TECHNICAL DEVELOPMENT

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USE OF 20% SE-30 ON CHROMOSORB P-AW-DMCS, 60/80 MESH, FOR SEPARATION OF n-ALKANES (C_6 - C_{17}), 1-ALKENES (C_5 - C_{10}), AROMATICS (BENZENE AND MONOSUBSTITUTED n-ALKYL (C_1 - C_{10}) BENZENES)

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Abstract

The 20% SE-30 on Chromosorb P-AW-DMCS, 60/80 mesh as a column packing in six feet, ¼" O.D. glass column at the optimum conditions, i.e., temperature programmed between 60°C - 300°C, detector temperature 310°C, injection port temperature 320°C, helium carrier gas flow rate 65 ml/minute, flow ratio of H_2 *: He : Air, 1 : 2 : 7 and dual flame ionization detector gave baseline separation of n-alkanes (*C_6 *-* C_{17}*), 1-alkenes (*C_5 *-* C_{10}*) and aromatics (benzene and monosubstituted n-alkyl (*C_1 *-* C_{10}*) benzene). The separation of the hydrocarbon mixture of n-alkanes (*C_6 *-* C_{17}*), 1-alkenes (*C_5 *-* C_{10}*) and aromatics (benzene and monosubstituted n-alkyl (*C_1 *-* C_{10}*) benzene) also can be achieved from this column.*

Introduction

Gas-liquid chromatography have been used for hydrocarbon separation since Janini *et al.*[1] applied the liquid crystal technology to chromatographic separation and McWilliams and Dewar[2,3] introduced the flame ionization detection method for hydrocarbons. Vigalok *et al.*[4] and Kuchhal *et al.*[5] worked with cyanoethylated polyols for the selective retention of aromatics. A comparison between poly (m-phenyl ether) and methyl silicones for the high temperature analysis of higher alkanes[6] was also reported. Boksanyi and Kovats[7] introduced a synthetic C_{87} hydrocarbon phase. Banerjee *et al.*[8] evaluated 3-isoalkoxypropionitriles as a liquid phase for the analysis of light hydrocarbons. Millen and Hawkes[9] studied the diffusion of linear alkanes in methyl silicone stationary phases. A direct analysis method for non-reactive hydrocarbon in air was described by Black *et al.*[10], and Cudney *et al.*[11] described a rapid gas chromatographic method of analysis for C_2 - C_6 alkanes and alkenes in air. In the petroleum industry most analyses use capillary column[12], Rang *et al.*[13] have used the capillary gas chromatographic technique to separate C_6 - C_{14} alkanes on polyphenyl ether. Sojak and Krupcik[14] used carbowax 20 M as a stationary phase in 300 m glass capillary column at temperature below its lower temperature limit (60°C) to analyses of isomeric C_{10} - C_{13} n-alkanes. Analysis of hydrocarbon fraction has been made by using a combination of a fused silica capillary gas chromatography and microcomputer to obtain resolution of the four basic hydrocarbon groups: paraffins, olefins, napthenes and aromatics.[15]

Usually the separation of hydrocarbons are achieved by capillary column GC, but in this investigation we could achieve the separation of hydrocarbons, i.e., n-alkanes (C_6 - C_{17}), 1-alkenes (C_5 - C_{10}) and aromatics (benzene and monosubstituted n-alkyl (C_1 - C_{10}) benzenes) on packed column GC. by using a suitable column packing at optimum conditions.

Experimental

A. Equipment

All gas-liquid chromatographic analyses were performed on a Hewlett Packard, F and M, High Efficiency Gas Chromatograph, Model 402 equipped with dual columns and dual Flame Ionization Detectors (FID). The data was collected by H-P 3380 integrator.

1.0 microliter needle sluger wire syringes model 7101 N from Hamilton Company, Reno, Nevada was used for taking samples for gas chromatographic analysis.

A 0.10 ml (100 microliter) COREX® measuring pipet was used to pipet standard hydrocarbon to make the standard mixtures from Fisher Scientific Company, Pittsburgh, Pennsylvania.

The gas chromatographic column was 6 feet by 0.25 inch O.D. U-shaped glass columns for FID analyses.

The SE-30 liquid phase was available from Supelco, Inc., Supelco Park Bellefonte, Pa.

Solid support Chromosorb P-AW-DMCS 60-80 mesh was purchased from Supelco, Inc., Supelco Park, Bellefonte, Pa., 5% SE-30 on Chromosorb W-AW 80/100 mesh and 10% OV-101 on Chromosorb W-HP 80/100 mesh were supplied from Alltech Associates, Inc., Avondale, Pa.

B. Chemicals

All the n-alkanes (C_6 - C_{17}), 1-alkenes (C_5 - C_{10}) standards were chromatographic grade (99.6 + % pure) and obtained from Poly Science Corporation, Illinois.

Standard aromatic hydrocarbons, i.e., benzene, toluene, ethylbenzene, and propylbenzene were supplied from Chem. Service, Inc., West Chester, Pennsylvania. Butylbenzene, hexylbenzene, and decylbenzene were supplied from Poly Science Corporation, Niles, Illinois. Amylbenzene, heptylbenzene and nonylbenzene were obtained from Alfa Products, Danvers, Massachusetts.

The methylene chloride solvent used was UV spectrophotometric grade supplied from J.T. Baker Chemical Co., Phillipsbury, New Jersey.

C. Procedure

Preparation of Gas Chromatographic Column Packing, 20% SE-30 on Chromosorb P-AW-DMCS 60-80 Mesh.

The slurry technique was used for the preparation. 25.0 grams of liquid phase, SE-30, was dissolved in 450.0 ml chloroform. After all the SE-30 was dissolved one slowly pours 100.0 grams of Chromosorb P-AW-DMCS 60-80 mesh into the solution and resulting slurry was well stirred. The slurry was then transferred to an evaporation dish and air dried. Resulting packing, 20% SE-30 on Chromosorb P-AW-DMCS 60-80 mesh was stored in a clean dry bottle with a screw cap.

Preparation of Standard Hydrocarbon Mixtures

400 parts per million mixtures of n-alkanes (C_6 - C_{17}), 1-alkenes (C_5 - C_{10}) and aromatic (Bezene and alkyl (C_1 - C_{10}) bezene) were made by pipeting 0.10 ml of each hydrocarbon in the series transferred to a 250.0 ml volumetric flask. Each flask was filled to the mark with methylene chloride solvent and mixed well. The stopper of each volumetric flask wrapped with Teflon® tape, and kept in the refrigerator.

An equal amount of each hydrocarbon serie, i.e., n-alkanes (C_6-C_{17}), 1-alkenes (C_5-C_{10}) and aromatic (benzene, n-alkyl (C_1-C_{10}) benzene) was well mixed and wrapped the stopper with Teflon® tape.

Qualitative and Quantitative Analysis

Four column packings, i.e., 20% SE-30 on Chromosorb P-AW-DMCS 60/80 mesh, 10% TCEP on Chromosorb P-AW 100/120 mesh, 5% SE-30 on Chromosorb W-AW 80/100 mesh, and 10% OV-101 on Chromosorb W-HP 80/100 mesh were used to optimize the gas chromatographic conditions for the hydrocarbons. The 20% SE-30 on Chromosorb P-AW-DMCS 60/80 mesh was found to be the suitable column packing.

The optimum carrier gas flow rate was obtained by van Deemter plot, i.e., height equivalent to theoretical plate versus linear gas velocity of n-nonane (representative hydrocarbon compound). A plot of the HETP versus carrier gas flow rate is shown in Figure 1.

The flow ratio between the hydrogen, carrier gas, and air was adjusted until the maximum response was obtained.

The optimum temperature was obtained by separating each component of all three individual hydrocarbon series.

The optimum gas chromatographic conditions for these hydrocarbon series for flame ionization detection are shown in Table 1.

TABLE 1. THE OPTIMUM GAS CHROMATOGRAPHIC CONDITIONS FOR FID

Gas Chromatograph	H-P 402 equiped with FID.
Data Collector	H-P 3380 A Integrator.
Column	6 ft., ¼" O.D. Glass column packed with 20% SE-30 on Chromosorb P-AW-DMCS, 60/80 mesh.
Column Temperature	Temperature programmed between 60 - 300°C at a rate of 7.5°C per minute.
Injection Port Temperature	320°C.
Detector Temperature	310°C.
Helium Carrier Gas Flow Rate	65 ml/minute.
Flow Ratio of H_2 : He : Air	1 : 2 : 7

Results and Discussion

The analytical gas chromatographic column packing produced a good separation of the hydrocarbon mixtures studied, i.e., n-alkanes (C_6 - C_{17}), 1-alkenes (C_5 - C_{10}), and aromatics (benzene, n-alkyl (C_1 - C_{10}) benzenes). Four column packings were used, i.e., 10% TCEP (1, 2, 3-tris) 2-cyanoethoxy (propane) on Chromosorb P-AW 100/120 mesh, 5% SE-30 on Chromosorb W-AW 80/100 mesh and 10% OV-101 on Chromosorb W-HP 80/100 mesh, and the most suitable column packing for this hydrocarbons was 20% SE-30 on Chromosorb P-AW-DMCS, 60/80 mesh. This column packing was chosen over other column packings because it can be used at high temperature and gave satisfactory baseline resolution for all three series of hydrocarbon that were used

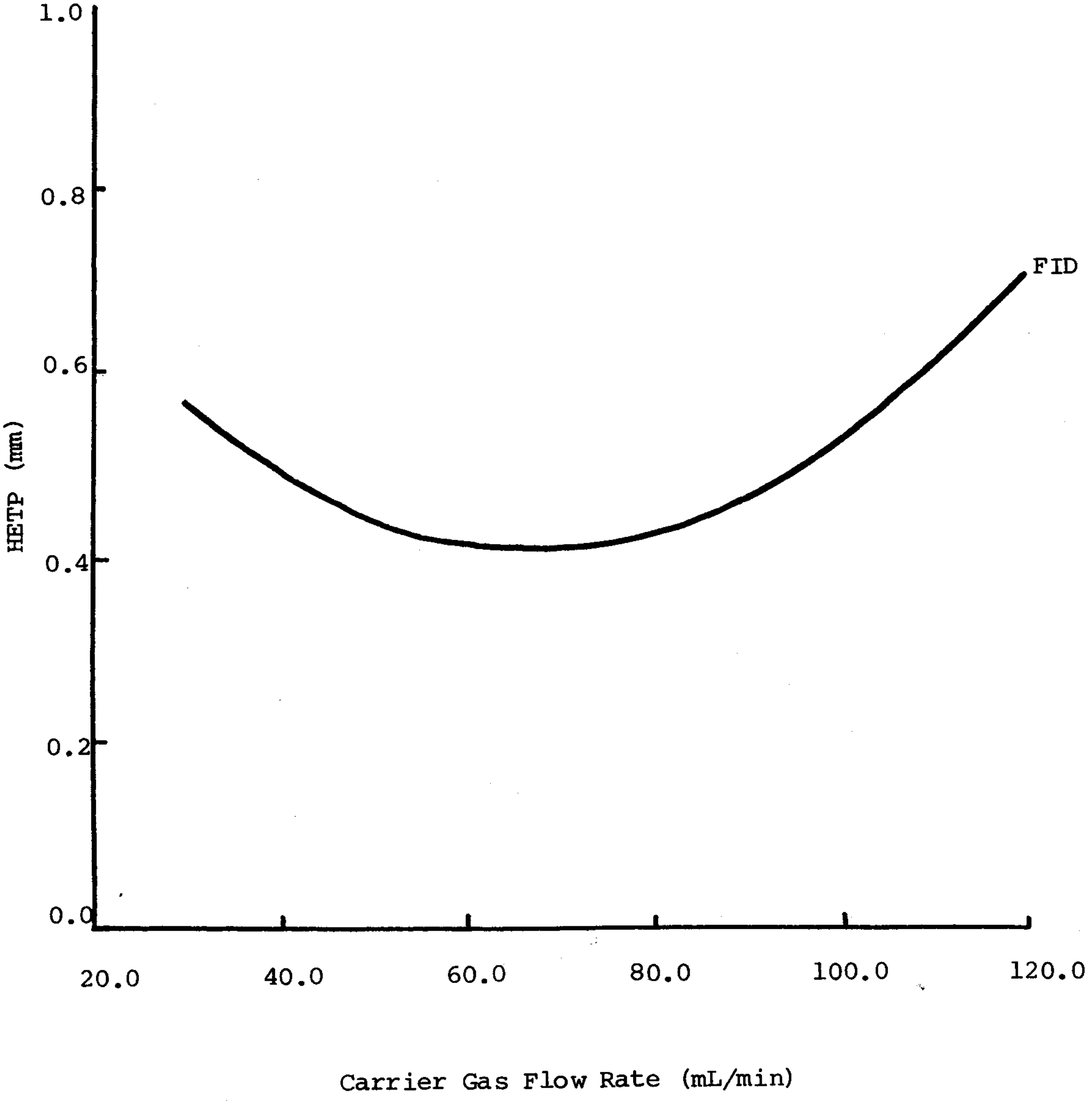


Fig. 1. van Deemter plot

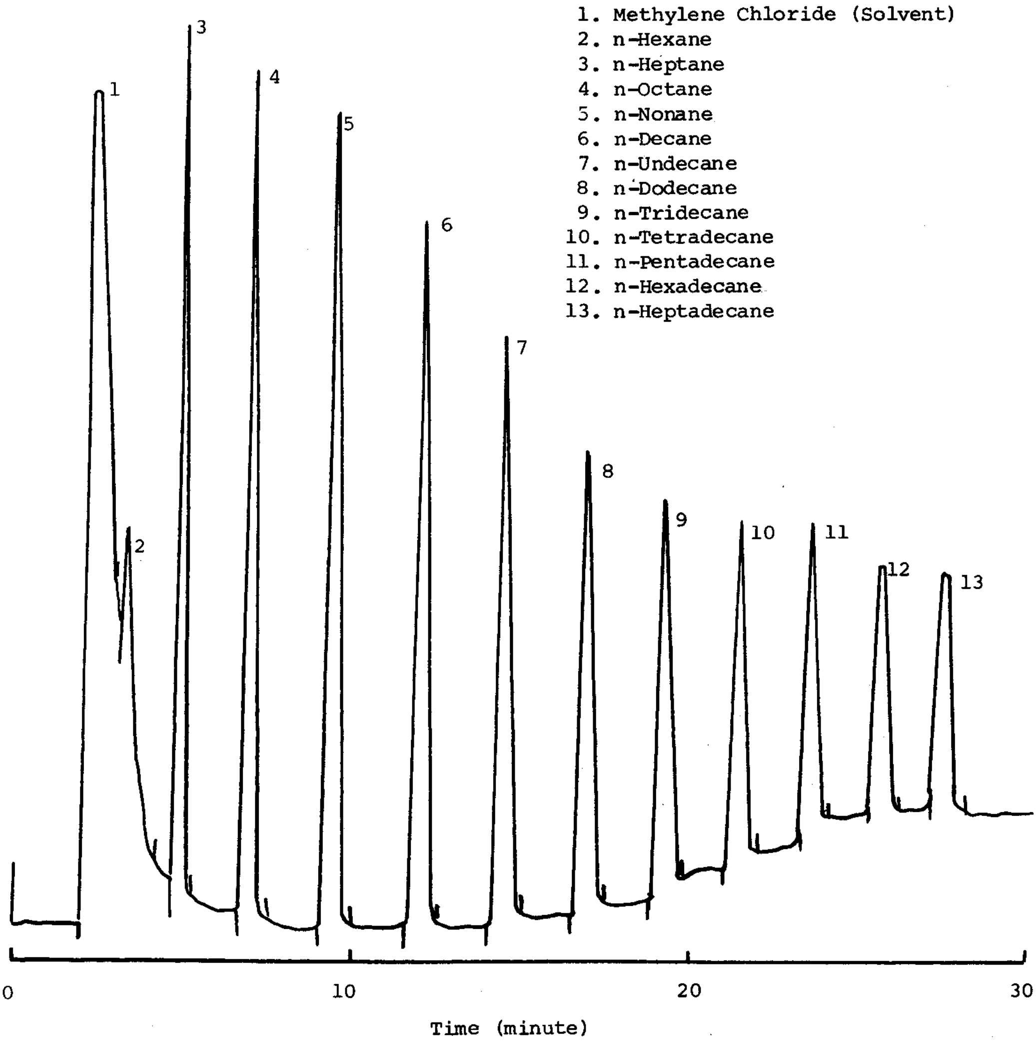


Fig. 2. Chromatogram of standard n-alkanes (C_6 - C_{17})mixture

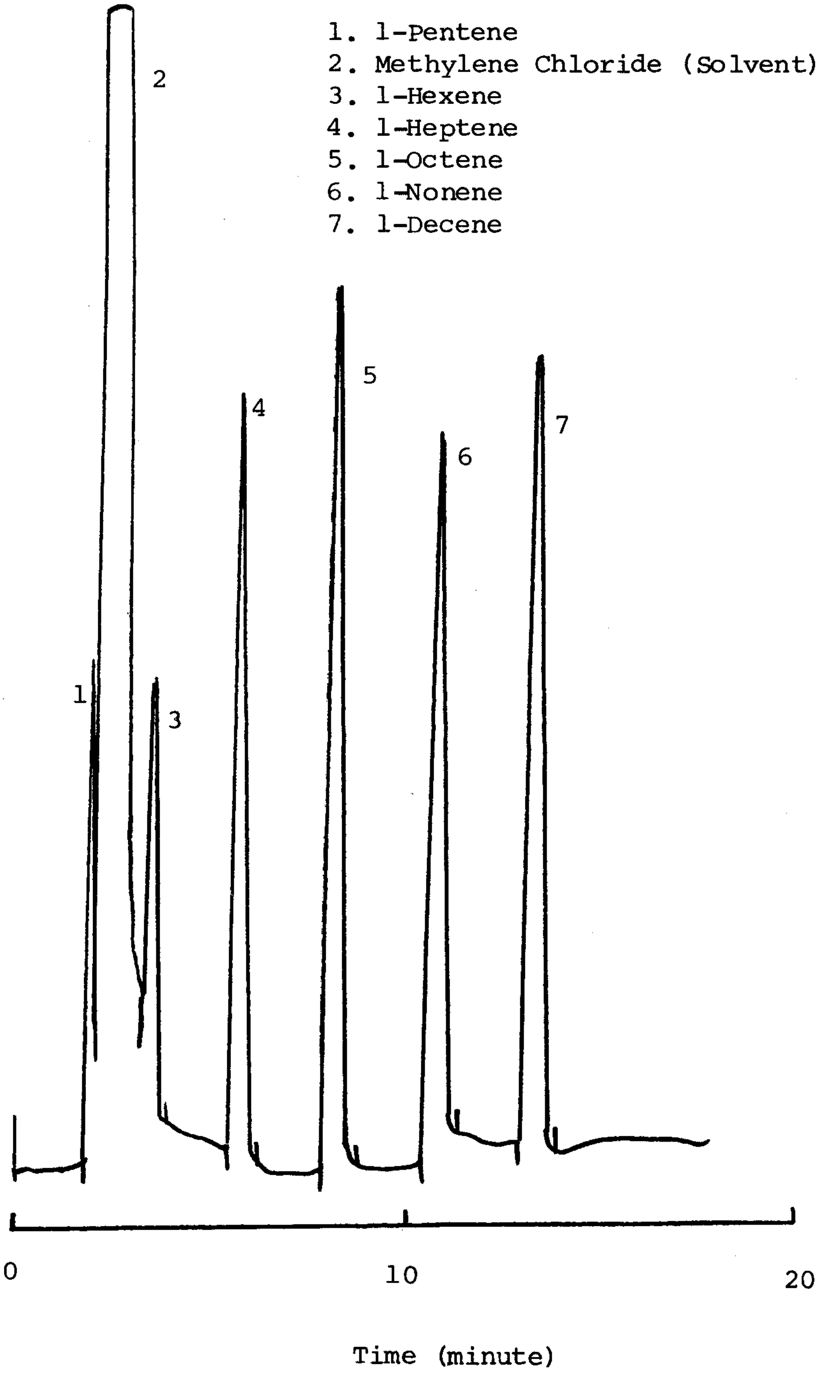


Fig. 3. Chromatogram of standard 1-alkenes (C_5 - C_{10})mixture

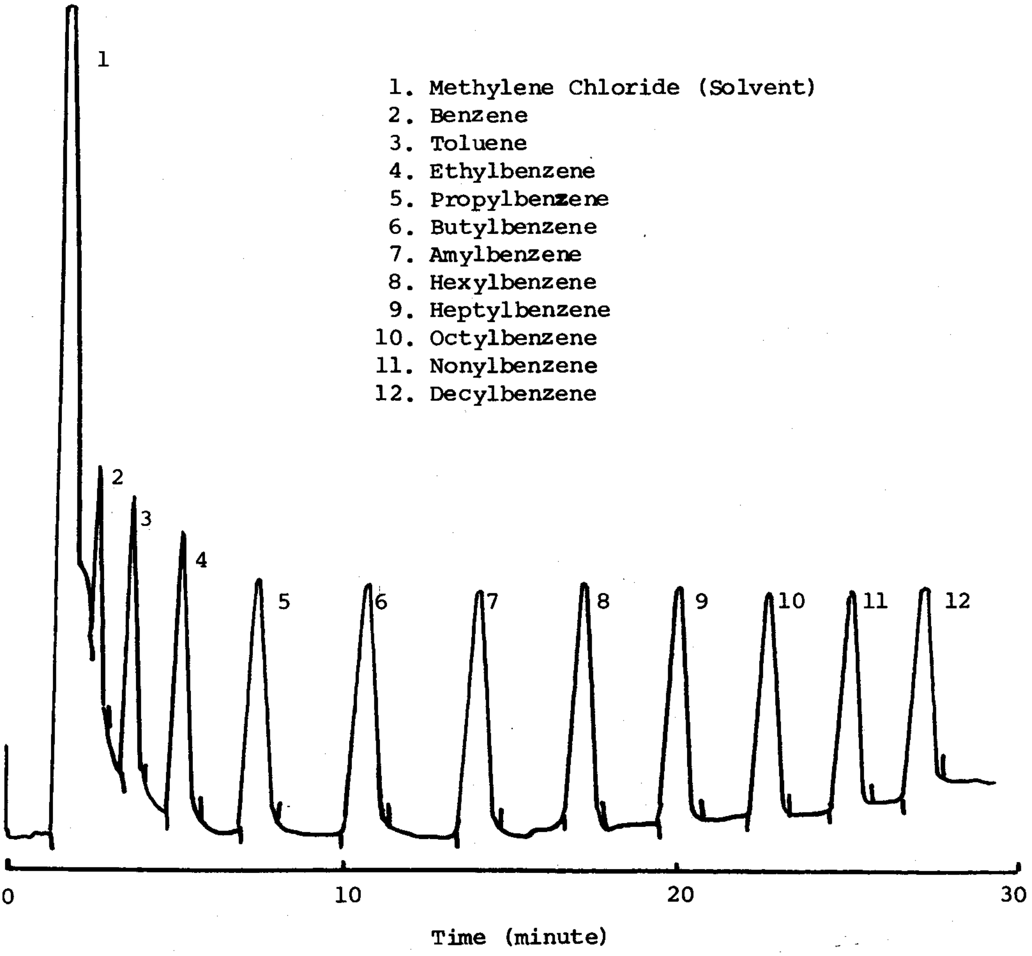
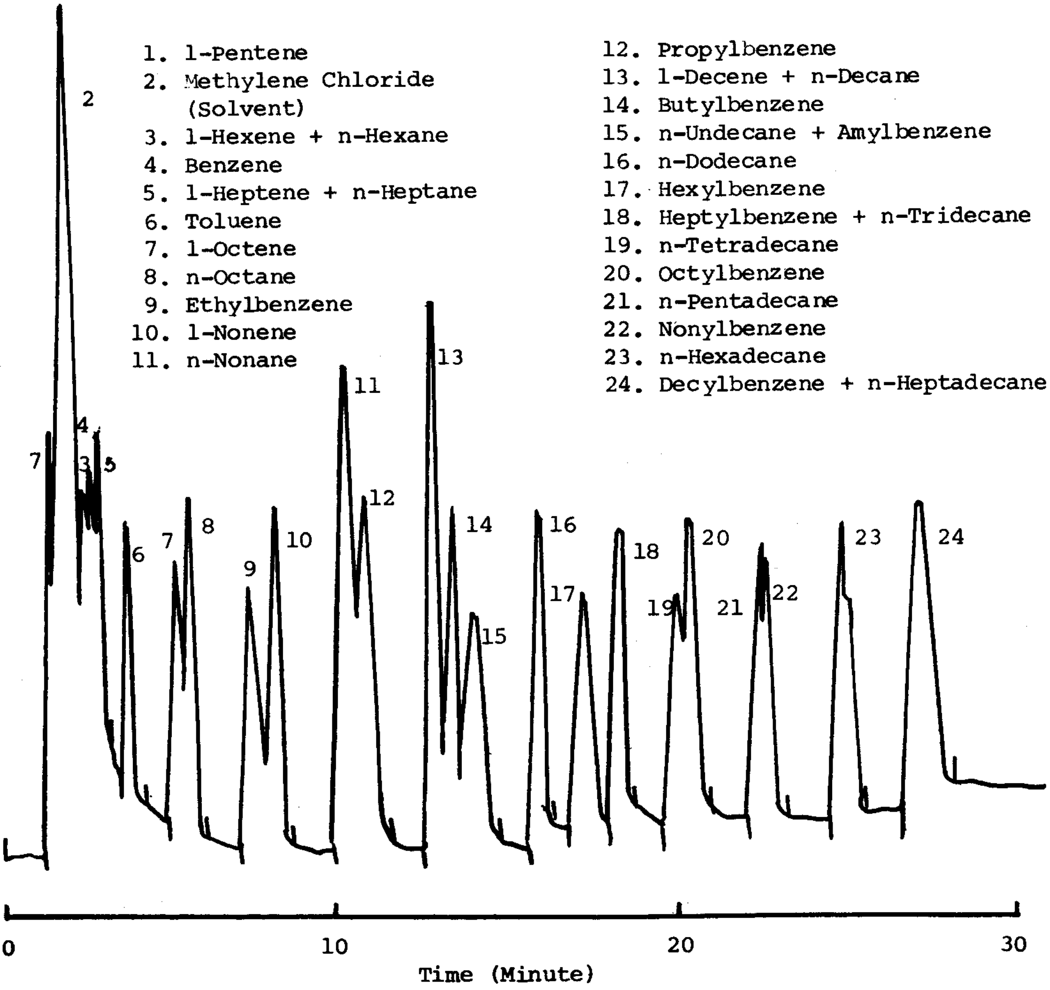


Fig. 4. Chromatogram of the standard benzene and n-alkyl (C_1 - C_{10}) benzenes mixture

6 ft x ¼" I.D., 20% SE-30 on Chromosorb P-AW-DMCS
60/80 mesh
Temperature:
  Detector = 310°C
  Injector = 320°C
  Column = 60°-300°C Programed 7.5°C/Min
  Helium Carrier Gas Flow Rate 65 mL/Min
  Flow Ratio of H_2:He:Air = 1:2:7



1. 1-Pentene
2. Methylene Chloride (Solvent)
3. 1-Hexene + n-Hexane
4. Benzene
5. 1-Heptene + n-Heptane
6. Toluene
7. 1-Octene
8. n-Octane
9. Ethylbenzene
10. 1-Nonene
11. n-Nonane
12. Propylbenzene
13. 1-Decene + n-Decane
14. Butylbenzene
15. n-Undecane + Amylbenzene
16. n-Dodecane
17. Hexylbenzene
18. Heptylbenzene + n-Tridecane
19. n-Tetradecane
20. Octylbenzene
21. n-Pentadecane
22. Nonylbenzene
23. n-Hexadecane
24. Decylbenzene + n-Heptadecane

Fig. 5. Chromatogram of standard hydrocarbon mixture

for this investigation as shown in chromatograms in Figures 2, 3 and 4. The SE-30 (methylsilicone) is a nonpolar liquid phase coated on Chromosorb P-AW-DMCS (which is the Chromosorb P washed with acid and dimethyldichlorosilane treated to make this solid support more inert). This column packing was chosen over 5% SE-30 on Chromosorb P-AW 80/100 mesh because no peak tailing occurred, while tailing occurred with the 5% SE-30 on Chromosorb W-AW 80/100 mesh column, probably because the percent loading of liquid phase (SE-30) was too low on the solid support and the solid support (Chromosorb W-AW) was not inert enough.

The chromatogram shown in Figure 5 shows the profile of all the hydrocarbons that were used in this study, i.e., n-alkanes (C_6 - C_{17}), 1-alkenes (C_5 - C_{10}) and benzene and n-alkyl (C_1 - C_{10}) benzenes. This chromatogram has 23 peaks (plus solvent peak); however, base line resolution could not be achieved for the low boiling hydrocarbons. This is attributed to the closeness of the boiling points of these compounds and the tailing of the solvent peak. Some of the peaks were not separated from the original sample, i.e., 30 compounds total. This resulted from the fact that six hydrocarbons came out at the same retention time as some of those 23 peaks. This investigation shows that separation can be achieved of hydrocarbon mixture (n-alkanes (C_6 - C_{17}), 1-alkenes (C_5 - C_{10}) and aromatics (benzene and n-alkyl (C_1 - C_{10}) benzenes) by using simple packed column GC instead of capillary GC which needs more experience to operate and a high cost of analysis.

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บทคัดย่อ

คอลัมน์แก้วยาว 6 ฟุต เส้นผ่าศูนย์กลาง $\frac{1}{4}$ นิ้ว ที่บรรจุด้วย 20% SE-30 บน Chromosorb P-AW-DMCS 60/80 mesh สภาพพอเหมาะ กล่าวคือโปรแกรมอุณหภูมิระหว่าง 60 - 300°C อุณหภูมิของตัวตรวจสาร (detector) 310°C อุณหภูมิของหัวที่จะฉีดสารเข้าไป 320°C อัตราความเร็วของฮีเลียม ก๊าซนำนั้น 65 cm^3/นาที อัตราความเร็วของ H_2 : He : Air เป็น 1 : 2 : 7 สามารถจะใช้แยกสารไฮโดรคาร์บอนชนิดอิ่มตัว (n-alkanes, C_6 - C_{17}) สารไฮโดรคาร์บอนชนิดไม่อิ่มตัว (1-alkenes, C_5 - C_{10}) และสารไฮโดรคาร์บอนชนิดอโรแมติก (benzene และ n-alkyl (C_1 - C_{10}) benzene) ได้อย่างดี และยังสามารถจะใช้แยกสารไฮโดรคาร์บอนทั้งสามอย่างดังกล่าวผสมอยู่ด้วยกันอีกได้ด้วย