane + 3-methyl-trans-2-hexene	0.25	3-Methylheptane + (3-methyl-3-ethylpentane)	1.54
1-trans-2-Dimethylcyclopentane	0.20	2,2,5-Trimethylhexane + (1-cis-2-cis-4-trimethylcyclopentane)	0.17
2,2,4-Trimethylpentane + (trans-3-heptene)	0.32	1,1-Dimethylcyclohexane + 1-trans-4-dimethylcyclohexane + 1-cis-3-dimethylcyclohexane	0. 27
cis-3-Heptene	0.17	1-Methyl-trans-3-ethylcyclopentane	0.12
3-Methyl-cis-3-hexene + 2-methyl-2-hexene + 3-methyl-trans-3-hexene	0.35	2,2,4-Trimethylhexane	0.18
3-Ethyl-2-pentene	0.04	1-Methyl-trans-2-ethylcyclopentane + 1-methyl-cis-3-ethylcyclopentane	0.13
trans-2-Heptene	0.10	Cycloheptane + 1-methyl-1-ethylcyclopentane	0.11
n-Heptane + (3-methyl-cis-2-hexene)	1.92	1-trans-2-Dimethylcyclohexane + 1-cis-2-cis-3-trimethylcyclopentane	0.18
2,3-Dimethyl-2-pentene + cis-2-heptene	0.14	n-Octane + (1-cis-4-dimethylcyclohexane)	1.43
1-cis-2-Dimethylcyclopentane	0.13	1-trans-3-Dimethylcyclohexane	0.12
Methylcyclohexane + 2,2-dimethylhexane + 1,1,3-trimethylcyclopentane	0.61	2,4,4-Trimethylhexane	0.04
2,5-Dimethylhexane	0.24	Isopropylcyclopentane	0.02
Ethylcyclopentane	0.14	2,3,5-Trimethylhexane	0.05
2,4-Dimethylhexane	0.34	2,2-Dimethylheptane	0.08
2,2,3-Trimethylpentane	trace	1-Methyl-cis-2-ethylcyclopentane	0.11
1-trans-2-cis-4-Trimethylcyclopentane	0.16	2,4-Dimethylheptane + 2,2,3-trimethylhexane	0.24
Toluene + (3,3-Dimethylhexane)	5.92	2,2-Dimethyl-3-ethylpentane + 2-methyl-4-ethylhexane	0.09
1-trans-2-cis-3-Trimethylcyclopentane	0.25	2,6-Dimethylheptane + (1-cis-2-dimethylcyclohexane)	0.20
2,3,4-Trimethylpentane	0.11	n-Propylcyclopentane	0.06
2,3,3-Trimethylpentane	0.05	Ethylcyclohexane	0.36
1,1,2-Trimethylcyclopentane	0.11	2,5-Dimethylheptane + 3,5-dimethylheptane	0.14
2,3-Dimethylhexane + 2-methyl-3-ethylpentane	0.39		
2-Methylheptane	1.05		
4-Methylheptane	0.52		
3,4-Dimethylhexane + (1-cis-2-trans-4-trimethylcyclopentane)	0.20		
3-Ethylhexane	trace		

Table 10. continued

Component	Weight %	Component	Weight %
Ethylbenzene	2.70	Isobutylbenzene	0.06
2,4-Dimethyl-3-ethyl-pentane	0.05	1-Methyl-3-isopropyl-benzene	0.12
3,3-Dimethylheptane	0.08	n-Decane	0.50
2,3,3-Trimethylhexane	0.12	1,2,3-Trimethylbenzene + 1-methyl-4-isopropyl-benzene	0.68
2-Methyl-3-ethylhexane	0.13	1-Methyl-2-isopropylben-zene + indan	0.35
p-Xylene	1.54	1,3-Diethylbenzene	0.25
m-Xylene + (3,3,4-tri-methylhexane)	3.87	1-Methyl-3-n-propylbenzene	0.48
2,3-Dimethylheptane	0.39	n-Butylbenzene	0.25
3,4-Dimethylheptane	0.33	1,2-Diethylbenzene + 1,4-diethylbenzene + 1-meth-yl-4-n-propylbenzene	0.44
4-Methyloctane	0.55	1-Methyl-2-n-propylbenzene	0.16
2-Methyloctane	0.62	1,3-Dimethyl-5-ethylbenzene	0.42
3-Ethylheptane	0.16	2-Methylindan	0.10
3-Methyloctane	0.85	1,4-Dimethyl-2-ethylbenzene	0.36
o-Xylene + (2,2,4,5-tetra-methylhexane)	2.05	1-Methylindan	0.10
2,2,4-Trimethylheptane	0.12	1-Methyl-3-tert-butyl-benzene	0.11
2,2,5-Trimethylheptane + 2,2,6-trimethylheptane	0.07	1,3-Dimethyl-4-ethylbenzene	0.27
2,5,5-Trimethylheptane + 2,4,4-trimethylheptane	0.06	1,3-Dimethyl-2-ethylbenzene + 1,2-dimethyl-4-ethyl-benzene	0.50
Isopropylbenzene	0.23	1-Methyl-4-tert-butyl-benzene	0.13
n-Nonane	0.83	1,2-Dimethyl-3-ethylbenzene	0.09
3,3,5-Trimethylheptane	0.05	n-Undecane	0.22
2,4,5-Trimethylheptane + 2,3,5-trimethylheptane	0.07	1,2,4,5-Tetramethylbenzene	0.21
n-Propylbenzene	0.72	1,2,3,5-Tetramethylbenzene	0.42
2,6-Dimethyloctane + (2,2,3,3-tetramethyl-hexane)	0.12	Isopentylbenzene	0.17
1-Methyl-3-ethylbenzene	1.84	5-Methylindan	0.30
1-Methyl-4-ethylbenzene	1.00	4-Methylindan	0.16
3,3,4-Trimethylheptane + 3,4,4-trimethylheptane + 3,4,5-trimethylheptane	0.08	n-Pentylbenzene	0.14
1-Methyl-2-ethylbenzene + 5-methylnonane	0.90	1,2,3,4-Tetramethylbenzene	0.19
4-Methylnonane	0.26	Tetralin	0.14
1,3,5-Trimethylbenzene	0.76	Napthalene	0.24
2-Methylnonane	0.41	1,3-Dimethyl-5-tert-butyl-benzene	0.16
3-Methylnonane	0.32	n-Dodecane	0.09
1,2,4-Trimethylbenzene	2.83		
sec-Butylbenzene	0.13		

following aromatic compounds: C_0 - C_{10} benzenes, C_0 - C_8 naphthalenes, C_0 - C_5 indans, C_0 - C_5 tetralins, acenaphthene, C_0 - C_3 fluorenes, and C_0 - C_3 phenanthrenes (291). Typical diesel fuels contain 30-70% naphthalenes; 16-21% acenaphthalenes; 6-10% phenanthrenes; 4-38% indans, tetralins, and indenes; and 2-32% alkyl benzenes (131).

The exhaust from internal combustion engines using gasoline and diesel fuel has been analyzed extensively. The exhaust coming out of an automobile tail pipe is more than 80% hydrocarbons on a mole basis (292). The composition of the exhaust has been found to be dependent upon the type of fuel used (293). The exhaust compounds either entirely or partially formed as combustion products comprise about 60% of the total exhaust; the remainder of the exhaust is similar in composition to the fuel used (292).

Several different methods have been used to collect automobile exhaust for analysis. Some of the more common sampling methods have been reviewed by Habibi (294) and Dimitriades et al. (4). Methods for collecting gaseous organic compounds (and suspended particulate matter) include adsorption on organic polymers such as Tenax (see Appendix) and Chromosorb resins (see Appendix), cryogenic trapping, and collection in bags and metal containers (295). In some cases, exhaust can be sampled continuously, especially in total hydrocarbon analyses (296). Eggertsen and Nelson trapped C_2 - C_5 hydrocarbons in engine exhaust in a short gas chromatographic column cooled in liquid oxygen (297). The sample was analyzed by elution with helium through a longer gas chromatographic column. Karasek and Smythe used a dual Friedrich condenser system to

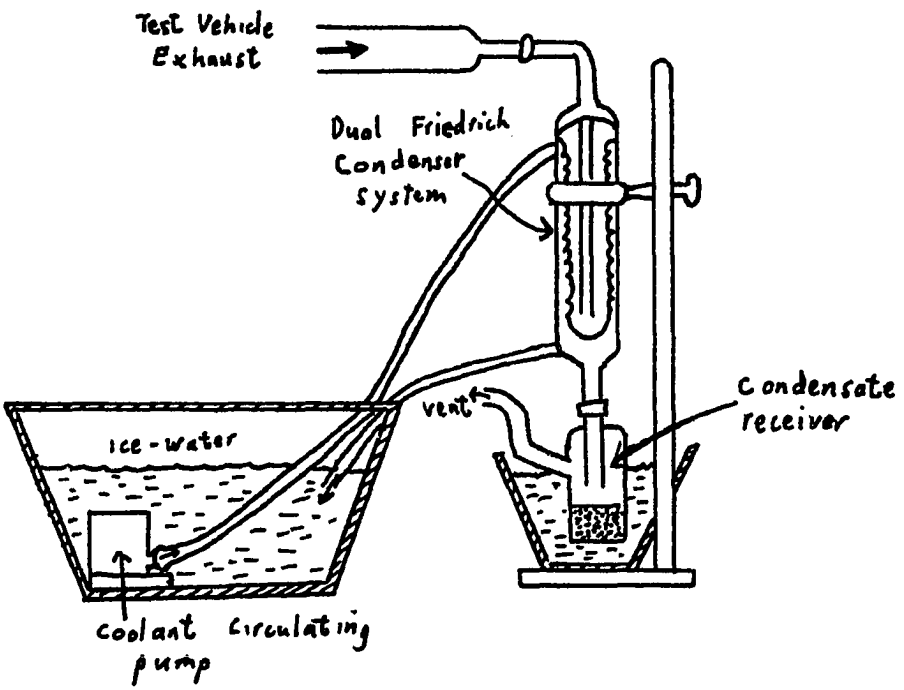


Figure 50. Automobile exhaust collection system used by Karasek and Smythe (44,134)

collect diesel exhaust (44,134). A diagram of the collection system is shown in Figure 50. They found that the contact of particulate matter and organic-aqueous condensates did not introduce any observable effects in the composition of organic compounds found in the liquid phase or adsorbed on the particulate matter. However, other workers have noted that there may be problems with side effects when organic material is condensed along with water (295). Some of the problems which can occur in the sampling of organic compounds include failure to collect

quantitatively, chemical changes in the sample, and a failure to regenerate completely the substances collected (298). Calvin et al. tested various sampling devices, including evacuated glass bulbs, aluminized Mylar bags (Mylar is a registered trademark of DuPont), gas sampling loops, gas chromatographic column traps, and gas washing bottles containing cyclohexane (283). They found that bubbling the exhaust through cyclohexane was the best method for collecting the higher molecular-weight materials.

Automobile exhaust contains a mixture of aliphatic, aromatic, olefinic, and oxygenated compounds. Boyer and Laitenin found that the composition of exhaust from a gasoline engine was about 50% saturated aliphatic compounds, 5% PAH's, and 30% oxygenated compounds (122). Most of the hydrocarbons in exhaust from spark-ignition engines are in the carbon number range of C_1 - C_{12} (4). Jacobs used gas chromatography to analyze the C_1 to C_{10} hydrocarbons in automobile exhaust (299). Caplin determined the concentrations of many hydrocarbons in automobile exhaust (300). He found that the total concentrations of paraffins, acetylenes, aromatics, and olefins were 324 ppm, 118 ppm, 206 ppm, and 310 ppm, respectively. Calvin et al. chromatographed a sample of automobile exhaust and found 28 major components (283). One of the components which they found was indene, a compound which was not found in gasoline.

Subtractor columns have been used to analyze automobile exhaust. Coulson used subtractor columns in combination with gas chromatography and mass spectrometry to analyze auto exhaust according to the following types:

paraffins, cycloparaffins, mono-olefins, acetylenes, cyclo-olefins, and aromatics (6). He collected the exhaust sample in a one-liter stainless steel cylinder held at 100 °C. Innes et al. used parallel subtractors combined with dual flame ionization detectors to analyze auto exhaust continuously for paraffins and olefins (10). Raible and Seizinger used a subtractor column to separate diesel exhaust into saturated and unsaturated compounds (17). Subtractor columns were used by McEwen (7) and Klosterman and Sigsby (11) in their analyses of auto exhaust.

Methods have been developed for analyzing the individual components of automobile exhaust. Papa developed a gas chromatographic method for analyzing compounds in exhaust, and he found more than 200 compounds (301). Papa, Dinsel, and Harris (302) analyzed the C_1 - C_{12} hydrocarbons in automobile exhaust. Table 11 lists the names of the compounds which they identified in the exhaust. Nebel used gas chromatography to measure benzene in the exhaust of five different cars (303). The average benzene emission of the five cars while being driven was found to be 19.9 mg per mile. Barber et al. used paper chromatography and gas chromatography to determine phenols in automobile exhaust (304). They collected the exhaust samples in a series of impingers containing aqueous solutions of sodium hydroxide.

The composition of diesel exhaust differs significantly from that of gasoline exhaust. Table 12 lists some of the typical exhaust data for gasoline engines and diesel engines (305). In general, the gasoline engines emit more hydrocarbons than do diesel engines, but diesel engines

Table 11. Some hydrocarbons found to be in gasoline-engine automobile exhaust by Papa *et al.*

Hydrocarbon	Hydrocarbon
Methane	3-Methyl-*trans*-2-pentene and/or
Ethane	3-Methyl-*cis*-2-pentene
Ethylene	Methylcyclopentane
Acetylene	2,4-Dimethylpentane
Propylene	2,2,3-Trimethylbutane
Propane	3,4-Dimethyl-1-pentene
Cyclopropane	4,4-Dimethyl-*cis*-2-pentene
Propadiene	3,3-Dimethylpentane
Methylacetylene	Benzene
Isobutane	Cyclohexane
Isobutylene and/or 1-Butene	3-Ethyl-1-pentene
1,3-Butadiene	5-Methyl-1-hexene
n-Butane	4-Methyl-1-hexene
trans-2-Butene	2-Methylhexane and/or
cis-2-Butene	2,3-Dimethylpentane
3-Methyl-1-butene	Cyclohexene
Isopentane	3-Methylhexane
1-Pentene	2,2,4-Trimethylpentane
2-Methyl-1-butene	1-Heptene
n-Pentane	*trans*-3-Heptene
2-Methyl-1,3-butadiene	n-Heptane
trans-2-Pentene	*cis*-3-Heptene and/or
cis-2-pentene	3-Ethyl-*trans*-2-pentene
2-Methyl-2-butene	2,4,4-Trimethyl-1-pentene and/or
2,2-Dimethylbutane	*trans*-2-Heptene
Cyclopentene	*cis*-2-Heptene
4-Methyl-1-pentene and/or	2,5-Dimethyl-*trans*-3-hexene
3-Methyl-1-pentene	Methylcyclohexane
Cyclopentane	2,4,4-Trimethyl-2-pentene
2,3-Dimethylbutane	4-Methyl-1-cyclohexene
2-Methylpentane	2,4-Dimethylhexane and/or
4-Methyl-*cis*-2-pentene	2,5-Dimethylhexane
3-Methylpentane	2,2,3-Trimethylpentane
2-Methyl-1-pentene and/or	4-Methylheptane
1-Hexene	2,3,4-Trimethylpentane
2-Ethyl-1-butene	Toluene
n-Hexane	2,3,3-Trimethylpentane
trans-3-Hexene	2,5-Dimethyl-*trans*-2-hexene
trans-2-Hexene	2-Methyl-3-ethylpentane and/or
2-Methyl-2-pentene	2,3-Dimethylhexane
cis-3-Hexene	3,4-Dimethylhexane and/or
cis-2-Hexene	3-Methylheptane

Table 11. continued

Hydrocarbon	Hydrocarbon
2,2,5-Trimethylhexane	1-Methyl-2-ethylbenzene
1-Octene	t-Butylbenzene
trans-2-Octene	1,2,4-Trimethylbenzene
Dimethylheptane	Isobutylbenzene
cis-2-Octene	sec-Butylbenzene
cis-1,2-Dimethylcyclohexane	1-Methyl-3-isopropylbenzene
Ethylcyclohexane	n-Decane
Ethylbenzene	1,2,3-Trimethylbenzene
m-Xylene and p-Xylene	1-Methyl-4-isopropylbenzene
o-Xylene	1,3-Diethylbenzene
2-Methyloctane	n-Butylbenzene and/or 1-Methyl-4-n-propylbenzene
n-Nonane	1,3-Dimethyl-5-ethylbenzene and/or 1,2-Diethylbenzene
Isopropylbenzene	1-Methyl-2-n-propylbenzene
n-Propylbenzene	Durene
1-Methyl-4-ethylbenzene and/or 1-Methyl-3-ethylbenzene	1-Dodecene
1,3,5-Trimethylbenzene	

Table 12. Comparison of some of the exhaust components of gasoline engines and diesel engines (305)

Component	Gasoline Engine	Diesel Engine
Carbon monoxide	0.5 - 12% by vol.	0.01 - 0.50 by vol.
Aldehydes	0 - 0.2 mg/l	0.001 - 0.009 mg/l
Hydrocarbons	0.2 - 3.0% by vol.	0.009 - 0.5% by vol.
Nitrogen oxides (as N_2O_5)	0 - 0.8% by vol.	0.0002 - 0.5% by vol.
Water vapor	3 - 5.5% by vol.	0.5 - 4.0% by vol.
Carbon dioxide	5 - 12% by vol.	1 - 10% by vol.
Soot	0 - .04 g/m^3	0.01 - 1.1 g/m^3
3,4-Benzpyrene	10 - 20 $\mu g/m^3$	0 - 10 $\mu g/m^3$

emit more particulate matter (306). Karasek et al. analyzed organic compounds on particulate matter from diesel exhaust (134). They identified 35 hydrocarbons, including alkanes, PAH's, and phenols. Mentser and Sharkey used high resolution mass spectrometry to characterize organic compounds on diesel exhaust particulates (289).

Carbonyl compounds in the exhaust from gasoline and diesel engines have been studied. Aldehydes are present in the exhaust gases mainly in the form of formaldehyde and acrolein (307). The aldehydes and ketones are formed as a result of incomplete combustion of fuel components (38,308). In many cases, carbonyl compounds in auto exhaust are analyzed after they are converted to their 2,4-dinitrophenylhydrazine (DNP) derivatives. Oberdorfer measured exhaust aldehydes as their DNP derivatives and found that the total aldehyde content (as HCHO) of automobile exhaust ranged from 20 to several hundred ppm depending upon such engine variables as the air-to-fuel ratio, spark timing, and the presence of exhaust control devices (38). Carbonyl compounds can be isolated from automobile exhaust by bubbling the exhaust through a solution of DNP (32,34). Some of the carbonyl compounds found in automobile exhaust (and their concentrations) during one study (32) included formaldehyde (46.3 ppm), acetaldehyde (9.1 ppm), acrolein and acetone (4.0 ppm), butyraldehyde (1.5 ppm), and benzaldehyde (4.3 ppm). Smythe and Karasek analyzed diesel exhaust carbonyls as their DNP derivatives, and found that the exhaust contained formaldehyde at a concentration of about 25 mg per kiloliter (44). Papa collected exhaust carbonyl compounds in DNP scrubbers, and used a colorimetric method

to measure the compounds (40). Barber and Lodge collected exhaust carbonyls in aqueous solutions of sodium bisulfite (33). They regenerated the aldehydes by adding sodium carbonate. The aldehydes were converted to their DNP derivatives and analyzed by paper chromatography. Hoshika and Takata collected automobile exhaust in a cold trap using liquid oxygen (36). The condensate was dissolved in ethanol and mixed with a solution of DNP. The DNP derivatives of the carbonyl compounds were isolated and analyzed by capillary gas chromatography. Kuwata et al. collected exhaust carbonyls in DNP bubblers and analyzed the DNP derivatives by reversed-phase liquid chromatography (309). Erickson et al. used a variety of instrumental techniques to analyze alkyl-9-fluorenones in diesel exhaust (253). Kashiwagi (73) and Day et al. (71) used chemical ionization mass spectrometry to analyze carbonyl compounds in automobile exhaust.

The relationship between exhaust components and the type of fuel used is difficult to determine when the fuels are complex mixtures such as gasoline and diesel fuel. Because of that, several workers have done studies of exhaust from engines fueled with individual hydrocarbons or simple hydrocarbon mixtures (310-312). In two studies (310,311), oxygenates in exhaust from nine different fuels were determined. The fuels tested were benzene-pentane (71:29), toluene-pentane (3:2), isooctane-toluene-isooctene (2:2:1), 2-methyl-2-butene, isooctane, isooctene, benzene, toluene, and o-xylene. Identified oxygenated compounds included saturated and unsaturated aldehydes, ketones, alcohols, ethers, esters, nitroalkanes, and phenols. Exhaust from aromatic fuels

contained lower levels of aliphatic aldehydes than exhaust from non-aromatic fuels. Aromatic oxygenates were found in the exhaust of nonaromatic fuels.

The effects of automobile engine parameters on the exhaust have been studied. Lewis reviewed some of the studies which had been done in the automobile industry (313). Hass et al. determined the effects of the intake manifold vacuum, engine rpm, vehicle speeds, and acceleration rates on the emissions of hydrocarbons (314). Jackson et al. measured the influences of the air-fuel ratio, spark timing, and combustion chamber deposits on exhaust hydrocarbon emissions (315). They found that increasing the air-fuel ratio and/or retarding the spark timing reduced exhaust hydrocarbon emissions. Hagen and Holiday investigated the effects of the following variables on exhaust emissions: air-fuel ratio, power output, engine speed, spark timing, exhaust back-pressure, valve overlap, combustion chamber deposits, and intake manifold pressure (316). Hydrocarbon concentrations in the exhaust were found to be affected considerably by changes in the air-fuel ratio, spark timing, intake manifold pressure, and combustion chamber deposits. The relationship between the fuel and the composition of exhaust was studied by Wigg et al. (317). They found that the aromatic hydrocarbon and aromatic aldehyde emissions were related linearly to the fuel aromatic content, while exhaust olefin and aliphatic aldehyde emissions showed an inverse relationship. Similar results were obtained by Hosaka et al. (318). Heuss et al. compared tetraethyl lead with aromatic hydrocarbons used to increase the octane rating of gasoline (319). They

found that adding aromatics to a low-aromatic gasoline increased the exhaust reactivity associated with eye irritation. However, the addition of tetraethyl lead to an unleaded gasoline did not affect the exhaust reactivity.

Several analysts have attempted to identify the major odor-producing components of automobile exhaust. O'Donnell and Dravnieks diluted diesel automobile exhaust with nitrogen and collected the organic compounds on Chromosorb 102 (see appendix) (290,320). They found the major odor contributors to be aliphatic aldehydes, olefins, alkyl benzenes, indans, tetralins, naphthalenes, aromatic aldehydes and ketones, sulfur compounds, and aliphatic acids. Several workers have placed diesel exhaust components in the odor categories of "smoky-burnt" and "oily-kerosene" (129-132,321). The "oily-kerosene" odor group includes alkyl indans, alkyl tetralins, and alkyl benzenes. The "smoky-burnt" odor group includes alkyl, hydroxy, and methoxy-substituted indanones, phenols, benzaldehyde, and alkenones. The effects of some engine variables on the odor of diesel exhaust were studied by Rounds and Pearsall (322).

Polynuclear aromatic hydrocarbons are the most widely studied class of compounds in automobile exhaust. Many PAH's have been shown to be carcinogenic, the most well-known compound being 3,4-benzpyrene. Automobile exhaust is a major source of PAH's in the environment (77, 323-325). Several different methods have been used to analyze PAH's in automobile exhaust. Gladen used column chromatography to isolate PAH's in auto exhaust; UV spectrometry was used to measure the PAH's (174). Nielsen developed an HPLC method for analyzing PAH's in auto

exhaust (219). A combination of HPLC and capillary gas chromatography was used by Doran and McTaggert in their analysis of PAH's in exhaust condensate (326). Colmsjo and Stenberg identified six PAH's in automobile exhaust by measuring the sharp fluorescence emission of the PAH's in an alkane matrix at low temperature (Shipol'skii effect) (327). Delvecchio et al. used column chromatography to separate PAH's in gasoline engine and liquified petroleum gas engine exhausts (328). The PAH's were measured by a spectrophotometric method. Candeli et al. used thin layer chromatography and gas chromatography to analyze PAH's in four different fuels and the exhaust from those fuels (228). They found that the PAH content of exhaust increased with increasing PAH content of the fuel used. Grimmer et al. used gas chromatography and mass spectrometry to identify about 150 PAH's in automobile exhaust (329). They compared the PAH content of the exhaust with that of the fuel used; the results indicated that most of the PAH's in the exhaust were produced in the engine during combustion. Gross studied the effects of various fuel and vehicle variables on the exhaust emission of PAH's (330). He found that the amount of PAH's in the exhaust was related to the level of carbon monoxide in the exhaust. In addition, he found that increasing the fuel aromaticity from 12% to 46% increased the PAH emission by 36% to 74% in a vehicle with no emission controls. Begeman and coworkers measured the concentration of 3,4-benzpyrene and 1,2-benzanthracene in fuels and in exhaust (331-333). Using radioactive tracers, Begeman and Colucci found that about 36% of the 3,4-benzpyrene in auto exhaust comes from 3,4-benzpyrene originally in the gasoline (332).

They analyzed the exhaust from 25 cars, and found that the average 3,4-benzpyrene emission rate was 6.6 micrograms per cubic meter of exhaust (333). The emission rate of 1,2-benzanthracene was found to be about four times higher than that of 3,4-benzpyrene. Bricklemyer and Spindt used ^{14}C radioactive tracers to measure PAH's in diesel exhaust (229, 230). Brown et al. used low voltage mass spectrometry to analyze PAH's in automobile exhaust, gasoline, and crankcase oil (135). Foster et al. analyzed the particulate matter in the exhaust from both leaded and unleaded gasoline (334). They used cascade impactors to collect exhaust particulates in various size ranges. They found that 3,4-benzpyrene was found only in the smallest (0.25 μm) size fraction.

Polynuclear aromatic hydrocarbons are produced by high temperature pyrolysis or incomplete combustion of many different fuels (97,335). PAH's have even been found in soot from a methane flame (336). Several factors affecting the formation of PAH's during the combustion of fuels have been studied in an attempt to determine the reactions which lead to the formation of the PAH's. Inefficient combustion has been shown to promote the formation of PAH's, and aromatic fuels have been shown to produce higher levels of PAH's than nonaromatic fuels (97). Commins studied the effects of temperature and air-to-fuel ratios on the formation of PAH's (337). Dubay and Hites studied the combustion products of aromatic fuels doped with 6-30% pyridine (338). They identified four cyanonaphthalenes in the soot generated by the combustion of the fuels.

Various hypotheses have been proposed for the formation of PAH's,

emphasis having been placed upon intermediates such as acetylene, ethylene, and 1,3-butadiene (339). Most proposed mechanisms involve chain-lengthening reactions followed by cyclization (339). Figure 51 shows the mechanism proposed by Badger et al. for the formation of 3,4-benzpyrene (340). Schmeltz and Hoffmann proposed a mechanism which involved a benzyne intermediate (341). Their proposed mechanism for the formation of naphthalene is shown in Figure 52. They based their mechanism upon the fact that the pyrolysis of benzene in nitrogen gives predominantly one product, biphenyl, whereas the pyrolysis of benzene in air produces high yields of phenol in addition to a complex mixture of PAH's, including a sizable amount of naphthalene.

During the past several years, alcohols and alcohol-gasoline blends have been tested as fuels for automobiles. Allsup and Eccleston analyzed the exhaust from an automobile using gasoline and 10% ethanol-90% gasoline (Gasohol) blends (342). They found that the addition of ethanol to gasoline (at 10% concentration) had very little effect on the levels of unburned hydrocarbons in auto exhaust. Stamper studied the aldehyde emissions of an automobile using 10% methanol-90% gasoline blends (343). He found that the concentration of aldehydes were higher in the methanol blend exhausts than in gasoline exhaust. Brinkman et al. tested various methanol-gasoline and ethanol-gasoline blends and found little difference between the two alcohols with respect to hydrocarbon emissions (344). Other analysts have studied the emissions of automobiles using only methanol as the fuel (345,346).

Because automobile exhaust is a major source of air pollution,

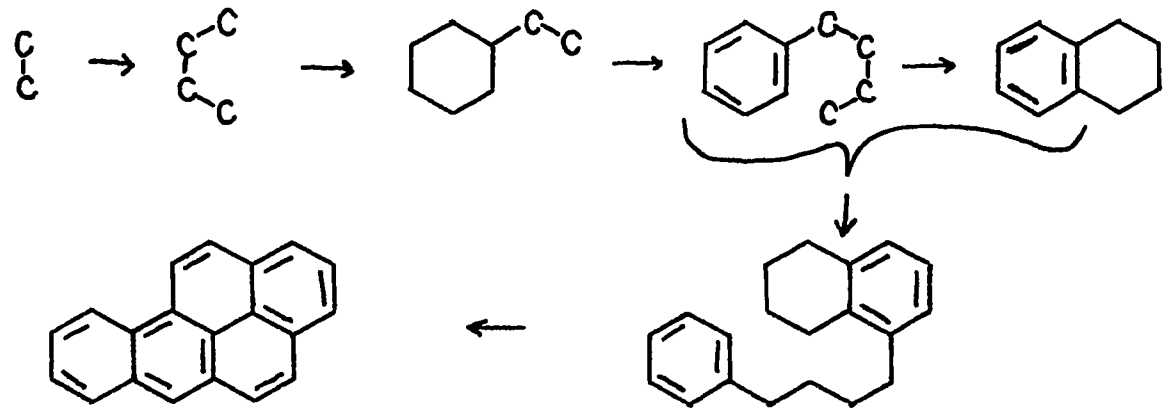


Figure 51. Badger's mechanism for the formation of 3,4-benzpyrene during combustion processes

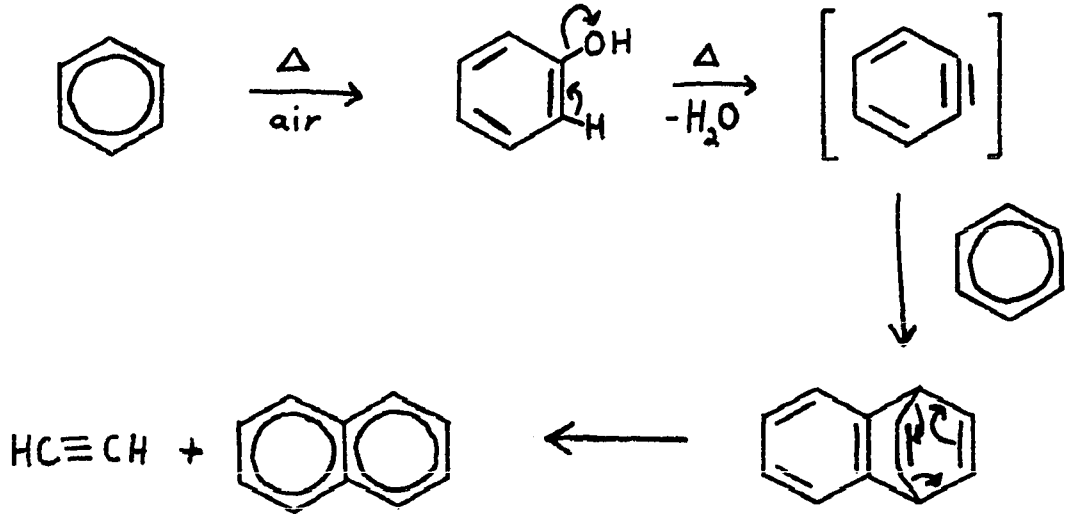


Figure 52. Mechanism proposed by Schmeltz and Hoffmann for the formation of naphthalene from benzene in air

attempts have been made to reduce the emissions of new cars. The maximum allowed emission of hydrocarbons for 1980 automobiles is 0.41 grams per mile (347). For the most part, the emission standards have been met by the use of catalytic converters containing noble metal oxidation catalysts (347). Platinum and palladium are the most widely used oxidation catalysts in catalytic converters (305,347). Gabele et al. used a nickel-copper alloy reduction catalyst in combination with a Pt-Pd oxidation catalyst to reduce auto exhaust emissions (348). However, they found the emissions of nickel in the exhaust were high. Bechtold and Pullman analyzed the exhaust from an automobile equipped with a catalytic converter, and found that the levels of unburned hydrocarbons in the exhaust were about the same for methanol, ethanol, and gasoline fuels (349). Jackson measured the reactivity of exhaust from cars with and without catalytic converters (350). He found that the hydrocarbons in the exhaust of cars with catalytic converters were from 10 to 35% less reactive than those in exhaust of cars without the converters. Seizinger and Dimitriades studied the exhaust from automobiles using hydrocarbons, mixtures of hydrocarbons, and gasoline as fuels (312). They found that catalytic converters reduced both carbonyl and total oxygenate content of the exhaust samples. However, they noted that the compositional character of the oxygenates could differ significantly between the exhaust of cars with and without catalytic converters.

Experimental

Apparatus and reagents

Gas chromatography A Tracor model 560 gas chromatograph, equipped with a linear temperature programmer, dual columns (one packed column and one capillary column), and dual FIDs was used to analyze samples.

Gas chromatography/mass spectrometry A Finnigan model 4000 GC/MS instrument with an INCOS data system was used to identify unknowns in samples.

Solution concentrators The solution concentrators which were used to reduce the volumes of sample solutions are described on page 41.

Solvents Benzene, dimethyl sulfoxide, methanol, methylene chloride, pentane, and water were used in the analysis of samples. These solvents are described on pp. 41-42.

Reagents The reagents used in the analysis of samples are described on pp. 42-43.

Sampling method

Exhaust samples were collected from the following automobiles: a 1973 Mercury Capri 2600, a 1973 Plymouth station wagon, a 1979 Fiat station wagon equipped with a catalytic converter, and a 1979 Volkswagen Diesel Rabbit. The exhaust samples were obtained by condensing the exhaust in a cold trap. The sampling apparatus is shown in Figure 53. The apparatus was made from a powder funnel, a glass joint, and a cold trap. The cold trap was held in a bucket containing a mixture

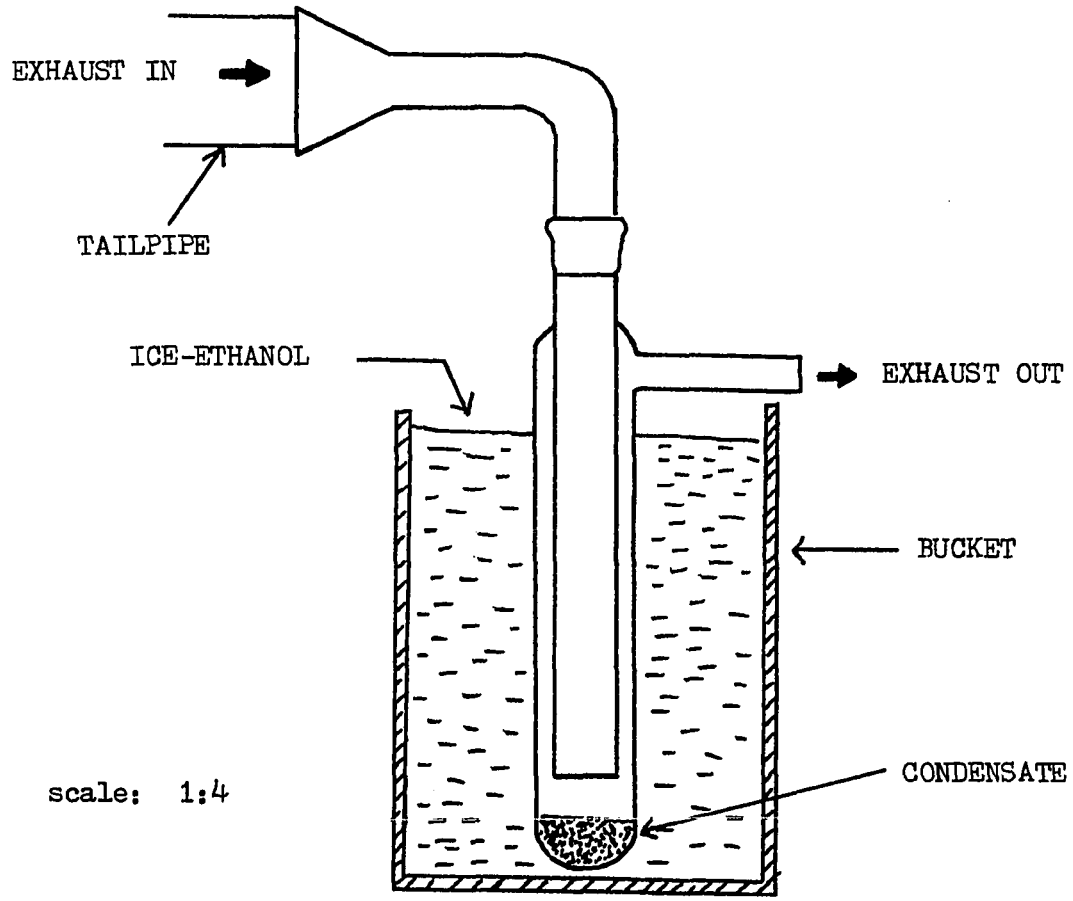


Figure 53. Diagram of automobile exhaust sampling apparatus

of ice and ethanol. In most cases, the temperature of the mixture was between -10 and -15 °C during the sampling period. Because of the high flow of exhaust through the sampling device, not all of the organic components would condense. However, sufficient amounts of organic compounds could be obtained during a 15 minute sampling period to test the fractionation method. In addition, the more volatile components of the exhaust (compounds with boiling points below 80 °C) were difficult to separate completely from the solvent during gas

chromatographic analysis; therefore, the loss of volatile components was not considered to be important.

All of the exhaust samples were collected for fifteen-minute intervals while the automobile engines were in an idle mode. Diesel fuel was used in the Volkswagen Diesel Rabbit, unleaded gasoline was used in the Fiat station wagon, and regular gasoline was used in the Mercury Capri and the Plymouth station wagon. In addition, a sample was obtained from the Plymouth station wagon using Gasohol (10% ethanol-90% gasoline) as the fuel.

Each exhaust sample collected in the cold trap was transferred to a separatory funnel. A total of about 40 ml of methylene chloride was used to rinse the contents of the sampling apparatus into the separatory funnel. The funnel was shaken, and the layers were allowed to separate. The methylene chloride layer was transferred to a clean separatory funnel. The aqueous layer was extracted again with a 20 ml volume of methylene chloride. The two methylene chloride extracts were combined and dried with anhydrous magnesium sulfate. The filtrate was concentrated to 1.0 ml using a Kuderna-Danish concentrator heated in a water bath at about 70 ^{o}C. The solution was analyzed by gas chromatography. Most of the samples were were chromatographed on both SE-54 (see Appendix) and SP-1000 (see Appendix) glass capillary columns.

Fractionation procedure

Exhaust samples obtained from the Mercury Capri, the Plymouth station wagon, and the Volkswagen Diesel Rabbit were fractionated according to the procedure given on pp. 46-49. However, during the

acid-base-neutral fractionation, 20 ml volumes of methylene chloride were used instead of the 30 ml volumes; and 20 ml and 25 ml volumes of the aqueous reagents were used instead of the 30 ml and 35 ml volumes, respectively. In addition, the bisulfite extracts were not washed with 5 ml of methylene chloride as suggested on page 48.

One hundred microliters of gasoline was dissolved in 20 ml of methylene chloride, and the solution was fractionated using the same procedure used to fractionate the exhaust samples from the Mercury Capri, the Plymouth station wagon, and the Volkswagen Diesel Rabbit. One hundred microliters of #2 diesel fuel was dissolved in 5 ml of pentane. The solution was extracted with dimethyl sulfoxide according to the polar-nonpolar fractionation procedure given on the last half of page 49.

The exhaust sample obtained from the Fiat station wagon was not fractionated.

Identification of sample components

With the exception of one of the Plymouth station wagon samples (the one obtained with Gasohol as the fuel), the samples were analyzed by GC/MS. The various fractions were chromatographed on an SE-54 glass capillary column. Some of the fractions were also chromatographed on a CP Wax-51 glass capillary column (see Appendix). The mass spectra of the sample components were compared with standards in the library of the INCOS data system. Some of the compounds in the samples did not have mass spectra in the data system library. Attempts were made to identify those compounds by interpreting the fragmentation patterns

of the mass spectra.

In most cases, positive identifications of sample components could not be obtained using mass spectral data alone. Whenever possible, the gas chromatographic behavior of the sample components was compared with that of standards. Gas chromatographic retention information was obtained for most samples using both a polar and a nonpolar capillary column. The peaks in the chromatograms were identified by a "retention index" system similar to the one proposed by Kovats in 1958 (351). The retention times of the sample components, $T_{R\ samp}$, were compared with the retention times of n-alkanes, $T_{R\ C_n}$. During a temperature programmed analysis, the following equation is usually used to calculate the retention index, R.I., of a component (352):

$$R.I. = \frac{100\ (T_{R\ comp} - T_{R\ C_n})}{(T_{R\ C_{n+1}} - T_{R\ C_n})} + 100n \qquad [4]$$

where $T_{R\ comp}$ is the retention time of the component

$T_{R\ C_n}$ is the retention time of the n-alkane which elutes just before the component

$T_{R\ C_{n+1}}$ is the retention time of the n-alkane which elutes just after the component

and n is the number of carbons in the n-alkane having the retention time of $T_{R\ C_n}$.

The equation given above implies that the retention index is a linear function. However, when a series of n-alkanes were chromatographed

on SE-54 and SP-1000 capillary columns (using temperature program rates of 8 degrees/minute and 6 degrees/minute, respectively), the retention index was not a linear function. Figure 54 shows the graphs of retention index versus the retention time of a series of n-alkanes on both SE-54 and SP-1000 columns. The data points were fitted to quadratic curves using the method of least squares.

The retention indices of sample components and standards were calculated using the quadratic equations obtained with the n-alkane mixture. The standard curves could be used as much as a few weeks before the calculated retention indices of standards deviated significantly from their original values.

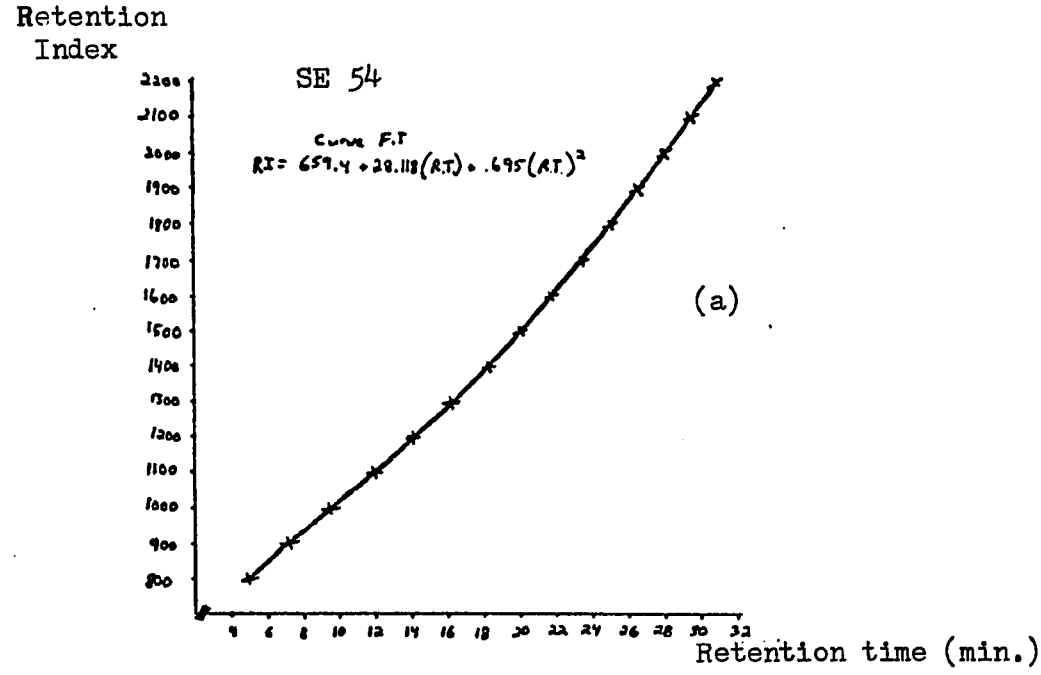
The major advantage of using retention indices is that they are independent of the gas chromatographic column constants and the type of gas chromatograph used (351). The retention index can also provide information about the chemical nature of the substances involved (351).

Positive identifications of sample components could be made by combining the mass spectral data with the retention index data for two different gas chromatographic columns.

Results and Discussion

Analysis of fuels

Gasoline The gasoline sample was found to contain a mixture of aliphatic, olefinic, and aromatic hydrocarbons. Trace levels of compounds were found in the strong acid, weak acid, base, and ketone fractions. However, most of the compounds were alkyl benzenes, which



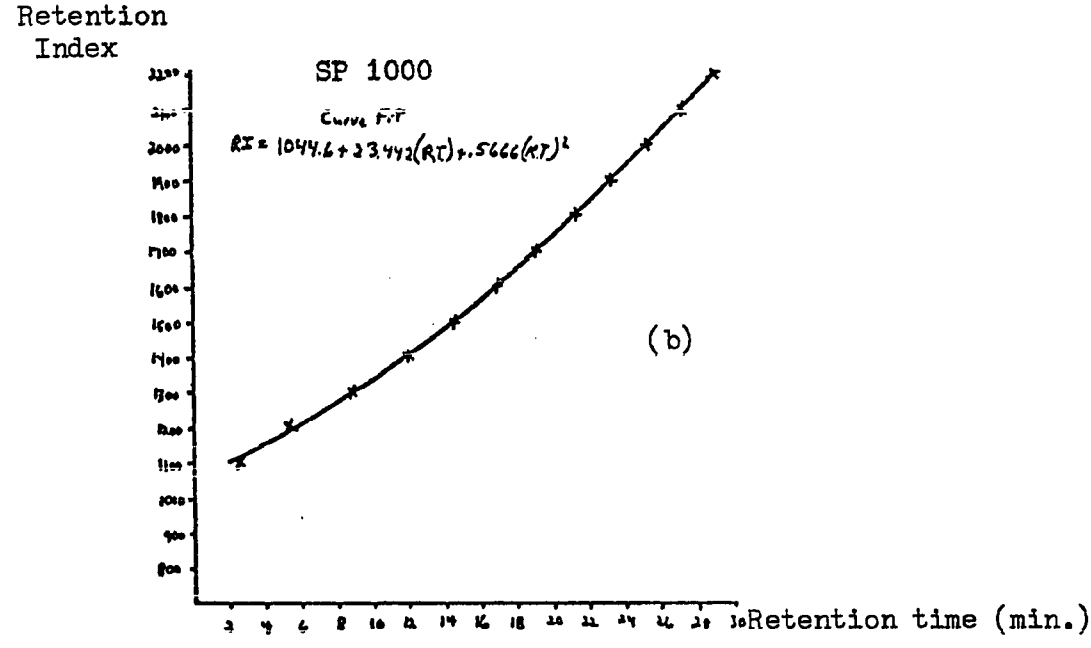


Figure 54. Graphs of retention index versus retention time for n-alkanes on SE-54 and SP-1000 gas chromatographic columns

had not been removed completely during the washing steps of the fractionation procedure. Most of the residual compounds in the acid, base, and ketone fractions had chromatogram peaks which were barely perceptible above the baseline. However, the aldehyde fraction contained residual compounds at fairly high levels. Apparently, some of the alkyl benzenes, naphthalenes, and aliphatic hydrocarbons had been suspended in the aqueous layer during the bisulfite extraction of the sample. A washing step was added to the fractionation procedure in order to minimize the amount of noncarbonyl compounds in the aldehyde fraction.

No acids, bases, aldehydes, or ketones were found in the gasoline sample. Most of the sample components were isolated in the nonpolar and polar fractions. The SE-54 capillary column chromatograms of the nonpolar and polar fractions are shown in Figures 55 and 56, respectively. Some of the major components of the nonpolar fraction were toluene, m-xylene, 4-ethyltoluene, 1,2,4-trimethylbenzene, and some aliphatic hydrocarbons which could not be positively identified. A series of n-alkanes up to n-heptadecane was present. Most of the hydrocarbons in the nonpolar fraction had fewer than 12 carbons.

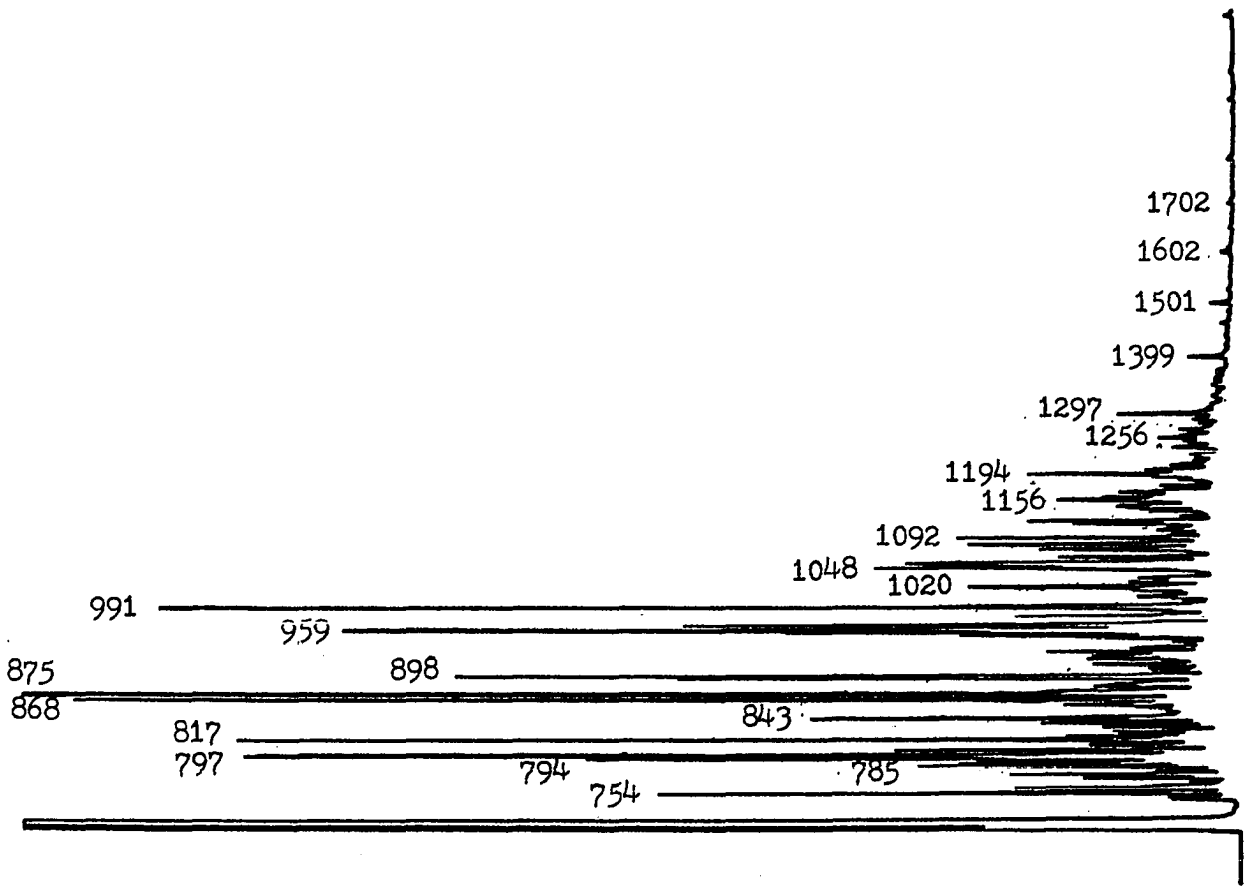
The major components in the polar fraction were toluene, the 3 xylenes, trimethylbenzenes, ethyltoluenes, indan, naphthalene, and methylnaphthalenes. There were no significant levels of compounds with boiling points higher than those of trimethylnaphthalenes.

The retention index for each peak in the SE-54 chromatograms, $R.I._{SE\ 54}$; the retention index for each peak in the SP-1000 chromatograms, $R.I._{SP\ 1000}$; and the corresponding compound identifications

Figure 55. Chromatogram of the nonpolar fraction of gasoline

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 32
detector:	FID
chart speed:	0.25 in./minute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875
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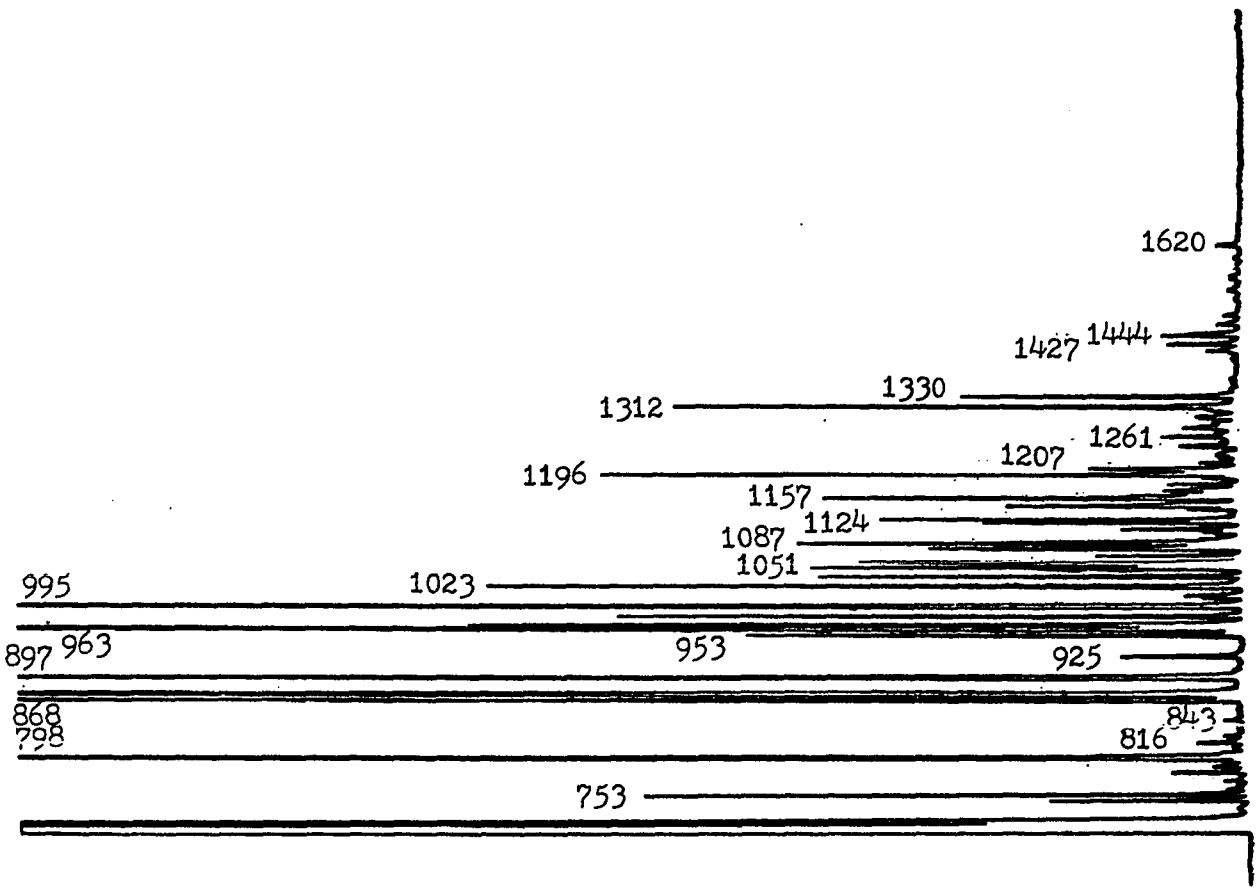
817
797
794
785
754

Figure 56. Chromatogram of the polar fraction of gasoline

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial hold:	2 minutes
initial temp.:	55 °C
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 32
detector:	FID
chart speed:	0.25 in./minute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925
868
843
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753

for the nonpolar and polar fractions of the gasoline sample are listed in Table 13. The compound identifications for the peaks in the SE-54 chromatograms were based upon the results of GC/MS analysis and upon the comparison of gas chromatographic retention indices with those of standards. The compound identifications for the peaks in the SP-1000 chromatograms were based only on retention index data. Many of the GC/MS data for the aliphatic hydrocarbons were inconclusive, and, with the exception of n-alkanes, most aliphatic hydrocarbon standards were unavaliable for determining retention index data.

#2 Diesel fuel The #2 diesel fuel differed significantly from the gasoline sample. Most of the compounds in the diesel fuel had boiling points which were higher than those of compounds in gasoline. Most of the diesel fuel components were in the carbon number range of C_8 to C_{20}. The diesel fuel sample was partitioned between pentane and dimethyl sulfoxide. The major components of the pentane layer, the "aliphatic fraction," were n-alkanes. The entire series of n-nonane through n-tricosane was found. The SE-54 capillary column chromatogram of the aliphatic fraction is shown in Figure 57. The evenly-spaced peaks in the chromatogram correspond to the n-alkanes. Most of the peaks between the n-alkanes correspond to branched isomers.

The major components of the DMSO layer, the "aromatic fraction," were naphthalenes and phenanthrenes. The SE-54 capillary column chromatogram of the aromatic fraction is shown in Figure 58. The amounts of aromatic compounds in the diesel fuel sample were lower than in the gasoline sample (relative to the aliphatic compounds). In addition,

Table 13. Components of gasoline

Nonpolar Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
749[a]	Cyclohexane?	1114	unknown
750[a]	3-Methylhexane?	1125	unknown
754[a]	Cyclohexene	1129	Toluene
760	C_8H_{18}?	1135	unknown
762	C_7H_{16}? C_8H_{18}?	1141	unknown
767	C_7H_{14}? (3-Ethyl-1-pentene?)	1146	unknown
772	Methylcyclohexane?	1159	unknown
776	2,4-Dimethylhexane?	1166	unknown
780	C_8H_{16}?	1178	unknown
785	4-Methylheptane?	1184	unknown
788	C_8H_{16}? C_8H_{18}?	1194	Ethylbenzene?
791	C_8H_{14}?	1202	p-Xylene?
794	C_8H_{18}?	1208	m-Xylene
797	Toluene	1220	unknown
799	3-Ethyl-3-methyl-pentane?	1227	unknown
805	C_8H_{18}?	1235	unknown
812	C_8H_{16}?	1239	unknown
817	n-Octane?	1243	o-Xylene
821	a dimethyl cyclo-hexane?	1252	unknown
825	a dimethyl cyclo-hexene?	1262	unknown
833	2,4-Dimethylheptane?	1270	unknown
838	unknown	1275	3-Ethyltoluene &/or 4-Ethyltoluene
843	3,5-Dimethylheptane?	1285	unknown
854	C_9H_{18}?	1291	1,3,5-Trimethylbenzene
858	2,3-Dimethylheptane?	1298	unknown
860	4-Ethylheptane?	1305	2-Ethyltoluene?
865	C_9H_{20}?	1311	n-Tridecane?
868	C_9H_{20}? & Ethylbenzene?	1322	1,2,4-Trimethylbenzene
875	m-Xylene & p-Xylene?	1331	unknown
879	$C_{10}H_{22}$? C_9H_{20}?	1334	unknown
885	C_9H_{20}? $C_{10}H_{22}$?	1340	unknown
		1349	unknown
		1359	unknown
		1369	1,2,3-Trimethylbenzene
		1384	unknown
		1390	Indan
		1397	unknown
		1405	unknown
		1410	unknown
		1413	n-Tetradecane?
		1418	unknown

[a]In blank.

Table 13. continued

Nonpolar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
889	C_9H_{18}?	1423	unknown
890	C_9H_{18}?	1426	unknown
895	o-Xylene	1434	unknown
898	n-Nonane	1449	unknown
906	an ethyl methyl cyclohexane?	1459	unknown
909	C_9H_{16}? C_9H_{20}?	1470	unknown
914	C_9H_{20}?	1490	unknown
921	C_9H_{16}?	1495	unknown
924	$C_{10}H_{22}$? (2,5-Dimethyloctane?)	1501	unknown
929	3-Methylnonane?	1506	n-Pentadecane?
935	$C_{10}H_{20}$?	1519	unknown
944	3-Ethyl-2-Methylheptane?	1524	unknown
951	n-Propylbenzene?	1534	unknown
956	2,3-Dimethyloctane?	1538	unknown
959	4-Ethyltoluene	1541	unknown
966	1,3,5-Trimethylbenzene	1556	unknown
985	C_9H_{12} (C_3 subst. benzene?)	1567	unknown
991	1,2,4-Trimethylbenzene	1572	unknown
999	n-Decane?	1583	unknown
1006	$C_{10}H_{20}$?	1592	unknown
1012	$C_{10}H_{22}$?	1604	unknown
1020	1,2,3-Trimethylbenzene	1612	unknown
1027	Indan	1621	unknown
1036	$C_{10}H_{20}$?	1626	unknown
1048	$C_{10}H_{14}$ (1-Methyl-4-propylbenzene?)	1642	unknown
1052	$C_{10}H_{14}$ (C_4 subst. benzene?)	1647	unknown
1056	$C_{10}H_{14}$ (C_4 subst. benzene)	1658	unknown
1063	$C_{11}H_{24}$?	1674	unknown
		1706	n-Heptadecane?
		1711	unknown
		1719	unknown
		1752	unknown
		1801	n-Octadecane?
		1896	n-Nonadecane?
		1972	unknown
		2010	unknown

Table 13. continued

Nonpolar Fraction - continued

$R.I._{SE\ 54}$	Compound
1076	1,3-Dimethyl-4-Ethylbenzene?
1083	a dimethyl ethyl benzene?
1092	n-Hendecane
1105	$C_{11}H_{24}$?
1114	1,2,4,5-Tetramethylbenzene
1119	1,2,3,5-Tetramethylbenzene
1127	$C_{11}H_{16}$ (C_5 subst. benzene?)
1132	$C_{11}H_{16}$ $C_{10}H_{12}O$?
1142	$C_{12}H_{26}$?
1145	$C_{11}H_{16}$ (C_5 subst. benzene?)
1150	$C_{10}H_{12}$ (a methyl indan?)
1160	n-Pentylbenzene?
1165	$C_{12}H_{26}$?
1175	2-Methyl-2-Phenylbutane?
1184	$C_{11}H_{20}O$?
1189	$C_{11}H_{14}$ (a dimethyl indan?)
1194	n-Dodecane
1199	$C_{11}H_{16}$ (C_5 subst. benzene?)
1209	$C_{12}H_{26}$?
1238	$C_{12}H_{18}$? (C_6 subst. benzene?)
1251	$C_{12}H_{18}$ (C_6 subst. benzene?)
1256	$C_{12}H_{18}$ (C_6 subst. benzene?)
1260	$C_{13}H_{28}$? (2-Methyldodecane?)
1270	$C_{13}H_{28}$?
1281	$C_{12}H_{18}$ (C_6 subst. benzene?)
1288	Pentamethylbenzene
1297	n-Tridecane
1349	1-Hendecanol?
1399	n-Tetradecane
1463	$C_{15}H_{32}$?
1501	n-Pentadecane
1602	n-Hexadecane
1702	n-Heptadecane

Table 13. continued

Polar Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
739	unknown	1131	Toluene
748	Benzene	1195	Ethylbenzene
753[a]	Cyclohexene	1202	p-Xylene
766	Methylcyclohexane?	1210	m-Xylene
780[a]	$(CH_3O)_2C{=}CH_2$?	1233	Cumene
787	C_7H_{12}?	1242	o-Xylene
798	Toluene	1260	n-Propylbenzene?
816	n-Octane?	1273	3-Ethyltoluene &/or 4-Ethyltoluene
824	2,3-Dimethyl-1,4-hexadiene?	1285	unknown
843	C_8H_{16}?	1288	1,3,5-Trimethylbenzene
868	Ethylbenzene	1302	2-Ethyltoluene
877	p-Xylene & m-Xylene	1308	p-Cymene?
897	o-Xylene	1319	1,2,4-Trimethylbenzene
925	Cumene	1338	1,4-Diethylbenzene?
953	n-Propylbenzene	1346	1,3-Diethylbenzene?
963	3-Ethyltoluene &/or 4-Ethyltoluene	1356	1,2-Diethylbenzene?
968	1,3,5-Trimethylbenzene	1366	1,2,3-Trimethylbenzene
980	2-Ethyltoluene	1376	unknown
995	1,2,4-Trimethylbenzene	1381	unknown
1007	$C_{10}H_{14}$ (2-Methyl-1-phenylpropane?)	1386	unknown
1010	2-Phenylbutane?	1394	Indan & 1,3-Dimethyl-4-ethylbenzene
1023	1,2,3-Trimethylbenzene	1402	unknown
1037	Indan	1407	unknown
1051	1-Methyl-4-propyl-benzene?	1419	unknown
1056	n-Butylbenzene?	1422	unknown
1058	1,4-Diethylbenzene &/or 1-Methyl-2-propylbenzene?	1432	unknown
1068	1,3-Diethylbenzene	1445	1,2,4,5-Tetramethyl-benzene
1078	a dimethyl ethyl benzene?	1455	1,2,3,5-Tetramethyl-benzene
1080	1,2-Diethylbenzene?	1466	unknown
1084	$C_{10}H_{12}$ (a dimethyl styrene?)	1474	unknown
1087	1,3-Dimethyl-4-Ethyl-benzene	1491	unknown
		1500	unknown
		1504	unknown
		1515	a methyl indan?
		1520	unknown
		1530	unknown
		1534	unknown
		1537	unknown

Table 13. continued

Polar Fraction - continued

$R.I._{SE\ 54}$	Compound	$R.I._{SP\ 1000}$	Compound
1089	1-Methylindan	1548	unknown
1103	unknown	1568	unknown
1106	$C_{11}H_{16}$ (C_5 subst. benzene?)	1572	unknown
		1578	unknown
1110	1,4-Dimethyl-2-Ethyl-benzene?	1588	unknown
		1593	unknown
1119	1,2,4,5-Tetramethyl-benzene	1599	unknown
		1606	unknown
1124	1,2,3,5-Tetramethyl-benzene	1610	unknown
		1615	unknown
1139	$C_{11}H_{16}$ (2-Methyl-2-phenylbutane?)	1634	unknown
		1636	unknown
		1642	Pentamethylbenzene?
1145	$C_{10}H_{10}$ (a methyl indene?)	1654	unknown
		1668	unknown
1157	$C_{10}H_{12}$ (a methyl indan?)	1685	unknown
		1689	unknown
		1699	unknown
1165	1-Methylindene?	1714	unknown
1170	$C_{11}H_{16}$ (C_5 subst. benzene?)	1728	unknown
		1734	unknown
		1745	Naphthalene
1180	$C_{11}H_{16}$ (2-Methyl-2-phenylbutane?)	1772	unknown
		1794[a]	unknown
1190	a dimethyl indan?	1809	unknown
1196	Naphthalene	1855	2-Methylnaphthalene
1207	$C_{11}H_{16}$ (C_5 subst. benzene?)	1876	unknown
		1889	1-Methylnaphthalene
		1918	unknown
1217	$C_{11}H_{16}$ (C_5 subst. benzene?)	1923	unknown
		1933	unknown
1227	a dimethyl isopropyl benzene?	1947	2-Ethylnaphthalene
		1959	1-Ethylnaphthalene
1231	unknown	1964	2,6-Dimethylnaphthalene?
1246	$C_{11}H_{14}$ (C_2 subst. indan?)	1994	unknown
		2002	1,3-Dimethylnaphthalene?
1261	a dimethyl indan?	2038	a dimethyl naphthalene
1267	$C_{11}H_{14}O$? (a methyl 1,2,3,4-tetrahydro-1-napthol?)	2057	unknown
		2066	unknown
		2091	unknown
		2097	unknown
1275	a dimethyl indan?	2106	unknown

Table 13. continued

Polar Fraction - continued			
R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1286	$C_{12}H_{18}$ (C_6 subst. benzene?)	2112	unknown
		2138	unknown
1293	Pentamethylbenzene (& a dimethyl indan?)	2147	unknown
		2168	unknown
		2177	unknown
1300	$C_{12}H_{16}$ (a dimethyltetralin?)		
1312	2-Methylnaphthalene		
1320	C_9H_8S (a methyl benzothiophene?)		
1330	1-Methylnaphthalene		
1410	1-Ethylnaphthalene		
1416	2-Ethylnaphthalene		
1427	a dimethyl naphthalene		
1444	1,3-Dimethylnaphthalene?		
1447	a dimethyl naphthalene		
1465	1,4-Dimethylnaphthalene?		
1482	a dimethyl naphthalene		
1531	$C_{13}H_{14}$ (C_3 subst. naphthalene?)		
1559	unknown		
1577	unknown		
1595[a]	2,3,5-Trimethylnaphthalene?		
1620[a]	Diethylphthalate		

the major aromatic components of the gasoline sample were alkyl benzenes, whereas naphthalenes were the major aromatic components of the diesel fuel sample.

The compound identifications for the chromatogram peaks (both SE-54 and SP-1000) in the aliphatic and aromatic fractions are listed in Table 14. The compound identifications for the SE-54 column chromatogram peaks were based on mass spectral and retention index data. The compound identifications for the SP-1000 column chromatogram peaks were

Figure 57. Chromatogram of the aliphatic fraction of #2 diesel fuel

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	11 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure	20 p.s.i.
attenuation:	X 32
detector:	FID
chart speed:	0.25 in./minute

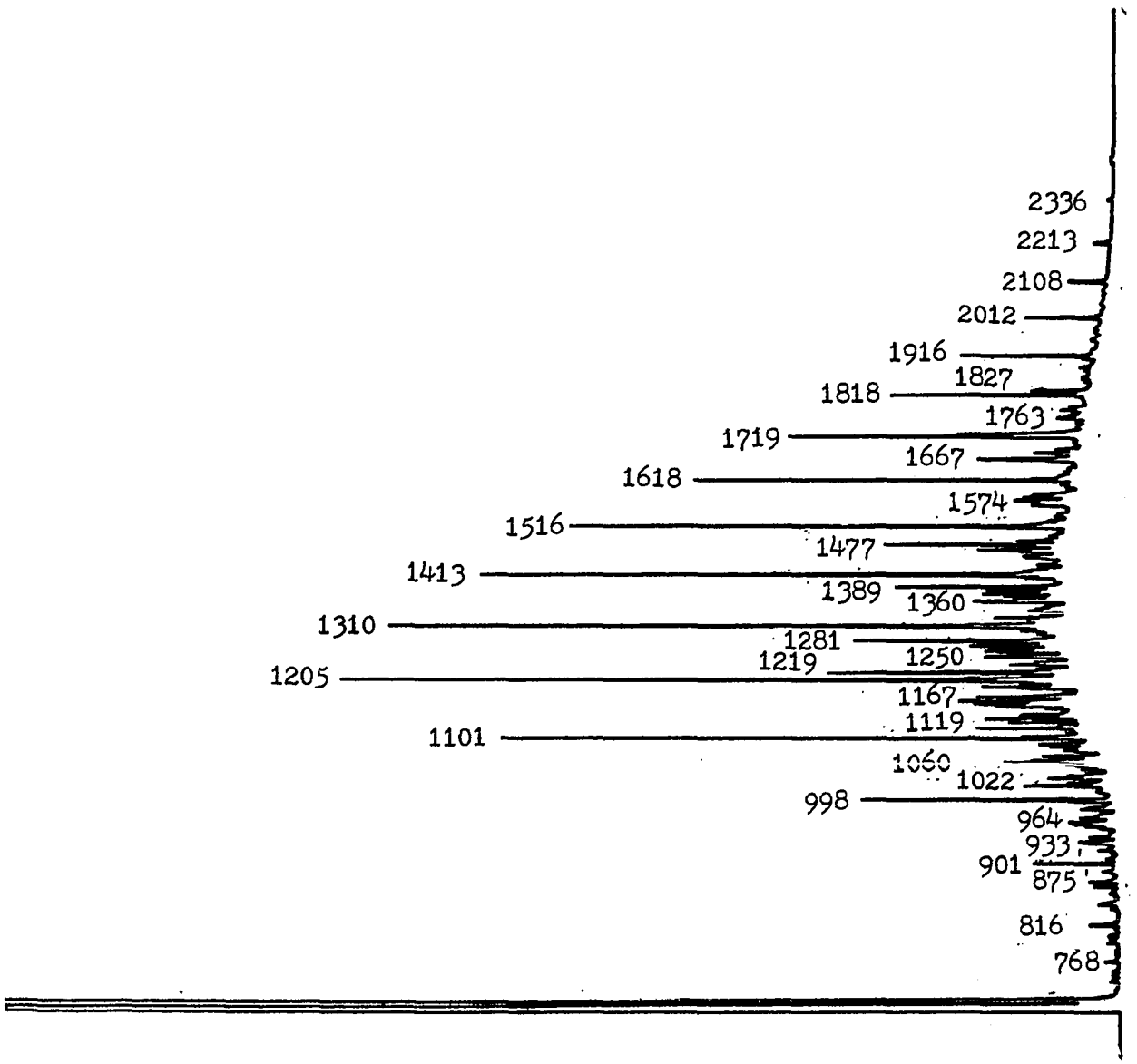

2336
2213
2108
2012
1916
1827
1818
1763
1719
1667
1618
1574
1516
1477
1413
1389
1360
1310
1281
1219
1250
1205
1167
1119
1101
1060
1022
998
964
933
901
875
816
768

Figure 58. Chromatogram of the aromatic fraction of #2 diesel fuel

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	11 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure	20 p.s.i.
attenuation:	X 16
detector:	FID
chart speed:	0.25 in./minute

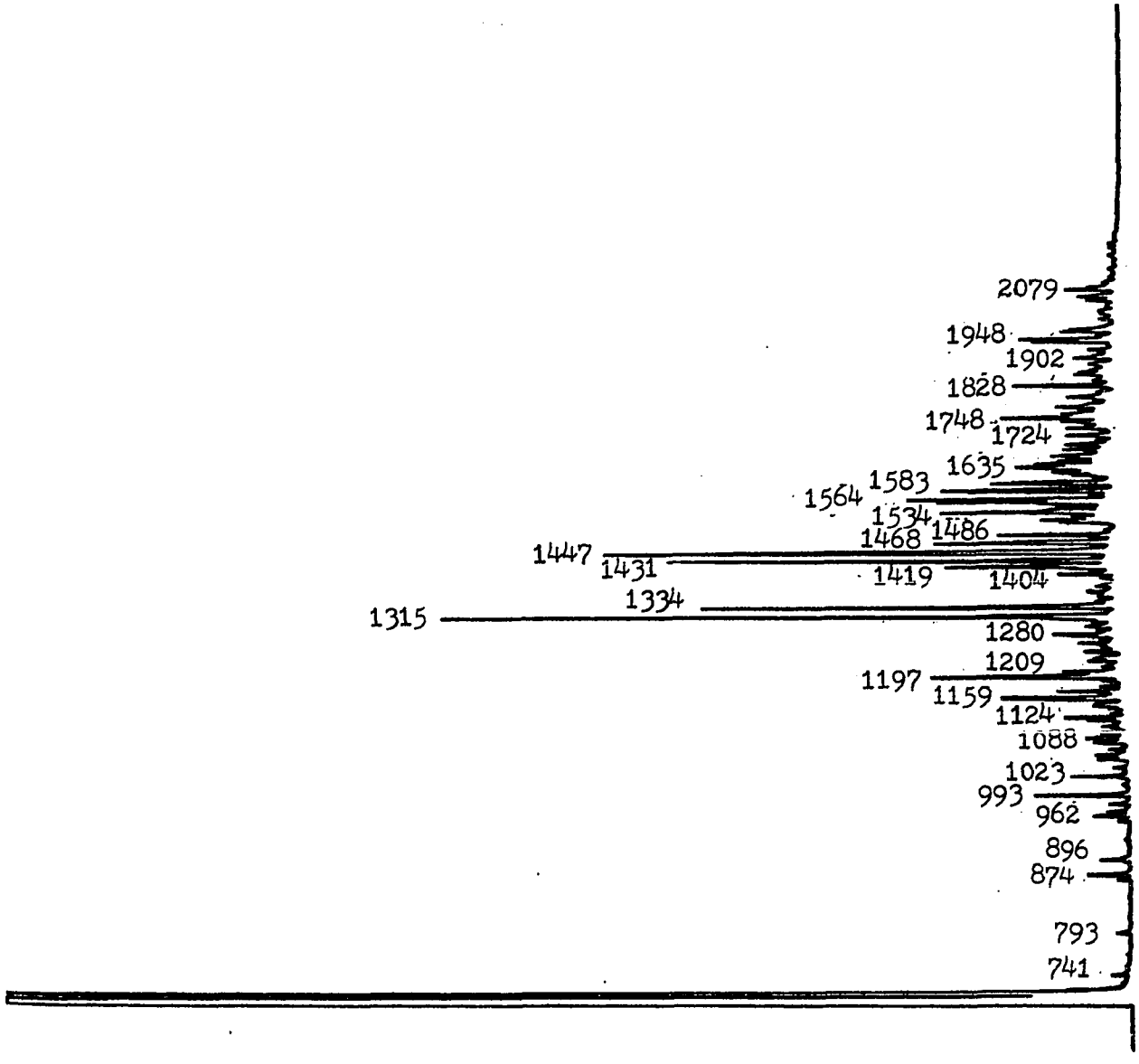

2079
1948
1902
1828
1748
1724
1635
1583
1564
1534
1486
1468
1447
1431
1419
1404
1334
1315
1280
1209
1197
1159
1124
1088
1023
993
962
896
874
793
741

Table 14. Components of #2 diesel fuel

Aliphatic Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
741	Benzene?	1102	unknown
745	Cyclohexene	1118	unknown
749	unknown	1121	unknown
755	methylcyclohexane?	1134	n-Hendecane
768	unknown	1145	unknown
792	unknown	1160	unknown
797	1,3-Dimethylcyclo-hexane?	1171	unknown
		1186	unknown
801	unknown	1193	unknown
811	unknown	1208	unknown
816	3-Ethylhexane?	1229	n-Dodecane
843	Ethylcyclohexane?	1238	unknown
846	unknown	1261	unknown
859	unknown	1285	unknown
868	C_9H_{20}	1300	unknown
		1316	unknown
875	3-Methyloctane?	1333	n-Tridecane
891	unknown	1347	unknown
901	n-Nonane	1354	unknown
909	an ethyl methyl cyclohexane?	1364	unknown
		1369	unknown
921	C_9H_{16}?	1380	unknown
933	$C_{10}H_{22}$?	1390	unknown
		1399	unknown
940	3-Ethyl-2-Methyl-heptane?	1410	unknown
		1420	n-Tetradecane
961	2,3-Dimethyloctane?	1428	unknown
964	2-Methylnonane?	1441	unknown
970	3-Methylnonane?	1453	unknown
984	1-Methyl-4-Isopropyl-cyclohexane?	1460	unknown
		1469	unknown
998	n-Decane	1475	unknown
1012	$C_{10}H_{22}$?	1480	unknown
1014	unknown	1488	unknown
1022	4-Methyldecane?	1494	unknown
1027	$C_{10}H_{22}$? $C_{11}H_{24}$?	1500	unknown
		1512	n-Pentadecane
1033	Butylcyclohexane?	1529	unknown
1038	2-Methylhendecane?	1536	unknown
1048	1-Methyl-4-propyl-benzene?	1547	unknown
		1552	unknown
1054	$C_{11}H_{22}$? $C_{10}H_{18}O$?	1559	unknown

Table 14. continued

Aliphatic Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1057	4-Methyldecane?	1563	unknown
1060	$C_{12}H_{26}$?	1574	unknown
1064	$C_{11}H_{22}$?	1580	unknown
1070	$C_{11}H_{24}$?	1596	unknown
1084	1,3-Dimethyl-4-ethyl-benzene?	1607	n-Hexadecane
1087	5-Methyl-1-decene?	1625	unknown
1091	$C_{11}H_{22}$ (C_5 subst. cyclohexane?)	1632	unknown
1101	n-Hendecane	1637	unknown
1119	$C_{12}H_{26}$?	1642	unknown
1125	$C_{12}H_{26}$?	1658	unknown
1130	4-Methylhendecane?	1670	unknown
1136	2-Methyldecalin?	1686	unknown
1140	$C_{11}H_{22}$ (C_5 subst. cyclohexane?)	1695	unknown
1143	$C_{12}H_{24}$?	1703	n-Heptadecane
1153	$C_{12}H_{24}$?	1715	unknown
1158	$C_{12}H_{26}$?	1727	unknown
1162	$C_{12}H_{24}$?	1737	unknown
1167	2-Methylhendecane?	1744	unknown
1174	$C_{12}H_{26}$?	1755	unknown
1185	2-Methyl-2-phenyl-butane?	1773	unknown
1194	2,6-Dimethyldecalin?	1785	unknown
1199	a methyl pentyl cyclohexane?	1789	unknown
1205	n-Dodecane	1801	n-Octadecane
1219	$C_{13}H_{28}$?	1820	unknown
1228	$C_{13}H_{28}$?	1826	unknown
1235	2-Butyl-1,1,3-tri-methylcyclohexane?	1834	unknown
1242	$C_{13}H_{28}$?	1842	unknown
1250	$C_{12}H_{24}$?	1851	unknown
1261	2,5-Dimethylhendecane?	1866	unknown
1266	4,8-Dimethylhendecane?	1887	unknown
		1899	n-Nonadecane
		1916	unknown
		1931	unknown
		1962	unknown
		1993	unknown
		1998	n-Eicosane
		2039	unknown
		2055	unknown
		2070	unknown
		2098	n-Heneicosane
		2111	unknown
		2146	unknown
		2168	unknown
		2176	unknown

Table 14. continued

Aliphatic Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1272	2-Methyldodecane?	2197	n-Docosane
1281	$C_{13}H_{28}$?	2290	unknown
1294	2,6,10-Trimethylhendecane?	2303	n-Tricosane
1302	5-Butyl-4-nonene?	2321	unknown
1305	a trimethyl indan?		
1310	n-Tridecane		
1323	$C_{13}H_{26}$?		
1328	$C_{13}H_{28}$? $C_{14}H_{30}$?		
1341	$C_{13}H_{26}$?		
1346	unknown		
1350	$C_{14}H_{30}$?		
1360	$C_{13}H_{26}$ (C_7 subst. cyclohexane?)		
1365	$C_{14}H_{30}$?		
1370	a methyl tridecane?		
1374	a methyl tridecane?		
1382	$C_{14}H_{30}$?		
1389	2,6,11-trimethyldodecane?		
1404	$C_{14}H_{26}$? $C_{14}H_{28}$?		
1408	2-Cyclohexyloctane?		
1413	n-Tetradecane		
1423	$C_{14}H_{30}$?		
1429	unknown		
1436	$C_{14}H_{30}$? $C_{15}H_{32}$?		
1455	$C_{14}H_{30}$? $C_{15}H_{32}$?		
1467	n-octylcyclohexane?		
1477	$C_{15}H_{32}$?		
1486	$C_{15}H_{32}$?		
1498	$C_{15}H_{32}$? $C_{16}H_{34}$?		
1508	unknown		
1516	n-Pentadecane		
1525	$C_{15}H_{30}$? $C_{16}H_{32}$?		
1530	$C_{15}H_{32}$?		
1540	unknown		
1545	$C_{15}H_{32}$? $C_{16}H_{34}$?		

Table 14. continued

Aliphatic Fraction - continued

R.I.$_{SE\ 54}$	Compound
1563	$C_{16}H_{34}$?
1569	$C_{16}H_{34}$?
1574	n-nonylcyclohexane?
1581	2-Methylpentadecane?
1588	$C_{16}H_{34}$?
1604	$C_{16}H_{34}$?
1618	n-Hexadecane
1638	unknown
1649	unknown
1656	$C_{16}H_{34}$?
1667	5-Propyltridecane?
1680	n-Decylcyclohexane?
1689	$C_{17}H_{36}$?
1703	unknown
1709	$C_{17}H_{36}$?
1719	n-Heptadecane
1724	$C_{17}H_{36}$?
1745	unknown
1753	unknown
1763	$C_{17}H_{36}$? $C_{18}H_{38}$?
1771	$C_{18}H_{38}$?
1782	2-Methylheptadecane?
1789	$C_{18}H_{38}$?
1818	n-Octadecane
1827	$C_{18}H_{38}$?
1853	unknown
1864	$C_{18}H_{38}$? $C_{19}H_{40}$?
1880	$C_{19}H_{40}$?
1889	2-Methylheptadecane
1910	$C_{19}H_{40}$?
1916	n-Nonadecane
1956	$C_{20}H_{42}$?
1978	unknown
1992	unknown
2012	n-Eicosane

Table 14. continued

Aliphatic Fraction - continued

R.I.$_{SE\ 54}$	Compound
2052	$C_{20}H_{42}$? $C_{21}H_{44}$?
2091	unknown
2108	n-Heneicosane
2213	n-Docosane
2336	n-Tricosane?

Aromatic Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
741	Benzene	1132	unknown
793	Toluene	1141	unknown
867	p-Xylene?	1150	unknown
874	m-Xylene	1194	p-Xylene?
896	o-Xylene	1219	m-Xylene
926	Cumene	1242	o-Xylene
954	3-Ethyltoluene	1264	3-Ethyltoluene &/or 4-Ethyltoluene
962	4-Ethyltoluene		
968	1,3,5-Trimethylbenzene	1284	1,3,5-Trimethylbenzene
981	2-Ethyltoluene	1294	2-Ethyltoluene
993	1,2,4-Trimethylbenzene	1306	1,2,4-Trimethylbenzene
1013	unknown	1332	1,4-Diethylbenzene?
1023	1,2,3-Trimethylbenzene	1343	unknown
1038	Indan?	1354	1,2-Diethylbenzene?
1052	1-Methyl-4-propyl-benzene?	1363	1,2,3-Trimethylbenzene
		1379	unknown
1059	unknown	1384	unknown
1069	1-Methyl-2-propyl-benzene?	1392	Indan &/or 1,3-Dimethyl-4-Ethyl-benzene
1082	$C_{10}H_{14}$ (C_4 subst. benzene?)	1396	unknown
		1410	unknown
1088	1-Methylindan?	1417	unknown
1097	n-Hendecane?	1429	unknown
iiii	a dimethyl indan?	1442	1,2,4,5-Tetramethylbenzene
1120	1,2,4,5-Tetramethyl-benzene	1452	1,2,3,5-Tetramethylbenzene
		1463	unknown
1124	1,2,3,5-Tetramethyl-benzene	1487	unknown
		1500	unknown
1133	2-Methyldecalin?	1510	1,2,4-Triethylbenzene?
1141	unknown	1515	unknown
1147	a methyl indan?	1534	unknown

Table 14. continued

Aromatic Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1150	2-Methyl-2-phenyl-butane?	1543	unknown
1159	1,3-Dimethyl-5-Ethyl-benzene?	1557	unknown
1171	Tetralin? 1,2-Dihydro-naphthalene?	1565	unknown
1181	1,3-Dimethyl-4-Ethyl-benzene?	1572	unknown
1192	a dimethyl indan?	1582	unknown
1197	Naphthalene	1594	unknown
1209	$C_{11}H_{14}$ (a dimethyl indan?)	1602	unknown
1219	1,1-Dimethylindan?	1610	1,2-Dihydronaphthalene?
1229[a]	a methyl tetralin?	1631	unknown
1233	a sulfur compound?	1635	unknown
1247	1,2,4-Triethylbenzene?	1647	unknown
1258	unknown	1663	unknown
1268	1,3-Dimethylindan?	1668	unknown
1270	$C_{12}H_{18}$?	1693	unknown
1280	5-Methyltetralin?	1708	unknown
1289	$C_{12}H_{18}$ (C_6 subst. benzene?)	1724	unknown
1296	Pentamethylbenzene	1739	Naphthalene
1305	Tridecane?	1768	unknown
1311	6-Methyltetralin?	1780	unknown
1315	2-Methylnaphthalene	1787	unknown
1334	1-Methylnaphthalene	1797	unknown
1348	unknown	1825	unknown
1358	$C_{13}H_{18}$?	1849	2-Methylnaphthalene
1366	unknown	1871	unknown
1385	unknown	1884	1-Methylnaphthalene
1399	$C_{13}H_{18}$ (a cyclohexyl toluene?)	1918	unknown
1404	Biphenyl	1942	2-Ethylnaphthalene?
1409	$C_{14}H_{30}$?	1954	unknown
1416	$C_{12}H_{16}$?	1960	2,6-Dimethylnaphthalene?
		1989	Biphenyl
		1998	1,3-Dimethylnaphthalene?
		2028	a dimethyl naphthalene?
		2033	a dimethyl naphthalene?
		2044	unknown
		2052	unknown
		2061	unknown
		2065	unknown
		2085	unknown
		2091	unknown
		2101	unknown

[a] Impurity in DMSO?

Table 14. continued

Aromatic Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1419	2-Ethylnaphthalene?	2108	unknown
1424	$C_{13}H_{12}$?	2133	unknown
		2143	unknown
1431	2,6-Dimethylnaphthalene?	2165	unknown
		2172	unknown
1447	1,3-Dimethylnaphthalene?	2186	2,3,5-Trimethylnaphthalene?
		2194	unknown
1451	a dimethyl naphthalene?	2201	unknown
1468	a dimethyl naphthalene?	2211	unknown
1486	a dimethyl naphthalene?	2217	unknown
1498	unknown	2224	unknown
1514	unknown	2231	unknown
1518	$C_{13}H_{14}$? $C_{12}H_{10}O$?	2238	4,4'-Dimethylbiphenyl?
1526	$C_{13}H_{14}$ (C_3 subst. naphthalene?)	2246	unknown
		2261	unknown
		2268	unknown
1534	2-Isopropylnaphthalene?	2277	unknown
		2289	unknown
1540	unknown	2318	unknown
1554	unknown	2330	unknown
1558	a trimethyl naphthalene?	2344	Fluorene
		2357	unknown
1564	a trimethyl naphthalene?	2366	unknown
		2382	unknown
1572	a trimethyl naphthalene?	2393	unknown
		2404	unknown
1580	unknown	2410	unknown
1583	a trimethyl naphthalene?	2427	unknown
		2442	unknown
1598	2,3,5-Trimethylnaphthalene	2477	unknown
		2503	unknown
1617	unknown	2537	unknown
1622	$C_{16}H_{34}$?	2554	unknown
1624	Fluorene	2578	unknown
1635	$C_{13}H_{12}$?	2630	unknown
		2662	unknown
1642	4,4'-Dimethylbiphenyl?	2705	unknown
1650	unknown	2786	unknown
1656	$C_{14}H_{16}$ (C_4 subst. naphthalene?)	2803	unknown
		2832	unknown
1660	unknown	2864	unknown

Table 14. continued

Aromatic Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1675	unknown	2905	unknown
1686	$C_{14}H_{16}$ (C_4 subst. naphthalene?)	2948	unknown
		2993	unknown
		3116	Phenanthrene
1697	unknown	3228	unknown
1724	$C_{14}H_{16}$ (C_4 subst. naphthalene?)	3380	unknown
		3558	unknown
		3613	unknown
1731	$C_{14}H_{16}$? $C_{15}H_{16}$?	3788	unknown
1741	unknown	3834	unknown
1748	$C_{14}H_{14}$? $C_{15}H_{16}$?	4289	unknown
1760	unknown	4367	unknown
1769	unknown	4566	unknown
1776	2-Ethylbiphenyl?		
1802	unknown		
1816	unknown		
1828	Phenanthrene		
1843	unknown		
1857	$C_{15}H_{14}$?		
1864	unknown		
1872	unknown		
1888	unknown		
1902	$C_{13}H_{10}S$ (a methyl dibenzothiophene?)		
1923	unknown		
1943	a methyl phenanthrene		
1948	a methyl phenanthrene		
1959	unknown		
1969	unknown		
1974	unknown		
2002	unknown		
2016	unknown		
2026	unknown		
2033	unknown		
2051	unknown		
2060	unknown		
2079	a dimethyl phenanthrene		
2085	unknown		
2102	unknown		
2139	unknown		
2175	unknown		

Table 14. continued

Aromatic Fraction - continued

$R.I._{SE\ 54}$	Compound
2196	unknown
2207	unknown

based only on retention index data. As can be seen from the Table, no aromatic compounds with boiling points higher than those of dimethyl phenanthrenes were found in the diesel fuel sample. No acids, bases, aldehydes, or ketones were found in the sample. At least one sulfur compound, possibly a methyl dibenzothiophene, was found in the sample.

Analysis of automobile exhaust

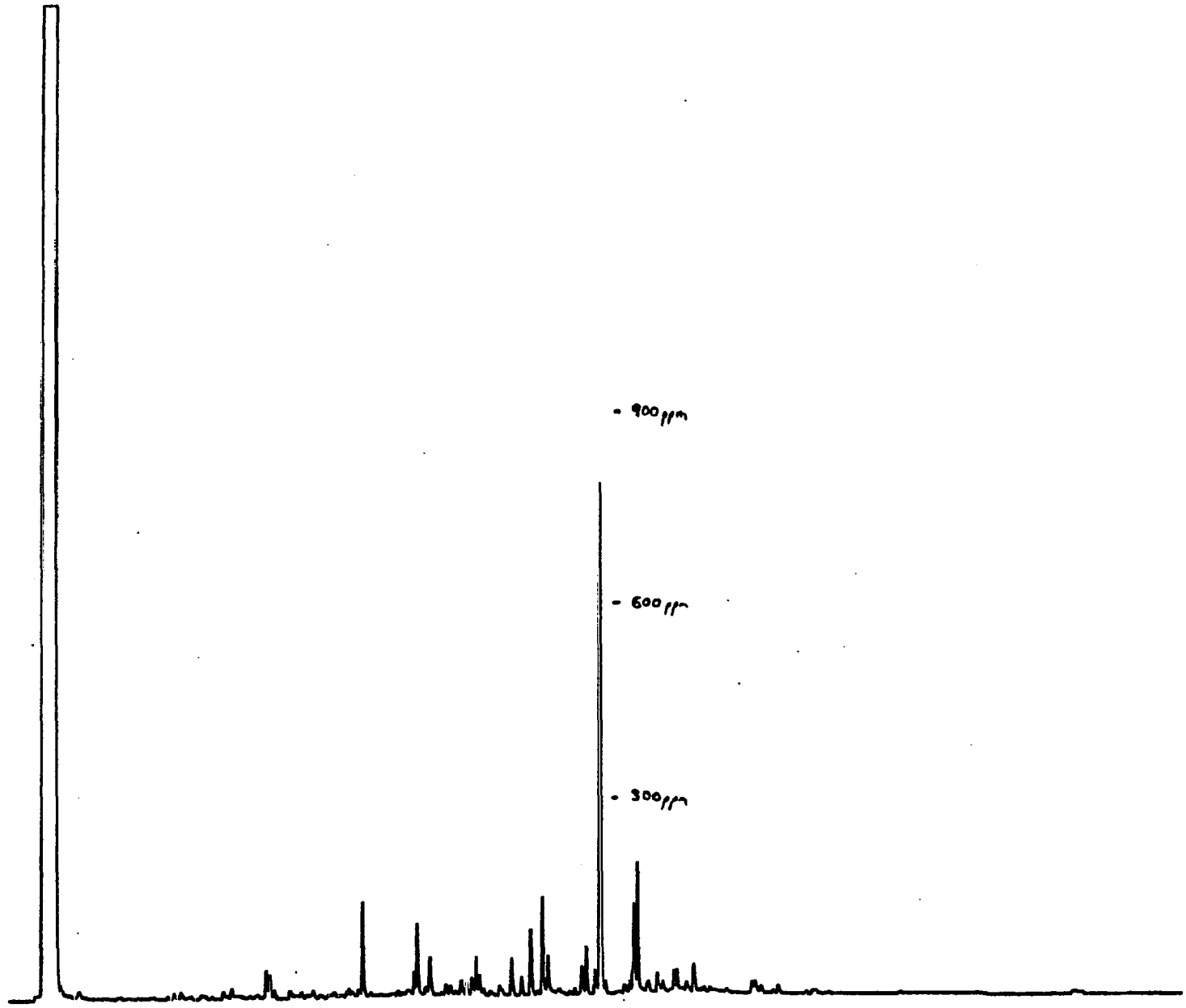
1973 Mercury Capri 2600 exhaust The SP-1000 capillary column chromatogram of the Mercury Capri exhaust sample is shown in Figure 59. The major component of the exhaust was found to be phenol. As can be seen in the Figure, the concentration of phenol is about 800 ppm, which corresponds to a total mass of about 800 micrograms. Other major components of the exhaust sample were cresols, benzaldehydes, and naphthalenes.

The strong acid fraction of the Mercury Capri exhaust contained phenol, the three cresols, some C_2-substituted phenols, salicylaldehyde, and some methyl and dimethyl benzoic acids. The SE-54 capillary column chromatograms of the strong acid fraction before and after methylation

Figure 59. Chromatogram of 1973 Mercury Capri 2600 exhaust

Gas chromatographic conditions:

amount:	1 microliter
column:	glass capillary, 30 meter
liquid phase:	SP-1000
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	6 degrees/minute
final temp.:	220 °C
final hold:	22 minutes
detector temp.:	300 °C
injector temp.:	250 °C
split ratio:	50:1
He Pressure:	20 p.s.i.
attenuation:	X 32
detector:	FID
chart speed:	0.25 in./minute


900 ppm
600 ppm
300 ppm

are shown in Figures 60 and 61, respectively. The chromatograms of the blanks appear below the chromatograms of the samples. The blank for the methylated fraction is fairly high. Most of the compounds in the blank were aliphatic methyl esters, which were probably present in the BF_3-methanol reagent used to methylate the sample.

The weak acid fraction of the Mercury Capri exhaust sample contained phenol, the three cresols, C_2-substituted phenols, C_3-substituted phenols, and 2-napthol. The SE-54 capillary column chromatogram of the weak acid fraction of the exhaust sample (and the blank) is shown in Figure 62.

No basic compounds were found in the Mercury Capri exhaust sample. The SE-54 capillary column chromatogram of the base fraction (and the blank) is shown in Figure 63. The chromatogram contains two significant peaks which were not in the blank. However, the concentrations of the compounds were too low to be positively identified. One of the compounds had a mass spectrum which was very similar to that of benzyl alcohol.

The aldehyde fraction of the Mercury Capri exhaust contained benzaldehyde, the three methyl benzaldehydes, C_2-substituted benzaldehydes, 1,3- and 1,4-benzenedicarboxylaldehyde, some methylbenzenedicarboxylaldehydes, and 1- and 2-naphthaldehyde. The SE-54 capillary column chromatogram of the aldehyde fraction (and the blank) is shown in Figure 64.

Most of the compounds in the ketone fraction of the Mercury Capri exhaust were aldehydes. The compounds in the ketone fraction included

Figure 60a. Chromatogram of the strong acid fraction (not methylated) of 1973 Mercury Capri 2600 exhaust

Figure 60b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	1 microliter
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	11 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 8
detector:	FID
chart speed:	0.25 in./minute

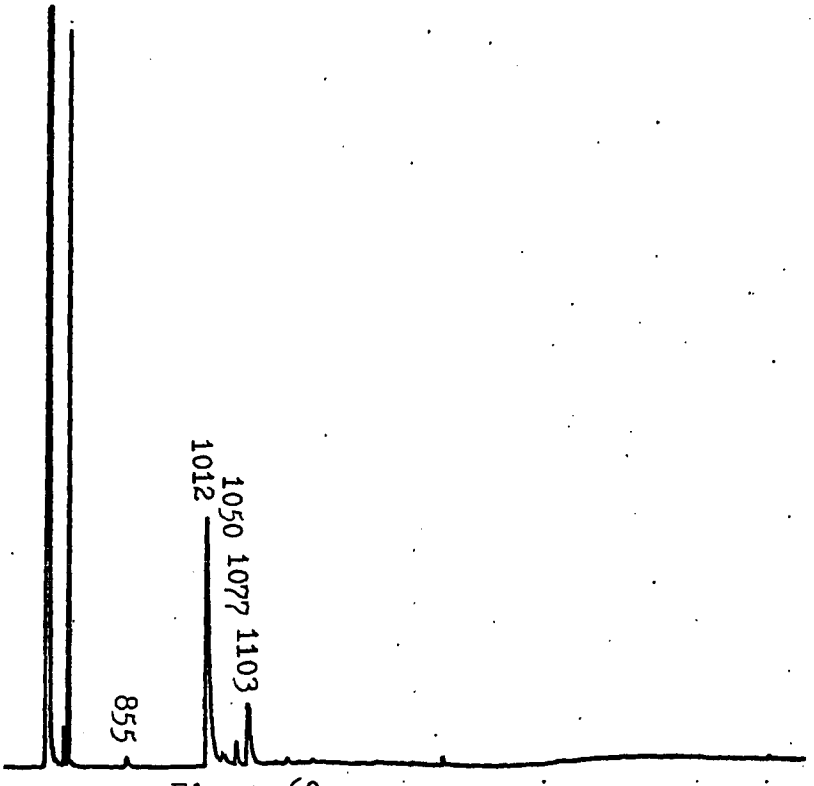


Figure 60a

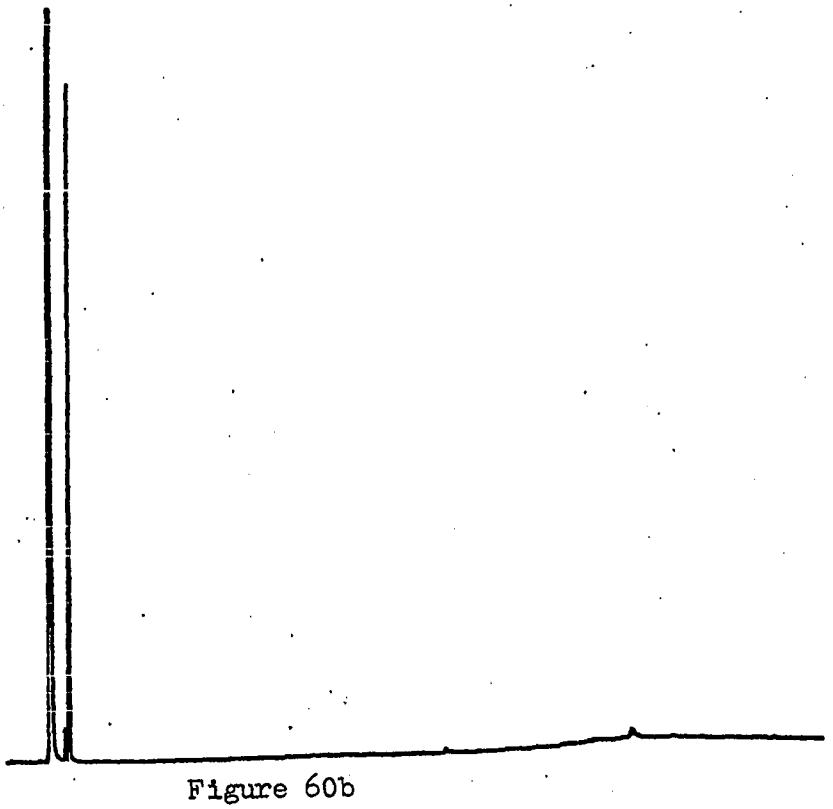


Figure 60b

Figure 61a. Chromatogram of the strong acid fraction (methylated) of 1973 Mercury Capri 2600 exhaust

Figure 61b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	7 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 8
detector:	FID
chart speed:	0.25 in./minute

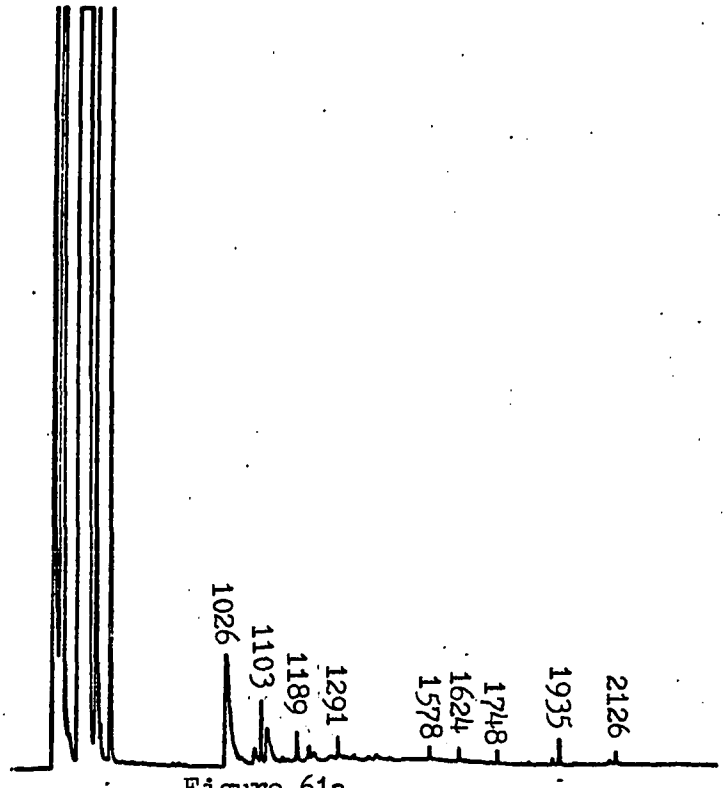


Figure 61a

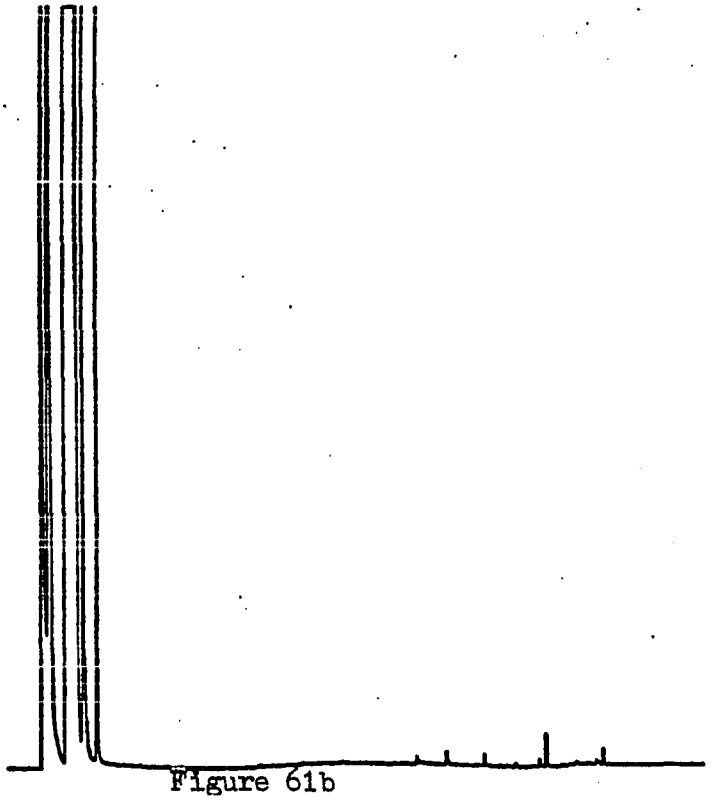


Figure 61b

Figure 62a. Chromatogram of the weak acid fraction of 1973 Mercury Capri 2600 exhaust

Figure 62b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 8
detector:	FID
chart speed:	0.25 in./minute

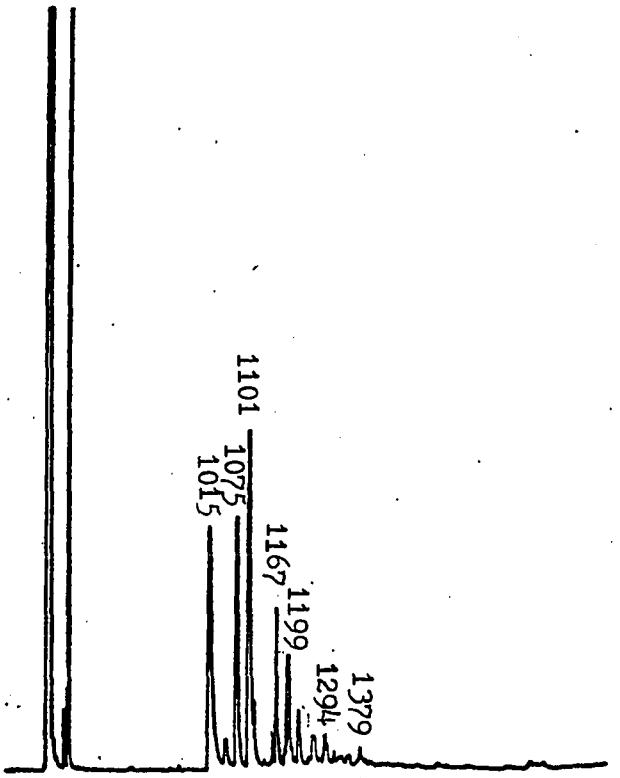


Figure 62a

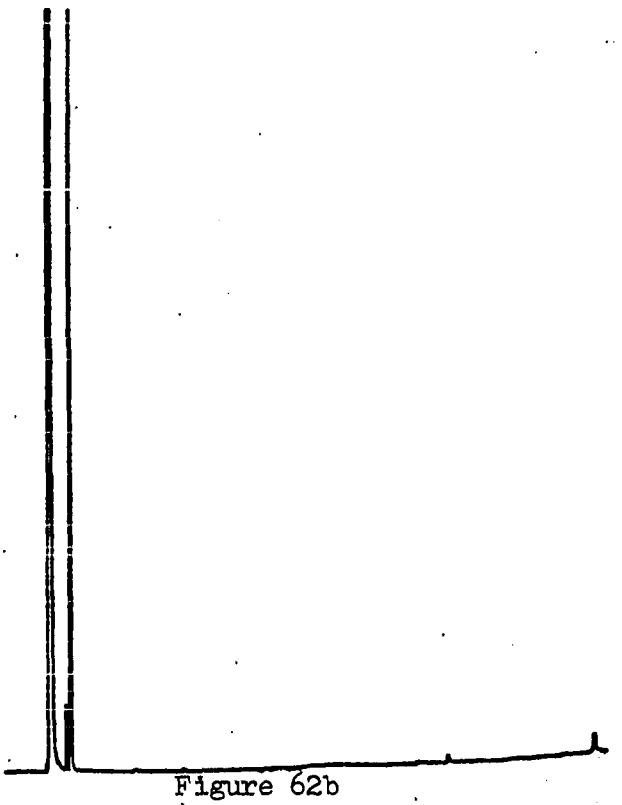


Figure 62b

Figure 63a. Chromatogram of the base fraction of 1973 Mercury Capri 2600 exhaust

Figure 63b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

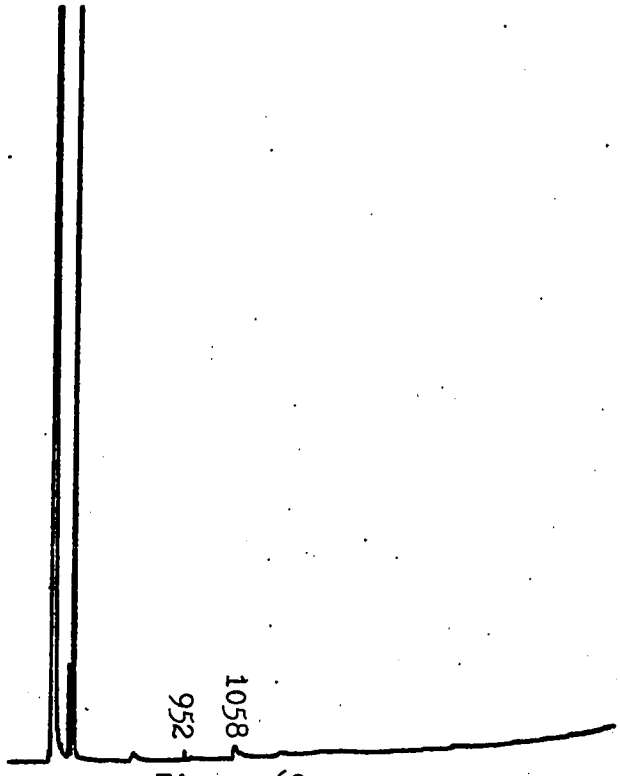


Figure 63a

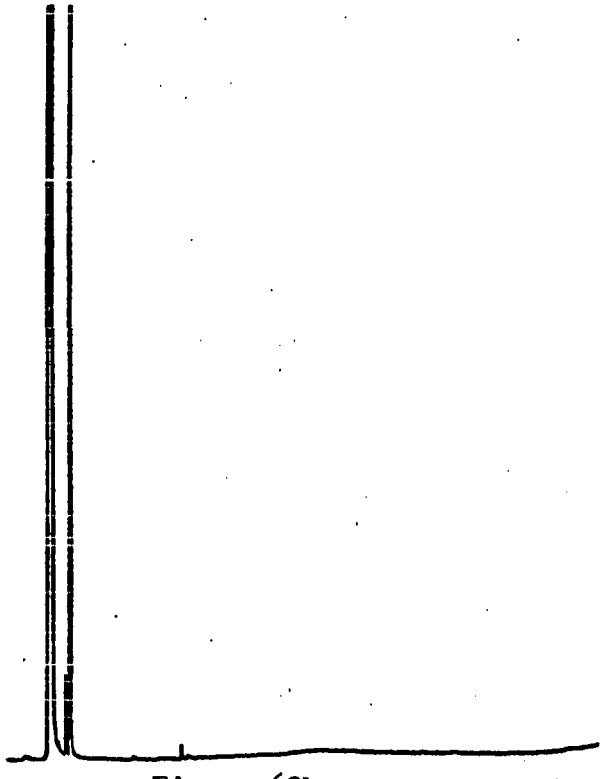


Figure 63b

Figure 64a. Chromatogram of the aldehyde fraction of 1973 Mercury Capri 2600 exhaust

Figure 64b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

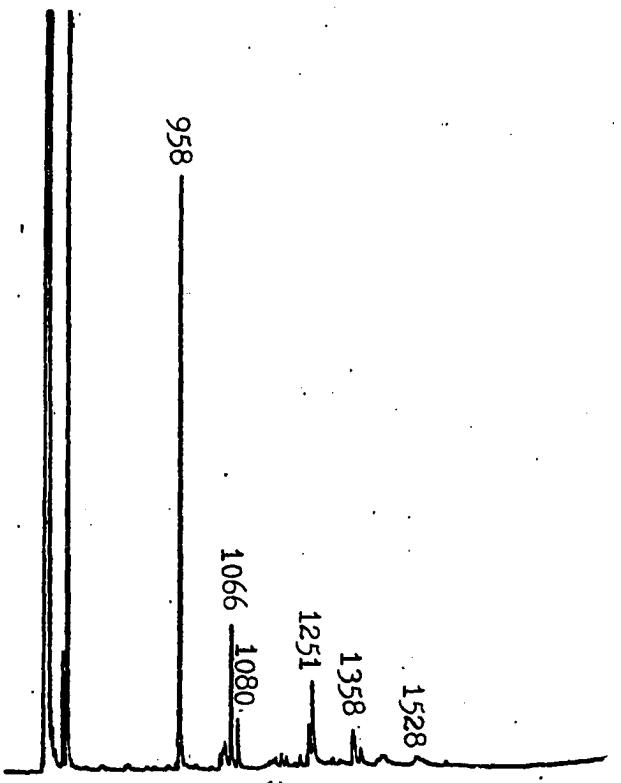


Figure 64a

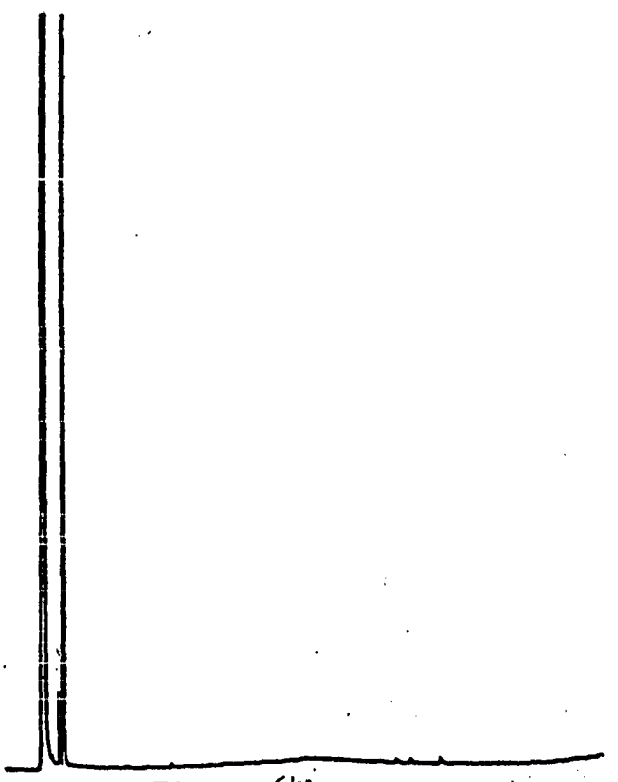


Figure 64b

benzaldehyde, C_1 to C_3-substituted benzaldehydes, methyl acetophenones, 1-indanone, and 1- and 2-naphthaldehyde. The SE-54 capillary column chromatogram of the ketone fraction (and the blank) is shown in Figure 65.

The concentrations of compounds in the nonpolar fraction were relatively low. The nonpolar fraction contained the series of n-alkanes from n-dodecane to n-eicosane. Branched hydrocarbons were also present, but at lower concentrations. The SE-54 capillary column chromatogram of the nonpolar fraction (and the blank) is shown in Figure 66. Many compounds were found in the blank; most of them were impurities found in DMSO.

The major component of the polar fraction of the Mercury Capri exhaust was 2-methylnaphthalene. Other major components included naphthalene, 1-methylnaphthalene, and some dimethylnaphthalenes. The concentrations of the alkyl benzenes were lower than those of most of the naphthalenes. The SE-54 capillary column chromatogram of the polar fraction (and the blank) is shown in Figure 67. The blank contained many compounds which were found to be impurities in DMSO.

The compound identifications for the chromatogram peaks (both SE-54 and SP-1000) for all of the various fractions of the Mercury Capri exhaust are listed in Table 15. The compound identifications for the SE-54 column chromatograms were based on mass spectral and retention index data. The compound identifications for the SP-1000 column chromatograms of the strong acid, base, and nonpolar fractions were based only on retention index data; the identifications of peaks in the

Figure 65a. Chromatogram of the ketone fraction of 1973 Mercury Capri 2600 exhaust

Figure 65b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	5 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

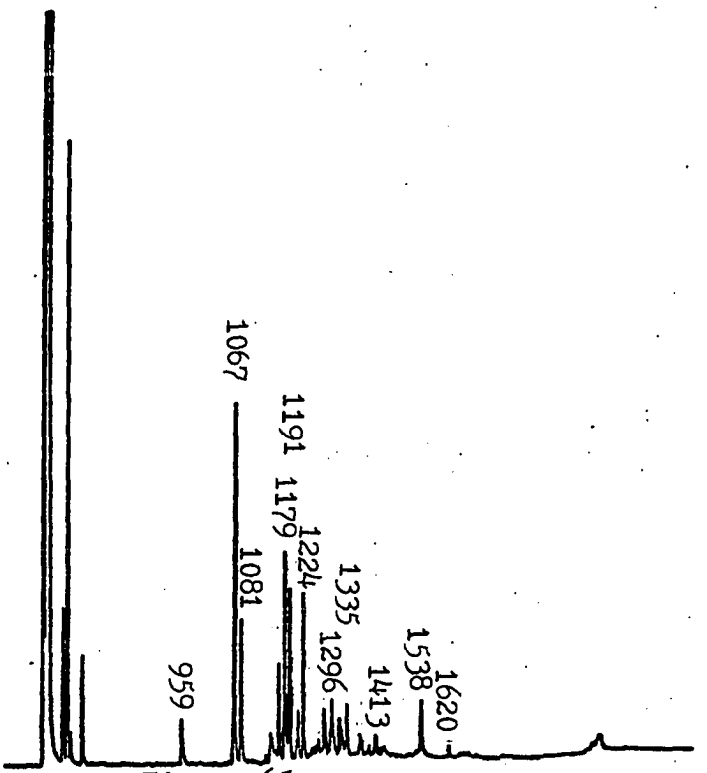


Figure 65a

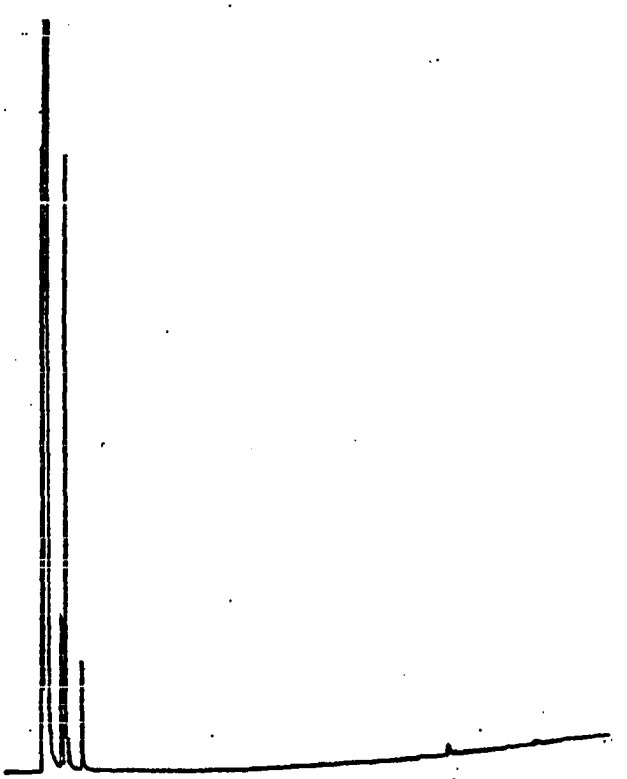


Figure 65b

Figure 66a. Chromatogram of the nonpolar fraction of 1973 Mercury Capri 2600 exhaust

Figure 66b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	11 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

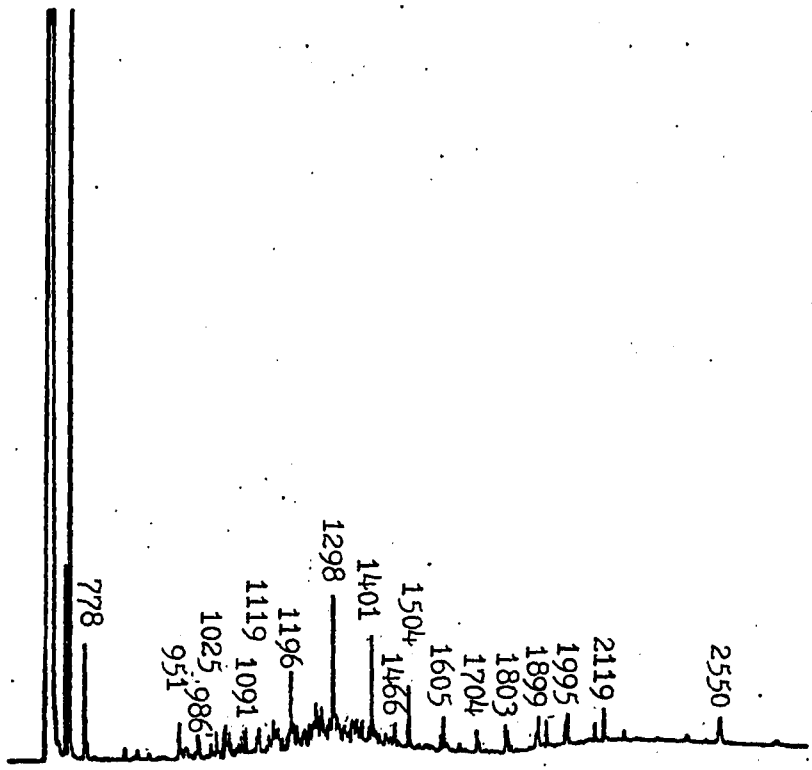


Figure 66a

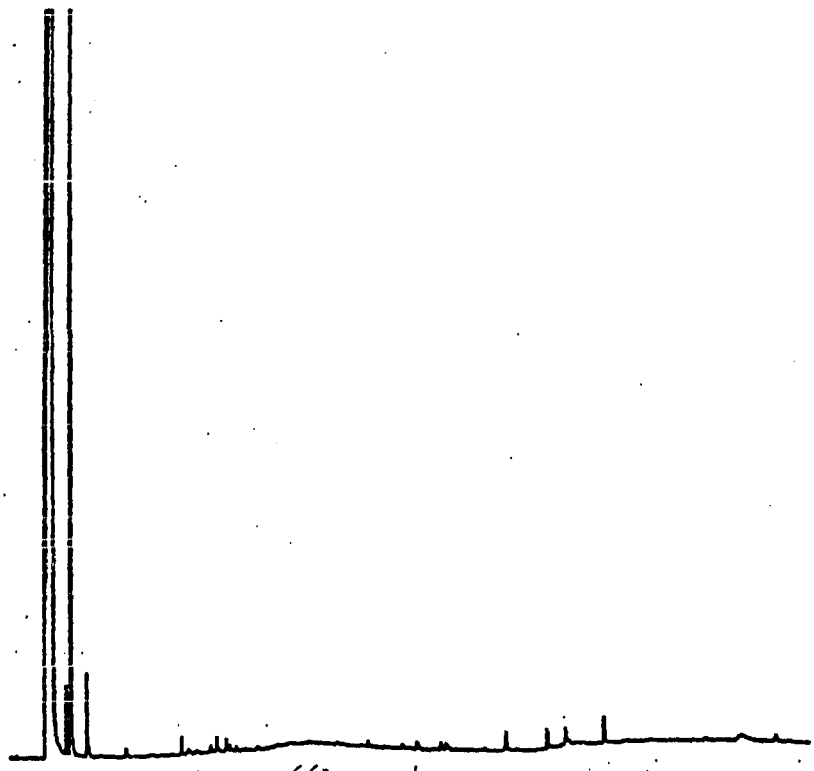


Figure 66b

Figure 67a. Chromatogram of the polar fraction of 1973 Mercury Capri 2600 exhaust

Figure 67b. Chromatogram of the blank

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	11 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

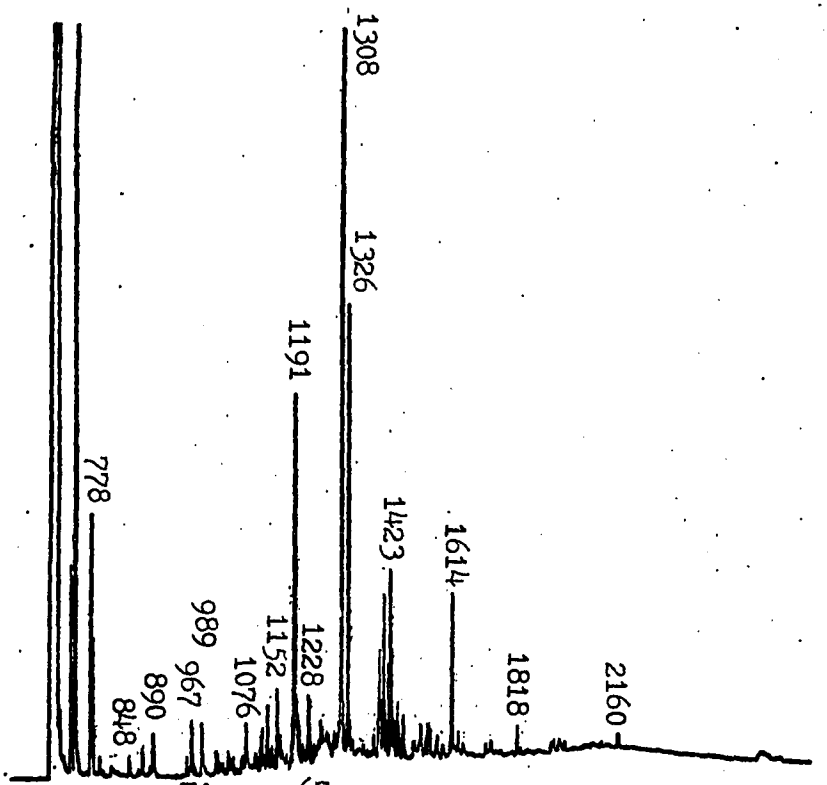


Figure 67a

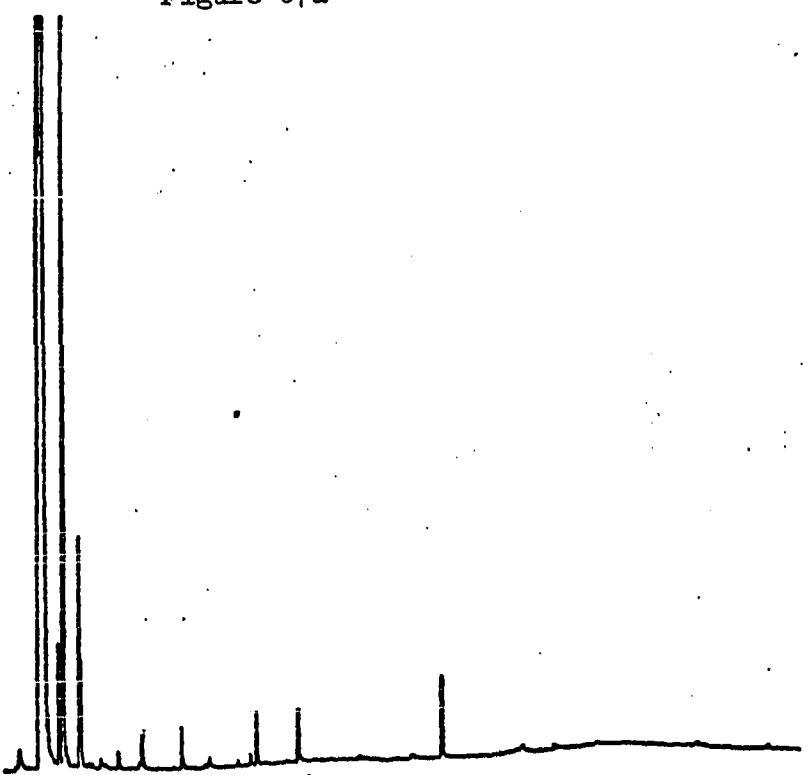


Figure 67b

Table 15. Components of 1973 Mercury Capri 2600 exhaust

Strong Acid Fraction (not methylated)

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
855	unknown	1378	unknown
1012	Phenol	1379	unknown
1050	Salicylaldehyde	1683	Salicylaldehyde
1077	o-Cresol	1874	unknown
1103	m-Cresol & p-Cresol	1969	unknown
1151	unknown	1997	Phenol
1170	unknown	2072	p-Cresol
1199	3-Ethylphenol?	2080	m-Cresol
1224	3,4-Dimethylphenol	2164	4-Ethylphenol
1237	unknown	2171	3-Ethylphenol &/or 3,5-Dimethylphenol
1257	unknown	2192	unknown
		2210	3,4-Dimethylphenol
		2360	unknown
		2374	unknown
		2395[a]	Diethylphthalate
		2522	unknown
		2579	unknown
		2626	unknown
		2682	unknown
		2722	unknown
		2346	unknown

Strong Acid Fraction (methylated)

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
929	unknown	1416	Methyloctanoate?
943	unknown	1512	Methylnonanoate?
1026	Phenol	1540	unknown
1060	Salicylaldehyde	1608	Methyldecanoate
1089	o-Cresol	1621	unknown
1103	Methylbenzoate	1636	Methylbenzoate
1117	m-Cresol & p-Cresol	1691	2-Methylmethylbenzoate
1127	unknown	1747	3-Methylmethylbenzoate or 4-Methylmethylbenzoate
1156	unknown		
1167	2-Ethylphenol?		
1184	2-Methylmethylbenzoate?	1758	unknown
1189	Methylphenylacetate	1773	Methylphenylacetate

[a] In blank.

Table 15. continued

Strong Acids Fraction (methylated) - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1215	3-Methylmethylbenzoate or 4-Methylbenzoate	1802	unknown
		1815[a]	Methyllaurate
1230[a]	Methylnonanoate?	1828	unknown
1235	unknown	1845	unknown
1269	unknown	1863	unknown
1277	unknown	1868	unknown
1291	2,6-Dimethylmethyl-benzoate?	1875	unknown
		1887	unknown
1317[a]	Methyldecanoate?	1936	unknown
1330	3,5-Dimethylmethyl-benzoate	1965	unknown
		1972	unknown
1334	unknown	1982	unknown
1371	unknown	2011	Phenol & o-Cresol
1393	unknown	2020[a]	Methylmyristate
1428	unknown	2038	unknown
1538[a]	Methyllaurate	2077	2-Ethylphenol &/or 2,5-Dimethylphenol
1624[a]	Diethylphthalate		
1748[a]	Methylmyristate	2086	p-Cresol
1839	unknown	2093	m-Cresol
1915[a]	unknown	2125	unknown
1935[a]	Methylpalmitate	2179	4-Ethylphenol?
2104[a]	unknown	2186	3-Ethylphenol &/or 3,5-Dimethylphenol?
2126[a]	Methylstearate		
		2227[a]	Methylpalmitate (& 3,4-Dimethylphenol?)
		2251[a]	unknown
		2322	unknown
		2380	unknown
		2396[a]	Diethylphthalate
		2478[a]	unknown
		2512[a]	unknown

Table 15. continued

Weak Acid Fraction

$R.I._{SE\ 54}$	Compound	$R.I._{SP\ 1000}$	Compound
862	unknown	1214	unknown
937	unknown	1376	unknown
953	unknown	1448	unknown
966	Benzaldehyde	1533	Benzaldehyde
1015	Phenol	1682	Salicylaldehyde
1053	Salicylaldehyde	1717	unknown
1075	o-Cresol	1791	unknown
1101	m-Cresol & p-Cresol	1792	unknown
1116	2,6-Dimethylphenol	1855	unknown
1142	unknown	1876	Benzylalcohol
1155	unknown	1906	2,6-Dimethylphenol
1159	2-Ethylphenol	1954	unknown
1167	2,4-Dimethylphenol &/ or 2,5-Dimethyl-phenol?	1961	4-Ethyl-2-methylphenol?
		1970	4-Methylbenzylalcohol
		1977	3-Methylbenzylalcohol
1189	4-Ethylphenol	1992	2-Methylbenzylalcohol
1196	3-Ethylphenol	1998	Phenol & o-Cresol
1199	2,3-Dimethylphenol & 3,5-Dimethylphenol	2039	2,3,6-Trimethylphenol?
		2061	unknown
1216	2,4,6-Trimethylphenol	2064	2-Ethylphenol
1223	3,4-Dimethylphenol	2070	unknown
1248	2,3,6-Trimethylphenol?	2074	p-Cresol & 2,5-Dimethyl-phenol
1256	3-Isopropylphenol &/or 4-Isopropylphenol?	2081	m-Cresol & 2,4-Dimethyl-phenol?
1260	unknown	2133	unknown
1286	an ethylmethyl phenol?	2139	2,3-Dimethylphenol
1287	an ethylmethyl phenol?	2166	3,5-Dimethylphenol & 4-Ethylphenol
1294	2,3,5-Trimethylphenol? an ethylmethyl phenol?	2172	3-Ethylphenol
		2193	C_8H_8O?
1310	unknown	2209	2,4,6-Trimethylphenol
1324	unknown	2210	3,4-Dimethyphenol
1331	unknown	2212	2,3,5-Trimethylphenol
1346	unknown	2248	2-Ethyl-5-methylphenol?
1351	unknown	2256	unknown
1379	unknown	2279	an ethylmethyl phenol?
1394	unknown	2290	4-Ethyl-2-methylphenol?
1408	unknown	2340	$C_9H_{10}O$ (2-(2-propenyl)-phenol?)
1595	2-Naphthol	2353	unknown
		2360	C_8H_8O? $C_9H_{10}O$?

Table 15. continued

Base Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
857	unknown	1376	unknown
952[a]	$C_{10}H_{22}$?	1381	unknown
965[a]	$C_{12}H_{18}$?	1884	Benzylalcohol?
1056	unknown		
1159	unknown		

Aldehyde Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
862[a]	unknown	1250	unknown
896	unknown	1386	$C_6H_{12}O_2$?
910	unknown	1393	unknown
937	2,5-Hexanedione?	1436	$C_7H_{10}O$?
951[a]	unknown	1484	$C_7H_{10}O$?
958	Benzaldehyde	1490	C_6H_8O?
993	unknown	1499	$C_7H_{10}O$? C_8H_{14}?
1027	unknown	1516	$C_8H_{12}O$
1044	Phenylacetaldehyde	1520	2,5-Hexanedione
1050	unknown	1532	$C_{10}H_{20}O$?
1055	3-Methyl-2-cyclohexenone?	1536	Benzaldehyde
1066	2-Methylbenzaldehyde 3-Methylbenzaldehyde	1604	3-Methyl-2-cyclohexenone?
1080	4-Methylbenzaldehyde	1627	2-Methylbenzaldehyde
1154	a methylbenzyl alcohol	1633	3-Methylbenzaldehyde
1166	$C_9H_{10}O$ (C_2 subst. benzaldehyde)	1653	unknown
1178	2,5-Dimethylbenzaldehyde	1656	4-Methylbenzaldehyde
1190	2,4-Dimethylbenzaldehyde & 4-Ethylbenzaldehyde	1716	$C_9H_{10}O$ (C_2 subst. benzaldehyde?)
1213	Naphthalene?	1728	2,5-Dimethylbenzaldehyde
1224	3,4-Dimethylbenzaldehyde?	1738	4-Ethylbenzaldehyde
1243	1,4-Benzenedicarboxylaldehyde	1747	Naphthalene
		1753	2,4-Dimethylbenzaldehyde
		1793	a dimethyl benzaldehyde
		1818	3,4-Dimethylbenzaldehyde?
		1857	2-Methylnaphthalene

Table 15. continued

Aldehyde Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1251	1,3-Benzenedicarboxyl-aldehyde	1880	Benzylalcohol
		1893	1-Methylnaphthalene
1306	2-Methylnaphthalene	1930	$C_9H_{10}O$?
1326	$C_{10}H_{10}O$? (a methyl indanone?)	1965	4-Methylbenzylalcohol
		1974	3-Methylbenzylalcohol
1358	$C_9H_8O_2$ (a methyl benzenedicarboxyl-aldehyde?)	2002	2-Methylbenzylalcohol
		2006	$C_{12}H_{12}$? (a dimethyl naphthalene?)
1362	a methyl benzenedi-carboxylaldehyde?	2017	1-Indanone?
		2108	1,4-Benzenedicarboxyl-aldehyde
1377	a methylbenzenedi-carboxylaldehyde?	2130	1,3-Benzenedicarboxyl-aldehyde
1435	unknown		
1528	1-Naphthaldehyde & 2-Naphthaldehyde	2208	2-Methyl-1,4-Benzene-dicarboxylaldehyde?
1620[a]	Diethylphthalate	2216	a methyl benzenedicarbox-ylaldehyde?
		2230	1-phenyl-1,2-propanedione?
		2239	a methyl benzenedicarbox-ylaldehyde?
		2255	a methyl benzenedicarbox-ylaldehyde? a methyl benzofuranone?
		2380[a]	Diethylphthalate
		2426	1-Naphthaldehyde & 2-Naphthaldehyde
		2524	$C_9H_{10}O$?
		2551	unknown

Ketone Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
778[a]	$C_6H_{12}O$?	1110	unknown
		1119	unknown
959	Benzaldehyde	1388	4-Hydroxy-4-Methyl-2-pentanone?
1067	2-Methylbenzaldehyde & 3-Methylbenzaldehyde		
		1420	unknown
1081	4-Methylbenzaldehyde	1432	unknown
1139	2-Methylacetophenone		

Table 15. continued

Ketone Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1150	unknown	1448	unknown
1160	unknown	1531	Benzaldehyde
1166	2-Ethylbenzaldehyde &/ or 3-Ethylbenzaldehyde	1549	unknown
		1588	unknown
		1622	2-Methylbenzaldehyde
1179	2,5-Dimethylbenzaldehyde	1627	3-Methylbenzaldehyde
		1650	4-Methylbenzaldehyde & Acetophenone
1191	2,4-Dimethylbenzaldehyde & 4-Ethylbenzaldehyde	1678	2-Ethylbenzaldehyde?
		1687	2-Methylacetophenone
1208	Decanal?	1710	3-Ethylbenzaldehyde?
1212	4-Methylacetophenone & a dimethylbenzaldehyde?	1721	2,5-Dimethylbenzaldehyde
		1732	$C_9H_{10}O$ (C_2 subst. benzaldehyde)
1224	3,4-Dimethylbenzaldehyde	1739	4-Ethylbenzaldehyde
		1746	2,4-Dimethylbenzaldehyde
1241	$C_9H_{10}O$	1755	3-Methylacetophenone
1248	2-Indanone?	1775	4-Methylacetophenone
1260	$C_9H_8O_2$ (a methyl benzenedicarboxylaldehyde?)	1786	a dimethylbenzaldehyde?
		1792	$C_9H_8O_2$ (5-methylisobenzofuranone?)
1276	$C_{10}H_{12}O$ (C_3 subst. benzaldehyde?)	1806	$C_{10}H_{12}O$ (C_3 subst. benzaldehyde)
1291	$C_{10}H_{12}O$ (C_3 subst. benzaldehyde?) or $C_9H_8O_2$ (a methyl benzenedicarboxylaldehyde?)	1811	3,4-Dimethylbenzaldehyde
		1826	C_3 subst. benzaldehyde?
		1831	C_9H_8O? (a phenyl propenal?)
1296	1-Indanone	1840	unknown
1314	2,4,6-Trimethylbenzaldehyde	1851	2-Methylnaphthalene
		1864	C_9H_8O? (a phenyl propenal?)
1325	a trimethylbenzaldehyde?	1871	2,4,6-Trimethylbenzaldehyde
1335	a trimethylbenzaldehyde?	1880	a trimethyl benzaldehyde?
1362	$C_{10}H_{10}O$? $C_{11}H_{14}$?	1888	a trimethyl benzaldehyde?
1372	a trimethylbenzaldehyde?	1908	$C_{10}H_{12}O$ (C_3 subst. benzaldehyde?)
1395	$C_{10}H_{10}O$? (C_3 subst. benzaldehyde?)	1932	$C_{10}H_{10}O$? (4,7-Dimethylbenzofuran?)

Table 15. continued

Ketone Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1413	$C_{10}H_{10}O$? (C_3 subst. benzaldehyde?)	1933	4-Ethylacetophenone? 2,4-Dimethylacetophenone?
1422	$C_{12}H_{18}$? $C_{11}H_{14}O$?	1951	$C_{10}H_{10}O$
1431	$C_{10}H_{10}O$? (C_3 subst. benzaldehyde?)	1958	4-Methylbenzylalcohol
1435	$C_{10}H_{10}O$?	1967	3-Methylbenzylalcohol
1538	1-Naphthaldehyde & 2-Naphthaldehyde	1979	a trimethyl benzaldehyde?
1620[a]	Diethylphthalate	1986	2-Methylbenzylalcohol?
		2008	1-Indanone
		2022	unknown
		2040	$C_{10}H_{10}O$? $C_{11}H_{12}O$?
		2051	unknown
		2062	unknown
		2069	unknown
		2076	2,4-Dimethylbenzylalcohol
		2081	2,5-Dimethylbenzylalcohol
		2106	1,4-Benzenedicarboxylaldehyde
		2116	3,5-Dimethylbenzylalcohol?
		2133	1,3-Benzenedicarboxylaldehyde
		2153	$C_{11}H_{14}$? (an ethyl indan?) $C_{10}H_{10}O$?
		2165	unknown
		2170	$C_{10}H_{10}O$
		2178	$C_{10}H_8O$?
		2213	$C_9H_{10}O$?
		2248	$C_9H_8O_2$
		2261	unknown
		2287	unknown
		2309	unknown
		2341	unknown
		2354	unknown
		2373	$C_8H_6O_2$ (Isobenzofuranone?)
		2394[a]	Diethylphthalate
		2403	1-Naphthaldehyde

Table 15. continued

Ketone Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
		2417	2-Naphthaldehyde
		2488	unknown
		2513	unknown
		2529	unknown
		2548	$C_9H_8O_2$? (a methyl isobenzofuranone?)
		2560	$C_{12}H_{10}O$?
		2585	unknown
		2610	unknown
		2621	2-Acetonaphthone?
		2643	unknown
		2656	unknown

Nonpolar Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
778[a]	$C_6H_{12}O$?	1160[a]	Dimethyldisulfide?
845[a]	a methoxy compound?	1171	unknown
869	p-Xylene	1201	unknown
891	o-Xylene	1206	unknown
909	unknown	1213	unknown
919	unknown	1236	n-Dodecane
951[a]	C_9H_{20}? $C_{10}H_{22}$?	1260	unknown
955	3-Ethyltoluene & 4-Ethyltoluene	1274	o-Xylene
963[a]	Dimethyltrisulfide	1280	unknown
974	2-Ethyltoluene	1289	3-Ethyltoluene & 4-Ethyltoluene
982	$C_{10}H_{22}$?	1304	1,3,5-Trimethylbenzene?
986	1,2,4-Trimethylbenzene	1316	n-Tridecane
1006	unknown	1342	unknown
1013	$C_{10}H_{22}$?	1352	unknown
1016	1,2,3-Trimethylbenzene?	1364	1,2,3-Trimethylbenzene?
1025	$C_{10}H_{22}$? $C_{11}H_{24}$?	1372	unknown
1045[a]	unknown	1379[a]	unknown
1054[a]	$C_{10}H_{22}$? $C_{11}H_{24}$?	1398	unknown
		1403	n-Tetradecane
		1416	unknown
		1430	unknown
		1440	unknown

Table 15. continued

Nonpolar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1062	$C_{10}H_{22}$? $C_{11}H_{24}$? (2-Methyldecane?)	1447	unknown
1068[a]	$C_{11}H_{22}$?	1450[a]	unknown
1071	1,2-Diethylbenzene?	1466	unknown
1080	1,3-Dimethyl-4-Ethyl-benzene?	1471	unknown
1091	$C_{11}H_{22}$?	1476	unknown
1104	2,5-Dimethyl-1-Ethyl-benzene?	1489	unknown
1114	$C_{10}H_{14}$ (C_4 subst. benzene)	1496	n-Pentadecane
1119	$C_{10}H_{14}$ (C_4 subst. benzene)	1504	unknown
1127	a sulfur compound	1508	unknown
1135	1-Nitropropylbenzene? (1-Ethylpropyl)benzene?	1518	unknown
1142	$C_{11}H_{16}$ (C_5 subst. benzene)	1522	unknown
1150	unknown	1536	unknown
1156	$C_{12}H_{26}$?	1552	unknown
1164	$C_{12}H_{26}$?	1568	unknown
1175	$C_{11}H_{16}$ ((1,1-Dimethyl-(propyl)benzene?)	1572	unknown
1196	n-Dodecane	1584	unknown
1201	$C_{11}H_{16}$ (C_5 subst. benzene)	1591	n-Hexadecane
1209	$C_{13}H_{28}$? (2,6-Dimethylundecane?)	1600	unknown
1219	$C_{12}H_{26}$? $C_{13}H_{28}$?	1604	unknown
1226	unknown	1612	unknown
1230	$C_{12}H_{18}$? (C_6 subst. benzene?)	1621	unknown
1239	$C_{11}H_{16}$ (C_5 subst. benzene)	1626	unknown
		1638[a]	unknown
		1657	unknown
		1669	unknown
		1674	unknown
		1684	unknown
		1688	n-Heptadecane
		1732	unknown
		1760	unknown
		1772	unknown
		1777	unknown
		1787	n-Octadecane
		1836	2-Methylnaphthalene?
		1840[a]	unknown
		1866[a]	unknown
		1875	unknown
		1885	n-Nonadecane
		1934	unknown
		1950	unknown
		1985	n-Eicosane
		2000[a]	unknown

Table 15. continued

Nonpolar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1251	$C_{12}H_{18}$ (C_6 subst. benzene?)	2038[a]	unknown
		2084	unknown
1256	$C_{12}H_{16}$ (an ethylmethyl indan?)	2137	unknown
		2167	unknown
		2185	unknown
1261	$C_{13}H_{28}$?	2206[a]	unknown
		2288	unknown
1270	$C_{12}H_{26}$? $C_{13}H_{28}$?	2371[a]	Diethylphthalate
1282	$C_{12}H_{18}$? $C_{11}H_{14}O$?	2446[a]	unknown
1289	$C_{12}H_{18}$?		
1298	n-Tridecane		
1309	2-Methylnaphthalene		
1318	$C_{11}H_{10}$? (a methylnaphthalene?)		
1330	$C_{12}H_{16}$?		
1342	$C_{12}H_{16}$?		
1351	$C_{13}H_{28}$? $C_{14}H_{30}$?		
1360	$C_{13}H_{28}$? $C_{14}H_{30}$?		
1364	$C_{13}H_{28}$? $C_{14}H_{30}$?		
1371	$C_{13}H_{28}$? $C_{14}H_{30}$?		
1378	$C_{13}H_{28}$? $C_{14}H_{30}$?		
1394	Nonanol?		
1401	n-Tetradecane		
1414	a dimethyl naphthalene?		
1425	a dimethyl naphthalene?		
1441	a dimethyl naphthalene?		
1453	a dimethyl naphthalene?		
1457	unknown		
1466	$C_{14}H_{30}$? $C_{15}H_{32}$?		
1475	unknown		
1504	n-Pentadecane		
1534	unknown		
1552	$C_{13}H_{14}$ (C_3 subst. naphthalene?)		
1598	Tridecanol?		
1605	n-Hexadecane		
1613[a]	Diethylphthalate		

Table 15. continued

Nonpolar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1655	$C_{15}H_{32}$? $C_{16}H_{34}$?		
1670	unknown		
1704	n-Heptadecane		
1711	$C_{17}H_{36}$?		
1734	unknown		
1753	unknown		
1797	Pentadecanol?		
1803	n-Octadecane		
1814	unknown		
1832	unknown		
1875	unknown		
1894[a]	unknown		
1899	n-Nonadecane		
1916	unknown		
1926[a]	unknown		
1989	unknown		
1995	n-Eicosane		
2089	unknown		
2119[a]	unknown		
2191	unknown		
2421	unknown		
2491	unknown		
2550	an ester?		

Polar Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
747[a]	Cyclohexane?	1136[a]	unknown
750[a]	Cyclohexene	1158[a]	Dimethyldisulfide
778[a]	$C_6H_{12}O$?	1196	p-Xylene
782[a]	Dimethyldisulfide?	1201	unknown
795	Toluene	1205	m-Xylene
816[a]	unknown	1236	o-Xylene
848[a]	a methoxy compound?	1268	3-Ethyltoluene & 4-Ethyltoluene
865	Ethylbenzene	1283	1,3,5-Trimethylbenzene
871	p-Xylene	1297	2-Ethyltoluene
885[a]	$C_4H_8S_2$? $C_5H_{12}SO$? $C_4H_8O_2S$?	1313	1,2,4-Trimethylbenzene
		1318[a]	$CH_3SCH_2SCH_3$

Table 15. continued

Polar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
890[a]	$CH_3SCH_2SCH_3$ (& o-Xylene?)	1333	a dimethylethyl benzene?
938	unknown	1342	unknown
950	unknown	1348[a]	$C_3H_8S_2$? $C_4H_{10}OS$?
957	3-Ethyltoluene	1352	$C_{10}H_{14}$ (C_4 subst. benzene?)
964	4-Ethyltoluene	1361	1,2,3-Trimethylbenzene
967[a]	Dimethyltrisulfide (& 1,3,5-Trimethyl-benzene?)	1372	unknown
976	2-Ethyltoluene	1382	$C_{10}H_{14}$ (C_4 subst. benzene?)
989	1,2,4-Trimethylbenzene	1390	Indan (& 1,3-Dimethyl-4-ethylbenzene?)
1018	1,2,3-Trimethylbenzene	1400[a]	Dimethyltrisulfide
1027[a]	unknown	1414[a]	unknown
1033	Indan	1418	$C_{10}H_{16}O$?
1043	Indene	1428	$C_{11}H_{16}$ (C_5 subst. benzene?)
1055	1,4-Diethylbenzene? a methylpropyl benzene?	1441	$C_{10}H_{14}$ (C_4 subst. benzene?)
1075	unknown	1451	1,2,4,5-Tetramethylbenzene
1076	$C_{10}H_{14}$ (C_4 subst. benzene?)	1462	$C_3H_{16}OS_2$?
1083	unknown	1477	$C_{11}H_{16}$ (C_5 subst. benzene?)
1101	$C_{10}H_{12}$ (a dimethyl styrene?)	1487	$C_{10}H_{12}$ (a methyl indan?)
1105	$C_{10}H_{14}$ (C_4 subst. benzene?)	1496	Indene
1115	$C_{10}H_{14}$ (C_4 subst. benzene?)	1500	$C_{10}H_{14}$ (C_4 subst. benzene?)
1119	1,2,4,5-Tetramethyl-benzene	1511	$C_{10}H_{12}$ (1-Methylindan?)
1130[a]	$CH_3SCH_2SSCH_3$?	1516	$C_{11}H_{16}$ (C_5 subst. benzene?)
1141	1-Methylindan?	1534	$C_{11}H_{14}$ (1,1-Dimethyl-indan?)
1152	a methyl indan?	1548	$C_{11}H_{16}$ (C_5 subst. benzene?)
1160	1-methylindene?	1564	$C_{10}H_{14}$? $C_9H_{10}O$?
1176	$C_{11}H_{16}$ (2-methyl-2-phenylbutane?)	1576	unknown
1185	1,1-Dimethylindan?		
1191	Naphthalene		

Table 15. continued

Polar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1197	$C_9H_{10}O$ (C_2 subst. benzaldehyde?)	1584	$C_{11}H_{14}$ (a methyl indan?)
1203	unknown	1595	C_8H_8O? $C_{10}H_{10}$?
1228[a]	$C_4H_{10}S_3$?	1612	$C_{11}H_{14}$ (a dimethyl indan?)
1241	$C_{11}H_{14}$?	1634	$C_{11}H_{14}$ (a dimethyl-indan?)
1248	unknown	1640	$C_{11}H_{14}$ (a methyl tetra-lin?)
1253	$C_{11}H_{12}$?	1645	unknown
1257	$C_{11}H_{14}$?	1650	$C_{11}H_{16}$? (C_5 subst. benzene?)
1263	unknown	1666[a]	$CH_3SCH_2SSCH_3$?
1272	$C_{11}H_{12}$?	1675	$C_{11}H_{12}$ (a dimethyl indan? a methyl tetralin?)
1276	$C_{11}H_{12}$?	1686	$C_{11}H_{12}$ (a methyl tetralin?)
1282	unknown	1701	$C_9H_{10}O$?
1290	unknown	1707	2,5-Dimethylbenzaldehyde
1292	$C_{11}H_{14}$ (a dimethyl indan?)	1717	$C_{11}H_{12}$ (a dimethyl indan? a methyl tetralin?)
1302	C_9H_8S (a methyl benzo-thiophene?)	1731	$C_{11}H_{12}$ (a dimethyl indan? a methyl tetralin?)
1308	2-Methylnaphthalene	1742	Naphthalene
1319	C_9H_8S (a methyl benzo-thiophene?)	1774	$C_{11}H_{12}$ (a dimethyl indan? a methyl tetralin?)
1326	1-Methylnaphthalene	1783[a]	$C_4H_{10}S_3$?
1339	unknown	1807	$C_{12}H_{16}$ (a trimethyl indan?)
1355	unknown	1825	a sulfur compound?
1362	unknown	1830	$C_{10}H_{12}O$?
1370	$C_{11}H_{14}$ (1-Ethyl-indan?)	1853	2-Methylnaphthalene
1380[a]	$C_7H_{10}S_2$? $C_6H_6OS_2$? $C_2H_6O_2S_3$?		
1389	unknown		
1396	Biphenyl		
1408	$C_{12}H_{18}$? $C_{11}H_{14}O$?		
1411	2-Ethylnaphthalene		
1412	1-Ethylnaphthalene		
1415	a dimethylnaphthalene		
1423	a dimethylnaphthalene		

Table 15. continued

Polar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1438	$C_{12}H_{18}$?	1868	2,4,6-Trimethylbenzaldehyde?
1442	$C_{12}H_{10}$?	1874	C_9H_8S? (a methyl benzothiophene?)
1450	a dimethylnaphthalene	1887	1-Methylnaphthalene
1460	1,4-Dimethylnaphthalene	1916	C_9H_8S (a methyl benzothiophene?)
1476	Acenaphthylene	1922	C_9H_8S? (a methyl benzothiophene?)
1505	3-Phenyltoluene	1931	C_9H_8S? (a methyl benzothiophene?)
1510	Acenaphthene	1945	2-Ethylnaphthalene
1521	$C_{13}H_{14}$ (C_3 subst. naphthalene?)	1957	1-Ethylnaphthalene
1526	$C_{13}H_{14}$ (C_3 subst. naphthalene?)	1962	a dimethyl naphthalene
1538	$C_{13}H_{14}$ (C_3 subst. naphthalene?)	1992	a dimethyl naphthalene
1548	unknown	2000	1,3-Dimethylnaphthalene
1554	$C_{13}H_{14}$ (C_3 subst. naphthalene?)	2025	$C_{11}H_{14}$ (an ethyl indan?)
1563	unknown	2035	a dimethyl naphthalene
1573	unknown	2054	$C_{13}H_{14}$ (C_3 subst. naphthalene)
1574	unknown	2064	a dimethyl naphthalene
1589	$C_{13}H_{14}$ (C_3 subst. naphthalene?)	2083	a dimethylbenzyl alcohol?
1608	Fluorene?	2092	$C_{12}H_{10}$?
1614[a]	Diethylphthalate	2103	3-Phenyltoluene
1633	$C_{15}H_{16}$?	2110	a trimethyl naphthalene?
1651	unknown	2141	$C_{13}H_{14}$ (C_3 subst. naphthalene?)
1671	unknown	2145	a trimethyl naphthalene?
1678	unknown	2158	unknown
1702	n-Heptadecane?	2166	$C_{13}H_{14}$ (C_3 subst. naphthalene?)
1720	unknown	2174	$C_{13}H_{14}$ (a trimethyl naphthalene?)
1737	$C_{16}H_{18}$?	2186	unknown
1766	$C_{16}H_{18}$?	2190	Acenaphthylene
1804	unknown	2204	$C_{15}H_{16}$? $C_{10}H_{14}$?
1818	Methylpentadecanoate?		
1829	Anthracene		
1852	unknown		
1932	unknown		
1938	unknown		

Table 15. continued

Polar Fraction - continued			
R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1958	unknown	2216	$C_{14}H_{14}$ (an ethyl biphenyl?)
1975	unknown		
2068	unknown	2239	$C_{13}H_{12}$
2103	n-Eicosane?	2259	$C_{13}H_{12}$
2160	unknown	2268	unknown
		2275	unknown
		2287	unknown
		2314	unknown
		2323	unknown
		2336	Fluorene
		2377[a]	Diethylphthalate
		2399	unknown
		2418[a]	unknown
		2494	unknown
		2553[a]	unknown
		2632[a]	unknown

chromatograms of the remaining fractions were based on mass spectral data and retention index data.

The oxygenated compounds in the Mercury Capri exhaust were partial oxidation products of compounds in the gasoline. The most likely precusors of the phenols, the benzoic acids, and the benzaldehydes were alkyl benzenes. The low concentrations of oxygenated products with more than one aromatic ring and the high concentrations of naphthalenes (relative to the alkyl benzenes) in the polar fraction indicated that the alkyl benzenes underwent combustion with a greater efficiency than did aromatic compounds with more than one ring. The low concentrations of aliphatic compounds in the nonpolar fraction of the exhaust relative

to the concentrations of aliphatic compounds in the nonpolar fraction of gasoline indicated that the aliphatic compounds underwent combustion with high efficiency. The presence of fluorene, acenaphthene, acenaphthylene, anthracene, and indene, all of which were not found in gasoline, indicated that pyrosynthesis of aromatic compounds had occurred.

1973 Plymouth station wagon exhaust The exhaust from a 1973 Plymouth station wagon was similar in composition to the exhaust of the Mercury Capri. The major component in the exhaust from the Plymouth station wagon was phenol when both regular gasoline and gasohol were tested as fuels. The compositions of the regular gasoline exhaust and the gasohol exhaust were very similar. Because the two samples were obtained at different times and the engine operating variables could not be controlled, it was difficult to compare the total amounts of organic material in the exhaust of the two fuels. However, the relative concentrations of the components of the various fractions could be compared.

The profiles of the chromatograms of the strong acid fractions of the regular gasoline and the gasohol exhaust were almost identical. The SE-54 capillary chromatograms for the strong acid fractions of both exhaust samples are shown in Figure 68.

The total concentration of m-cresol plus p-cresol (relative to the concentration of phenol) was higher in the gasohol sample than it was in the regular gasoline sample. Also, the relative concentration of 2-naphthol was higher in the gasohol sample than in the regular gasoline sample. The SE-54 chromatograms of the weak acid fractions of the two

Figure 68a. Chromatogram of the strong acid fraction (methylated) of 1973 Plymouth station wagon exhaust - regular gasoline

Figure 68b. Chromatogram of the strong acid fraction (methylated) of 1973 Plymouth station wagon exhaust - gasohol

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	30:1 (Fig. 68a) 50:1 (Fig. 68b)
He pressure:	20 p.s.i.
attenuation:	X 4
detector	FID
chart speed:	0.25 in./minute

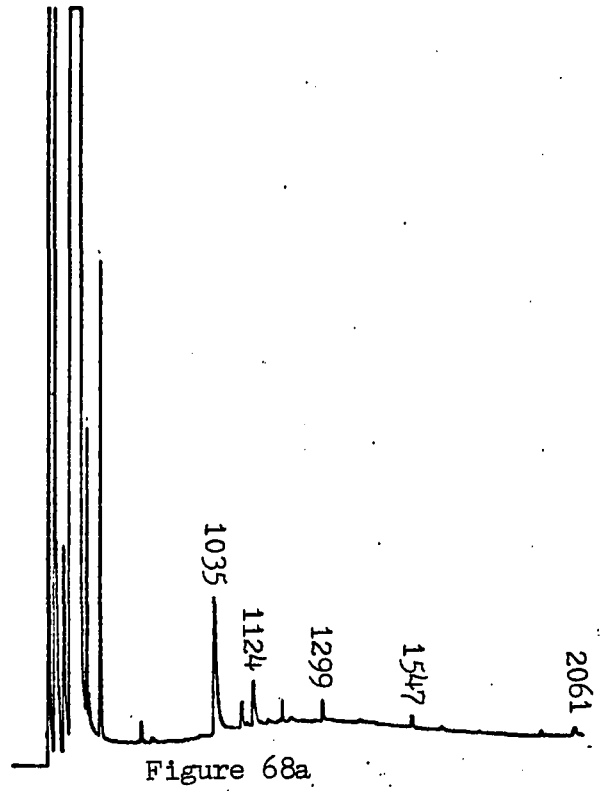


Figure 68a

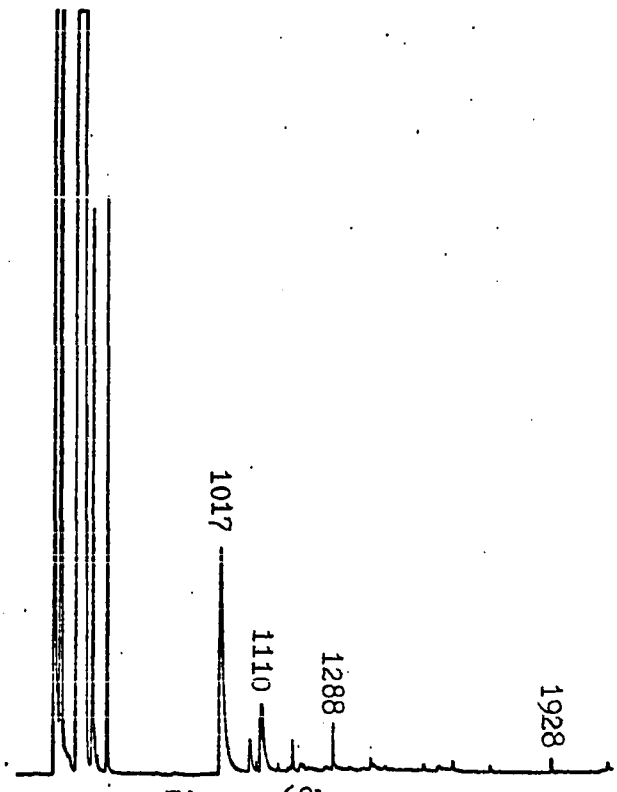


Figure 68b

samples are shown in Figure 69.

No significant amounts of bases were found in either of the two exhaust samples. Figure 70 shows the SE-54 capillary column chromatograms of the base fractions of the two exhaust samples. The two small peaks in the chromatograms of each sample corresponded to the same peaks found in the base fraction of the Mercury Capri exhaust base fraction.

The SE-54 capillary column chromatograms of the aldehyde fractions of the regular gasoline and gasohol exhaust samples are shown in Figure 71. The chromatogram profiles are almost identical. The major components were benzaldehyde and the three methyl benzaldehydes.

The ketone fractions of the two exhaust samples were similar in composition. However, the relative concentrations of 1-indanone and 1- and 2-naphthaldehyde were higher in the gasohol sample. Figure 72 shows the SE-54 capillary column chromatograms of the ketone fractions of the two samples.

The concentrations of aliphatic hydrocarbons in the gasohol exhaust appeared to be lower than they were in the regular gasoline exhaust. The SE-54 capillary column chromatograms of the nonpolar fractions of the two exhaust samples are shown in Figure 73. Most of the hydrocarbons in the regular gasoline exhaust sample had carbon numbers in the range of C_8 to C_{14}. The gasohol exhaust, on the other hand, had relatively high concentrations of hydrocarbons in the carbon number range of C_{15} to C_{21}.

The regular gasoline exhaust contained relatively higher concentrations of alkyl benzenes than did the gasohol exhaust. However,

Figure 69a. Chromatogram of the weak acid fraction of 1973 Plymouth station wagon exhaust - regular gasoline

Figure 69b. Chromatogram of the weak acid fraction of 1973 Plymouth station wagon exhaust - gasohol

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	0 minutes (Fig. 69a) 5 minutes (Fig. 69b)
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	30:1
He pressure:	20 p.s.i.
attenuation:	X 4 (Fig. 69a) X 8 (Fig. 69b)
detector:	FID
chart speed:	0.25 in./minute

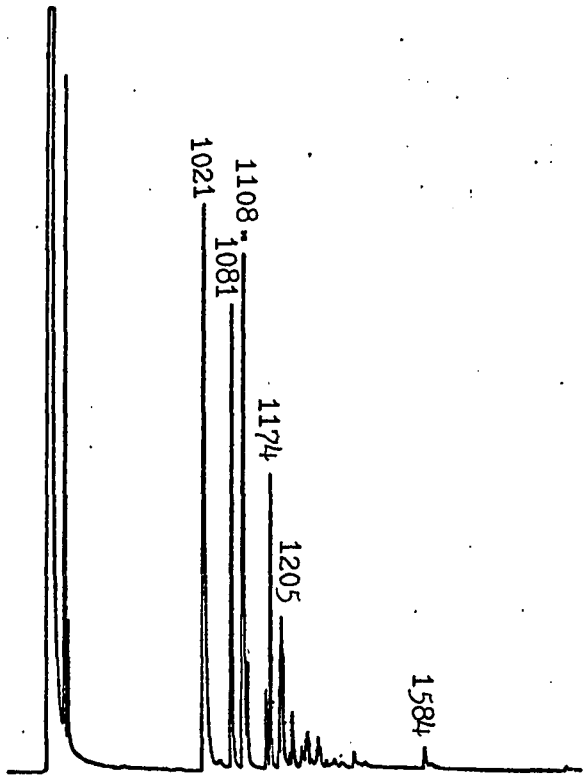


Figure 69a

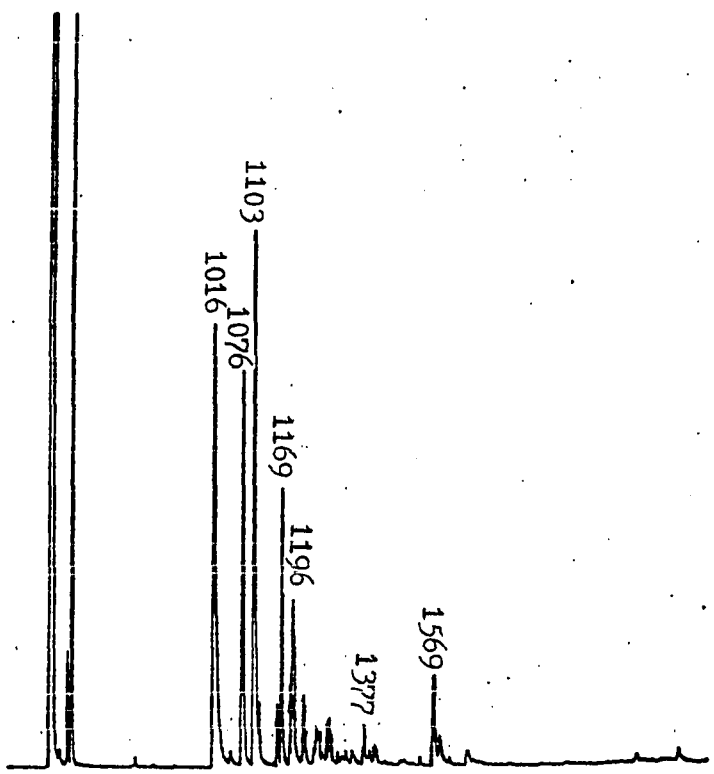


Figure 69b

Figure 70a. Chromatogram of the base fraction of 1973 Plymouth station wagon exhaust - regular gasoline

Figure 70b. Chromatogram of the base fraction of 1973 Plymouth station wagon exhaust - gasohol

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	0 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	30:1
He pressure:	20 p.s.i.
attenuation:	X 4 (Fig. 70a) X 8 (Fig. 70b)
detector:	300 °C
chart speed:	0.25 in./minute

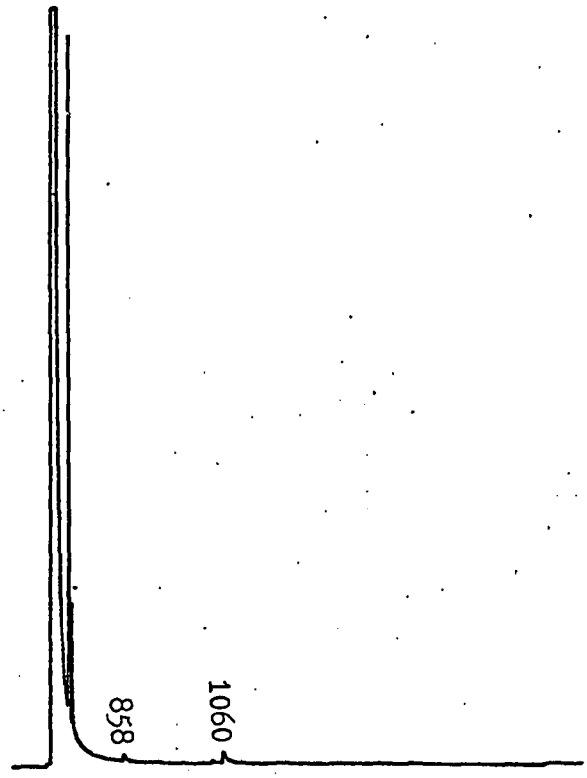


Figure 70a

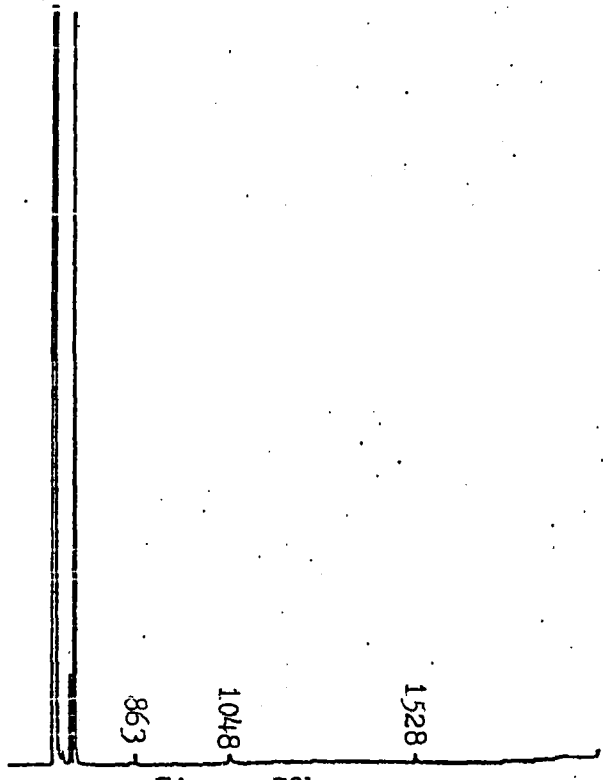


Figure 70b

Figure 71a. Chromatogram of the aldehyde fraction of 1973 Plymouth station wagon exhaust - regular gasoline

Figure 71b. Chromatogram of the aldehyde fraction of 1973 Plymouth station wagon exhaust - gasohol

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	0 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	30:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

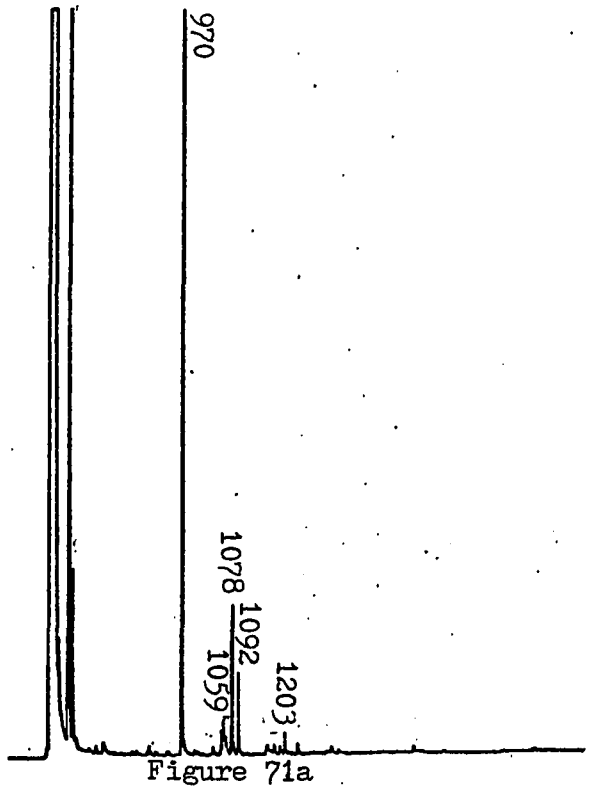


Figure 71a

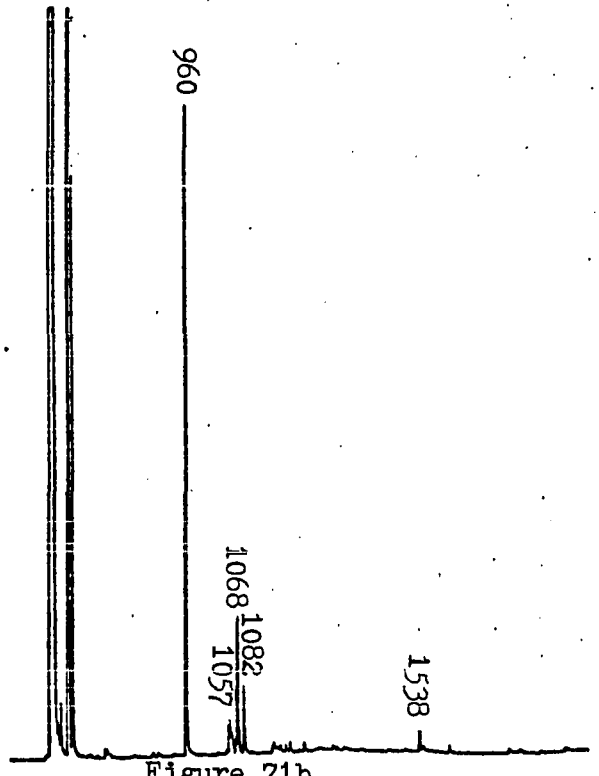


Figure 71b

Figure 72a. Chromatogram of the ketone fraction of 1973 Plymouth station wagon exhaust - regular gasoline

Figure 72b. Chromatogram of the ketone fraction of 1973 Plymouth station wagon exhaust - gasohol

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	0 minutes
detector temp.:	300 °C
injector temp.:	275:
split ratio:	30:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

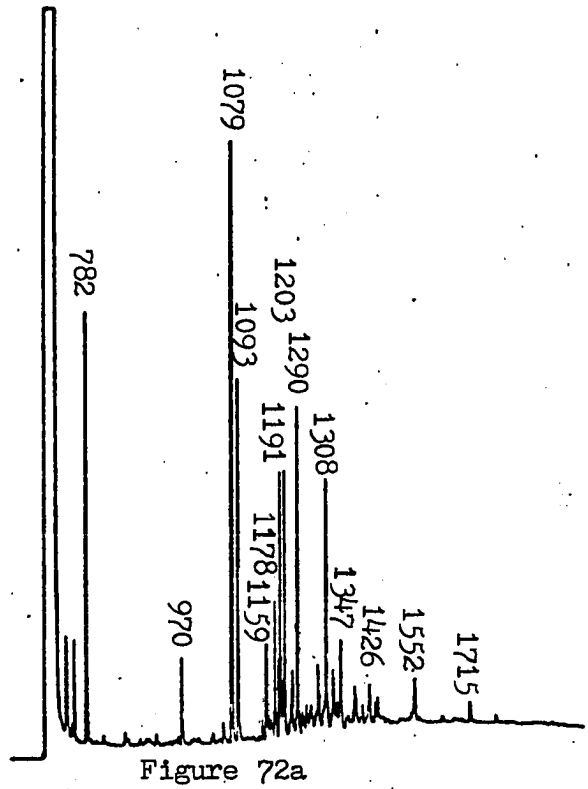


Figure 72a

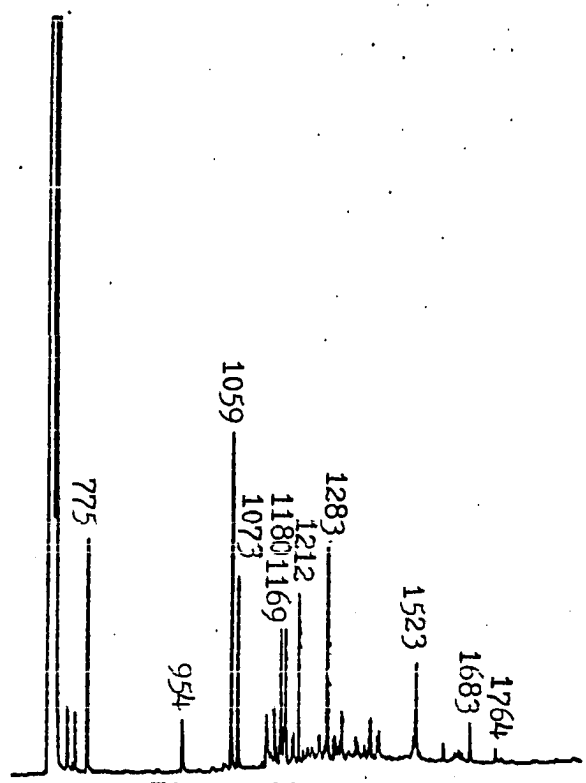


Figure 72b

Figure 73a. Chromatogram of the nonpolar fraction of 1973 Plymouth station wagon exhaust - regular gasoline

Figure 73b. Chromatogram of the nonpolar fraction of 1973 Plymouth station wagon exhaust - gasohol

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	0 minutes (Fig. 73a) 6 minutes (Fig. 73b)
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	30:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

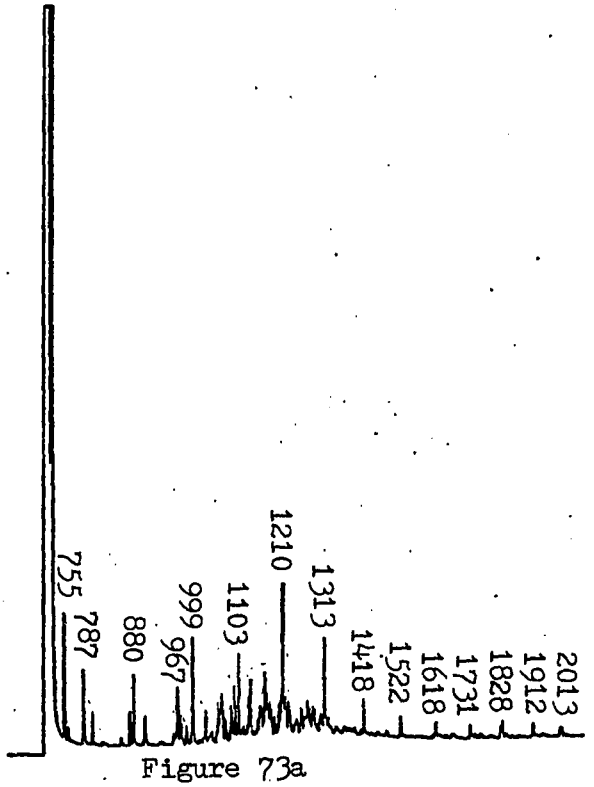


Figure 73a

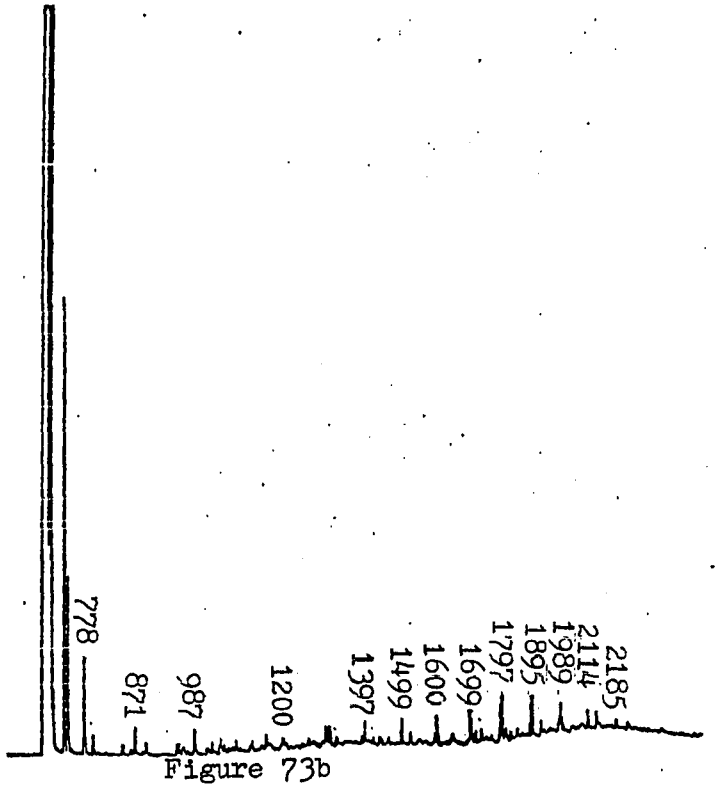


Figure 73b

the gasohol exhaust contained higher relative concentrations of higher molecular-weight aromatic compounds such as phenathrene and pyrene. Figure 74 shows the SE-54 capillary column chromatograms of the polar fractions of the two exhaust samples.

The compound identifications for the SE-54 capillary column chromatogram peaks are listed in Table 16. The regular gasoline exhaust sample was analyzed by GC/MS. The compound identifications for the peaks in the gasohol exhaust sample chromatograms were based on retention index data and the comparison of the retention indices with those of the peaks in the regular gasoline exhaust sample.

The major differences between the regular gasoline exhaust and the gasohol exhaust were seen in the nonpolar and polar fractions. It appeared that the presence of ethanol in the fuel increased the efficiency of the combustion of alkyl benzenes and of lower molecular-weight aliphatic compounds. However, The formation of higher molecular-weight PAH's was increased in the presence of ethanol.

1979 Fiat station wagon exhaust The total amount of organic material obtained from the 1979 Fiat station wagon was much lower (by at least a factor of ten) than the amounts obtained with the Mercury Capri and the Plymouth station wagon. Undoubtedly, the low concentrations of organic compounds in the exhaust of the Fiat station wagon were due to the presence of the catalytic converter. Because the concentrations of organic copounds in the exhaust were so low, the sample was not fractionated. Figures 75 and 76 show the SE-54 and SP-1000 capillary column chromatograms, respectively, of the exhaust sample. The sample

Figure 74a. Chromatogram of the polar fraction of 1973 Plymouth station wagon exhaust - regular gasoline

Figure 74b. Chromatogram of the polar fraction of 1973 Plymouth station wagon exhaust - gasohol

Gas chromatographic conditions:

amount:	2 microliters	
column:	glass capillary, 30 meter	
liquid phase:	SE-54	
mode:	temperature programmed	
initial temp.:	55 °C	
initial hold:	2 minutes	
rate:	8 degrees/minute	
final temp.:	270 °C	
final hold:	6 minutes (Fig. 74a)	11 minutes (Fig. 74b)
detector temp.:	300 °C	
injector temp.:	275 °C	
split ratio:	30:1	
He pressure	20 p.s.i.	
attenuation:	X 4	
chart speed:	0.25 in./minute	

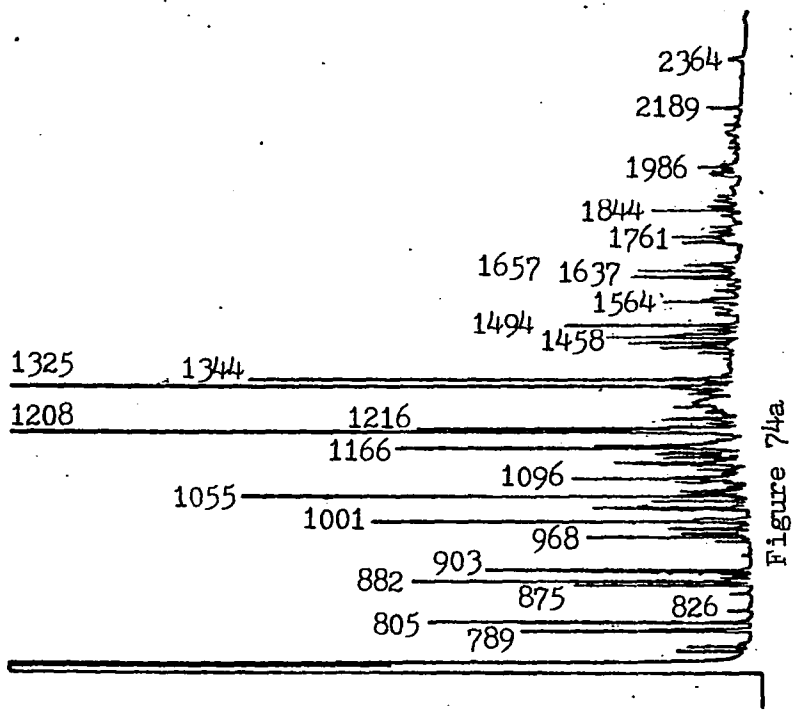


Figure 74a

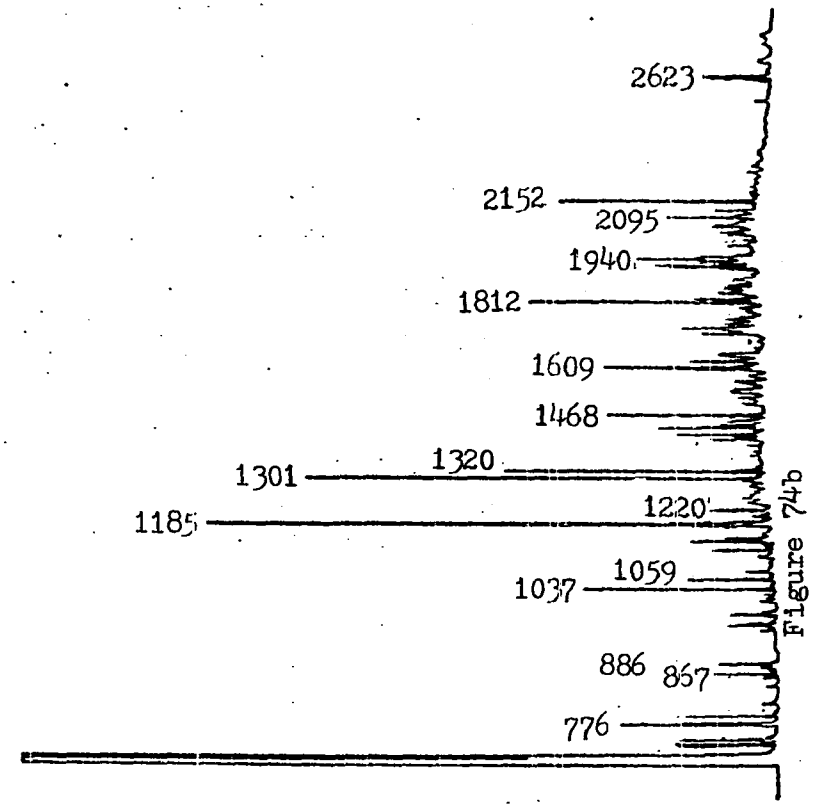


Figure 74b

Table 16. Components of 1973 Plymouth station wagon exhaust

Strong Acid Fraction (methylated)

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
800[a]	799[a]	Toluene
883[a]		m-Xylene & p-Xylene
903[a]	894[a]	o-Xylene
	927[a]	unknown
1035	1017	Phenol
1096	1084	o-Cresol
1110	1099	methylbenzoate
1124	1110	m-Cresol & p-Cresol
1163	1151	2-Ethylphenol? (& propylbenzene[a]?)
1190	1178	4-Ethylphenol?
1195	1185	Methylphenylacetate & 3-Ethylphenol?
1220	1208	Methyl(3-methylbenzoate)?
	1215	unknown
	1227	unknown
	1270	unknown
1299	1288	Methyl(2,4-dimethylbenzoate)?
1402	1387	unknown
	1395	unknown
	1426	unknown
1547[a]	1534[a]	Methyllaurate
	1582	unknown
1636[a]	1620[a]	Diethylphthalate
	1739[a]	Methylmyristate
1944[a]	1928[a]	Methylpalmitate
2061		unknown

Weak Acid Fraction

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
	863[a]	unknown
1021	1016	Phenol
1059	1054	Salicylaldehyde?
1081	1076	o-Cresol
1108	1103	m-Cresol & p-Cresol
1122	1118	2,6-Dimethylphenol
	1155	unknown
1164	1160	2-Ethylphenol
1174	1169	2,5-Dimethylphenol

[a]In blank.

Table 16. continued

Weak Acid Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
1196	1190	C_8H_8O?
1205	1196	4-Ethylphenol
1208	1201	3-Ethylphenol
1215	1208	2,3-Dimethylphenol
1230	1224	3,4-Dimethylphenol
1254	1249	2,3,6-Trimethylphenol
1268		C_3 subst. phenol?
1272	1256	C_3 subst. phenol?
1275	1261	C_3 subst. phenol?
1288	1264	C_3 subst. phenol?
1301	1286	an ethylmethyl phenol?
	1289	an ethylmethyl phenol?
1307	1294	an ethylmethyl phenol?
1315	1310	an ethylmethyl phenol?
1326	1321	unknown
1340	1329	C_3 subst. phenol?
	1344	unknown
1363	1352	unknown
1387	1377	C_3 subst. phenol?
	1392	unknown
1420	1407	C_3 subst. phenol?
	1437	unknown
	1453	unknown
	1476	unknown
	1489	unknown
	1532[a]	unknown
1584	1569	2-Naphthol
1608	1587	$C_{10}H_8O$?

Table 16. continued

Base Fraction

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
858	849	$C_8H_{18}O$? (4-Methyl-3-heptanol?)
	863[a]	unknown
971		unknown
1038		$C_6H_{11}OCl$? (a chloro cyclohexanol?)
1060	1048	Benzylalcohol?
	1528[a]	unknown

Aldehyde Fraction

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
790		unknown
805		unknown
817	810	unknown
819		unknown
868		p-Xylene & unknown[a]?
878		m-Xylene
908		$C_6H_{10}O$ (an unsaturated aldehyde?)
918	906	unknown
939		unknown
970	960	Benzaldehyde
998		C_9H_{12} (C_3 subst. benzene?)
1037[a]		$C_6H_{11}OCl$? (a chloro cyclohexanol?)
1053		unknown
1059	1050	Phenylacetaldehyde?
1066	1057	$C_7H_{10}O$? (3-Methyl-2-cyclohexenone?)
	1063	unknown
1078	1068	2-Methylbenzaldehyde & 3-Methylbenzaldehyde
1092	1082	4-Methylbenzaldehyde
1162	1150	unknown
1178	1167	2,5-Dimethylbenzaldehyde
1194	1179	2,4-Dimethylbenzaldehyde
1203	1190	Naphthalene
1236	1223	3,4-Dimethylbenzaldehyde?
1310	1296	C_9H_8O? (1-Indanone?) $C_{10}H_{10}O$?

Table 16. continued

Aldehyde Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
1321	1307	2-Methylnaphthalene
1340	1327	1-Methylnaphthalene
1545[a]	1538[a]	unknown
	1625[a]	Diethylphthalate

Ketone Fraction

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
782	775	$C_5H_8O_2$? $C_6H_{12}O$?
819		unknown
858		unknown
888		$C_6H_{12}O$?
916		C_6H_{12}?
970	954	Benzaldehyde
992		unknown
998		unknown
1008		unknown
1039[a]		unknown
1060	1044	Acetophenone?
1079	1059	2-Methylbenzaldehyde & 3-Methylbenzaldehyde
1093	1073	4-Methylbenzaldehyde
1146		2-Methylacetophenone
1150	1130	unknown
1159	1138	unknown
1175	1149	3-Methylacetophenone & 3-Ethylbenzaldehyde?
1178	1156	2,5-Dimethylbenzaldehyde
1191	1169	2,4-Dimethylbenzaldehyde
1203	1180	4-Methylacetophenone?
1220	1197	unknown
1224	1202	C_2 subst. benzaldehyde?
1236	1212	3,4-Dimethylbenzaldehyde
1248	1225	2-Indanone
1259	1236	Terephthalicdicarboxylaldehyde?
1271	1248	Isophthalicdicarboxylaldehyde?
1290	1264	C_3 subst. benzaldehyde?

Table 16. continued

Ketone Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
	1277	unknown
	1279	unknown
1308	1283	1-Indanone
1327	1305	2,4,6-Trimethylbenzaldehyde
1339	1313	unknown
1347	1322	2,4,5-Trimethylbenzaldehyde
	1343	unknown
1385	1359	unknown
1408	1382	$C_{10}H_{10}O$? (a dimethylbenzofuran?)
1426	1399	$C_{11}H_{14}$ (an ethyl indan?)
1442	1415	unknown
1449	1421	$C_{11}H_{14}$ (an ethyl indan?)
	1514	unknown
1552	1523	1-Naphthaldehyde & 2-Naphthaldehyde
1632[a]	1608[a]	Diethylphthalate
	1639	unknown
	1650	unknown
	1659	unknown
1715	1683	$C_{12}H_8O$?
1800	1764	9-Fluorenone?

Nonpolar Fraction

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
755[a]	745[a]	unknown
760[a]	751[a]	Cyclohexene
787[a]	778[a]	$C_4H_8O_2$? $C_6H_{14}O_2$? (1,1-Dimethoxy-isobutane?)
803	794	Toluene
823		unknown
863[a]	845[a]	unknown (a methoxy compound?)
868	864	Ethylbenzene
880	871	m-Xylene & p-Xylene
	888	unknown
901	892	o-Xylene
928		C_9H_{20}?

Table 16. continued

Nonpolar Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
931		C_9H_{20}?
959		C_9H_{20}? (4-Ethylheptane?)
967	956	3-Ethyltoluene & 4-Ethyltoluene?
976	966	1,3,5-Trimethylbenzene & Dimethyl-sulfide[a]
985	974	2-Ethyltoluene
999	987	1,2,4-Trimethylbenzene & n-Decane
1028	1013	1,2,3-Trimethylbenzene
	1020	unknown
1047	1026	unknown
1057		n-Butylbenzene
1062	1042	$C_{11}H_{24}$? (2,5-Dimethylnonane?)
1064	1044	1,4-Diethylbenzene
1073		$C_{11}H_{24}$?
1086		1,3-Dimethyl-4-Ethylbenzene?
1093	1073	a dimethylethyl benzene?
1103	1080	n-Hendecane
1116		1,2,4,5-Tetramethylbenzene
1126	1111	1,2,3,5-Tetramethylbenzene
1131	1117	$C_{11}H_{16}$ (C_5 subst. benzene?)
1147		unknown
1156	1139	$C_{10}H_{12}$ (a methyl indan?)
1164	1150	$C_{10}H_{12}$ (1-Methyl-2-(2-propenyl)-benzene?)
1171	1158	$C_{12}H_{26}$? $C_{13}H_{28}$?
1178		$C_{12}H_{26}$? $C_{13}H_{28}$?
1188		C_5 subst. benzene?
1210	1200	n-Dodecane
1215		C_5 subst. benzene?
1222	1211	$C_{12}H_{26}$? $C_{13}H_{28}$?
1245	1227	$C_{12}H_{26}$? $C_{13}H_{28}$?
1254	1238	C_5 subst. benzene? 1,2,4-Triethyl-benzene?
1265		$C_{13}H_{28}$?
1271	1254	$C_{11}H_{14}$ (a dimethyl indan?)

Table 16. continued

Nonpolar Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
1276		$C_{13}H_{28}$?
1285		$C_{13}H_{28}$?
1304	1288	Pentamethylbenzene?
1313	1294	n-Tridecane
	1305	unknown
1340	1317	unknown
1366		$C_{12}H_{16}$? (C_2 subst. tetrahydro-naphthalene?)
1418	1397	n-Tetradecane
	1420	unknown
	1435	unknown
1489	1462	$C_{14}H_{30}$? $C_{15}H_{32}$?
1522	1499	n-Pentadecane
	1528[a]	unknown
	1546	unknown
	1553	unknown
1614	1593	$C_{13}H_{28}O$? (an alcohol?)
1618	1600	n-Hexadecane
	1631	unknown
1678	1649	$C_{17}H_{36}$?
	1693	unknown
1731	1699	n-Heptadecane
	1705	unknown
	1716	unknown
	1732	unknown
	1746	unknown
	1763	unknown
1824[a]	1790[a]	$C_{15}H_{32}O$? (an alcohol?)
1828	1797	n-Octadecane
1912	1895	n-Nonadecane
	1922	unknown
	1935	unknown
	1961	unknown
2010[a]	1977[a]	$C_{17}H_{36}O$? (an alcohol?)
2013	1989	n-Eicosane
	2029	unknown
	2050	unknown

Table 16. continued

Nonpolar Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
	2064	unknown
	2084	unknown
	2114	n-Heneicosane
	2125	unknown
	2185	n-Docosane?
	2298	unknown

Polar Fraction

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
735[a]	744[a]	unknown
739[a]	750[a]	unknown
	752[a]	unknown
	753[a]	unknown
789[a]	776[a]	unknown (a methoxy compound?)
793[a]	780[a]	Dimethyldisulfide
805	792	Toluene
	800	unknown
826[a]	813[a]	unknown
858[a]	844[a]	unknown (a methoxy compound?)
875	861	Ethylbenzene
882	867	m-Xylene & p-Xylene
890[a]	876[a]	unknown
894[a]	879[a]	unknown
	882[a]	unknown
	886[a]	unknown
903	888	o-Xylene
932		unknown
961		Propylbenzene?
968	952	3-Ethyltoluene & 4-Ethyltoluene
976	959	1,3,5-Trimethylbenzene
979[a]	962[a]	Dimethyltrisulfide
987	970	2-Ethyltoluene
1001	984	1,2,4-Trimethylbenzene
1031	1013	1,2,3-Trimethylbenzene
1038[a]	1020[a]	$C_8H_{18}O$? (2-Ethyl-1-hexanol?)
1045	1028	Indan
1055	1037	Indene

Table 16. continued

Polar Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
1066	1049	$C_{10}H_{14}$ (1-Methyl-4-propylbenzene?)
1076	1059	$C_{10}H_{14}$ (1-Methyl-2-propylbenzene?)
1087		1,4-Dimethyl-2-ethylbenzene?
1089	1071	1,3-Dimethyl-4-ethylbenzene
1096	1076	1-Methyl-3-propylbenzene?
1106		$C_{10}H_{12}$? (2-Methylindan?)
1114		unknown
1118		$C_{10}H_{14}$ (a dimethyl ethyl benzene?)
1128	1110	1,2,4,5-Tetramethylbenzene
1133		1,2,3,5-Tetramethylbenzene
1143[a]	1124[a]	a sulfur compound
1154		$C_{10}H_{12}$ (a methyl indan?)
1166		$C_{10}H_{10}$ (3-Methylindene?)
1171	1146	$C_{10}H_{10}$ (1-Methylindene?)
1175	1153	unknown
1180		$C_{11}H_{16}$ (C_5 subst. benzene?)
1185		$C_{11}H_{16}$ (C_5 subst, benzene?)
1190	1166	unknown
1208	1185	Naphthalene
1216	1195	$C_{11}H_{16}$ (C_5 subst. benzene?) & a sulfur compound
1231	1209	$C_{11}H_{16}$ (a dimethyl cumene?)
1242[a]	1220[a]	a sulfur compound
1258		$C_{10}H_{12}$ (a methyl indan?)
1263	1242	unknown
1267		$C_{11}H_{22}$ (a methyl dihydronaphthalene?)
1273	1250	$C_{11}H_{14}$ (a dimethyl indan?)
1276	1255	$C_{11}H_{12}$ (a dimethyl indene?)
1282	1261	$C_{11}H_{14}$ (a dimethyl indan?)
	1270	unknown
1288		$C_{11}H_{12}$ (a methyl dihydronaphthalene?)

Table 16. continued

Polar Fraction - continued		
Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
1299		$C_{11}H_{16}$ (C_5 subst. benzene?)
	1284	unknown
1319	1295	C_9H_8S (a methyl benzothiophene?)
1325	1301	2-Methylnaphthalene
1336	1312	C_9H_8S (a methyl benzothiophene?)
1344	1320	1-Methylnaphthalene
1350		unknown
	1334	unknown
1374		unknown
1388	1362	unknown
1400[a]	1374[a]	a sulfur compound?
1414	1390	Biphenyl
1430	1405	1-Ethylnaphthalene &/or 2-Ethyl-naphthalene
	1410	unknown
1442	1416	1,3-Dimethylnaphthalene?
	1426	unknown
1458	1433	1,2-Dimethylnaphthalene?
1460	1435	unknown
	1435	unknown
1470	1444	$C_{12}H_{10}$?
1480	1454	$C_{12}H_{12}$? (1,4-Dimethylnaphthalene?)
1494	1468	Acenaphthylene
1525	1499	3-Phenyltoluene
1531	1504	Acenaphthene
1534		unknown
1543[a]	1519[a]	unknown
1546		$C_{13}H_{14}$ (C_3 subst. naphthalene?)
	1533	unknown
1564	1537	$C_{14}H_{14}$ (1,2-Diphenylethane?)
1567	1542	$C_{14}H_{14}$
1572	1548	$C_{13}H_{14}$
	1558	unknown
	1568	unknown
	1583	unknown
1603	1588	$C_{13}H_{14}$

Table 16. continued

Polar Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
1618		unknown
1635	1602	Fluorene
1637[a]	1609[a]	Diethylphthalate
1645		unknown
1657	1628	$C_{15}H_{16}$? (1,2-Diphenylpropane?)
1674	1645	$C_{15}H_{16}$? (1,2-Diphenylpropane?)
1680	1651	$C_{13}H_{10}$?
1690		$C_{14}H_{12}$?
	1670	unknown
1720	1692	unknown
	1708	unknown
1744	1715	$C_{16}H_{18}$? $C_{15}H_{14}O$?
	1726	unknown
1761	1730	$C_{16}H_{18}$? $C_{15}H_{14}O$?
1775	1744	$C_{16}H_{18}$? $C_{15}H_{14}O$?
1792	1761	$C_{16}H_{18}$? $C_{15}H_{14}O$?
	1768	unknown
	1786	unknown
	1787	unknown
1828		$C_{17}H_{20}$? $C_{16}H_{16}O$?
1844	1812	Phenanthrene
1857	1823	$C_{17}H_{20}$? $C_{16}H_{16}O$?
1869	1841	$C_{17}H_{20}$? $C_{16}H_{16}O$?
1881	1846	$C_{17}H_{20}$? $C_{16}H_{16}O$?
	1857	unknown
1905	1873	unknown
	1886	unknown
	1907	unknown
1959	1927	$C_{18}H_{22}$?
1963	1932	$C_{15}H_{12}$ (a methyl phenanthrene?)
1969		$C_{17}H_{16}$? $C_{15}H_{12}$?
	1940	unknown
1986	1954	a methyl phenanthrene?
	1957	unknown

Table 16. continued

Polar Fraction - continued

Retention Index (Regular Gasoline)	Retention Index (Gasohol)	Compound
2005		$C_{18}H_{22}$?
2035	1997	unknown
2044		unknown
	2018	unknown
2068	2033	unknown
2082	2042	unknown
	2061	unknown
2101	2068	unknown
2107	2074	unknown
	2081	unknown
2130	2095	Fluoranthene
	2106	unknown
2158	2121	unknown
	2143	unknown
2189	2152	Pyrene
	2176	unknown
	2188	unknown
	2209	unknown
	2231	unknown
	2260	unknown
	2280	unknown
	2296	unknown
2364	2327	unknown
	2335	unknown
	2525	unknown
	2623	unknown
	2653	unknown
	2685	unknown
	2757	unknown
	2790	unknown

was analyzed by GC/MS on both SE-54 and CP Wax-51 (which gives separations similar to those obtained on SP-1000). The compound identifications for the chromatogram peaks are listed in Table 17.

The major components of the Fiat exhaust sample were phenol, the cresols, benzaldehyde, methyl benzaldehydes, and naphthalene. Some

Figure 75. Chromatogram of 1979 Fiat station wagon exhaust (SE-54)

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 2
detector:	FID
chart speed:	0.25 in./minute

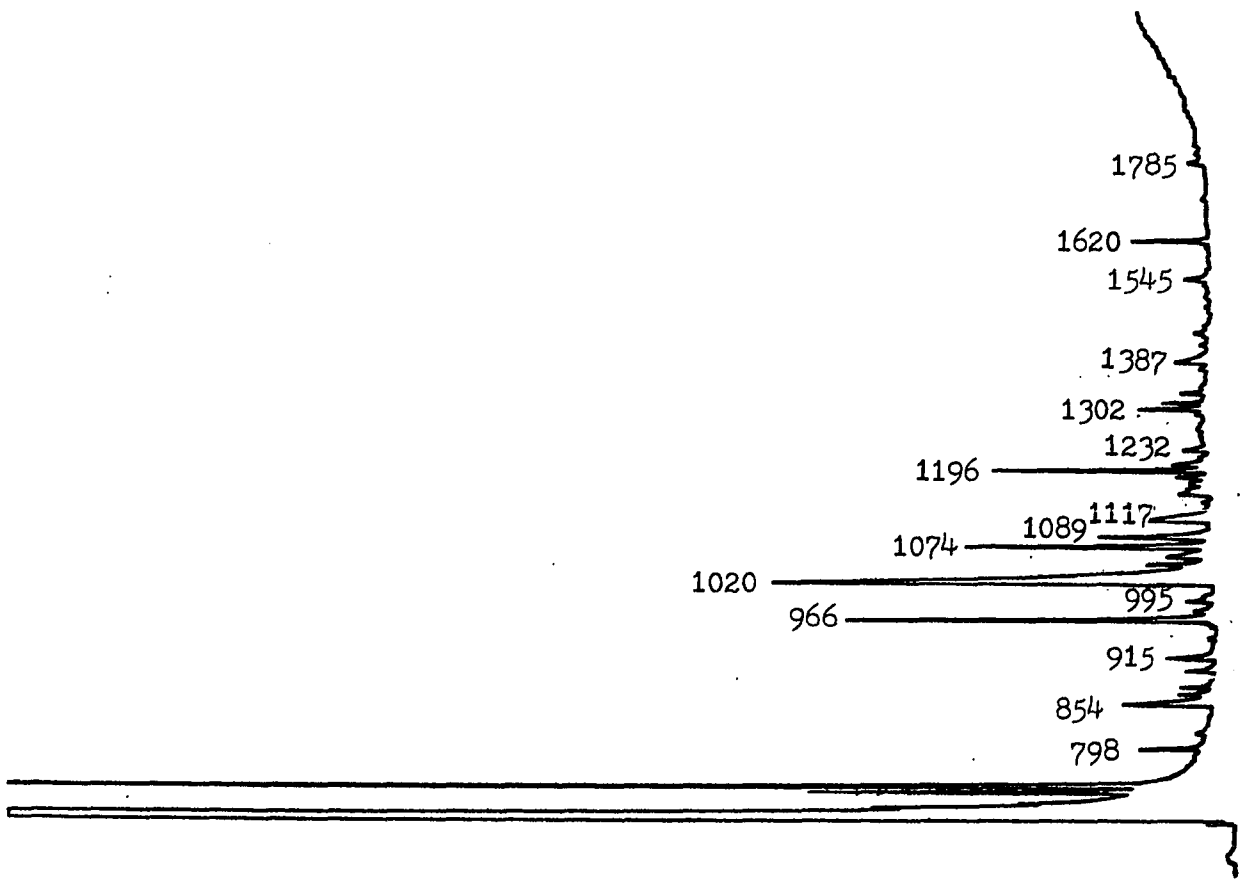

1785
1620
1545
1387
1302
1232
1196
1117
1089
1074
1020
995
966
915
854
798

Figure 76. Chromatogram of 1979 Fiat station wagon exhaust (SP-1000)

Gas chromatographic conditions:

amount:	2 microliters (soln. concentrated to 0.5 ml)
column:	glass capillary, 30 meter
liquid phase:	SP-1000
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	6 degrees/minute
final temp.:	220 °C
final hold:	12 minutes
detector temp.:	300 °C
injector temp.:	250 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

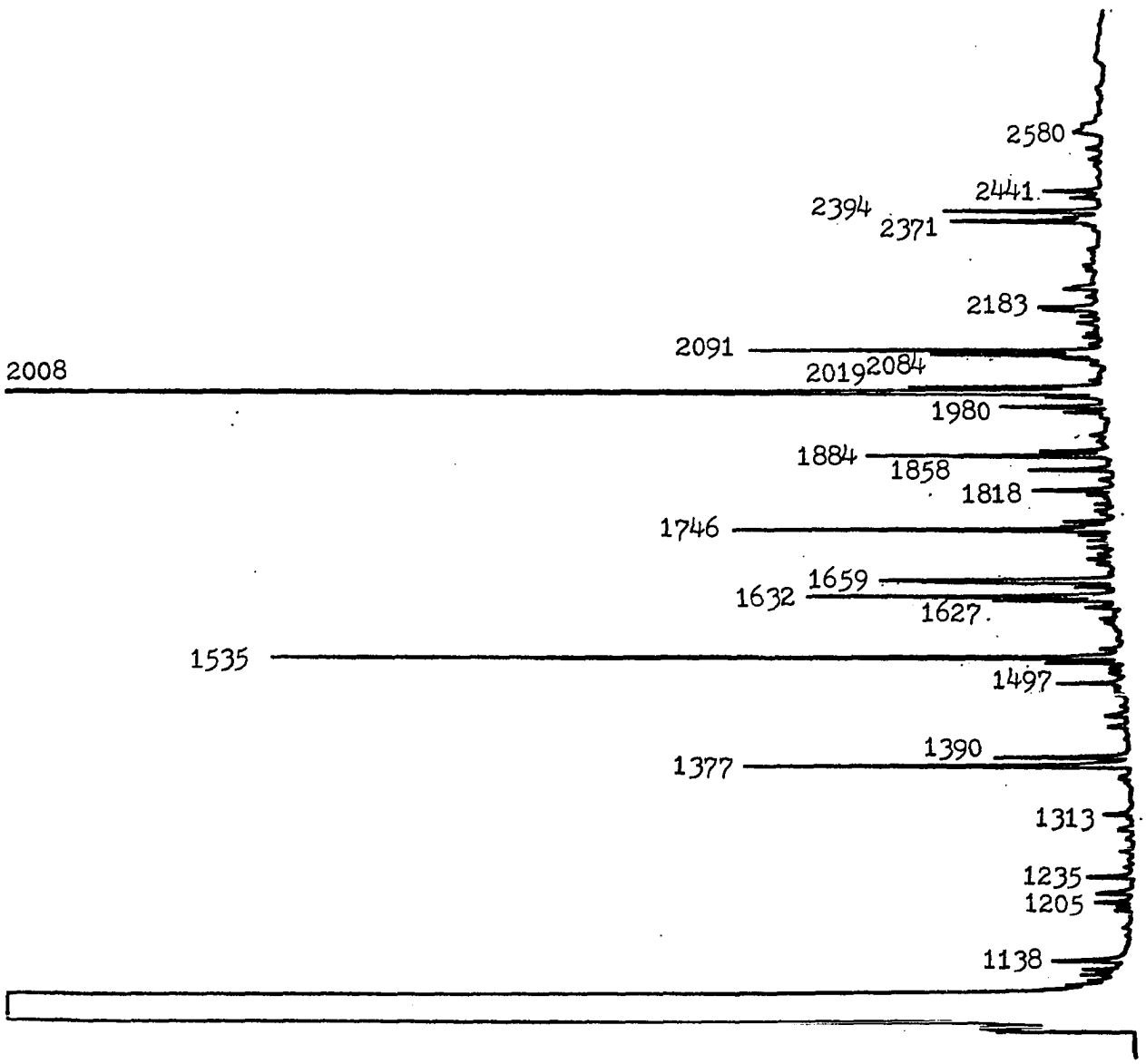

2580
2441
2394
2371
2183
2091
2008
2019
2084
1980
1884
1858
1818
1746
1659
1632
1627
1535
1497
1390
1377
1313
1235
1205
1138

Table 17. Components of 1979 Fiat station wagon exhaust[a]

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
798	Toluene	1124	unknown
818	unknown	1129	unknown
854	2-Cyclopentenone	1138	Toluene
866	p-Xylene	1167	unknown
876	m-Xylene	1175	unknown
898	o-Xylene	1195	p-Xylene
915	2-Methyl-2-cyclo-pentenone?	1200	unknown
943	$C_{10}H_{14}$?	1205	m-Xylene
966	Benzaldehyde	1215	unknown
981	Benzonitrile	1229	Cumene?
995	Benzylalcohol	1235	o-Xylene
1002	unknown	1248	unknown
1020	Phenol	1256	unknown
1048	Indene	1267	3-Ethyltoluene & 4-Ethyltoulene?
1060	o-Cresol	1294	2-Ethyltoluene?
1074	Acetophenone & 2-Methylbenzaldehyde & 3-Methylbenzaldehyde?	1309	unknown
		1313	1,2,4-Trimethylbenzene
		1356	a methyl cyclohexene?
1089	4-Methylbenzaldehyde	1362	1,2,3-Trimethylbenzene
1117	m-Cresol & p-Cresol	1377	2-Cyclopentenone
1146	4-Methylbenzylalcohol?	1390	2-Methyl-2-cyclopentenone
1159	3-Methylbenzylalcohol &/or 2-Ethylphenol	1416	unknown
		1434	C_7H_{10}? C_6H_6O?
1167	2,4-Dimethylphenol?	1443	1,2,4,5-Tetramethylbenzene
1178	2,5-Dimethylphenol?	1450	1,2,3,5-Tetramethylbenzene
1187	4-Ethylphenol?	1464	unknown
1196	Naphthalene	1482	unknown
1208	2,4,6-Trimethylphenol?	1488	unknown
1221	3,4-Dimethylphenol?	1494	2-Acetylfuran?
1232	unknown	1497	Indene
1302	2-Methylnaphthalene	1513	1-Methylindan?
1313	2,4,6-Trimethylbenzaldehyde?	1520	unknown
		1528	C_7H_{12}? C_6H_8O?
1332	1-Methylnaphthalene	1535	Benzaldehyde
1376	unknown	1550	C_8H_{14}?
1387	unknown	1566	unknown
1421	unknown	1584	unknown
1492	unknown	1592	C_7H_8O?
1513	unknown	1598	unknown
1545	1-Naphthaldehyde & 2-Naphthaldehyde	1608	unknown

[a]Sample not fractionated.

Table 17. continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1620	Diethylphthalate	1615	Benzonitrile
1785	Dibutylphthalate?	1627	2-Methylbenzaldehyde
		1632	3-Methylbenzaldehyde
		1648	$NCCH_2CH_2CH_2CHO$??
		1656	4-Methylbenzaldehyde
		1659	Acetophenone
		1673	unknown
		1688	unknown
		1695	2-Methylacetophenone
		1705	2-Methylbenzonitrile?
		1716	2- or 3- Ethylbenzaldehyde?
		1728	2,5-Dimethylbenzaldehyde
		1738	4-Ethylbenzaldehyde?
		1746	Naphthalene
		1753	2,4-Dimethylbenzaldehyde
		1762	3-Methylacetophenone
		1776	unknown
		1782	4-Methylacetophenone
		1794	a dimethylbenzaldehyde?
		1806	unknown
		1811	unknown
		1818	3,4-Dimethylbenzaldehyde?
		1840	$C_{11}H_{16}$? (C_5 subst. benzene?)
		1858	2-Methylnaphthalene
		1876	unknown
		1884	Benzylalcohol
		1893	1-Methylnaphthalene
		1906	unknown
		1911	unknown
		1914	unknown
		1918	2,6-Dimethylphenol
		1925	unknown
		1962	unknown
		1970	4-Methylbenzylalcohol
		1980	3-Methylbenzylalcohol
		1999	2-Methylbenzylalcohol
		2008	Phenol
		2019	o-Cresol
		2034	an ethyl indan?
		2041	unknown
		2048	unknown
		2064	4-Ethylbenzylalcohol
		2075	2,4-Dimethylbenzylalcohol?

Table 17. continued

R.I.$_{SP\ 1000}$	Compound
2084	p-Cresol
2091	m-Cresol
2105	unknown
2120	3,4- or 3,5- Dimethyl-benzylalcohol?
2128	unknown
2137	unknown
2151	$C_{11}H_{14}$? $C_{10}H_{10}O$?
2164	2-Ethylphenol?
2178	4-Ethylphenol?
2183	3,5-Dimethylphenol?
2206	unknown
2223	3,4-Dimethylphenol
2228	unknown
2241	unknown
2264	3-Phenyl-2-butanone?
2273	unknown
2310	unknown
2355	unknown
2365	unknown
2371	3-Coumaranone?
2381	C_8H_8O?
2394	Diethylphthalate
2416	unknown
2427	1-Naphthaldehyde
2441	2-Naphthaldehyde
2504	a methyl 2-coumaranone?
2517	unknown
2542	unknown
2580	unknown
2600	unknown

of the compounds found in the Fiat exhaust which had not been found in other exhaust samples were 2-cyclopentenone, benzonitrile, and some substituted benzyl alcohols. Most of those compounds would have been lost during fractionation.

In general, the composition of the Fiat exhaust was not much

different from the composition of the other gasoline exhaust samples. While the catalytic converter did reduce the concentrations of organic compounds in the exhaust of the Fiat station wagon, it did not appear to remove any particular class of compounds in preference to any other class.

1979 Volkswagen Diesel Rabbit exhaust The composition of the Volkswagen Diesel Rabbit exhaust differed significantly from the composition of gasoline engine exhaust. The SE-54 capillary column chromatogram of the Volkswagen Diesel Rabbit exhaust is shown in Figure 77. Most of the compounds in the exhaust had higher boiling points than those found in gasoline engine exhaust. Phenol, which was the major component in the gasoline engine exhaust samples, was only a minor component of the diesel engine exhaust. The major compounds were n-alkanes in the carbon number range of C_{12} to C_{23}.

Figure 78 shows the strong acid fraction of the Diesel Rabbit exhaust. The only significant acidic compounds in the strong acid fraction were phenol, m-cresol, and p-cresol. Small amounts of residual aliphatic compounds were also found in the fraction.

The weak acid fraction contained phenol, o-cresol, m-cresol, p-cresol, some C_2-substituted phenols, and some residual aliphatic hydrocarbons. The SE-54 capillary column chromatogram of the weak acid fraction of the Diesel Rabbit exhaust is shown in Figure 79.

No significant amounts of basic materials were found in the Diesel Rabbit exhaust. Figure 80 shows the SE-54 capillary column chromatogram of the base fraction of the exhaust. Most of the peaks in the

Figure 77. Chromatogram of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	6 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 16
detector:	FID
chart speed:	0.25 in./minute

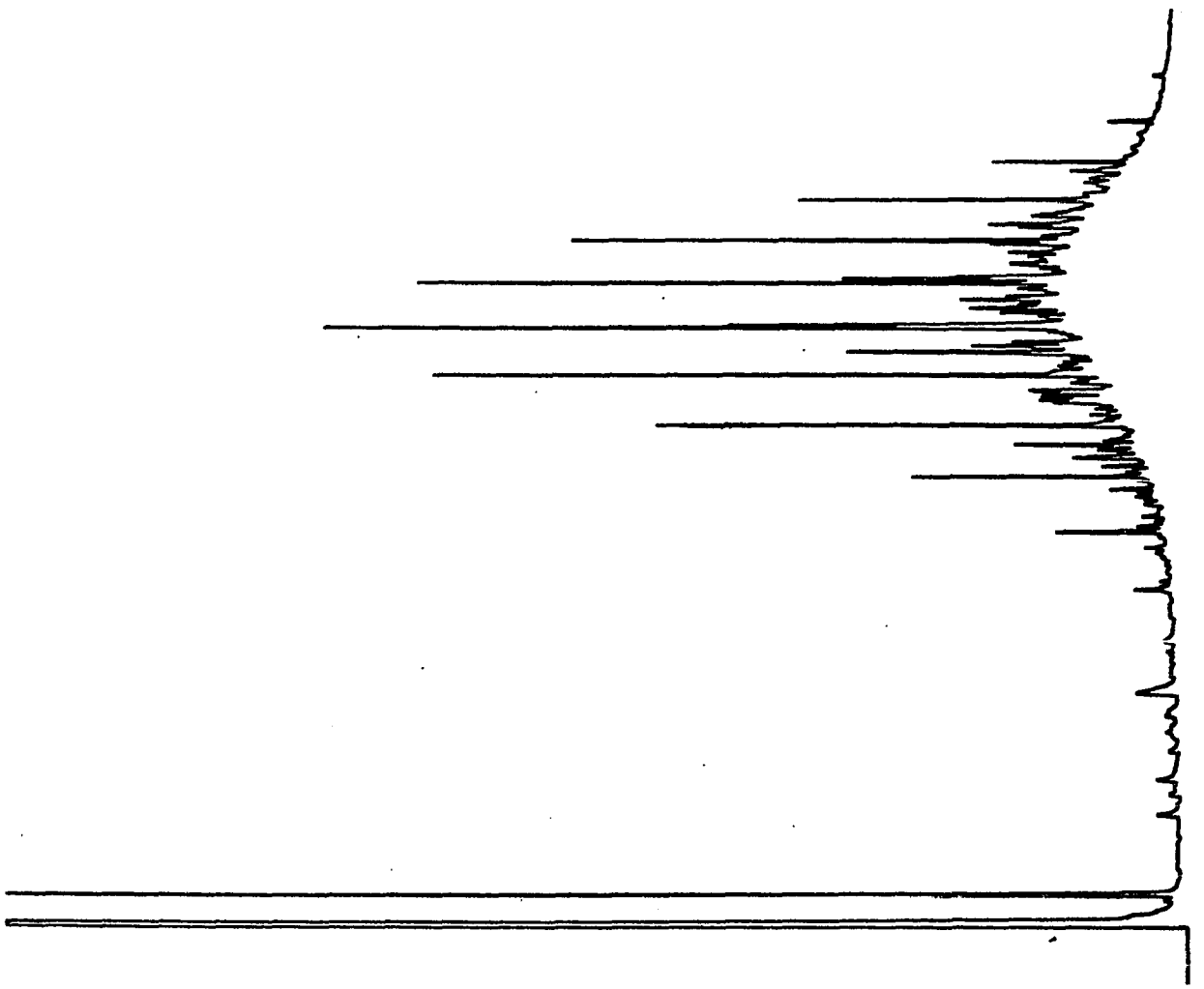


Figure 78. Chromatogram of the strong acid fraction (not methylated) of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

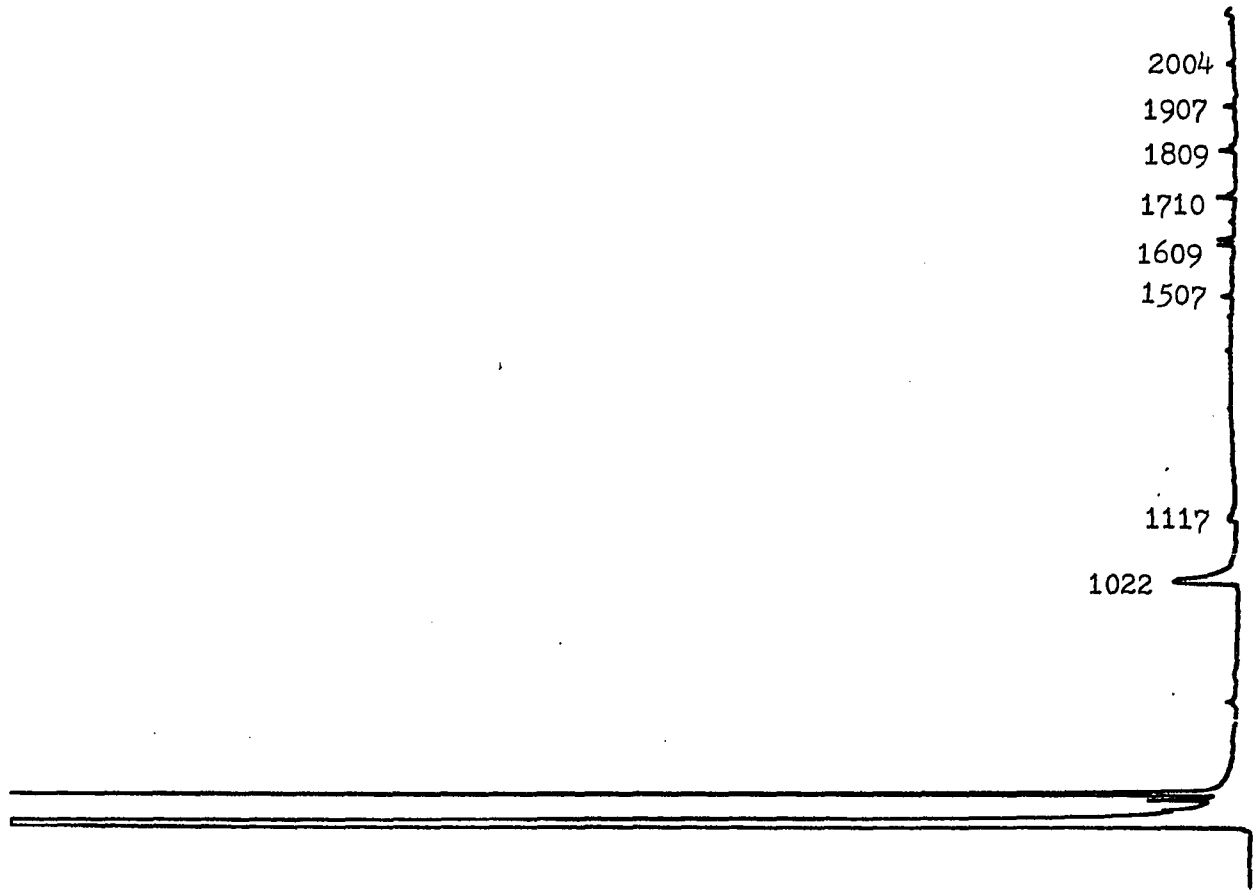

2004
1907
1809
1710
1609
1507
1117
1022

Figure 79. Chromatogram of the weak acid fraction of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 2
chart speed:	0.25 in./minute

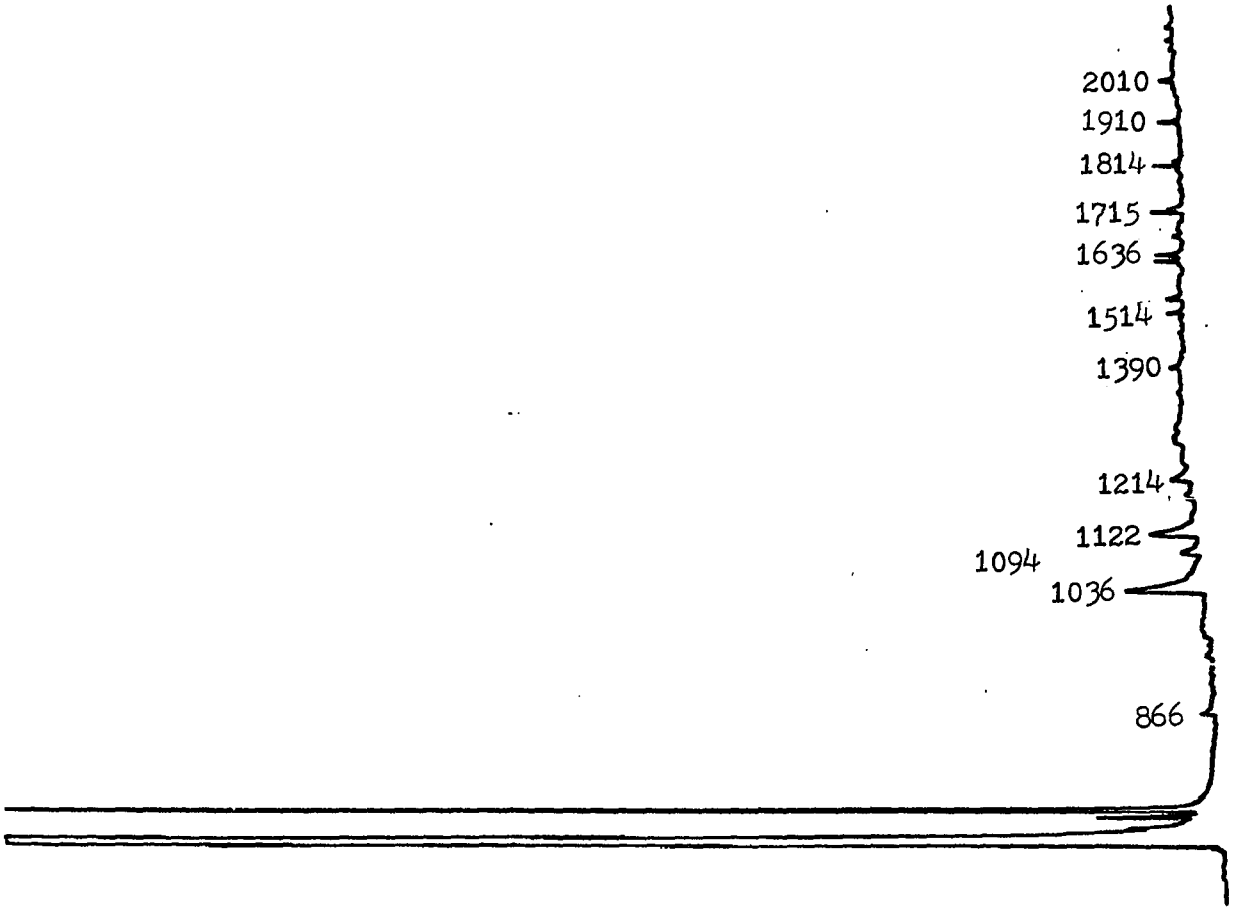
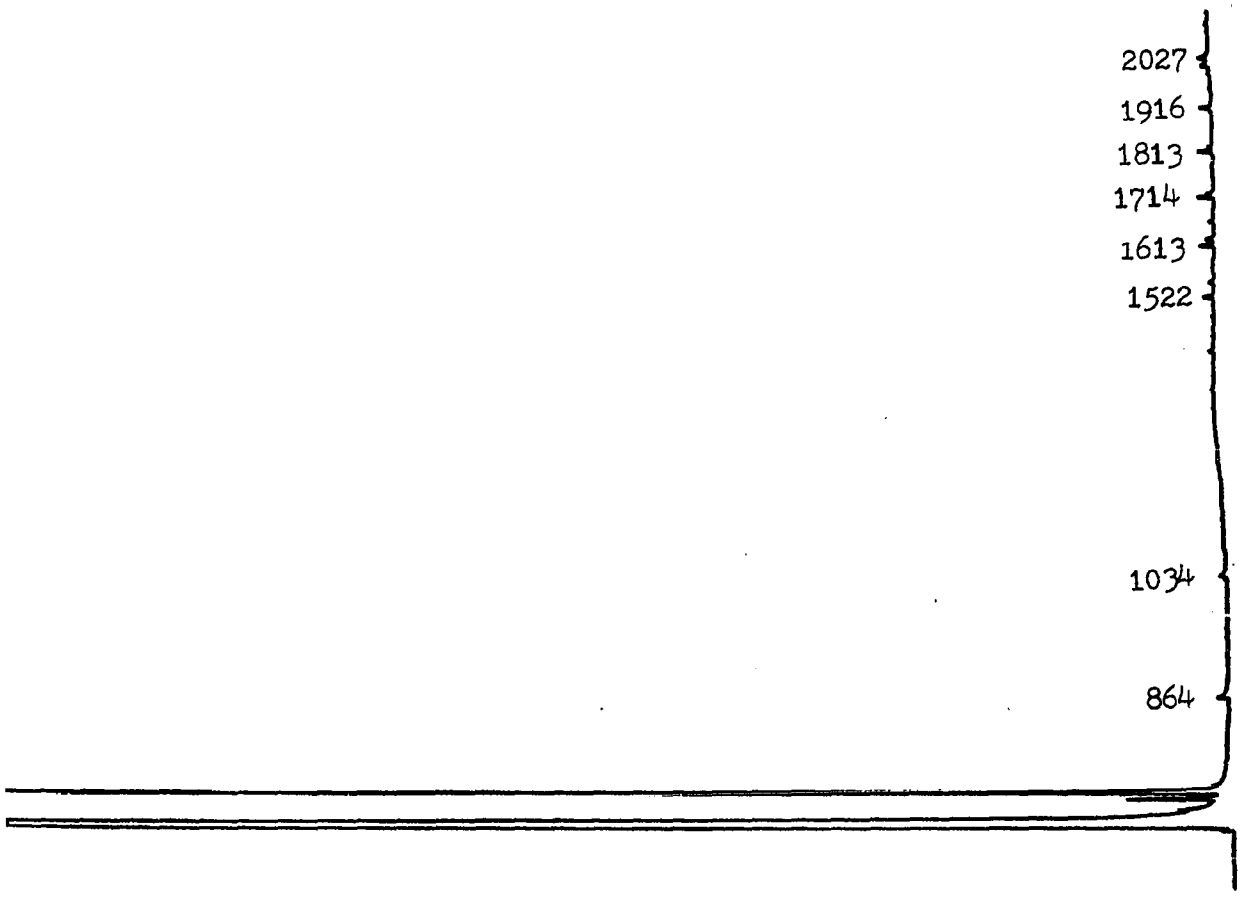

2010
1910
1814
1715
1636
1514
1390
1214
1122
1094
1036
866

Figure 80. Chromatogram of the base fraction of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	1 minute
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute


2027
1916
1813
1714
1613
1522
1034
864

chromatogram correspond to residual aliphatic hydrocarbons.

The aldehyde fraction of the Diesel Rabbit exhaust contained residual aliphatic hydrocarbons and a small amount of benzaldehyde. The SE-54 capillary column chromatogram of the aldehyde fraction is shown in Figure 81. The ketone fraction of the Diesel Rabbit exhaust contained small amounts of 1- and 2-naphthaldehyde, methyl naphthaldehydes, C_2-substituted naphthaldehydes, and 9-fluorenone. The SE-54 capillary column chromatogram of the ketone fraction is shown in Figure 82.

The largest amounts of compounds were found in the nonpolar fraction of the exhaust sample. The SE-54 capillary column chromatogram of the nonpolar fraction is shown in Figure 83. The large, evenly-spaced peaks correspond to n-alkanes. Almost all of the compounds in the nonpolar fraction contained between 12 and 23 carbons. So many compounds were present in the nonpolar fraction that they were not completely resolved by the capillary column. As a result, the GC/MS analysis was difficult.

A large number of compounds were also present in the polar fraction of the exhaust sample. Most of the polar fraction components were naphthalenes or phenanthrenes. The SE-54 capillary column of the polar fraction of the Diesel Rabbit exhaust is shown in Figure 84.

The compound identifications of the SE-54 and SP-1000 capillary column chromatograms are listed in Table 18. The identifications of the peaks in the strong acid, weak acid, and base fractions were based only on retention index data. The identifications for the SE-54 column chromatograms of the aldehyde, ketone, nonpolar, and polar

Figure 81. Chromatogram of the aldehyde fraction of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	6 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
detector:	FID
chart speed:	0.25 in./minute

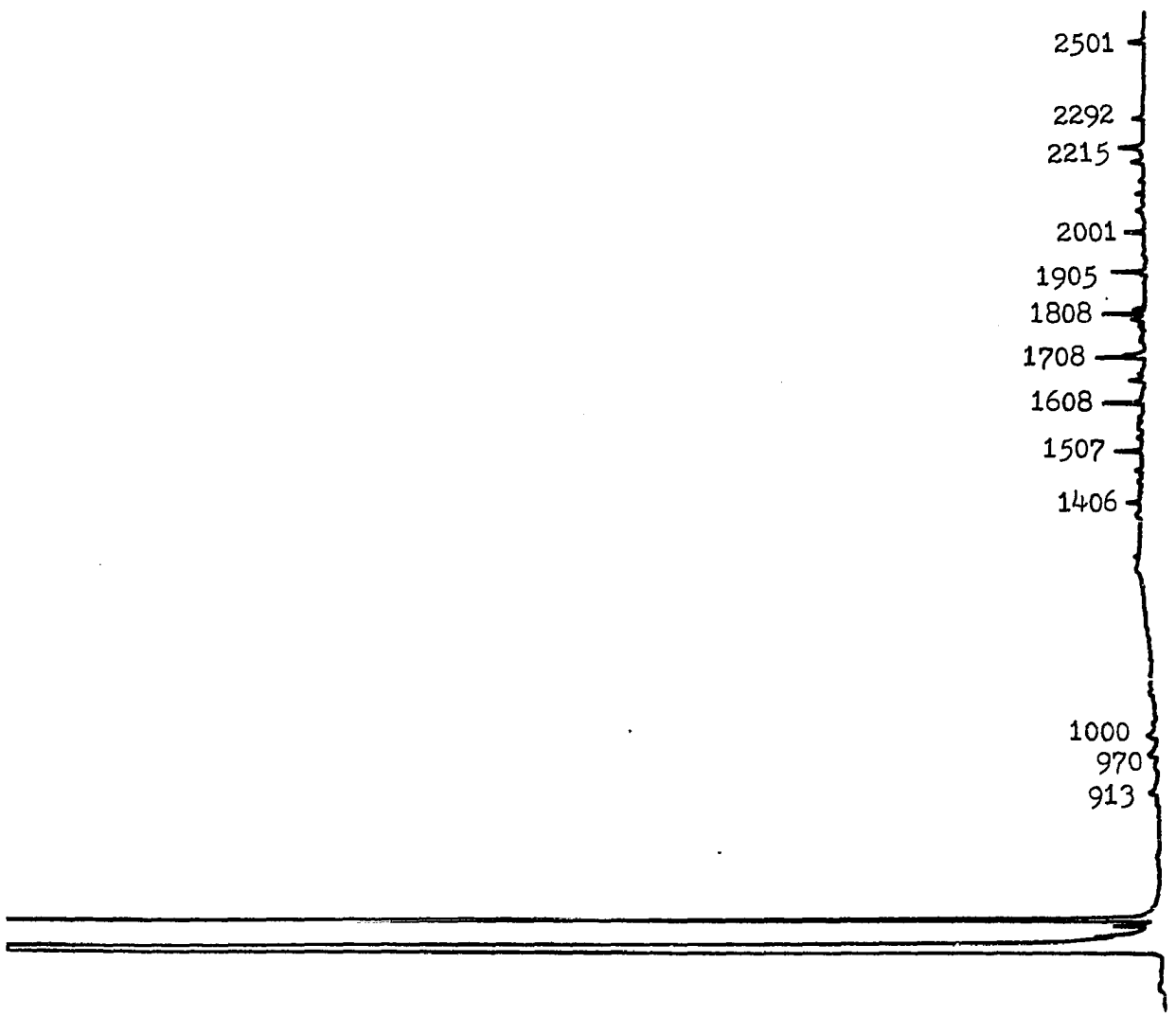

2501
2292
2215
2001
1905
1808
1708
1608
1507
1406
1000
970
913

Figure 82. Chromatogram of the ketone fraction of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	5 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
chart speed:	0.25 in./minute

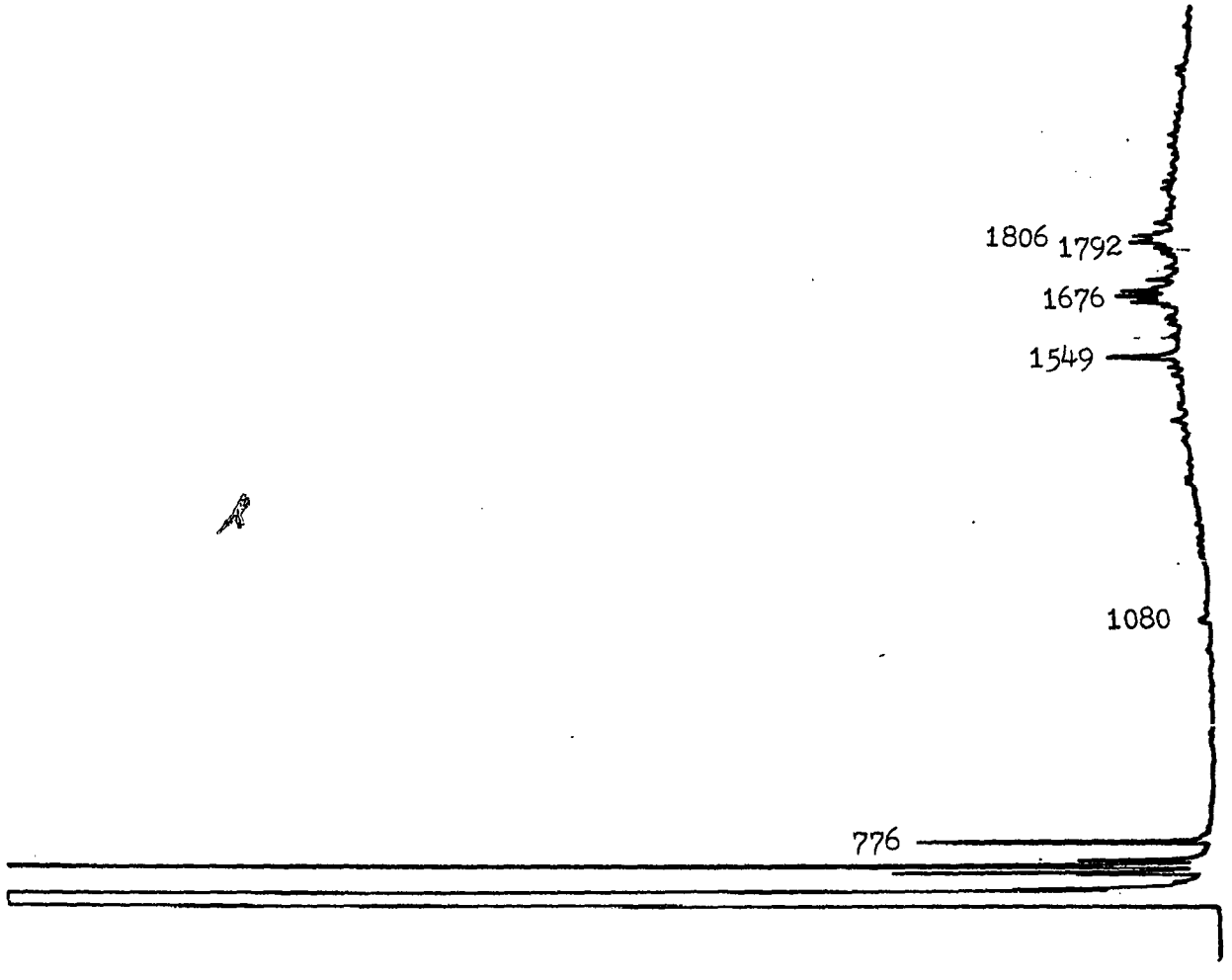

1806
1792
1676
1549
1080
776

Figure 83. Chromatogram of the nonpolar fraction of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	11 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 8
chart speed:	0.25 in./minute

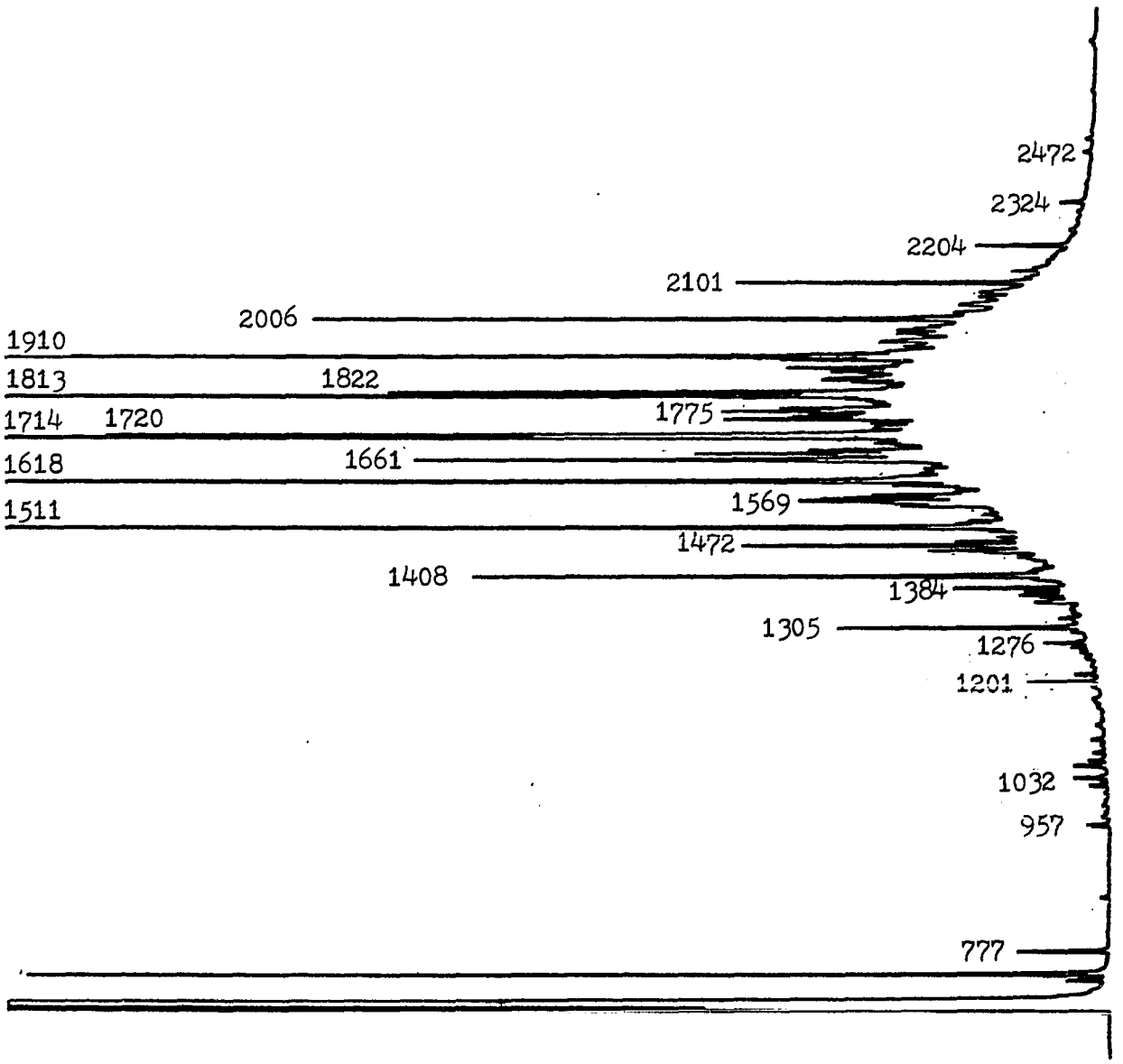

2472
2324
2204
2101
2006
1910
1813
1822
1714
1720
1775
1618
1661
1511
1569
1472
1408
1384
1305
1276
1201
1032
957
777

Figure 84. Chromatogram of the polar fraction of 1979 Volkswagen Diesel Rabbit exhaust

Gas chromatographic conditions:

amount:	2 microliters
column:	glass capillary, 30 meter
liquid phase:	SE-54
mode:	temperature programmed
initial temp.:	55 °C
initial hold:	2 minutes
rate:	8 degrees/minute
final temp.:	270 °C
final hold:	11 minutes
detector temp.:	300 °C
injector temp.:	275 °C
split ratio:	40:1
He pressure:	20 p.s.i.
attenuation:	X 4
chart speed:	0.25 in./minute

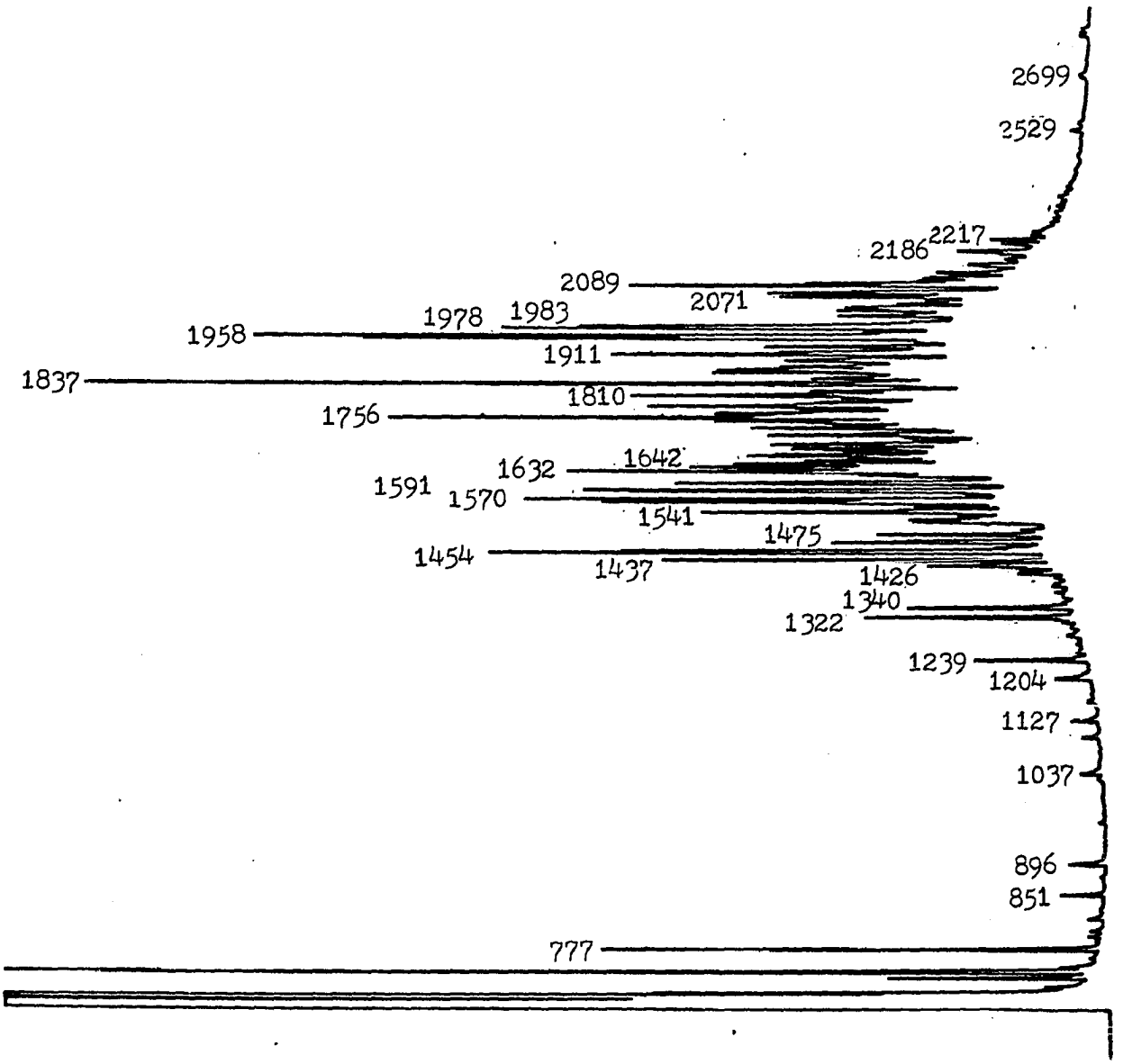

2699
2529
2217
2186
2089
2071
1983
1978
1958
1911
1837
1810
1756
1642
1632
1591
1570
1541
1475
1454
1437
1426
1340
1322
1239
1204
1127
1037
896
851
777

Table 18. Components of 1979 Volkswagen Diesel Rabbit exhaust

Strong Acid Fraction (not methylated)

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
858[a]	unknown	1487	unknown
1022	Phenol	1510	n-Pentadecane
1117	m-Cresol & p-Cresol	1607	n-Hexadecane
1405	n-Tetradecane	1649	unknown
1507	n-Pentadecane	1661	unknown
1609	n-Hexadecane	1672	unknown
1621[a]	Diethylphthalate	1687	unknown
1660	unknown	1705	n-Heptadecane
1710	n-Heptadecane	1754	unknown
1809	n-Octadecane	1776	unknown
1907	n-Nonadecane	1805	n-Octadecane
2004	n-Eicosane	1863	unknown
		1905	n-Nonadecane
		1927	unknown
		2006	Phenol & o-Cresol & n-Eicosane
		2074	2,5-Dimethylphenol?
		2086	p-Cresol
		2091	m-Cresol
		2109	n-Heneicosane
		2181	unknown
		2232	unknown
		2290	unknown
		2381	unknown
		2396[a]	Diethylphthalate

Strong Acid Fraction (methylated)

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1037	unknown	1321	unknown
1082	Phenol	1384[a]	unknown
1134	m-Cresol & p-Cresol	1410	unknown
1239	Methyl(3-methylbenzoate)?	1434	unknown
		1504	n-Pentadecane
1343	unknown	1530[a]	unknown
1447	unknown	1541	unknown
1518	n-Pentadecane	1602[a]	Methyldecanoate
1543[a]	Methyllaurate	1611	n-Hexadecane
1619	n-Hexadecane	1635	unknown
1631[a]	Diethylphthalate	1658[a]	unknown

[a]In blank.

Table 18. continued

Strong Acid Fraction (methylated) - continued			
R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1720	n-Heptadecane	1669	unknown
1748[a]	Methylmyristate	1683	unknown
1820	n-Octadecane	1700	n-Heptadecane
1916	n-Nonadecane	1735	Methyl(3-methylbenzoate)?
1943[a]	Methylpalmitate	1765	Methylphenylacetate?
1999	unknown	1773	unknown
2012	n-Eicosane	1788	unknown
2135[a]	Methylstearate	1801	n-Octadecane
2294	unknown	1807[a]	Methyllaurate
2306[a]	unknown	1861	unknown
		1868	unknown
		1901	n-Nonadecane
		1930[a]	unknown
		1942[a]	unknown
		1958[a]	unknown
		1970	unknown
		2004	Phenol & o-Cresol & n-Eicosane
		2015[a]	Methylmyristate
		2074	2,5-Dimethylphenol?
		2082	p-Cresol
		2089	m-Cresol
		2121	unknown
		2131	2,3-Dimethylphenol?
		2154	unknown
		2183	unknown
		2204	unknown
		2225[a]	Methylpalmitate
		2249[a]	unknown
		2271	unknown
		2284	unknown
		2359	unknown
		2379	unknown
		2395[a]	Diethylphthalate
		2481[a]	Methylstearate
		2529	unknown
		2697[a]	unknown

Table 18. continued

Weak Acid Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
866[a]	unknown	1220	unknown
1036	Phenol	1382	unknown
1094	o-Cresol	1453	unknown
1122	m-Cresol & p-Cresol	1514	n-Pentadecane
1187	2,5-Dimethylphenol?	1573[a]	unknown
1214	3-Ethylphenol & 4-Ethylphenol	1603	n-Hexadecane
		1658[a]	unknown
1280	unknown	1669	unknown
1287	unknown	1683	Salicylaldehyde
1390	unknown	1702	n-Heptadecane
1514	n-Pentadecane	1800	n-Octadecane
1547	unknown	1901	n-Nonadecane
1625[a]	Diethylphthalate	2002	Phenol
1715	n-Heptadecane	2038	2,3,6-Trimethylphenol?
1814	n-Octadecane	2078	p-Cresol
1910	n-Nonadecane	2083	m-Cresol
2010	n-Eicosane	2103	n-Heneicosane
		2122	unknown
		2171	3-Ethylphenol &/or 4-Ethylphenol?
		2178	unknown
		2200	n-Docosane
		2216	3,4-Dimethylphenol?
		2224	unknown
		2372[a]	Diethylphthalate
		2388	unknown

Base Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
864[a]	unknown	1381	unknown
1034	unknown		
1414	n-Tetradecane		
1522	n-Pentadecane		
1613	n-Hexadecane		
1643	unknown		
1714	n-Heptadecane		
1813	n-Octadecane		
1916	n-Nonadecane		
2008	n-Eicosane		
2027	unknown		

Table 18. continued

Aldehyde Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
913	unknown	1326	unknown
970	Benzaldehyde?	1385[a]	unknown
1000	unknown	1392	unknown
1406	n-Tetradecane	1417	n-Tetradecane
1470	$C_{15}H_{32}$?	1451	unknown
1507	n-Pentadecane	1464	unknown
1608	n-Hexadecane	1488	unknown
1658	$C_{16}H_{34}$?	1510	n-Pentadecane
1708	n-Heptadecane	1519	unknown
1798	unknown	1539	Benzaldehyde?
1808	n-Octadecane	1606	n-Hexadecane
1905	n-Nonadecane	1627	unknown
2001	n-Eicosane	1672	unknown
2058	unknown	1705	n-Heptadecane
2101	n-Heneicosane	1777	unknown
2131	unknown	1804	n-Octadecane
2178	unknown	1857	unknown
2215	n-Docosane	1888	unknown
2292	unknown	1903	n-Nonadecane
2501	unknown	1929	unknown
		2004	n-Eicosane
		2105	n-Heneicosane
		2114	unknown
		2137	unknown
		2225	n-Docosane?
		2237[a]	unknown
		2393	unknown

Ketone Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
740	Benzene?	1382	unknown
747[a]	Cyclohexene	1416	unknown
754[a]	unknown	1514	unknown
776[a]	$C_6H_{12}O$? (2-hexanone?)	1537	Benzaldehyde?
1080	4-Methylbenzaldehyde?	1608	unknown
		1617	unknown

Table 18. continued

Ketone Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1549	1-Naphthaldehyde & 2-Naphthaldehyde	1634	unknown
1584	unknown	1662	4-Methylbenzaldehyde?
1617	n-Hexadecane?	1698	unknown
1628	1-Acetonaphthone?	1707	unknown
1635[a]	Diethylphthalate	1721	unknown
1654	a methyl naphthaldehyde?	1764	unknown
1664	a methyl naphthaldehyde?	1785	unknown
1670	a methyl naphthaldehyde?	1821	unknown
1676	a methyl naphthaldehyde?	1826	unknown
1686	a methyl naphthaldehyde?	1842	unknown
1696	$C_{12}H_8O$?	1891	unknown
1711	n-Heptadecane?	1928	unknown
1739	unknown	1934	unknown
1762	an ethyl naphthaldehyde?	1963	unknown
1772	9-Fluorenone	2008	n-Eicosane?
1782	a dimethyl naphthaldehyde?	2028	unknown
1792	unknown	2041	unknown
1806	n-Octadecane?	2168	unknown
1817	a dimethyl naphthaldehyde?	2229	unknown
1834	unknown	2398[a]	Diethylphthalate
1854	unknown	2429	1-Naphthaldehyde
1916	n-Nonadecane?	2441	2-Naphthaldehyde
1929	unknown	2564	unknown
2013	n-Eicosane?	2589	unknown
2040	unknown	2598	unknown
2193	unknown	2626	unknown
2204	unknown	2652	unknown
		2687	1-Acetonaphthone?
		2700	unknown
		2779	unknown
		2820	unknown
		2861	unknown
		2912	unknown
		3197	unknown
		3299	unknown

Table 18. continued

Nonpolar Fraction

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
748[a]	Cyclohexene	1221	unknown
777[a]	1,1-Dimethoxyisobutane? $CH_2=C(OCH_3)_2$??	1245	n-Dodecane
		1285	unknown
850	$C_4H_{10}O_3$? (a methoxy compound?)	1291	unknown
		1300	unknown
		1316	unknown
957	2,2,4-Trimethylhexane? 3-Methyloctane?	1327	n-Tridecane
		1364	unknown
980[a]	unknown	1375	unknown
990[a]	2,6-Dimethylheptane? 3-Methylnonane?	1388	unknown
		1406	unknown
1020[a]	2,2,5-Trimethylheptane?	1415	n-Tetradecane
1032[a]	$C_{10}H_{22}$? $C_{11}H_{24}$? (2-Methyldecane?)	1436	unknown
		1442	unknown
		1449	unknown
1052	$C_{10}H_{22}$? $C_{11}H_{24}$?	1457	unknown
1061[a]	$C_{10}H_{22}$? $C_{11}H_{24}$?	1466	unknown
		1471	unknown
1076[a]	$C_{10}H_{22}$? $C_{11}H_{24}$?	1476	unknown
1098	n-Hendecane	1488	unknown
1126	2,2,5-Trimethyloctane?	1507	n-Pentadecane
1172	unknown	1524	unknown
1195	unknown	1533	unknown
1201	n-Dodecane	1544	unknown
1216	$C_{12}H_{26}$? $C_{13}H_{28}$? (2,6-Dimethylhendecane?)	1549	unknown
		1559	unknown
		1570	unknown
1234	unknown	1576	unknown
1249	unknown	1594	unknown
1258	$C_8H_{18}O$? $C_9H_{20}O$? (an alcohol?)	1604	n-Hexadecane
		1622	unknown
1262	unknown	1640	unknown
1268	4-Methyldodecane?	1645	unknown
1276	6-Ethylhendecane?	1656	unknown
1298	unknown	1668	unknown
1305	n-Tridecane	1686	unknown
1324	5-Methyldodecane?	1692	unknown
1337	$C_{13}H_{28}$? $C_{14}H_{30}$?	1702	n-Heptadecane
		1712	unknown
1340	$C_{13}H_{28}$? $C_{14}H_{30}$?	1728	unknown
1358	n-Heptylcyclohexane?	1734	unknown

Table 18. continued

Nonpolar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1366	5-Ethyl-5-methyl-decane?	1742	unknown
1371	4-Methyltridecane?	1753	unknown
1378	$C_{13}H_{28}$? $C_{14}H_{30}$? 3-Methyltridecane?)	1771	unknown
1384	6-Methyltridecane? 2-Methyltridecane?	1799	n-Octadecane
1404	1-Tetradecene?	1809	unknown
1408	n-Tetradecane	1817	unknown
1417	unknown	1831	unknown
1425	$C_{14}H_{30}$? $C_{15}H_{32}$?	1840	unknown
1433	unknown	1849	unknown
1450	$C_{16}H_{26}$? (C_{10} subst. benzene?)	1864	unknown
1459	2,5-Dimethyltridecane?	1875	unknown
1462	Octylcyclohexane?	1883	unknown
1472	6-Ethyltridecane?	1898	n-Nonadecane
1482	2-Ethyltridecane?	1913	unknown
1490	1-Dodecanol?	1922	unknown
1504	1-Pentadecene?	1927	unknown
1511	n-Pentadecane	1933	unknown
1525	$C_{15}H_{30}$?	1937	unknown
1540	unknown	1949	unknown
1559	$C_{16}H_{34}$? $C_{15}H_{32}$?	1960	unknown
1569	$C_{13}H_{28}O$?	1973	unknown
1575	2-Methylpentadecane?	1982	unknown
1583	3-Methylpentadecane?	1996	n-Eicosane
1590	$C_{15}H_{24}$?	2014	unknown
1606	5-Methylpentadecane?	2017	unknown
1618	n-Hexadecane	2028	unknown
1636	$C_{16}H_{32}$?	2047	unknown
1639	$C_{16}H_{34}$?	2063	unknown
1643	unknown	2074	unknown
1650	$C_{16}H_{34}$? $C_{17}H_{36}$?	2079	unknown
1661	$C_{16}H_{34}$? $C_{17}H_{36}$?	2094	n-Heneicosane
1676	$C_{16}H_{34}$? $C_{17}H_{36}$? (3-Methylhexa-decane?)	2108	unknown
		2120	unknown
		2142	unknown
		2161	unknown
		2175	unknown
		2193	n-Docosane
		2213	unknown
		2225	unknown
		2247	unknown
		2286	n-Tricosane?
		2297	unknown
		2316	unknown
		2328	unknown

Table 18. continued

Nonpolar Fraction - continued

$R.I._{SE\ 54}$	Compound	$R.I._{SP\ 1000}$	Compound
1686	3-Methylhexadecane?	2361	unknown
1702	$C_{17}H_{34}$? $C_{17}H_{36}$?	2373	unknown
1714	n-Heptadecane	2384	unknown
1720	$C_{17}H_{36}$?	2402	unknown
1737	$C_{17}H_{34}$?	2426	unknown
1743	$C_{17}H_{34}$? $C_{17}H_{36}$?	2466[a]	unknown
1744	unknown		
1758	$C_{19}H_{36}$? $C_{18}H_{38}$?		
1764	unknown		
1770	$C_{18}H_{38}$?		
1775	$C_{18}H_{38}$?		
1785	$C_{17}H_{36}$? $C_{18}H_{38}$?		
1796	$C_{16}H_{30}$? $C_{17}H_{32}$? $C_{18}H_{34}$?		
1802	$C_{17}H_{36}$? $C_{18}H_{38}$?		
1807	unknown		
1813	n-Octadecane		
1822	$C_{18}H_{38}$?		
1840	unknown		
1848	$C_{18}H_{38}$? $C_{19}H_{40}$?		
1854	$C_{18}H_{38}$? $C_{19}H_{40}$?		
1869	$C_{18}H_{38}$? $C_{19}H_{40}$?		
1875	$C_{18}H_{38}$? $C_{19}H_{40}$? (4-Methyloctadecane?)		
1882	$C_{18}H_{38}$? $C_{19}H_{40}$? (3-Methyloctadecane?)		
1892	unknown		
1903	$C_{19}H_{40}$?		
1910	n-Nonadecane		
1920	$C_{19}H_{38}$?		
1925	$C_{19}H_{40}$? $C_{17}H_{36}O$?		
1937	$C_{17}H_{34}O_2$? (a methyl ester?)		
1949	$C_{19}H_{40}$? $C_{20}H_{42}$?		
1965	$C_{19}H_{40}$? $C_{20}H_{42}$?		

Table 18. continued

Nonpolar Fraction - continued

$R.I._{SE\ 54}$	Compound
1971	$C_{20}H_{42}$?
1978	$C_{20}H_{42}$?
1983	$C_{19}H_{38}$? $C_{20}H_{40}$?
1991	$C_{19}H_{40}$? $C_{20}H_{42}$?
2006	n-Eicosane
2079	unknown
2101	n-Heneicosane
2131	$C_{19}H_{38}O_2$? (a methyl ester?)
2166	unknown
2175	unknown
2204	n-Docosane
2248	unknown
2303	n-Tricosane
2324	unknown
2472	unknown
2510	unknown
2659	unknown
2808	unknown

Polar Fraction

$R.I._{SE\ 54}$	Compound	$R.I._{SP\ 1000}$	Compound
741[a]	Cyclohexane?	1317[a]	unknown
748[a]	Cyclohexene	1332	unknown
777[a]	1,1-Dimethoxyisobutane?	1420	unknown
	$CH_2=C(OCH_3)_2$??	1435	unknown
796[a]	unknown	1511[a]	unknown
802[a]	unknown	1575[a]	unknown
820[a]	unknown	1606	unknown
851[a]	a methoxy compound?	1625	unknown
896[a]	$CH_3SCH_2SCH_3$?	1640	unknown
961[a]	C_9H_{20}?	1660	unknown
		1671	unknown
1037[a]	C_9H_{20}? $C_{10}H_{22}$?	1688	unknown
1098[a]	$C_{10}H_{16}O$?	1697	unknown
		1702	unknown
1127[a]	$C_8H_{16}O$?	1727	unknown

Table 18. continued

Polar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1161[a]	$C_{10}H_{16}O$?	1743	Naphthalene
1204	Naphthalene	1773	unknown
1239[a]	$C_4H_{10}S_3$?	1783[a]	unknown
1260	unknown	1800	unknown
1272	a dimethyl indan?	1828	unknown
1288	unknown	1835	unknown
1304	unknown	1852	2-Methylnaphthalene
1311	$C_{13}H_{28}$?	1869	unknown
1318	a methyl tetralin?	1887	1-Methylnaphthalene
1322	2-Methylnaphthalene	1898	unknown
1340	1-Methylnaphthalene	1918	unknown
1366	an ethyl tetralin or a dimethyl tetralin?	1945	2-Ethylnaphthalene
1374	unknown	1956	unknown
1392	$C_{14}H_{30}$?	1963	1-Ethylnaphthalene
1404	Biphenyl	1988	Biphenyl
1411	n-Tetradecane	1992	unknown
1416	$C_{12}H_{16}$ (C_6 subst. benzene?)	2000	1,3-Dimethylnaphthalene?
1422	2-Ethylnaphthalene	2013	unknown
1426	1-Ethylnaphthalene	2031	unknown
1437	2,6- or 2,7- Dimethyl-naphthalene?	2035	unknown
1448	unknown	2047	unknown
1454	1,2- or 1,3- Dimethyl-naphthalene?	2054	unknown
1456	2,7- or 1,7- Dimethyl-naphthalene?	2064	unknown
1458	Hexamethylbenzene?	2067	unknown
1466	$C_{13}H_{12}$ (C_3 subst. naphthalene?)	2087	unknown
1475	1,4-Dimethylnaphtha-lene?	2093	unknown
1480	$C_{14}H_{22}$?	2103	unknown
1492	1,8-Dimethylnaphtha-lene?	2110	unknown
1505	a tetramethyl indan?	2135	unknown
1512	unknown	2139	unknown
		2144	unknown
		2166	unknown
		2174	unknown
		2187	unknown
		2195	unknown
		2202	unknown
		2211	unknown
		2217	unknown
		2224	unknown
		2231	unknown
		2246	unknown
		2255	unknown

Table 18. continued

Polar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1520	3-Phenyltoluene?	2260	unknown
1525	3-Bromodecane??	2268	unknown
1533	a trimethyl naphthalene? an isopropyl naphthalene?	2277	unknown
		2286	unknown
		2317	unknown
1538	unknown	2328	unknown
1541	an isopropyl naphthalene?	2342	Fluorene
		2355	unknown
1548	a phenyl ethyl benzene?	2365	unknown
		2387[a]	Diethylphthalate
1554	an isopropyl naphthalene?	2401	unknown
		2407	unknown
1562	a trimethyl naphthalene?	2423	unknown
		2437	unknown
1564	a trimethyl naphthalene?	2471	unknown
		2477	unknown
1570	a trimethyl naphthalene?	2499	unknown
		2525	unknown
1580	$C_{11}H_{12}O_2$? $C_{12}H_{16}O$?	2531	unknown
		2549	unknown
1588	unknown	2569	unknown
1591	a trimethyl naphthalene?	2581	unknown
		2610	unknown
1606	2,3,5- or 2,3,6- Trimethylnaphthalene?	2620	unknown
		2637	unknown
1621	$C_{14}H_{14}$? $C_{13}H_{10}O$? $C_{12}H_6O_2$?	2651	unknown
		2671	unknown
		2681	unknown
1625[a]	Diethylphthalate (& a trimethyl naphthalene?)	2694[a]	unknown
		2704	unknown
		2724	unknown
1632	$C_{13}H_{12}$ (C_3 subst. naphthalene? a methyl biphenyl?)	2746	unknown
		2774	unknown
		2789	unknown
1642	a trimethyl naphthalene?	2815	unknown
		2839	unknown
1650	unknown	2886	unknown
1658	$C_{13}H_{10}O$? $C_{14}H_{14}$?	2888	unknown
		2932	unknown
1664	a dimethyl ethyl naphthalene?	2974	unknown
		3002	unknown
1667	unknown	3044	unknown

Table 18. continued

Polar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1672	4-Methyldibenzofuran?	3063	unknown
1683	a methyl isopropyl naphthalene?	3093	Phenanthrene?
1695	unknown	3151	unknown
1712	unknown	3173	unknown
1716	a methyl isopropyl naphthalene?	3200	unknown
1721	a t-butyl naphthalene?	3242	unknown
1728	$C_{17}H_{36}$? $C_{18}H_{38}$?	3269	unknown
1733	a methyl isopropyl naphthalene? a t-butyl naphthalene?	3290	unknown
1739	a methyl fluorene?	3319	unknown
1750	1-Naphthalenyl-1-butanone?	3340	unknown
1756	an ethyl biphenyl? a dimethyl biphenyl?	3486	unknown
1763	a methyl dihydrophenanthrene?	3520	unknown
1767	$C_{15}H_{18}$? $C_{14}H_{14}$?	3574	unknown
1768	unknown	3660	unknown
1778	unknown	3695	unknown
1785	2-Ethylbiphenyl?	3737	unknown
1805	unknown	3785	unknown
1810	Dibenzothiophene? $C_{14}H_{16}$?	3805	unknown
1824	$C_{18}H_{38}$?	3913	unknown
1837	Phenathrene?	3966	unknown
1851	unknown	4010	unknown
1866	a methyl dihydrophenanthrene?	4105	unknown
1872	$C_{16}H_{18}$? $C_{15}H_{14}O$?	4146	unknown
1876	an ethyl dihydrophenanthrene?	4182	unknown
1882	$C_{15}H_{14}O$? $C_{16}H_{18}$?	4227	unknown
1896	unknown	4296	unknown
1911[a]	$C_{13}H_{10}S$ (a methyl dibenzothiophene?)	4332	unknown
1918	$C_{19}H_{40}$?	4384	unknown
		4501	unknown
		4553	unknown
		4598	unknown
		4606	unknown

Table 18. continued

Polar Fraction - continued

R.I.$_{SE\ 54}$	Compound	R.I.$_{SP\ 1000}$	Compound
1932	unknown		
1945	unknown		
1952	a methyl phenanthrene?		
1958	a methyl phenanthrene?		
1968	$C_{16}H_{16}$?		
1978	a methyl phenanthrene?		
1983	a methyl phenanthrene?		
2002	unknown		
2010	unknown		
2017[a]	$C_{14}H_{12}S$? (a dimethyl naphthothiophene?)	$C_{16}H_{20}$?	
2024	unknown		
2033	$C_{20}H_{42}$? $C_{21}H_{44}$?		
2043	unknown		
2051	$C_{16}H_{30}$?		
2060	a dimethyl phenanthrene?		
2071	a dimethyl phenanthrene?		
2089	a dimethyl phenanthrene?		
2096	a dimethyl phenanthrene?		
2103	unknown		
2111	unknown		
2124	unknown		
2137	$C_{21}H_{44}$? $C_{22}H_{46}$?		
2149	unknown		
2163	unknown		
2178	unknown		
2186	Pyrene?		
2207	unknown		
2217	a trimethyl phenanthrene?		
2230	unknown		
2241	unknown		
2260	unknown		
2277	unknown		
2297	unknown		
2313	unknown		
2340	unknown		
2355	unknown		
2368[a]	unknown		
2529	unknown		

Table 18. continued

Polar Fraction - continued	
$R.I._{SE\ 54}$	Compound
2556	unknown
2699[a]	unknown
2825[a]	unknown
2842[a]	unknown

fractions were based on mass spectral data and retention index data. The identifications of the SP-1000 column chromatograms for the aldehyde, ketone, nonpolar, and polar fractions were based only on retention index data.

In general, the composition of the Volkswagen Diesel Rabbit exhaust was very similar to the composition of the #2 diesel fuel sample. The diesel exhaust sample contained only small amounts of oxygenated compounds. Several factors may be used to explain the low levels of phenols, aldehydes, and ketones in the diesel exhaust sample relative to the levels of the oxygenated compounds in gasoline exhaust. First of all, the alkyl benzenes, which seemed to be the major source of oxygenated compounds in gasoline exhaust, were present only at low levels in the diesel fuel. In addition, the total concentration of aromatic compounds relative to the total concentration of saturates was lower in the diesel fuel sample than it was in the gasoline sample. Another factor which may have had an effect on the amount of oxygenates formed in the automobile exhaust was the air-to-fuel ratio in the

automobile engine. Diesel engines usually operate in a fuel-rich mode relative to the gasoline engines; in fact, the aeration of gasoline engines requires 50 to 100 times more air than in the case of diesel engines (305). A higher level of air in the automobile engine would lead to a greater level of oxygenates in the exhaust.

There did not appear to be a great amount of pyrosynthesis occurring during the combustion of the diesel fuel. The highest molecular-weight compound which was identified with any amount of certainty in the diesel exhaust sample was a trimethylphenanthrene, which could have been a component in the diesel fuel used in the automobile. The lack of higher molecular-weight PAH's, such as those found in the gasoline exhaust, may have been caused by the low air-to-fuel ratio. The PAH-formation mechanism proposed by Schmeltz and Hoffmann (341) (see page 131) would tend to support that conclusion.

CONCLUSIONS

The usefulness of liquid-liquid fractionation as a pre-separation method for GC/MS has been demonstrated by this work. Not only did the fractionation method simplify the mass spectral analysis of real samples, but also the method provided much chemical information about the samples. By fractionating various standard compounds, representing several chemical classes, it was possible to determine what types of compounds would be found in the seven fractions. In many cases, the number of possibilities for the identifications of sample components based on mass spectral data could be narrowed as a result of the chemical information provided by the fractionation method. In addition, the analysis of many trace compounds in the presence of major compounds, which would have been difficult using GC/MS alone, was made possible by the use of the fractionation method.

In most cases, fairly clean separations of various types of compounds were achieved with the fractionation method. Even when compounds would partition between two fractions, useful information could still be obtained about those compounds.

No alterations of compounds were observed during the fractionation of samples. Although some standard compounds had been shown to decompose under certain conditions, the fractionation method was designed to minimize such decompositions. However, some sample components may have been lost during the fractionation as a result of their solubility in water.

The major problem with the fractionation method was the introduction of impurities into the samples by solvents and reagents. The greatest amounts of impurities were introduced into the sample by the dimethyl sulfoxide used to extract polar materials. The impurities introduced into the samples could be determined by fractionating blanks along with the samples.

SUGGESTIONS FOR FUTURE WORK

Several improvements can be made in the fractionation method. One of the greatest improvements would be to find a way to remove all of the impurities from the solvents and reagents. Much work needs to be done in the identification of the impurities in order to find the best way to remove them. It is also important to determine what compounds, if any, would form in the reagents over a period of time. The reagents in methanol solutions presented the greatest problems with the formation of impurities. Perhaps some compounds could be added to the reagents to prevent the formation of impurities.

Another improvement which could be made would be to find a way to increase the extraction of aldehydes by bisulfite. It was found that the solvent was a factor in the reaction. Perhaps other variables could be found which would make the equilibrium more favorable for the extraction of aldehydes, and at the same time, not increase the chances of decomposing sample components.

Other reagents could be found to be used in the fractionation method. The fractionation method could be expanded to separate mixtures of compounds into smaller fractions. In addition, reagents could be found which might give better separations of mixtures than those already in the fractionation procedure. For example, it might be possible to remove ketones from an organic solvent by elution through a column containing a resin with a hydrazine functionality.

In this work, the fractionation method was tested with fuel and automobile exhaust samples. Other samples could be fractionated by

the method. A sample containing basic materials would be useful to test the feasibility of removing bases with HCl, a step which was not adequately tested by the fuel and automobile exhaust samples.

In summary, work could be done to test the fractionation method further, and to provide improvements in the separations of complex mixtures.

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APPENDIX

Some Chromatographic Materials Mentioned In This Dissertation

Amberlite MB-3 is a mixture of a strong-acid cation-exchange resin and a strong-base anion-exchange resin used for deionizing water. Amberlite is a trademark of Rohm and Haas Company.

Amberlite IRC-50 is a weak-acid cation-exchange resin. Amberlite is a trademark of Rohm and Haas Company.

Bio-Beads S is a series of neutral, porous styrene-divinylbenzene copolymer beads used in gel permeation chromatography. Bio-Beads is a trademark of Bio-Rad Laboratories.

Carbowax 20M is an ethylene glycol polymer used as a polar liquid phase in gas chromatography. Amines can be chromatographed on Carbowax 20M if it is made basic with KOH. Carbowax is a trademark of Union Carbide.

Chromosorb 102 is a porous styrene-divinylbenzene copolymer used as an adsorbent for organic compounds in gaseous samples and as a gas chromatographic packing. Chromosorb is a trademark of Johns-Manville.

CP Wax-51 is a high-temperature ethylene glycol polymer used as a liquid phase (polar) in gas chromatography. CP Wax is a trademark of Chromopack, Inc.

Dexsil 300 is a carborane-silicone liquid phase (nonpolar) used in high-temperature gas chromatographic separations. Dexsil is a trademark of Dexsil Chemical Corporation.

Florisil is a magnesium silicate material used as a liquid chromatography packing. Florisil is a trademark of Floridin Company.

OV-17 is a phenyl-methyl (50:50) silicone liquid phase (intermediate polarity) used in gas chromatography. OV is a trademark of Ohio Valley Specialty Chemical Company.

Poragels are high capacity, porous adsorbents made by copolymerizing styrene and divinylbenzene with a third monomer to provide specific functionalities. Poragel is a versatile packing used for both size exclusion and adsorption separations. Poragel is a trademark of Waters Associates, Inc.

SE-54 is a methyl phenyl vinyl (94:5:1) silicone liquid phase (nonpolar) used in gas chromatography.

Sephadex LH-20 is prepared by hydroxypropylation of Sephadex G-25. Sephadex is a bead-formed, dextran gel. The dextran chains are cross-linked to give a three-dimensional polysaccharide network. Sephadex LH-20 can be used in size exclusion, adsorption, and partition chromatography. Sephadex is a trademark of Pharmacia Fine Chemicals.

SP-1000 is a nitroterephthalic acid-modified polyethylene glycol (20M) liquid phase (polar) used in gas chromatography.

Styragel and micro-Styragel are rigid, porous gel particles of cross-linked co-polymer of styrene and divinylbenzene used in gel permeation chromatography. Styragel is a trademark of Waters Associates, Inc.

Tenax is a porous 2,6-diphenyl-p-phenylene oxide polymer used as a column packing material in gas chromatography and as an adsorbent for organic compounds in gaseous samples. Tenax has good thermal stability and does not have a strong affinity for water. Tenax is a trademark of Enka N. V. (The Netherlands).