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STATIONARY PHASE FOR GAS CHROMATOGRAPHY VII. PHENOL ALKYLATED WITH HALF EOUIVALENTLY CHLORINATED TO CARBON NUMBER OF n-ALKANES SEPARATED FROM KEROSENE. (PHECAK) PHASE

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ABSTRACT

PHECAK phase was prepared by alkylation of phenol with n-alkanes mixture, which was separated from kerosene and chlorinated in a manner that one of each two carbons is substituted. This phase contained less chlorine but unsubstituted methylene groups in the straight alkane chain.

PHECAK phase exhibits moderately polar phase properties by some additional Lewis acid character and better coataing property of the support material than other kerosene based chlorinated stationary phases.

This packing has been utilized for the separation of a number of compounds carrying different functional groups. McReynolds' conctants were given.

INTRODUCTION

Sporadic accounts of the use of halocarbon compounds as stationary phases have appeared almost from the inception of gas-liquid chromatography. Early reports dealt with the use of perhaloalkanes, especially fluoroalkanes for the analysis of corrosive and reactive chemicals, which could not be separated on conventional phases (Pappas, Million, 1968). Attempts to use these phases for more general applications were less successful due to a combination poor coating characteristics, and low column efficiencies. At about the same time purified high molecular weight polysiloxane and polyester phases became available and virtually eliminated futher interest in halocarbon phases. Recent research in the use of perfluorocarbon phases in gas chromatography has been directed toward their use for separation of low concentrations of halocarbon compounds, (Muller, et.al., 1983) which are potent environmental pollutants. Several new halocarbon stationary phases have been investigated (Dhanegar, Poole, 1983) and collected in a review (Yancey, 1985).

EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents were general laboratory or analytical grade. Kerosene was obtained from Orta Anadolu Rafinerisi (Kırıkkale-Ankara-Turkey) which was distilled from Kirkuk origin crudes. Specifications were B.P. range 152°–242° in which 20% distilles in the range 152°–167°, $D_{15} = 0.7826$. Chlorine was obtained in cylinder from Koruma Tarım İlaçları A.Ş. (Derince-Kocaeli-Turkey). Chromosorb 750. A.W. Sil. Tred. 100–120 mesh was obtained from Johns-Manville İnc. (USA), Squalane was obtained from MSwill. HGmbH. (Switzerland).

Infrared spectra were obtained with a Perkin Elmer Model 377 Grating Infrared Spectrophotometer Gas chromatographic work was done with a Perkin Elmer Model F11 chromatograph with temperature programmer and flame ionization detector connected to a Spectra Physıcs Autolab Minigrator in series with a 1 mv input sensitivity Perkin Elmer Model 54 linear Recorder. Chromatographic separation conditions are given in the figure captions.

Liquid phase was prepared as follows: n-alkane mixture (average M.W. = 164.273, carbon number = 11.5) (15 g, 91.3 mmol) was chlorinated until the total weight reached to 34 g (5.7 mol chlorine atom per mol alkane). Dissolved hydrogen chloride and chlorine were removed under reduced pressure. Alkylation of phenol with the above product was carried out by using the method given by Bann and. Thrower (1955) Chlorinated product (15 g, 40.2 mmol) and freshly distilled phenol (3.8 g, 40.3 mmol) and anhydrous zinc chloride dried at 110° overnight (5.4 g, 40.2 mmol) were put in 100 ml round-bottomed flask with a small magnet bar and closed with a stopper. Flask was kept at 100° for 6 h on a magnetic stirrer. After, the reaction mixture was washed with hot water twice and extracted with diethyl ether (3x50 ml). The ether extract was washed several times with cold water and dried over silicagel. Main part of ether was removed by distillation. The remained viscous liquid, was poured on a watch glass and the last portions of ether was evaporated under IR lamp.

Column packing containing 7% (w/w) of (PHECAK) on Chromosorb 750 was prepared by using the conventional rotary evaporator technique and toluene as solvent. The air dried packing was resieved to insure proper particle size. 1/8 in, 2 m stainless steel column was cleaned by toluene, methylene chloride, acetone repeatedly. Dried at

120° in the oven and filled with the prepared packing by gravity and gentle vibration by the aid of an electrical vibrator. Packed column was coiled and conditioned overnight with temperature programmed at 150° max. with nitrogen carrier gas flow rate 15 ml min^{-1}.

The maximum allowable operating temperature for the phase was established as the highest isothermal temperature at which column could be held for 24 h without changing retention indices of McReynolds test probe series. Under constant chromatograpic condition 1 μl water was injected ten times and peak areas were determined for Hexane-Hexanol 1/1 (w/w) mixture respectively to find out any change on support stationary phase surface.

RESULTS AND DISCUSSION

Chromatographic calculations were done according to procedures desribed in the first article of this series (Obalı, 1988). Phenol was alkylated with polychlorinated alkane mixture in the presence of equimolar anhydrous zinc chloride, in which polychlorinated alkane mixture was obtained by half equivalently chlorination to carbon number of n-alkanes mixtures separated from kerosene by successive urea adduction.

Figure 1. shows IR spectra of both polychlorinated n-alkane mixture and alkylated phenol product (PHECAK). Characteristic O–H stretchling vibration of phenolic hydroxy group is seen in the product spectrum as a broad band at 3250–3600 cm^{-1} frequency. Band

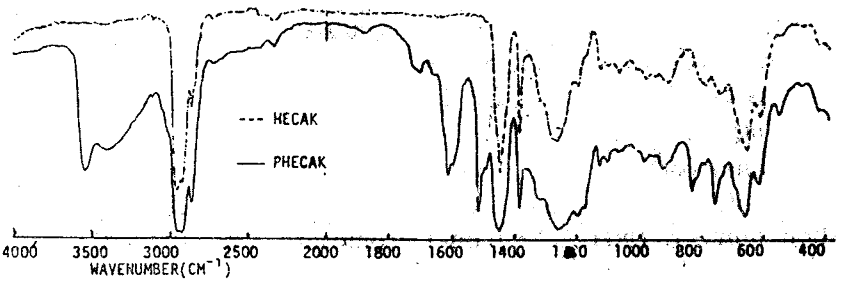


Figure 1. Infrared spectra of half equivalently chlorinated to carbon number of n-alkanes mixture separated from kerosene (HECAK) and its reaction product with phenol (PHECAK) by coating on KBr disc. Scan mode 5 min.

appeared in the product spectrum at 1650 cm^{-1} is the in plane stretching vibration of C=C of benzene ring of the phenolic moiety. Weak broad band between 1700–1500 cm^{-1} is the overtone of the CH out-of plane deformation frequency wichh is consistent and characteristic of the bustitutions of the benzene ring. Absorbtion band appeared in the product spectrum at 770 cm^{-1} shows monosubstitution to benzene ring.

7% (w/w) PHECAK packing having 1100 plates per meter was calculated for dodecane was prepared by standard procedure and without any particular difficulties. The McReynolds' constants of the phase are given in Table I. To make a comparison constants of PPCAK phase are also given (See, Stationary Phase for Gas Gromatography VI. Obalı, 1989). The only difference between the PPCAK phase and the PHECAK phase is their molar chlorination ratio, which is twice in the PPCAK phase. From the correlation of McReynolds' constants PHECAK phase is a moderately polar phase. Highest S' value among the others indicates its Lewis acidic character as in the PPCAK phase. But it is more profound, that this phase retards solutes having proton acceptor capability, more preferentially. This property of the phase is seen in the separation; of alcohols, Figure 2., where 1 pentanol (I(80) = 1049 u.i.) separated from its isomer 2–pentanol (I(80) = 966 i.u.), and aldehydes, where C_3–C_6 n-aldehydes are separated with tepperature programming, Figure 3. The symmetry of the solute peak eluating at high temperature indicates, the coating stability of the stationary phase on support material. This also shows the support deactivating potential of stationary phase, which is a desired property of commonly used favorable stationary phase, which is a desired property of commonly used favorable stationary phase.

Table I. McReynolds' Constants for PHECAK and PPCAK Phases and Capasity Ratio for PHECAK Phase.

	X'	Y'	Z'	U'	S'	J
PHECAK	162	352	355	356	446	172
PPCAK	127	247	277	286	381	158
k	2.56	6.27	8.56	10.94	31.5	8.67

t_m (cal) = 18 sec

U' value of PHECAK phase is 70 i.u. higher than that of the PPCAK phase which points out its more polar character. With this higher po-

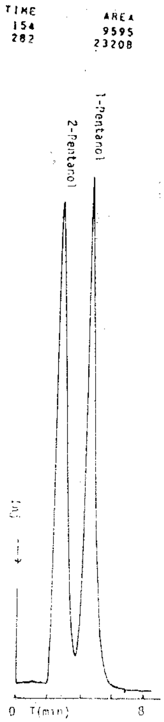


Figure 2. Separation of Pentanols at 80° with nitrogen carrier gas flow rate 3; ml min^{-1}.

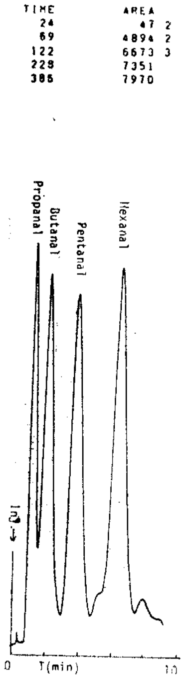
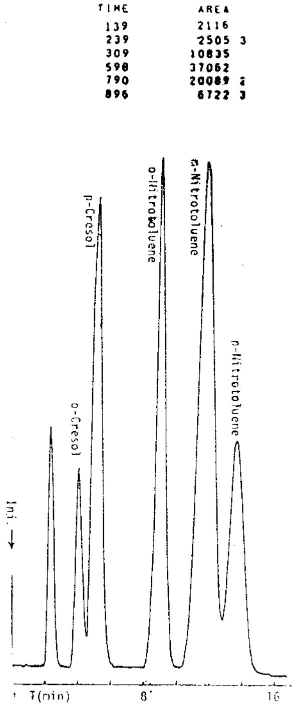


Figure 3. Separation of C_3–C_6 n-aldehydes. Temperature programing 60°–110° at 4°C min^{-1} with nitrogen carrier gas flow rate 30 ml min^{-1}.

lar property PHECAK phase can separate acidic compounds better, as it is seen in Figure 4. This phase is capable to separate cresol isomers, and all three nitrotoluene isomers, which haven't been achieved with the other chlorinated kerosene based phases. As it is seen in Figure 5. separation of underivatized carboxylic acids is also achieved. The separation of underivatized carboxylic acids is a particularly severe test of the support deactivating properties of this phase. It is noteworthy that no peak symmetry is observed. The more polar character is gained by the PHECAK phase because of methylene groups between two adjacent chlorine carrying carbon atoms. While in the PPCAK phase to every aliphatic carbon atom one chlorine atom is connected. As a final example, Figure 6 shows a separation of a homolog acetate esters with same peak symmetry under temperature programming condition.



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TIME        AREA
 139        2116
 239        2505 3
 309       10835
 598       37062
 790       20089 2
 896        6722 3
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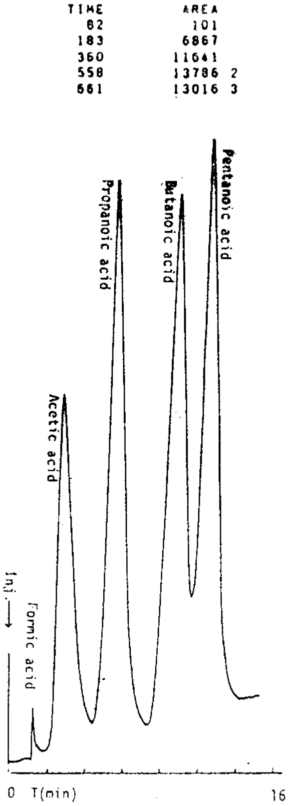
Figure 4. Separation of Nitrotoluenes and cresols at 130°, with nitrogen carrier gas flow rate 30 ml min^{-1}.



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TIME        AREA
  82         101
 183        6867
 360       11641
 558       13786 2
 661       13016 3
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Figure 5. Separation of C_1–C_5 carboxylic acids. Temperature program 60°–110° at 4°C min^{-1}, with nitrogen carrier gas flow rate 30 ml min^{-1}.

PHECAK phase is completely unaffected by repeated injection of water. No preconditioning of the packing with injections of water is necessary to obtain reproducible peak areas. Also no "ghosting" of components is observed when injections of water are made subsequent to sample injections.

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TIME      AREA
  75      3868 2
 125      5365 3
 234      5260
 398      6919
 600      7265
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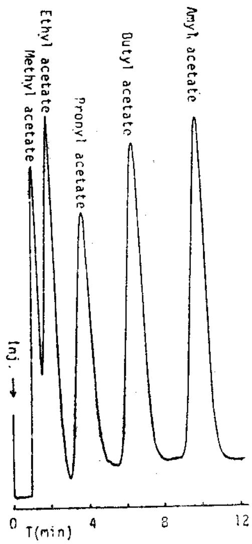

Figure 6. Separation of acetate esters Temperature pragram 60°–110° at 4°C min^{-1} with nitrogene carrier gas flow rate 30 ml min^{-1}.

CONCLUSION

Our work using kerosene originated polychlorine phases has led to several generalities which may be of use to other workers, in predicting the usability of polychlorinated liquids as stationary phases. First of all their support deactivating capability enabled the separation of high polar compounds. Less chlorinated phases achieved better separation than the more chlorinated phases. In the former phases chlorine atoms are seemed to take part more in the stationary phase, solute interactions. The former phases had more column bleeding at high temperatures. To avoid this undesired property, molecules can be enlarged by insertion of different functional group moieties. Polychlorinated alkanes gained better coating property of the solid support surface by the insertion of phenolic group. This increased the durability of the phase.

REFERENCES

BANN, B., THROWER, R.D., Industrie Chim Belg., 20. Spec. No. II., 155–8 (1955)

DHANESAR, S.C., POOLE, C.F., J. Chromatogr., 276, 388–94 (1983)

MULLER, I., DIETCRICH, P., PRESCHER, D., J. Chromatogr., 259, 243 (1983)

OBALI, M., Stationary Phase for Gas Chromatography I., Commun. Fac. Sci. Uni., Ankara., Series, B., 34, 1-10, (1988)

OBALI, M., Stationary Phase for Gas Chromatography VI., Commun. Fac., Sci., Uni., Ankara., Series B., 35, 25–32 (1989)

PAPPAS, W.S., MILLION, J.C., Anal. Chem., 40, 2176 (1968)

YANCEY, J.A., J. Chromatogr. Sci., 23, 370–377 (1985)