USE OF SOLVENT INJECTION CHROMATOGRAPHY FOR EVALUATING EXTRACTIVE DISTILLATION SYSTEMS

By

MEREDITH RAY SHEETS

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Thesis Approved:

R. N. Maddox
Thesis Adviser

John B. West

Lynn Mackenzie
Dean of the Graduate School

PREFACE

The gas chromatograph is rapidly becoming the most widely used analytical tool in the world. Acceptance of this new tool has occurred because it can quickly and economically separate many gaseous or volatile mixtures into their components. The separation efficiency obtained can be compared to a distillation tower containing hundreds of theoretical trays. The similarity between gas chromatography and distillation has prompted several vapor-liquid equilibrium studies to be performed on the gas chromatograph.

This thesis presents a technique which can be utilized to obtain equilibrium data for extractive distillation systems when using a volatile solvent. Investigations were also made to determine the reproducilibity of separation factors (chromatographic relative volatilities), to investigate the effect of temperature on the separation factors, and to determine if equilibrium still azeotropic composition can be obtained on the chromatograph.

I would like to express my sincere appreciation to Dr. R. N. Maddox and members of the Chemical Engineering staff at Oklahoma State University for their advice and direction of this investigation. I am particularly appreciative of the assistance given me by Dr. J. M. Marchello during the course of this study.

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CHAPTER I

INTRODUCTION

The gas chromatograph has been accepted by industry because of the time and money it saves. Its main function is the analysis of gaseous or volatile mixtures for individual components. Gas chromatography is employed in laboratories to help guide the operations of old processes and to develop new processes. Some of the process applications include checking absorber efficiencies, checking conversions in reactors, and controlling distillation towers. A recent application is the use of gas chromatography to obtain vapor-liquid equilibrium data for ideal and nonideal systems.

The term "gas chromatography," as used in this research, refers to a column in which there is a mobile gas phase passing over a liquid which is supported by an inert solid. The mobile gas contains the sample. The sample components are in equilibrium with the stationary and mobile phases, which causes a physical separation to occur between the components.

The specific goal of this research was to develop a technique which could be used to obtain vapor-liquid equilibrium data for extractive distillation systems when

using volatile solvents and the standard gas chromatograph. To reach the stated goal, it was necessary to determine the effects that certain procedures and variables would have on the chromatographic separation factor (relative volatility).

The objectives of this research were as follows:

A. Preliminary Investigations
   1. Determine the reproducibility of binary sample separation factors when the solvent is evenly distributed on the support and also when the solvent is injected into the operating column.
   2. Determine if azeotropic compositions exist in the field of gas chromatography.
   3. Investigate the influence of temperature on the separation factor for several binary samples when the solute is at infinite dilution in the solvent phase.
   4. Determine the effect of sample composition on the separation factor.

B. Solvent Injection
   1. Obtain separation factors for a binary system when injecting different amounts of solvent into a column which does not have liquid on the packing.

2. Obtain separation factors for an extractive distillation system when injecting different volumes of solvent into a column in which there is a heavy partitioning liquid already on the packing.

CHAPTER II

LITERATURE SURVEY

Gas Chromatography and Fractional Distillation

The relationship between gas-liquid chromatography and distillation was first suggested by Martin and Synge (17) in 1941 when they proposed the technique of using a gas instead of a liquid as the mobile phase. They suggested that a permanent gas be made to flow over gel impregnated with a nonvolatile solvent in which the substances to be separated approximately obeyed Raoult's Law. James and Martin (12) in 1952 referred to gas chromatography as "carrier distillation" when they developed the technique. The modifications which they made concerning chromatography could also be made in distillation. These modifications would be to replace the vapor with a permanent gas and the condensed liquid with a nonvolatile liquid. They found that, when volatile substances were blown through a gas chromatographic column, the more volatile components of the mixture would travel more rapidly than the less volatile components.

Because of the similarity between a gas chromatographic column and a distillation column, the efficiency is

usually referred to in terms of theoretical plates. This theoretical plate approach was defined by the nomenclature committee of the London symposium (2) and recommended for use by the Committee on Nomenclature of the Instrument Society of America Symposium (1). The number of theoretical plates can be obtained from the chromatogram data by the expression:

$$n_i = 16 \left(\frac{d_i}{\Delta d_i} \right)^2 \qquad (1)$$

Several investigators (6, 14, 17, 19, 24, 35) have used theoretical trays as a method for expressing the efficiency of a chromatographic column.

The theoretical plates needed for a specific separation are not the same for gas chromatography and distillation. Herington (10) stated, "If n theoretical plates are required in distillation to obtain a given separation, then approximately n^2 plates may be required in chromatography." This statement can be used to summarize the findings of van Deemter and his co-workers (33). The chromatographic plates, however, are easier to obtain and control. Distillation will probably never be replaced by gas chromatography, because gas chromatography is a discontinuous process and can utilize only small quantities of volatile materials.

Gas Chromatography and Packed Process Columns

Another plate theory used to describe the efficiency of a gas chromatographic column is known as the "height equivalent to a theoretical plate" or HETP. The HETP theory has been used by several investigators (13, 15, 33). This refers to a length of column which will produce the separation equivalent to that of one theoretical plate. This concept is important because it considers the effects of the column length and of the sample injection method. The HETP can be calculated by using Equation (2) if the number of theoretical plates, n, is known.

$$HETP = \frac{L}{n_i} \qquad (2)$$

Equations for finding the HETP when the number of theoretical plates is not known are discussed in the following Theoretical Background section of this chapter.

Gas Chromatography and Extractive Distillation

The technique of gas chromatographic separation is similar to extractive distillation due to the influence of the solvent phase. The application of gas chromatography for studying extractive distillation systems has been suggested by several writers (20, 31, 34, 36). Warren and others (34) compared relative volatilities obtained from

equilibrium still runs with separation factors obtained by gas chromatography. The separation factor could probably be called the "chromatographic effective relative volatility" as a more descriptive name. Throughout this research, the term separation factor, α, shall be used and will be expressed by:

$$\alpha_{2,1} = \frac{d_2 - d_a}{d_1 - d_a} \qquad (3)$$

The solvents employed by Warren were rather high boiling. Porter and Johnson (26, 27, 28) investigated several extractive distillation systems when using circular gas chromatography. This technique involves the use of a closed system in which there is circulated either the partitioning "liquid" in the gas phase or helium as the eluting gas. Circular gas chromatography permits the use of volatile partitioning liquids without allowing any of the liquids to leave the enclosed circuit. When working on the system methylcyclohexane-toluene and using aniline as the solvent, Porter and Johnson (28) reported a separation factor of 3.1 compared to an equilibrium still value of 2.59. For the system n-heptane-methylcyclohexane, they reported a separation factor of 1.65 compared to the equilibrium still value of 1.52. The authors concluded, "The excellent agreement indicates the potential of circular gas chromatography in developing correlations for several types of solvent separations." In each of the above cases, the separation factors obtained were considerably

higher than the relative volatility values obtained from the equilibrium still. The high values calculated from chromatographic data were probably caused by the infinite solvent dilution of the sample.

Gas Chromatography and Vapor-Liquid Equilibrium Constants

The potential application of gas chromatography for determining vapor-liquid equilibrium constants has been demonstrated. Mellado and Kobayashi (20) obtained chromatographic experimental K-values for the system n-butane in n-dodecane which compared favorably with the Natural Gasoline Association (21) K-value chart for the same conditions of temperature and pressure. A convergence pressure of 20,000 pounds was used. Similar runs made on methane, ethane, ethylene, and propane did not yield accurate K-values because the retention times were apparently too low. Preston (29) stated, "It is predicted that as chromatography data becomes available at elevated pressures, it will be found to be in agreement with comparable 'K' values." The basis for this prediction is the fact that the same factors which influence K-values, such as activity coefficients and compressibility factors, can also be made to influence retention times by the proper choice of carrier gas and stationary phase.

Theoretical Background

The efficiency of a distillation tower can be described in terms of the number of theoretical plates, and the degree of separation obtained in an equilibrium still can be expressed as relative volatility. After observing the separations obtained on a gas chromatograph, the question might be asked, "What can be used to describe these separations?" Several methods have been proposed which express the separations in terms of separation factors and which express the efficiency in terms of theoretical plates.

Relative Volatility and Separation Factor

The deviations of a liquid phase from Raoult's Law must be considered when doing research on extractive distillation systems. The deviations can be summed up by the introduction of the activity coefficient. The insertion of this factor into Raoult's Law gives:

$$p_i^\circ = y_i \pi = \gamma_i P_i^\circ x_i \tag{4}$$

The relative volatility, α, obtained from equilibrium still data for the separation of two components of a nonideal system can be expressed by:

$$\alpha_{1,2} = \frac{y_1 x_2}{x_1 y_2} = \frac{\gamma_1 P_1^\circ}{\gamma_2 P_2^\circ} \tag{5}$$

A term similar to relative volatility can be derived from gas chromatographic data for the separation of binary systems. This term is called the separation factor and requires the use of the partition coefficient, H°, at infinite solvent dilution as defined by Porter, Deal, and Stross (24). This definition is expressed by:

$$H_i^\circ = \frac{M_S RT}{\gamma_i^\circ P_i^\circ} \tag{6}$$

where: $H_i^\circ = \dfrac{\text{amount of solute per unit volume of stationary phase}}{\text{amount of solute per unit volume of moving phase}}$

The separation factor, α, can be obtained by employing Equation (6) to obtain the relative partition coefficient for two components by:

$$\frac{H_2^\circ}{H_1^\circ} = \frac{\gamma_1^\circ P_1^\circ}{\gamma_2^\circ P_2^\circ} = \alpha_{1,2} \tag{7}$$

Another important term used in gas chromatographic calculations is retention volume. This is the volume of carrier gas, measured at or corrected to column temperature and column outlet pressure, which passes through the column between the time the sample is injected and the peak maximum occurs. This is given by:

$$V_R = F_c \theta \tag{8}$$

James and Martin (11) introduced a pressure gradient correction for the compressibility of the carrier gas so that a

corrected retention volume could be obtained. The corrected retention volume, V_R°, is given by:

$$V_R^\circ = \frac{\frac{3}{2} V_R \left[\left(\frac{P_{in}}{P_{out}}\right)^2 - 1\right]}{\left[\left(\frac{P_{in}}{P_{out}}\right)^3 - 1\right]} \tag{9}$$

The partition coefficient is related to the corrected retention volume by:

$$H_i^\circ = \frac{V_{R_i}^\circ - V_a^\circ}{V_L} \tag{10}$$

The separation factor for a binary system can be obtained from the ratio of the partition coefficients. The following Equation (11) can be obtained by using Equation (10) for two components:

$$\alpha_{1,2} = \frac{H_2^\circ}{H_1^\circ} = \frac{V_{R_2} - V_a}{V_{R_1} - V_a} = \frac{d_2 - d_a}{d_1 - d_a} \tag{11}$$

A symposium (1) agreed upon Equation (11) as being the suitable standard nomenclature for the separation factor.

Several other methods have been used to describe the separations achieved by a gas chromatograph column in terms of a "separation factor." The following approaches were not employed in this research and are presented here as equations which might warrant further investigation. Figure 1 will be employed to define several of these methods which have been used to describe gas chromatographic column performance.

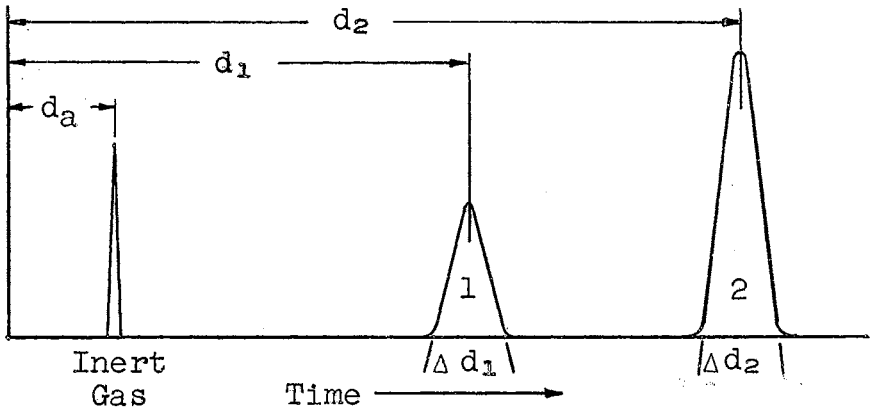


Figure 1

Terms Used in Calculating Column Efficiencies

A. Martin (1) used the following separation factor, F, which is based upon the uncorrected retention times:

$$F = \frac{\Theta_2 - \Theta_1}{\Theta_1} = \frac{d_2 - d_1}{d_1} \qquad (12)$$

where: Θ = uncorrected retention times.

B. Golay (1) proposed the following definition which is the ratio of the distance between peak maxima to the width of the first peak:

$$F = \frac{d_2 - d_1}{\Delta d_1} \qquad (13)$$

where: Δd_1 = peak width of first component.

C. A symposium committee (3) suggested that an obvious way for expressing column resolution would be as follows:

$$F = \frac{2(d_2-d_1)}{\Delta d_2+\Delta d_1} \qquad (14)$$

where: Δd = intercepts cut on the base line by the tangents to the peak.

Column Efficiency

A symposium committee (3) recommended that the chromatographic column efficiency should be related to individual peaks and not to any separations achieved. Another symposium (1) agreed upon the following theoretical plate equations as being suitable as standard nomenclature:

$$n_i = 16\left(\frac{d_i}{\Delta d_i}\right)^2 \qquad (15)$$

This expression defines the efficiency in terms of the column's ability to produce narrow peaks.

Golay (1, 8) originated an efficiency equation which might warrant some attention. This equation expresses efficiency as the performance index, PI, and is as follows:

$$PI = \frac{(\Delta d_1)^4}{d_1} \cdot \frac{d_a \Delta P}{d_1 - \frac{15}{16} d_a} \qquad (16)$$

where: ΔP = pressure drop across column.

The performance index was not intended to substitute for the theoretical plate Equation (15) and is simply a general

guide to how well a column will perform. Golay stated that "Its smallness gives us a measure of intrinsic goodness of a column, which can constitute the criterion on the basis of which a certain type of column is selected."

Van Deempter and others (33) proposed an equation which expresses the relationship between the height equivalent to a theoretical plate and the diffusional effects in a chromatographic column. This equation reads:

$$HETP = \underbrace{2\lambda d_p}_{\text{Eddy Diffusion}} + \underbrace{\frac{2\bar{\gamma}D_g}{u}}_{\text{Molecular Diffusion}} + \underbrace{\frac{8\,k'}{\pi^2\,(1+k')^2} \cdot \frac{d_f^{\,2}}{D_L}\,u}_{\text{Resistance to Mass Transfer}} \qquad (17)$$

where: d_f = statistical average of liquid film thickness

d_p = particle diameter

D_g = molecular diffusivity in gas

D_L = molecular diffusivity in liquid

k' = effect of changing the distribution ratio

u = linear gas velocity

λ = measure of packing irregularities

$\bar{\gamma}$ = tortuosity of the packing.

Jones (13) developed an equation similar to Equation (17) to allow for column pressure drop. The integrated equation is as follows:

$$HETP = A + B\frac{D_{g_o}}{u_o} + C\frac{S_{ax}}{(1+S_{ax})^2}\cdot\frac{d_f^2 u_o}{D_L}\cdot\frac{2\,P_{out}}{P_{in}+P_{out}} + D\frac{S_{ax}}{(1+S_{ax})^2}\cdot\frac{d_m^2 u_o}{D_{g_o}} + E\frac{1}{(1+S_{ax})^2}\cdot\frac{d_s^2 u_o}{D_{g_o}} \quad (18)$$

where: A = velocity-independent constant of random flow pattern in a packed column

B = coefficient of axial or longitudinal diffusion in a gas phase

C = coefficient of resistance to mass transfer in liquid phase

D = coefficient of resistance to mass transfer in moving gas phase

D_{g_o} = diffusion coefficient of sample into carrier gas at column outlet pressure

d_m = effective moving-gas diffusional path length

d_s = effective stagnant-gas diffusional path length

E = coefficient of relatively stagnant gas within column packing

S_{ax} = relative separation of sample peak from air peak = $\frac{d_1-d_a}{d_a}$

u_o = carrier gas velocity at outlet of column packing

The first three terms are essentially Equation (17). Jones obtained coefficients for air, butane, and cyclohexane; and these coefficients were apparently in excellent agreement with the column data.

Equations (17) and (18) are of particular value when studying the internal mechanism of columns. The HETP can also be calculated by employing Equation (15) and dividing by the column length. This simplified equation is expressed as follows:

$$\text{HETP} = \frac{16}{L}\left(\frac{d_i}{\Delta d_i}\right)^2 \qquad (19)$$

CHAPTER III

DESCRIPTION OF APPARATUS

The apparatus used in this research consisted primarily of a Perkin-Elmer Corporation Model 154 Vapor Fractometer (gas chromatograph) and a strip chart recorder. This equipment is shown on Plate I. The auxiliary equipment included a helium gas supply, pressure regulator, soap film meter, hot plate, stop watch, and syringes. Several chromatographic columns were constructed and used in this research.

A brief description of some of the chromatographic items is given below.

Detector

The thermal conductivity cell detector was used to follow the separations obtained in the chromatographic column. The detector contained a reference cell and a sensing cell, as shown in Plate II. Each detector contained a thermister. The electrical resistances of these heated thermisters were used to indicate the thermal conductivity of the atmosphere in each chamber. When a sample component would emerge from the column, the thermal conductivity of the sensing chamber would change. This change caused a variation in the resistance of the sensing thermister. The

unbalance in the thermister bridge circuit would then provide a signal to the recorder.

Heated Air Chamber

The column and the detector were enclosed in a heated air chamber in which the temperature could be accurately controlled from room temperature to 225°C. The temperature in the chamber was held uniform by means of a blower in the top of the oven.

The sample injection block was located in the chamber, and its temperature was maintained approximately 30°C. above the column temperature by utilizing a small element connected in parallel with the oven heating elements. The high temperature of the heating block caused the liquid samples to be rapidly vaporized.

Flow Control

The helium carrier gas flow rate was adjusted by using a pressure regulator connected in the gas input circuit. A rotameter was used to determine the approximate flow rate, and a soap film meter was employed to determine the exact flow rate. The flow rates were adjusted from 16 to 50 cc. per minute in this research.

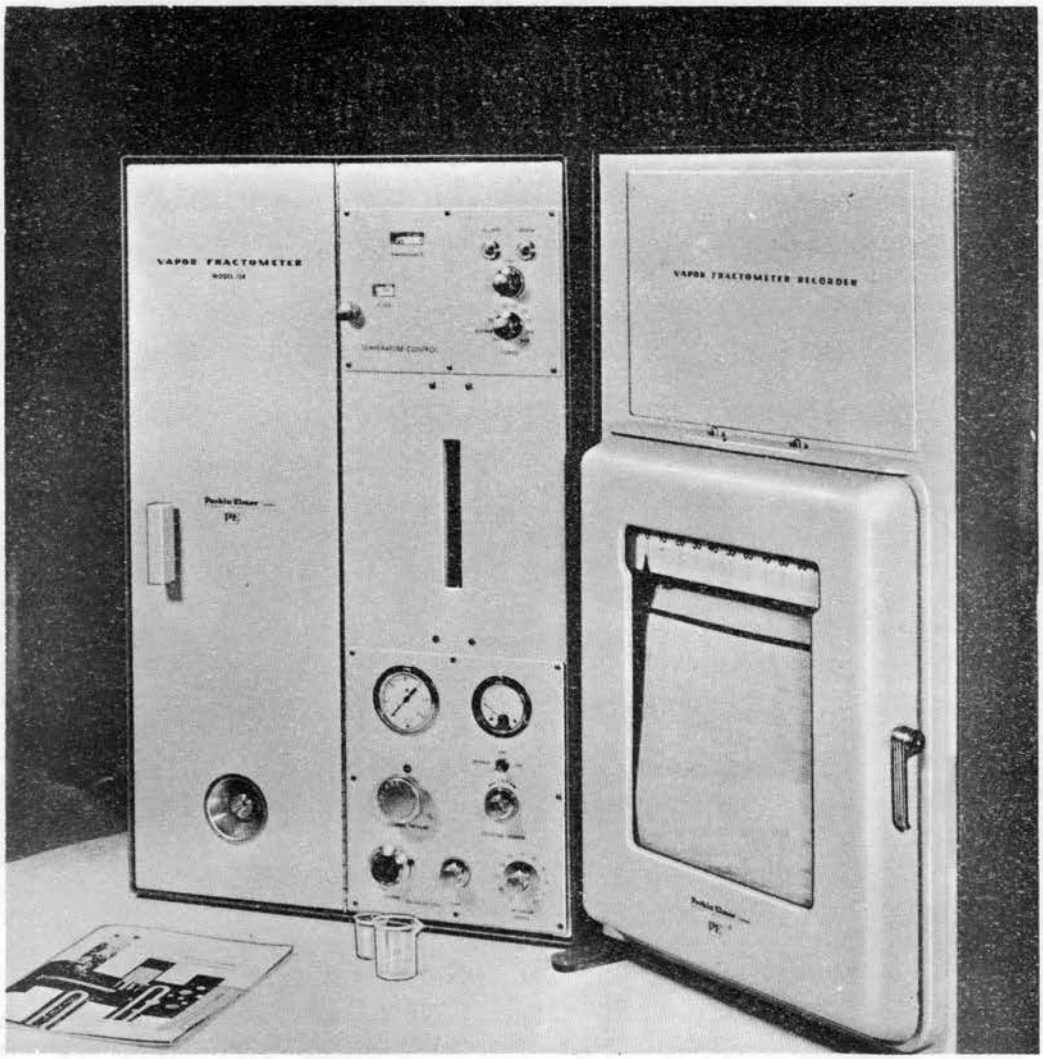


Plate I

Perkin-Elmer Corporation Model 154-D Vapor Fractometer

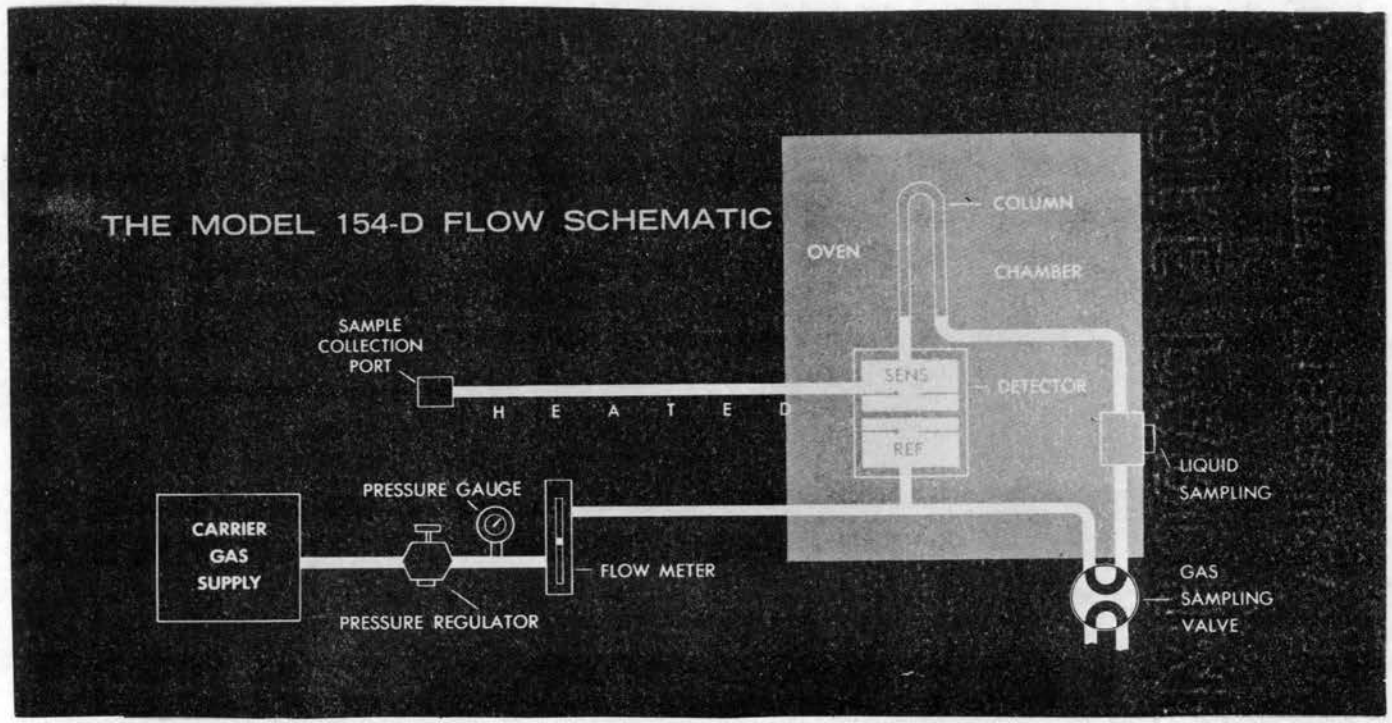


Plate II

Flow Schematic Of The Perkin-Elmer Corporation Model 154-D Vapor Fractometer

CHAPTER IV

EXPERIMENTAL PROCEDURES

General Description

The procedure outlined below was followed for all experimental runs. The first step was the preparation of the samples. The chromatographic column was then prepared and installed in the chromatograph. The temperature control dial was then set to give the desired temperature. Temperatures from 45°C. to 150°C. were used. The helium carrier gas flow rate was next adjusted to the desired value by means of a pressure regulator on the control panel. A soap film meter was used to check the flow rate. The flow rates were set from 16 to 50 cc. per minute at the flow meter conditions. When a change was made in the helium flow rate or the temperature, the equipment was allowed to reach equilibrium. Approximately 30 minutes were required to adjust to the desired conditions and to equilibrate the equipment.

Chromatogram Data

The following chromatogram data were recorded before a series of runs was made: column characteristics, carrier gas rate, column temperature, column inlet and outlet pressures, distance of air peak, chart speed, sample

volume to be used, voltage on the detector, rotameter reading, recorder range, and temperature in the soap film meter.

Flow Circuit

The flow circuit is shown on the flow schematic in Plate II. The carrier gas pressure was reduced from the pressure of the gas source down to 35 psig by employing a regulator. Helium flow through the system was then controlled by means of a pressure regulator on the control panel. The carrier gas next flowed to the heated air chamber where it was heated to the chamber temperature before entering the detector reference cell. The carrier gas then mixed with the vaporized liquid sample in the sample injection block. The volumes of the samples varied from 5 to 10 microliters. The sample and carrier gas flowed into the column for sample separation and then to the sensing side of the detector. The effluent from the detector was allowed to vent to the atmosphere or to a vacuum collecting system.

Injections of Samples and Solvents

The injection of the five to ten-microliter sample was performed by inserting the syringe needle through the septum and then rapidly depressing the plunger. The syringe was allowed to remain in the injected position for ten seconds to insure consistency between samples. The injections of from 100 to 1,200 microliters of phenol and furfural

required plunger depressing periods as long as twenty seconds. The solvents did not vaporize upon injection and were used to coat the stationary column packing. An electric heater was employed to heat the phenol and the phenol injection syringe to 65°C. This was necessary because the phenol melting point was 41°C. During some of the runs, phenol or furfural was venting from the column. These materials were condensed in a vacuum collecting system for safety reasons.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

Preliminary Investigations

Reproducibility of Separation Factors

Early in this investigation it was necessary to determine if gas chromatographic separation factors could be accurately reproduced. This was conducted in two parts. The first part was the injection of toluene and methylcyclohexane into a four-foot long column of Apiezon L on Perkin-Elmer Coarse Celite. The separation factors as shown on Table I were all the same. The second part was the injection of the same sample into the column at certain time intervals after a phenol solvent injection of 100 microliters. The relative volatilities obtained were reproducible within one per cent, as shown on Table I.

Azeotropes and Gas Chromatography

A series of runs was made employing each of the azeotropes presented in Table II. These runs were made to determine if azeotropic compositions exist in the field of gas chromatography.

TABLE I

SEPARATION FACTOR REPRODUCIBILITY

Chromatogram Data:

Column -	4-foot long by 0.25 inch O.D. 30 weight per cent Apiezon L on Perkin-Elmer Coarse Celite, 2 grams per foot Temperature, 100°C. Inlet pressure, 16.1 psia
Helium flow rate	20 cc./minute
Air peak distance	0.33 inch
Chart speed	0.5 inch/minute
Sample composition, weight per cent	50.0 toluene 50.0 methylcyclohexane
Sample volume	5 microliters
Phenol injection	100 microliters

Run Number	Sample Injection Point, Minutes After Phenol Injected	Chromatogram Peak Distance, Inches		Separation Factor
		Methyl-cyclohexane	Toluene	
70	Before	4.76	6.15	1.314
71	Before	4.69	6.06	1.314
72	Before	4.66	6.02	1.314
74	1.00	4.91	6.47	1.341
75	11.02	4.85	6.68	1.405
76	21.02	4.86	6.88	1.446
77	1.10	4.93	6.49	1.339
78	11.20	4.73	6.57	1.418
79	20.96	4.88	6.88	1.440

TABLE II

AZEOTROPES EMPLOYED FOR RUNS NUMBERED 283 THROUGH 302

Equilibrium Still Azeotropes, Weight Per Cent		Azeotropic Data		
Benzene	Cyclohexane	Boiling Point, °C.	Pressure, mm. Hg	Reference
51.8	48.2	77.7	760	16
49.7	50.3	77.4	760	30
	Methylcyclopentane			
90.58	9.42	71.39	760	9
91.00	9.00	72.00	1,019	22

The temperatures for the benzene-methylcyclopentane runs were varied incrementally from 70°C. to 73°C. in an attempt to find a temperature where the azeotrope would form. The samples were also run at 60°C. and 90°C. The four-foot long column of Apiezon L on Coarse Celite would not separate the benzene-cyclohexane system at any temperature. An inlet pressure of 863 mm. Hg was used for this part of the research. The Apiezon L column was chosen, because it should exhibit little or no special solvent effects on the samples.

The data indicated that gas chromatography can be used to resolve azeotropes. When a sample is being separated in a column, the sample composition passes through a wide range. At some point in the column the equilibrium still azeotropic composition is reached, if such a composition is possible. In spite of this, the benzene-methylcyclopentane system completely separated into its pure components.

This is an important difference between gas chromatography behavior and distillation tower behavior. The results of these runs are presented in Table III.

Influence of Temperature on the Separation Factor

Three binary systems were used in determining what effect different temperatures would have on the separation factors. The column used consisted of thirty weight per cent phenol on 60/80 mesh G-Cell. The results are given on Table IV and shown graphically in Figure 2. The temperatures were varied from 45°C. to 150°C. The phenol liquid on the packing vented rapidly from the column at temperatures above 100°C. The bleeding of phenol from the column at the high temperatures is believed not to have affected the separation factors because the data were reproducible. The separation factors were also considered to be accurate because the high temperature data points remained constant with the low temperature results. The findings of this investigation at high temperatures are in good agreement with circular gas chromatograph data obtained by Porter and Johnson (28). The low temperature results were lower than those obtained by Porter and Johnson and may have been caused by operating differences.

A comparison between gas chromatographic separation factors and equilibrium still relative volatilities for the system toluene-isooctane can be made by using Figure 3. Equilibrium still curves are shown when approximately 80 mole

per cent phenol is present and when no phenol is present. The separation factors are higher than the relative volatilities for all temperatures above 154°C. As can be seen in Figure 3, increasing the temperature increases the relative volatility and decreases the separation factor. The vapor pressure data curve, if plotted on Figure 3, would have a slope similar to the separation factor curve.

The equilibrium still data presented on Figure 3 are available in the 1945 Transactions of the American Institute of Chemical Engineers (4).

TABLE III

SEPARATION FACTORS FOR AZEOTROPES

Chromatogram Data:

Column -	4-foot long by 0.25 inch O.D. 30 weight per cent Apiezon L on Perkin-Elmer Coarse Celite, 2 grams per foot Inlet pressure, 863 mm. Hg Outlet pressure, 741 mm. Hg
Helium flow rate	16 cc. per minute
Chart speed	0.5 inch per minute
Sample volume	5 microliters

Run Number	Column Temperature, °C.	Azeotropic Compositions Weight Per Cent		Chromatogram Peak Distance, Inches		Air Peak Distance Inches	Separation Factor
		Methylcyclopentane	Benzene	Methylcyclopentane	Benzene		
283	70	9.42	90.58	6.45	8.26	0.5	1.304
284	70	9.00	91.00	6.40	8.20	"	1.305
285	71	9.42	90.58	6.23	7.96	"	1.302
286	71	9.00	91.00	6.27	7.98	"	1.296
287	71.4	9.42	90.58	6.17	7.89	0.49	1.303
288	71.4	9.00	91.00	6.14	7.84	"	1.301
289	72	9.42	90.58	6.02	7.71	"	1.305
290	72	9.00	91.00	6.08	7.74	"	1.297
291	73	9.42	90.58	5.94	7.56	"	1.297
292	73	9.00	91.00	5.96	7.59	"	1.298
293	90	9.42	90.58	4.21	5.18	0.5	1.261
294	90	9.00	91.00	4.23	5.23	"	1.268
295	60	9.42	90.58	7.86	10.26	0.49	1.326
296	60	9.00	91.00	7.85	10.19	"	1.318

TABLE III (Continued)

Run Number	Column Temperature, °C.	Azeotropic Compositions Weight Per Cent		Chromatogram Peak Distance, Inches		Air Peak Distance Inches	Separation Factor
		Cyclohexane	Benzene	Cyclohexane[1]	Benzene[1]		
297	90	49.7	50.3	5.11	5.11	0.5	1.0
298	90	51.8	48.2	5.20	5.20	"	1.0
299	76	49.7	50.3	7.02	7.02	"	1.0
300	76	51.8	48.2	7.18	7.18	"	1.0
301	60	49.7	50.3	10.27	10.27	"	1.0
302	60	51.8	48.2	10.40	10.40	"	1.0

[1]The cyclohexane and benzene did not separate in the column.

TABLE IV

EFFECT OF TEMPERATURE ON THE SEPARATION FACTOR

Chromatogram Data:

Column -	10-foot long by 0.25 inch O.D. 30 weight per cent phenol on 60/80 mesh G-Cell 22.027 grams total weight in column Inlet pressure, 1,103 mm. Hg Outlet pressure, 749 mm. Hg
Helium flow rate	50 cc. per minute
Temperature in soap film meter	22.5°C.
Air peak distance[2]	.47 to .53 inches
Chart speed	0.5 inch per minute
Liquid sample volume	5 microliters (1) 50.123 weight per cent toluene, 49.877 weight per cent methylcyclohexane (2) 50.0 weight per cent toluene, 50.0 weight per cent isooctane (2,2,4-trimethylpentane) (3) 51.8 weight per cent benzene, 48.2 weight per cent cyclohexane

Run Number	Column Temperature, °C.	Chromatogram Distance, Inches		Separation Factor
		Methylcyclohexane	Toluene	
207	45	15.98	80.2	5.151
210	45	16.02	80.0	5.125
212	45	15.90	79.0	5.100
215	65	9.62	43.22	4.696
218	65	9.22	42.69	4.825
221	100	3.80	13.60	3.943
224	100	3.65	13.19	4.000
227	125	2.15	6.65	3.678
229	150	1.83	4.54	2.993
234	150	1.77	4.42	3.038
236	150	1.66	3.18[3]	2.277

[2]The air peak distance was .51 inch through test run 212, then .53 inch through test run 218, and then .47 inch through test run 236.

[3]The remaining phenol on the column vented during runs 235 and 236.

TABLE IV (Continued)

Run Number	Column Temperature, °C.	Chromatogram Distance, Inches Iso-octane	Toluene	Separation Factor
208	45	8.21	79.9	10.310
211-1	45	8.14	79.8	10.392
213	65	5.11	43.6	9.404
216	65	5.04	42.5	9.293
219	100	2.28	13.6	7.254
222	100	2.22	13.29	7.326
226	125	1.47	6.76	6.760
230	150	1.32	4.54	4.788
232	150	1.34	4.32	4.678
235	150	1.33	3.28[3]	3.267
		Cyclo-hexane	Benzene	
209	45	10.28	31.23	3.146
211-2	45	10.28	31.20	3.141
214	65	6.35	18.43	3.076
217	65	6.21	17.66	3.132
220	100	2.72	6.63	2.738
223	100	2.63	6.43	2.759
225	100	2.57	6.24	2.748
228	125	1.65	3.55[4]	2.610
231	150	1.33	2.5	2.360
233	150	1.42	2.55	2.195

[3]The remaining phenol on the column vented during test runs 235 and 236.

[4]This peak was under a cyclohexane peak.

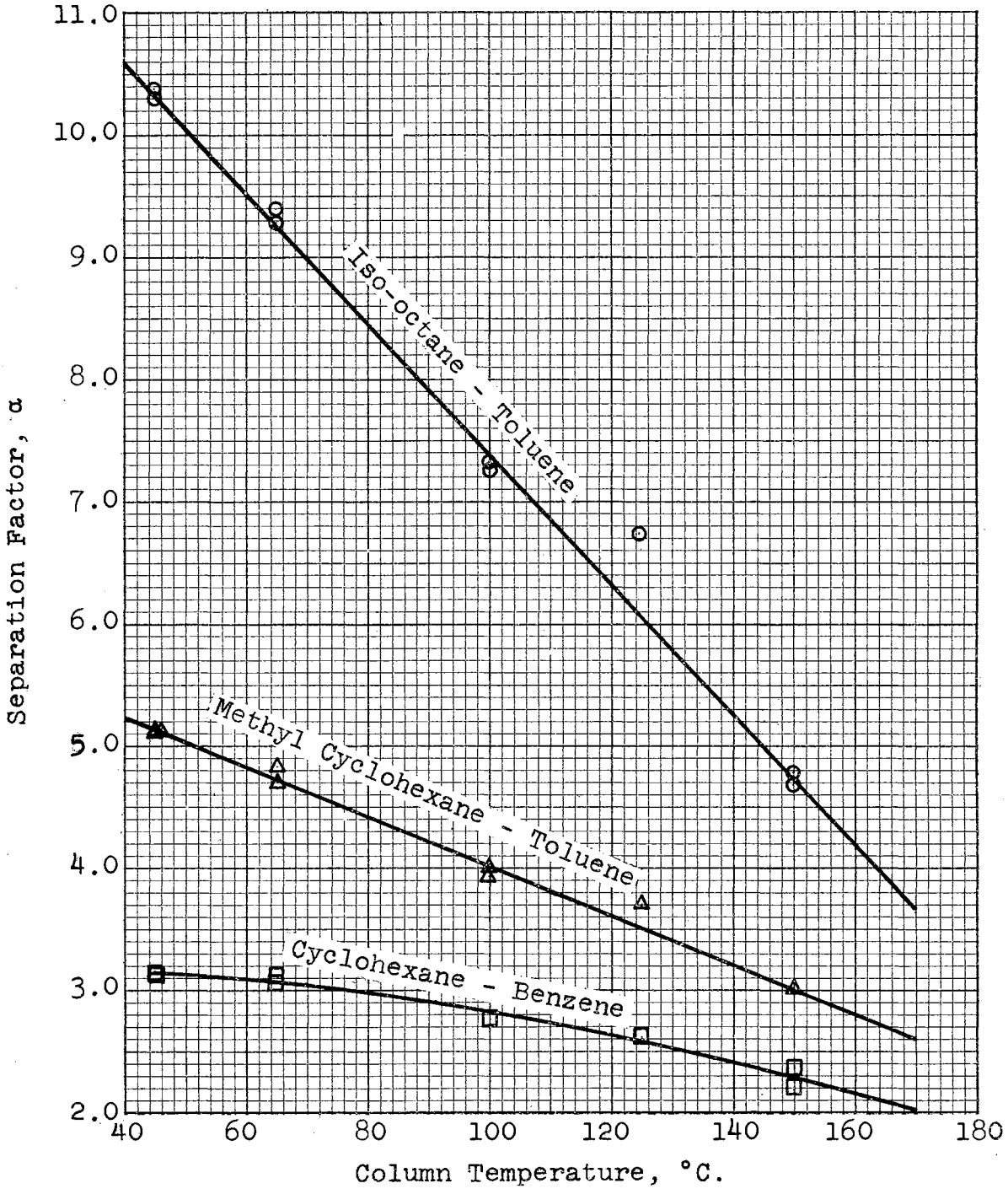


Figure 2 Separation Factor As A Function Of Temperature For Three Binary Systems

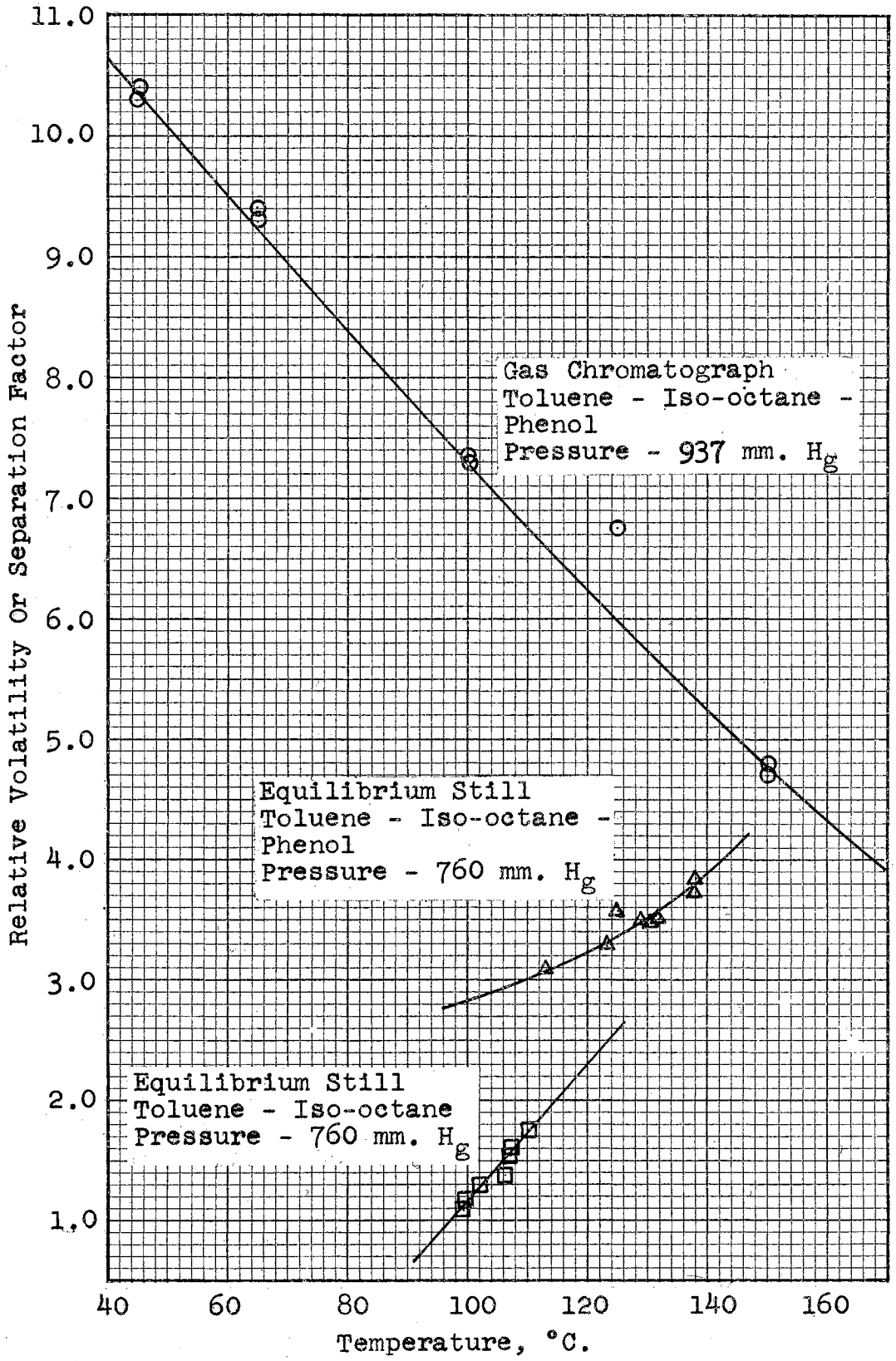


Figure 3 Vapor-Liquid Equilibria Comparison

Effect of Sample Composition on the Separation Factor

A series of runs was made using a four-foot long Apiezon L on Coarse Celite column to determine the effect of sample composition on the separation factors. The data presented on Table V indicate that sample composition had no effect. Several runs were also made when employing a phenol on a G-Cell packed column. Results of these runs are presented on Table VI. These runs indicate that the separation factors are a function of sample composition. This may have been caused by the venting of phenol from the column. In all cases, separation factors varied by approximately five per cent over a wide range of sample compositions.

Solvents Injected into Column Packing

The major effort in this research was to develop a technique for determining separation factor (relative volatility) data when using volatile extractive distillation solvents. The method proposed here is to inject the solvent into the column prior to the sample injections. This procedure would allow the use of standard chromatographic equipment.

Injecting Furfural into a Solvent-Free Column

A series of runs was made using the binary system benzene-cyclohexane. The furfural injections were made into a plain 60/80 mesh G-Cell packed column. The results of these

TABLE V

SEPARATION FACTOR AS A FUNCTION OF SAMPLE COMPOSITION

Chromatogram Data:

Column -	10-foot long by 0.25 inch O.D. 30 weight per cent Apiezon L on Perkin-Elmer Coarse Celite 2 grams per foot Temperature, 100°C. Inlet pressure, 1,364 mm. Hg Outlet pressure, 736 mm. Hg
Helium flow rate	50 cc. per minute
Temperature in soap film meter	23.5°C.
Air peak distance	0.5 inch
Chart speed	0.5 inch per minute
Sample volume	5 microliters

Run Number	Sample Weight Per Cent		Chromatogram Peak Distance, Inches		Separation Factor
	Methyl-cyclo-hexane	Toluene	Methyl-cyclo-hexane	Toluene	
265	19.82	80.18	6.83	8.75	1.303
268	19.82	80.18	6.82	8.73	1.302
266	49.877	50.123	6.80	8.69	1.300
269	49.877	50.123	6.81	8.69	1.298
267	80.293	19.707	6.82	8.68	1.294
270	80.293	19.707	6.82	8.70	1.297
	Methyl-cyclo-pentane	Benzene	Methyl-cyclo-pentane	Benzene	
271	9.0	91.0	3.30	3.97	1.239
274	9.0	91.0	3.30	3.97	1.239
272	49.99	50.01	3.30	3.98	1.243
275	49.99	50.01	3.30	4.00	1.250
273	78.87	21.13	3.27	4.08	1.292
276	78.87	21.13	3.29	4.12	1.297
	Cyclohexane		Benzene	Cyclohexane	
277	16.35	83.65	-	-	Peaked Together
280	16.35	83.65	-	-	" "
278	48.2	51.8	4.01	4.35	1.097
281	48.2	51.8	4.01	4.35	1.097
279	80.25	19.75	4.06	4.31	1.070
282	80.25	19.75	4.05	4.31	1.073

TABLE VI

EFFECT OF SAMPLE COMPOSITION AND COLUMN TEMPERATURE ON THE SEPARATION FACTOR

Chromatogram Data:

Column -	6-foot long by .25 inch O.D. 20.38 weight per cent phenol on 42/60 mesh firebrick, GC-22 Supersupport 25.1255 grams total weight in column Inlet pressure, 1,060 mm. Hg Outlet pressure, 750 mm. Hg Temperature of measured helium, 25°C.
Helium flow rate	50 cc. per minute at outlet conditions
Air peak distance	.59 inch
Chart speed	0.5 inch per minute
Sample volume	10 microliters

Sample Number	Column Temperature, °C.	Sample Weight Per Cent		Chromatogram Distance, Inches		Separation Factor
		Methylcyclohexane	Toluene	Methylcyclohexane	Toluene	
I	85	27.49	72.51	3.89	15.15	4.41
II	85	62.21	37.79	3.87	14.41	4.21
III	85	49.20	50.60	3.67	14.02	4.36

TABLE VI (Continued)

Sample Number	Column Temperature, °C.	Sample Weight Per Cent		Chromatogram Distance, Inches		Separation Factor
		2,2,4-trimethylpentane	Toluene	2,2,4-trimethylpentane	Toluene	
IV-a	85	50.276	49.724	1.97	11.47	7.88
V-a	85	33.209	66.791	1.85	10.70	8.02
VI-a	85	66.620	33.380	1.77	9.79	7.80
IV-b	95	50.276	49.724	1.33	6.41	7.86
V-b	95	33.209	66.791	1.33	6.15	7.51
VI-b	95	66.620	33.380	1.29	5.71	7.31

runs are given in Table VII and in Figure 4. The time between the furfural injections and the sample injections varied from 0 to 86 minutes. The separation factor was 1.0 for the solvent-free column, indicating that no separation was obtained. When 1,000 microliters of furfural were injected, the separation factors varied from 3.17 to 3.90, depending upon the sample injection time. The separation factors ranged from 2.5 to 3.875 for the injection of 400 microliters of furfural. The separation factors shown in Figure 4 had their highest value when a sample was injected shortly after the solvent injection. As indicated in Figure 4, the separation factors decreased rapidly after the major portion of the solvent had bled from the column.

Injecting Phenol into a Column of Apiezon L on Coarse Celite

An injection of 100 microliters of phenol was made into a four-foot long column of Apiezon L on Coarse Celite. The samples used for these runs were composed of toluene and methylcyclohexane. The results are shown in Table VIII and in Figure 5. A similar series of runs was made using 400 microliters of phenol. The results are shown in Table IX and in Figure 5. The separation factors varied from an Apiezon L base line of 1.319 to 1.445 for the 100 microliters of solvent injection. When 400 microliters were injected, the separation factors varied from 1.316 to 1.611. As shown in Figure 5, the separation factors rose sharply with time and then passed through a maximum after approximately fifty

TABLE VII

SEPARATION FACTOR AS A FUNCTION OF FURFURAL INJECTIONS

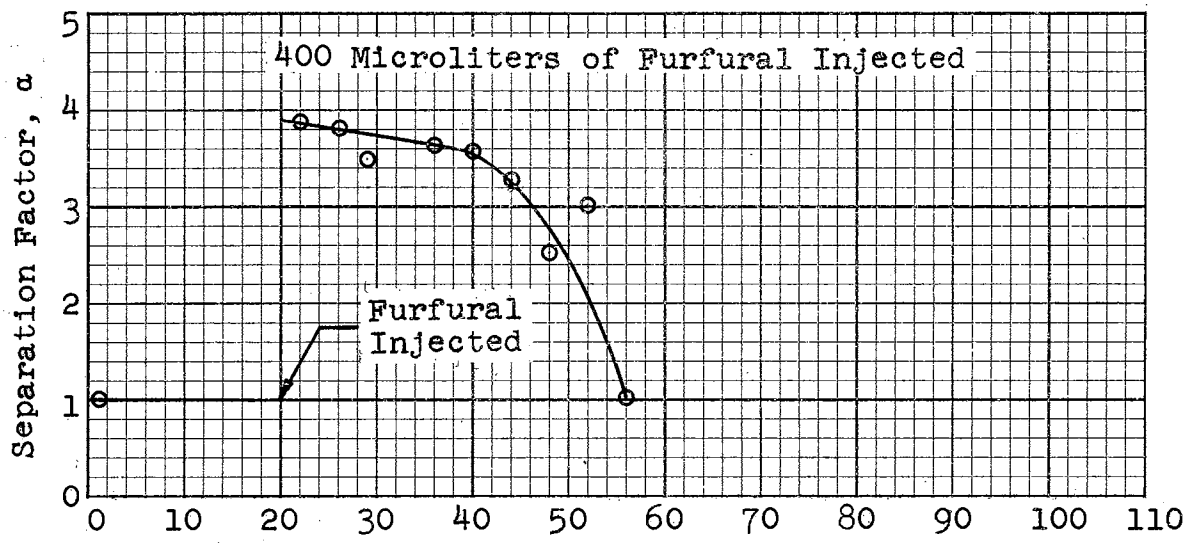
Chromatogram Data:

Column -	10-foot long by 0.25 inch O.D. Plain 60/80 mesh G-Cell 17.3 grams used in column Temperature, 100°C. Inlet pressure, 1,618 mm. Hg Outlet pressure, 749 mm. Hg
Helium flow rate	50 cc. per minute
Sample volume	5 microliters
Temperature in soap film meter	23.4
Sample composition	51.8 weight per cent benzene 48.2 weight per cent cyclohexane

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Distance, Inches		Air Peak Distance Inches	Separation Factor α
		Cyclohexane	Benzene		
237	0	.57	.57	.56	1.000
238	2	.57	.57	.56	1.000
239	4	.57	.57	-	1.000
	20	1,000 microliters of furfural injected			
240	21	1.04	2.17	.52	3.173
241	24	.97	2.18	-	3.666
242	29	1.05	2.20	-	3.170
243	35	.91	2.01	-	3.820
244	43	.89	1.85	-	3.595
245	48	.85	1.74	-	3.697
846	55	.82	1.60	-	3.600
247	60	.78	1.50	-	3.770
248	73	.70	1.22	.52	3.888
249	76	.68	1.14	.52	3.875
250	80	.67	1.09	.52	3.800
251	90	.62	.88	-	3.600
252	98	.57	.715	-	3.900
253	102	.55	.62	-	3.300
254	106	.54	.54	.54	1.000
255	0	.56	.56	-	1.000
	20	400 microliters of furfural injected			
256	21	.70	1.16	-	3.875
257	26	.68	1.10	.53	3.800

TABLE VII (Continued)

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Distance, Inches		Air Peak Distance Inches	Separation Factor
		Cyclohexane	Benzene		
258	29	.67	1.07	.51	3.500
259	36	.63	.95	-	3.666
260	40	.61	.87	-	3.600
261	44	.60	.80	-	3.222
262	48	.59	.71	-	2.500
263	52	.56	.64	.52	3.000
264	56	.52	.53	-	1.000



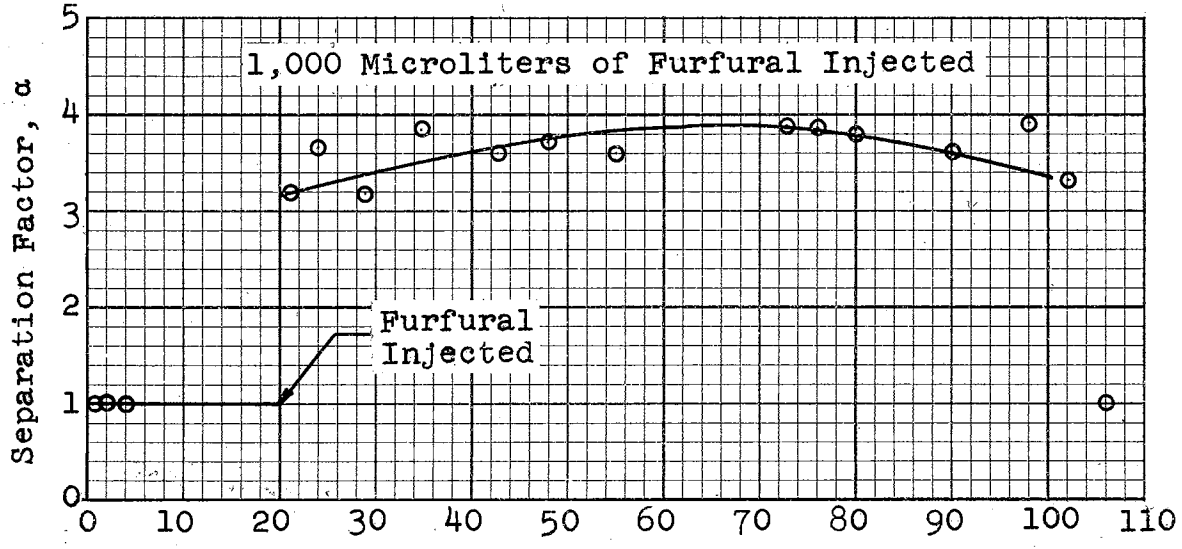


Figure 4 Separation Factor As A Function Of Time, Volume Of Furfural Solvent And Column Characteristics

TABLE VIII

EFFECT OF 100-MICROLITER PHENOL INJECTION ON THE SEPARATION FACTOR WHEN USING A FOUR-FOOT LONG COLUMN

Chromatogram Data:

Column -	4-foot long by .25 inch O.D. 30 weight per cent Apiezon L on Coarse Celite, 2 grams per foot Temperature, 100°C. Inlet pressure, 824 mm. Hg Outlet pressure, 736 mm. Hg
Helium flow rate	20 cc. per minute at outlet conditions
Phenol injection	100 microliters at 20-minute point
Temperature in soap film meter	23.5°C.
Air peak distance	0.390 inch
Chart speed	0.5 inch per minute
Sample composition	50.123 weight per cent toluene 49.877 weight per cent methylcyclohexane
Sample volume	5 microliters

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methylcyclohexane	Toluene		
188	0	5.19	6.72	1.319	-
189	5	5.185	6.72	1.320	-
190	10	5.16	6.72	1.327	-
191	21	5.45	7.26	1.358	No
192	29	5.39	7.40	1.402	No
193	39	5.39	7.58	1.438	No
194	49	5.40	7.63	1.445	No
195	59	5.39	7.56	1.434	Yes

TABLE VIII (Continued)

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methyl-cyclohexane	Toluene		
196	69	5.38	7.40	1.405	Yes
197	79	5.32	7.21	1.383	Yes
198	94	5.27	6.88	1.330	Yes
199	114	5.24	6.78	1.318	No
200	134	5.223	6.78	1.322	No

TABLE IX

EFFECT OF 400-MICROLITER PHENOL INJECTION ON THE SEPARATION FACTOR WHEN USING A FOUR-FOOT LONG COLUMN

Chromatogram Data:

Column -	4-foot long by .25 inch O.D. 30 weight per cent Apiezon L on Coarse Celite, 2 grams per foot Temperature, 100°C. Inlet pressure, 825 mm. Hg Outlet pressure, 737 mm. Hg
Helium flow rate	20 cc. per minute at outlet conditions
Phenol injection	400 microliters at 20-minute point
Temperature in soap film meter	25.4°C.
Air peak distance	0.385 inch
Chart speed	0.5 inch per minute
Sample composition	50.123 weight per cent toluene 49.877 weight per cent methylcyclohexane
Sample volume	5 microliters

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methylcyclohexane	Toluene		
168	0	5.10	6.605	1.319	-
169	5	5.105	6.610	1.319	-
170	15	5.125	6.625	1.316	-
171[5]	22	-	-	-	No

[5]Toluene peak under Run No. 172 methylcyclohexane peak.

TABLE IX (Continued)

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methyl-cyclohexane	Toluene		
172	27	5.78	8.46	1.497	No
173	36	5.87	9.07	1.583	No
174	46	5.92	9.28	1.607	No
175	56	5.84	9.17	1.610	Yes
176-a	66	5.78	9.08	1.611	Yes
176-b	80	5.73	8.98	1.608	Yes
177	95	5.70	8.84	1.591	Yes
178	110	5.65	8.69	1.577	Yes
179	125	5.62	8.51	1.552	Yes
180	140	5.54	8.30	1.535	Yes
181	155	5.47	8.006	1.499	Yes
182	170	5.37	7.61	1.449	Yes
183	185	5.26	7.20	1.398	Yes
184	200	5.18	6.81	1.340	Yes
185	215	5.17	6.68	1.316	Yes
186	231	5.14	6.66	1.320	No
187	245	5.14	6.66	1.320	No

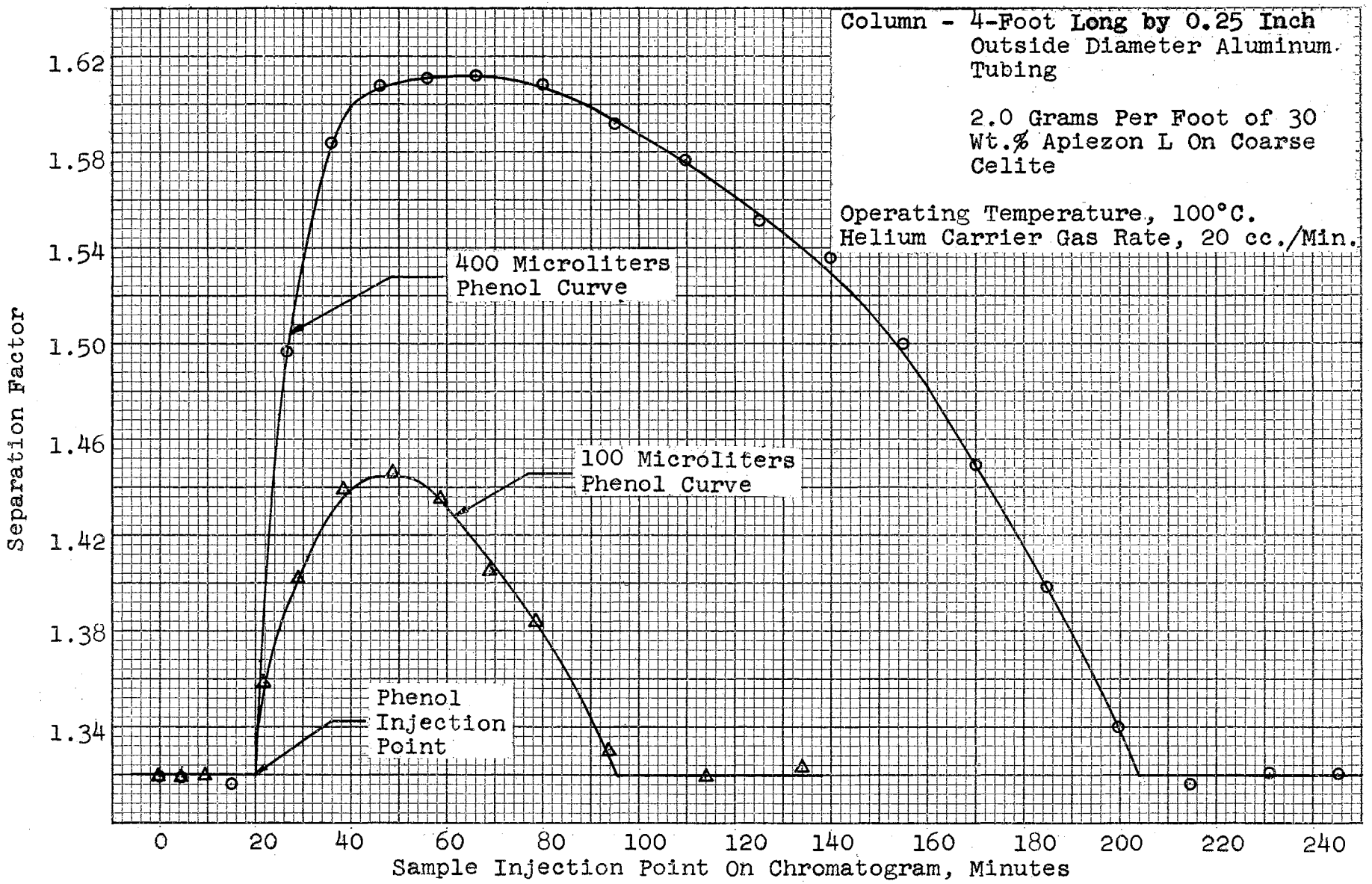


Figure 5 Separation Factor As A Function Of Time, Volume Of Phenol Solvent And Column Characteristics

minutes for the 100-microliter injection and approximately sixty minutes for the 400-microliter injection. Both runs dropped off to the Apiezon L separation factor of 1.316 after the solvent vented from the column. The conductivity cell thermisters gave no indication that any solvent was condensing in the cell. The gradual shifting of the base line was the only indication that solvent was leaving the column in each case during this research.

An extensive investigation was made to determine what effect the volume of the solvent injected would have on the separation factors. A ten-foot long column of Apiezon L liquid on Coarse Celite was employed. The volumes of the phenol solvent injections were 100, 400, 800, and 1,200 microliters. The results are presented in tables X, XI, XII, and XIII and in Figure 6. In all cases the separation factor was 1.305 for the Apiezon L liquid. The maximum values obtained for the phenol injections were 1.374 for 100 microliters, 1.488 for 400 microliters, 1.597 for 800 microliters, and 1.717 for 1,200 microliters.

The small difference between the 1.305 for the ten-foot column with 50 cc. per minute helium flow rate and the 1.316 for the four-foot long column with 20 cc. per minute helium flow rate indicated that the variation in length and flow rate compensated for each other.

Variation of maximum separation factor with volume of solvent injected is approximately linear, as shown in Figure 7, for the toluene-methylcyclohexane system when using an

TABLE X

SEPARATION FACTOR AS A FUNCTION OF A 100-MICROLITER PHENOL INJECTION WHEN USING A TEN-FOOT LONG COLUMN

Chromatogram Data:

Column -	10-foot long by .25 inch O.D. 30 weight per cent Apiezon L on Perkin-Elmer Coarse Celite, 2 grams per foot
Temperature	100°C.
Inlet pressure	1,383 mm. Hg
Outlet pressure	742 mm. Hg
Helium flow rate	50 cc. per minute at outlet conditions
Phenol injection	100 microliters at 20-minute point
Temperature in soap film meter	25°C.
Air peak distance	0.47 inch
Chart speed	0.5 inch per minute
Sample composition	50 weight per cent toluene 50 weight per cent methylcyclohexane
Sample volume	5 microliters

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methyl-cyclohexane	Toluene		
92	0	6.66	8.55	1.305	-
93	12	6.70	8.57	1.300	-
94	15	6.70	8.57	1.300	-
95	24	6.75	8.77	1.322	No
96	30	6.80	9.13	1.368	No
97	35	6.755	9.09	1.373	No
99	45	6.86	9.23	1.370	No
100	46	6.86	9.195	1.374	No

TABLE X (Continued)

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methyl-cyclohexane	Toluene		
102	55	6.82	9.04	1.350	No
103	63	6.82	8.98	1.340	Yes
104	76	6.78	8.75	1.312	Yes
105	102	6.77	8.625	1.294	Yes
106	112	6.72	8.58	1.298	Yes

TABLE XI

SEPARATION FACTOR AS A FUNCTION OF A 400-MICROLITER PHENOL INJECTION WHEN USING A TEN-FOOT LONG COLUMN

Chromatogram Data:

Column -	10-foot long by .25 inch O.D. 30 weight per cent Apiezon L on Perkin-Elmer Coarse Celite, 2 grams per foot Temperature, 100°C. Inlet pressure, 1,383 mm. Hg Outlet pressure, 742 mm. Hg
Helium flow rate	50 cc. per minute at outlet conditions
Phenol injection	400 microliters at 20-minute point
Temperature in soap film meter	25°C.
Air peak distance	0.47 inch
Chart speed	0.5 inch per minute
Sample composition	50 weight per cent toluene 50 weight per cent methylcyclohexane
Sample volume	5 microliters

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methylcyclohexane	Toluene		
107	21	7.02	9.78	1.420	No
109	29	7.01	9.99	1.456	No
110	36	7.065	10.15	1.466	No
111	45	7.14	10.32	1.475	No
113[6]	60	7.11	10.36	1.488	No
114	83	7.17	10.29	1.464	Yes

[6]A sample containing 79.7 weight per cent methylcyclohexane and 20.3 weight per cent toluene injected.

TABLE XII

SEPARATION FACTOR AS A FUNCTION OF AN 800-MICROLITER PHENOL INJECTION WHEN USING A TEN-FOOT LONG COLUMN

Chromatogram Data:

Column -	10-foot long by .25 inch O.D. 30 weight per cent Apiezon L on Perkin-Elmer Coarse Celite, 2 grams per foot Temperature, 100°C. Inlet pressure, 1,364 mm. Hg Outlet pressure, 733 mm. Hg
Helium flow rate	50 cc. per minute at outlet conditions
Phenol injection	800 microliters at 20-minute point
Temperature in soap film meter	25°C.
Air peak distance	0.49 inch
Chart speed	0.5 inch per minute
Sample composition	50 weight per cent toluene 50 weight per cent methylcyclohexane
Sample volume	5 microliters

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methyl-cyclohexane	Toluene		
117	0	6.85	8.75	1.299	-
118	11	6.84	8.75	1.301	-
119	15	6.85	8.75	1.299	-
123	30	7.58	11.66	1.575	No
124	40	7.61	11.86	1.597	No
125	50	7.64	11.91	1.597	No
126	60	7.68	11.97	1.597	No
127	70	7.66	11.94	1.597	Yes

TABLE XII (Continued)

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methylcyclohexane	Toluene		
129	90	7.63	11.74	1.578	Yes
130	100	7.61	11.64	1.566	Yes
131	111	7.58	11.51	1.554	Yes
132	124	7.54	11.34	1.539	Yes
133	138	7.49	11.14	1.521	Yes
134	154	7.43	10.89	1.499	Yes
135[7]	166	7.38	10.64	1.473	Yes
136	178	7.33	10.52	1.466	Yes
137	190	7.245	10.17	1.433	Yes
138	202	7.145	9.81	1.400	Yes
139	220	6.99	9.31	1.357	Yes
140	236	6.90	8.87	1.307	Yes
142	253	6.83	8.73	1.300	No
143	256	6.83	8.73	1.300	No
144	259	6.83	8.73	1.300	No

[7]A sample containing 79.7 weight per cent methylcyclohexane and 20.3 weight per cent toluene injected as a special test.

TABLE XIII

SEPARATION FACTOR AS A FUNCTION OF A 1,200-MICROLITER PHENOL INJECTION WHEN USING A TEN-FOOT LONG COLUMN

Chromatogram Data:

Column -	10-foot long by .25 inch O.D. 30 weight per cent Apiezon L on Perkin-Elmer Coarse Celite, 2 grams per foot Temperature, 100°C. Inlet pressure, 1,363 mm. Hg Outlet pressure, 735 mm. Hg
Helium flow rate	50 cc. per minute at outlet conditions
Phenol injection	1,200 microliters at 20-minute point
Temperature in soap film meter	24°C.
Air peak distance	0.49 inch
Chart speed	0.5 inch per minute
Sample composition	50 weight per cent toluene 50 weight per cent methylcyclohexane
Sample volume	5 microliters

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methyl-cyclohexane	Toluene		
145	0	6.89	8.82	1.302	-
146	12	6.88	8.81	1.302	-
147	17	6.875	8.775	1.298	-
149	30	8.15	13.16	1.654	No
150	45	7.90	13.21	1.717	No
151	60	8.02	13.35	1.708	No
152	102	8.17	13.15	1.648	Yes
153	118	7.89	12.80	1.664	Yes

TABLE XIII (Continued)

Run Number	Sample Injection Point on Chromatogram Minutes	Chromatogram Peak Distance, Inches		Separation Factor	Phenol Leaving Column When Sample Injected
		Methyl-cyclohexane	Toluene		
154	148	7.78	12.34	1.626	Yes
155	178	7.69	11.85	1.578	Yes
156	208	7.54	11.35	1.540	Yes
157	238	7.43	10.84	1.491	Yes
158	269	7.23	10.14	1.432	Yes
159	298	7.02	9.27	1.345	Yes
160	328	6.86	8.76	1.298	Yes
161	338	6.84	8.74	1.299	No
162	348	6.87	8.77	1.298	No

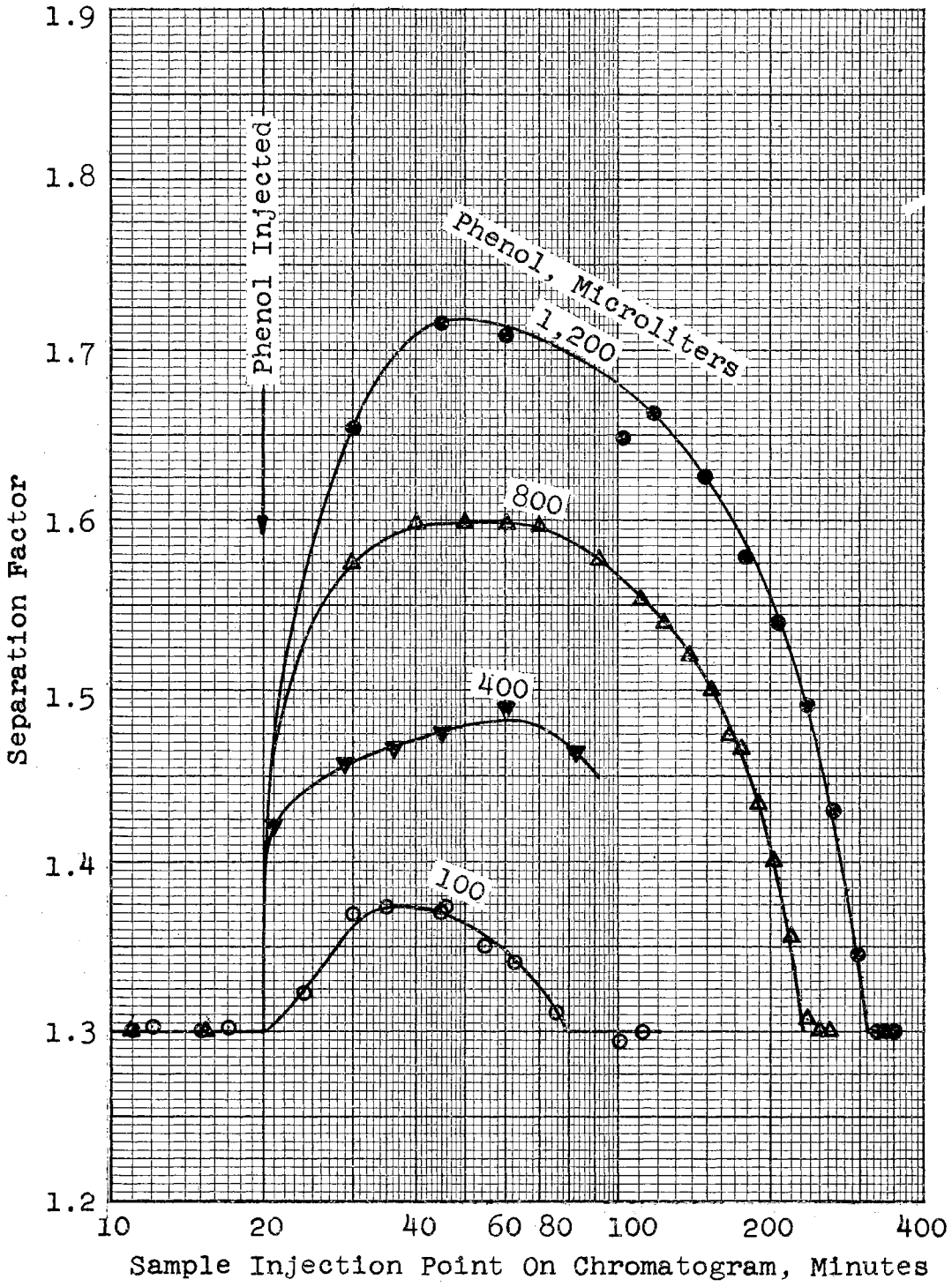


Figure 6 Separation Factor As A Function Of Time, Volume Of Phenol Solvent And Column Characteristics

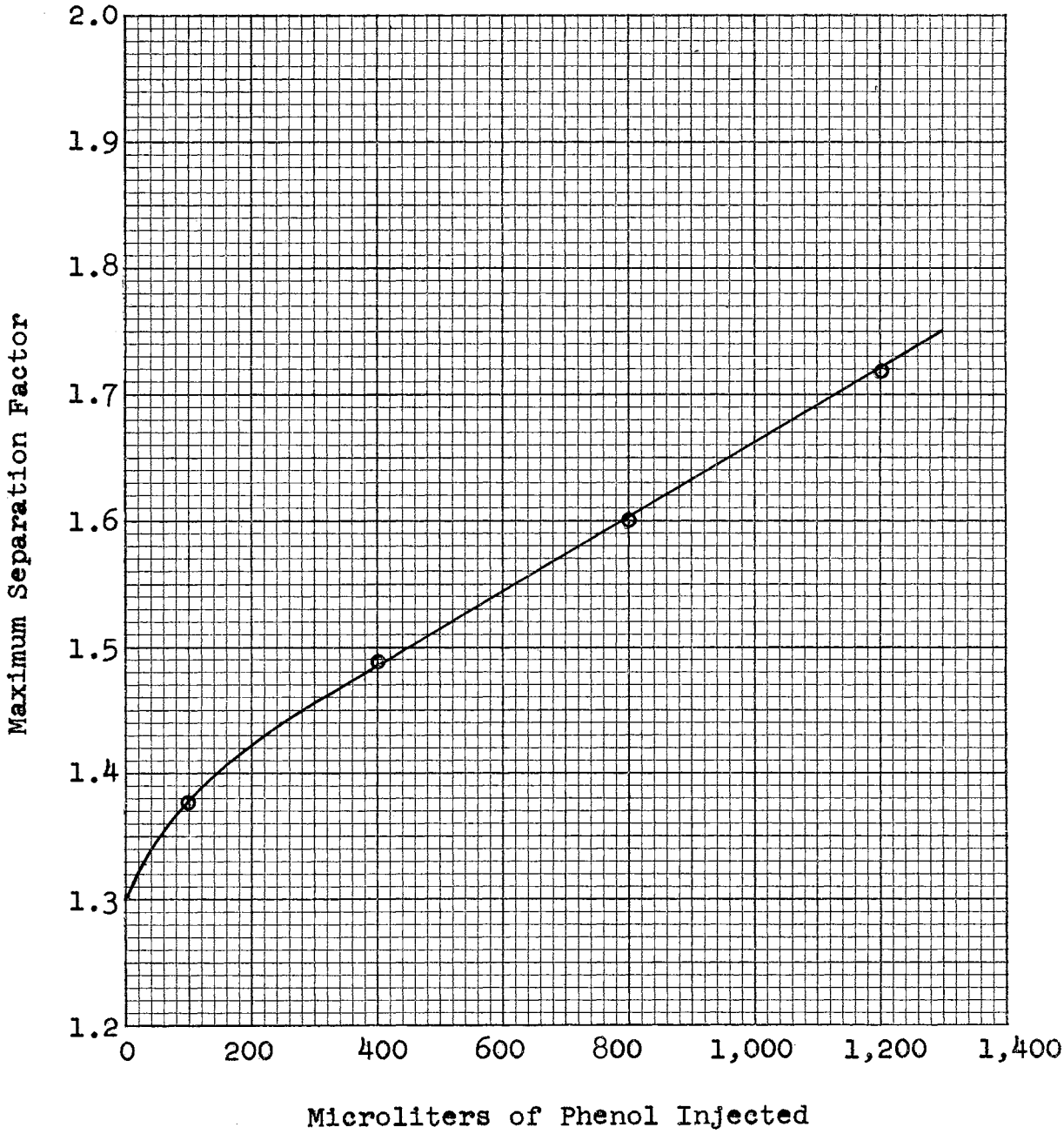


Figure 7 Maximum Separation Factor As A Function Of The Volume Of Phenol Solvent

Apiezon L liquid on Coarse Celite. It can also be noted that, when injecting solvent into a solvent-free column with a benzene-cyclohexane system, there was essentially no variation in the maximum separation factors with injected solvent size. The results are mentioned above and are presented in figures 4, 5, and 6.

The curve for the plain column in Figure 4 rises immediately to the maximum separation factor, while the curve for the column of Apiezon L on Coarse Celite rises slowly to a maximum and then starts decreasing. The influence of the Apiezon L partitioning liquid appears to be of no practical value and, in fact, seems to have an undesirable effect. The solvent injection technique works best with a plain column.

Vapor liquid equilibrium data for the phenol-toluene-methylcyclohexane system at high phenol concentrations are available in the 1945 Transactions of the American Institute of Chemical Engineers (4).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Restatement of Thesis Goals

The specific goal of this research was to determine if a technique could be developed whereby vapor-liquid equilibrium data could be obtained for extractive distillation systems when using volatile solvents and standard gas chromatography equipment. The objectives were:

A. Preliminary Investigations
   1. Determine the reproducibility of the separation factors calculated from gas chromatographic data.
   2. Determine if azeotropic compositions exist in the field of gas chromatography.
   3. Investigate the influence of temperature on the separation factor when the solute is at infinite dilution in the solvent phase.
   4. Determine the effect of sample composition on the separation factor.

B. Solvent Injection

1. Obtain separation factors for a binary sample when injecting different volumes of solvent into a column which does not have liquid on the packing.
2. Obtain separation factors for binary samples when injecting different volumes of solvent into a column which already has a partitioning liquid on the packing.

Conclusions

Based upon the information presented herein, it can be concluded that a new technique has been presented which, upon further development, can be used to obtain vapor-liquid equilibrium data for extractive distillation systems. This technique employs volatile solvents and standard chromatographic equipment. Since data were taken on only a limited number of systems, more experimental work will be necessary before the technique can be considered to be fully established.

This technique would be particularly useful in evaluating the relative merits of different solvents. For example, if you were required to find a solvent to be used in a commercial process unit to separate a binary mixture, this technique would help determine which solvent to use. Equilibrium still data would then be obtained, using only the best solvent.

The procedure for the new method is as follows:

1. Pack a 10-foot long by 0.25-inch outside diameter column with an inert packing material, such as diatomaceous earth. Place column in chromatograph.
2. Adjust the operating variables to the desired values.
3. Inject a minimum of 400 microliters of solvent into the carrier gas stream in the column.
4. Inject samples at intervals so that a curve may be obtained of separation factor versus time. This graph should be constructed similar to Figure 4.
5. The useful separation factor can then be easily obtained from the maximum point on the curve. The curve will reach a level maximum separation factor value, depending upon the amount of solvent injected.

To apply this technique, it will be necessary to determine experimentally the effect of sample volume, sample injection delay time, and several other gas chromatographic variables. As our understanding of the operation of chromatographic columns increases, it may become possible to calculate these effects from theoretical considerations. In

addition, a very important relationship which must be established is the correspondence between solvent injection quantity and the mole fraction in the equilibrium still. Eventually, when the chromatographic method has been refined, it will be possible to get all the information directly from this method without doing any equilibrium still distillation work.

Recommendations

Studying nonideal systems when using a volatile solvent might be simplified by passing the solvent continuously through the column with the carrier gas. This could be accomplished by passing the helium over hot solvent. The concentration of the solvent in the carrier gas could then be controlled by means of its temperature. The amount of solvent in the carrier gas could be indicated by a shift in the base line on the recording strip chart. Heating tape could be wrapped around the lines leading to the column to avoid condensation of the solvent.

The amount of solvent in the column could also be controlled by injecting the solvent into the column at frequent intervals.

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APPENDIX A

LIST OF NOMENCLATURE

A - Velocity-independent constant of random flow pattern in a packed column

B - Coefficient of axial or longitudinal diffusion in gas phase

C - Coefficient of resistance to mass transfer in liquid phase

D - Coefficient of resistance to mass transfer in moving gas phase

D_g - Diffusion coefficient of sample into carrier gas

D_L - Molecular diffusivity in liquid

d - Distance from the injection point to the middle of the component peak

d_f - Statistical average of the liquid film thickness

d_p - Particle diameter

d_m - Effective moving-gas diffusional path length

d_s - Effective stagnant-gas diffusional path length

Δd - Peak width measured on the base line by the intersection of tangents at the points of inflection to the component curve

E - Coefficient of relatively stagnant gas within column packing

F - Separation factor

F_c - Flow rate of carrier gas corrected to column temperature and outlet pressure

H° - Partition coefficient at infinite dilution, equals amount of solute per unit volume of stationary liquid phase divided by amount of solute per unit volume of moving phase

HETP - Height equivalent to a theoretical plate

k' - Effect of changing the distribution ratio = $H^{\circ}(X/Y)$

L - Effective length of column packing

M_s - Reciprocal molar volume of the solvent

n - Number of theoretical plates

P° - Vapor pressure

P_{in} - Column inlet pressure

P_{out} - Column outlet pressure

PI - Performance index

ΔP - Pressure drop across column

p° - Partial pressure

R - Gas constant

S_{ax} - Relative separation of sample peak from air peak = $(d_i - d_a)/d_a$

T - Temperature

u - Carrier gas velocity

V_a - Uncorrected retention volume for a nonabsorbed gas

V_a° - Corrected retention volume for a nonabsorbed gas

V_L - Volume occupied by the liquid phase in the column at the temperature of the column

V_R - Uncorrected retention volume, carrier gas which passes through the column between the time the sample is injected and the peak maximum occurs

V_R° - Corrected retention volume

X - Volume fraction of sample in liquid phase

x - Mole fraction of a component in liquid

Y - Volume fraction of sample in gas phase

y - Mole fraction of a component in vapor

α - Separation factor or relative volatility

γ - Activity coefficient

γ° - Activity coefficient of the solute at infinite dilution in the solvent

$\bar{\gamma}$ - Tortuosity of the packing

θ - Time elapsed between injection of sample and emergence of peak maximum

λ - Measure of packing irregularities

Subscripts

a - Inert gas, usually air

i - Component i

o - Column outlet

1,2 - Components numbered one and two

APPENDIX B

SAMPLE CALCULATION

Determine the separation factor, α, for a sample composed of 50 weight per cent toluene and 50 weight per cent methylcyclohexane.

Operating Conditions: Same as Table X

Step 1. Determine the distances on the chromatogram from the injection point to the middle of the component peak for air, methylcyclohexane, and toluene.

Air	$d_a = .49$ inch
Methylcyclohexane	$d_1 = 7.63$ inches
Toluene	$d_2 = 11.74$ inches

Step 2. Calculate the separation factor by employing Equation (11).

$$\alpha_{1,2} = \frac{d_2 - d_a}{d_1 - d_a}$$

$$\alpha_{1,2} = \frac{11.74 - .49}{7.63 - .49}$$

$$\alpha_{1,2} = 1.578$$

VITA

Meredith Ray Sheets

Candidate for the Degree of

Master of Science

Thesis: USE OF SOLVENT INJECTION CHROMATOGRAPHY FOR EVALUATING EXTRACTIVE DISTILLATION SYSTEMS

Major Field: Chemical Engineering

Biographical:

Personal data: Born in Geary, Oklahoma, September 2, 1930, the son of Harry G. and Addie E. Sheets; married to Ladona A. Coldiron, Oklahoma City, Oklahoma, in September, 1955.

Education: Attended grade school in El Reno and high school in Lawton, Oklahoma; graduated from Lawton High School in May 1949; attended Cameron State Agricultural College, Lawton, Oklahoma, 1949 to 1950; attended the University of Oklahoma, Norman, Oklahoma, 1952 to 1955; received the degree of Bachelor of Science in Chemical Engineering, May, 1955; completed the requirements for the Master of Science degree in May, 1962.

Professional experience: Employed as a Process Engineer in the Continental Oil Company Refinery at Ponca City, Oklahoma, 1955 to present; employed as a Process Engineer in the Process Center, 1955 to 1957; employed as a Division Process Engineer, 1957 to present.