Commun. Fac. Sci. Univ. Ank. Series B
V. 35, pp 25-32 (1988)

STATIONARY PHASE FOR GAS CHROMATOGRAPHY, VI. PHENOL ALKYLATED WITH POLYCHLORINATED n-ALKANES SEPARATED FROM KEROSENE (PPCAK) PHASE

METİN OBALI

Department of Chemistry, Faculty of Science University of Ankara, Ankara-Turkey

ABSTRACT

PPCAK, prepared by insertion of phenolic group to the polychlorinated n-alkanes spearated from kerosene by successive urea adduction, is shown to fuction effectively as a stationary liquid phase for gas chromatography. PPCAK is a medium polar phase possessing some additional Lewis acid character and produces a stable film at all operating temperatures on the support and exhibited support deactivating property.

This packing has been utilized for both high solubility polar components (e.g. alcohols) and low aqueous solubility hydrocarbons.
McReynolds' constants are given.

INTRODUCTION

Polychlorinated kerosene was shown to function effectively as a medium polar stationary phase within the usable temperature range from 50° to 150° imparting an unusually high degree of support deactivation property. Main disadvantage of polychlorinated kerosene was column bleeding at elevated temperatures. Modified phase PCAK, prepared by chlorination of n-alkanes mixture separated from kerosene showed less column beleding and chlorine atoms of the phase took part more effectively in solute stationary phase interactions. This made its use feasible in the separation of halogenated isomers (Obalı, 1988). By insertion of new functional groups to the latter phase, different chromatographic properties can be attained.

Alkylation of phenol with PCAK was carried out in the presence of anhydrous zinc chloride instead of anhydrous aluminum chloride given by Egorov, et.al. (1978). With the insertion of one phenolic group the polychlorinated molecule has gained some additional Lewis acid and asymmetric character. Stationary phase is attained better thermal stability on the support as the average molecular weight was increased As a result better separations were achieved at elevated temperatures.

EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents were general laboratory or analytical grade. Kerosene was obtained from Orta Anadoly 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 MSwil. GmbH. (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 Physics Autolab Minigrator in series with a 1 mv input sensitivity Perkin Elmer Model 54 linear Recorder.

99.8 % pure n-alkanes mixture was separated from kerosene by successive urea adduction and chlorinated with an equivalent amont to carbon number of n-alkanes mixture (Obalı, 1988).

n-Alkanes mixture (average M.W = 164.273, carbon number = 11.6) (15 g 91.3 mmol) was chlorinated until the total weight reached 51.3 g (11.6 mol chlorine per mol alkane) hydrochloric acid and unreacted chlorine was removed under reduced pressure.

Alkylation of phenol with the above product was carried out according to Bann, Thrower (1955).

Chlorinated product (15 g 26.6 mmol) and freshly distilled phenol (2.5 g, 26.6 mmol) and anhydrous zinc chloride (3.63 g, 26.6 mmol) were put in a 100 ml round-bottomed flask with a small magnetic bar and closed with a stopper. Flask was kept at 100° for 6 h on a magnetic stirrer. After, the mixture was washed with hot water twice and extracracted with diethyl ether (3x50 ml). The ether extract was washed several times with water and dried over silicagel overnight. Main part of ether was removed by distillation. The remained viscous liquid was poured on a watch glass and remained ether was evaporated under I.R. lamp. Product was dark brown coloured semisolid.

Column packing containing 7% (w/w) of phenol alkylated with polychlorinated alkanes (PPCAK) on Chromosorb 750 was prepared by using the conventional rotary evaporator technique and toluene as solvent. The air deried packing was resieved to insure proper particle size. 1/8 in, 2 m stainless steel column was cleaned by toluene, methylene chloride, and 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 with temperature programming conditioned overnight at 200° 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 calculatiols were done according to Obalı (1988). Attempts for alkylation of phenol with polychlorinated alkanes in the presence of anydrous aluminium chloride according to Egorev, et.al. (1978) were unsuccessful black tarry product was obtained. Alkylation product was obtained using anhydrous zinc chloride IR spectra of reactant polychlorinated n-alkanes of kerosene and alkylation product are given in Figure 1. O–H streching vibration of phenolic hydroxy group is seen as a broad band at 3250–3300 cm^{-1} frequency, sharp band at 3600 cm^{-1} is due to OH streching of free hydroxy group. Sharp band at 1600 cm^{-1} is the inplane streching vibration of C=C of benzene ring of phenol. There is no difference in the C–Cl streching vibrations at 800–700 cm^{-1} of the product and reactant.

7% (w/w) PPCAK packing having 1640 plates per meter calculated for tetradecand was prepared by standard procedures and without any particular difficulties. The plate count is the highest among other

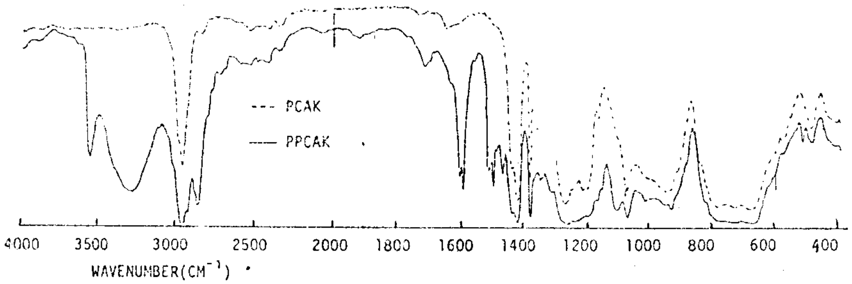

Figure 1. Infrared spectra of polychlorinated n-alkanes separated from kerosene. by successive urea adduction (PCAK) and its reaction product with phenol (PPCAK). By coating on KBr pressed disc. Scan mode 5 min.

kerosene originated stationary phases under investigation. Test chromatogram for efficiency, Figure 2. illustrate the chromatographic characteristics of PPCAK. At elevated temperatures no peak deformation is observed. It is noteworthy that this phase produces a stable film at all temperatures which may be due to the superior support wetting characteristics of PPCAK phase as compared to other kerosene originated phases.

The McReynolds' constants values for PPCAK are given in Table I. On the basis of these values PPCAK could be described as a medium polar phase possessing some additional Lewis acid character because S' value is the highest. By the insertion of the aromatic group, linear carbon chain has gained an asymmetric character and orientation properties are expected to effect the interraction with solute.

Table I. McReynolds' Constants for PPCAK Phase and Capacity Ratio.

	X'	Y'	Z'	U'	S'	J
PPCAK	127	247	277	286	381	158
k	1.37	2.26	4.11	5.63	13.21	6.95

t_M(cal) = 19 sec

PPCAK phase is suitable for the separation of many different functional groups because Y', Z', U' values are in the medium range and close to each other. Figure 3. shows the separation of underivatised chloropropanoic acids. The separation of underivatized halogenated carboxylic acids is a particularly severe test of the support deacti-

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TIME        AREA
  95         636  2
 163        4902
 266       11172
 383         867  3
 541        4263
 713        5405
 880        6615
1031        1085
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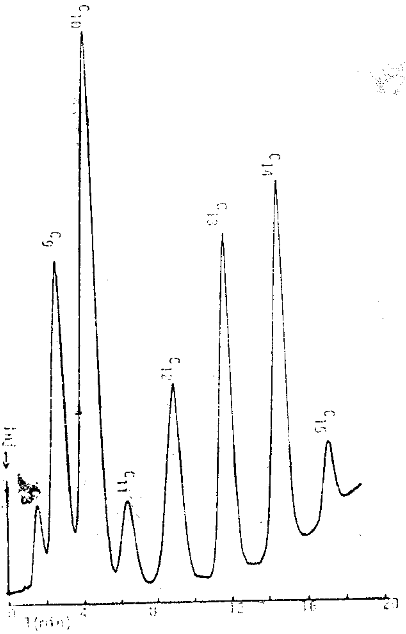

Figure 2. Test chromatogram illustrating column efficiency. Test mixture C_8–C_{15} n-alkanes. Temperature programmed from 80°–180° at 5°C min^{-1}.

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-   TIME      AREA
      33       726
     144      6129  3
     255     10394
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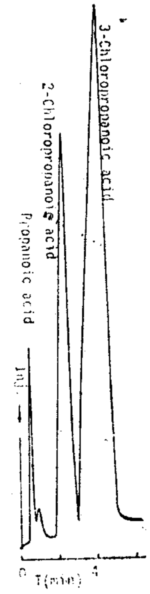


Figure3. Separation of chloropropanoic acid isomers at 120° with nitrogen carrier gas flow rate 30 ml min^{-1}.

vating properties of this phase. Because of high loading under isothermal conditions some peak asymmetry is observable. Figure 4 and 5 shows the separation of other acidic isomers dichlorophenols and nitrotoluenes respectively.

Figure 6. shows the separation of n-aldehydes with temperature programming the symmetry of the peaks do not differ considerably than the peaks of n-alkanes in test chromatogram in Figure 1. This

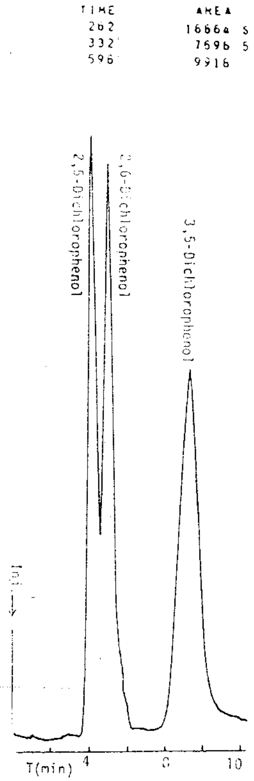


Figure 4. Separation of Dichlorophenol isomers at 150^{a} with nitrogen carrier gas flow rate 30 ml min^{-1}.

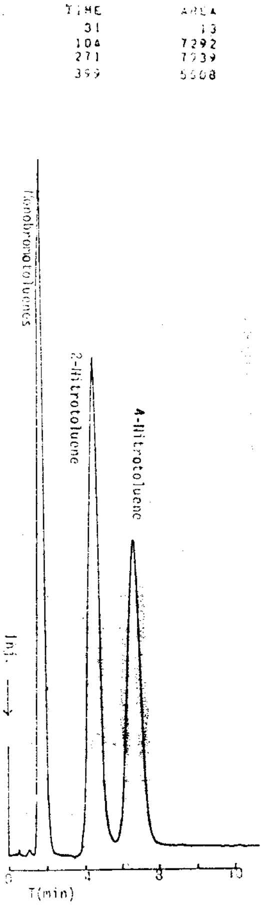
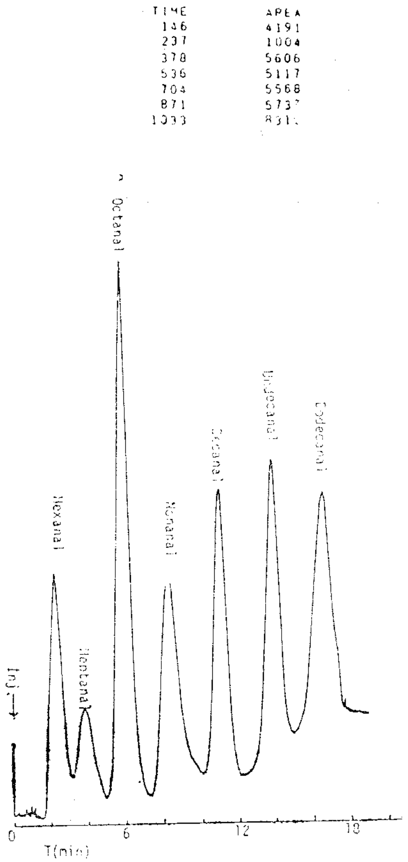


Figure 5. Sepration of Nitrotoluenes at 150° with nitrogen carrier gas flow rate 30 ml min^{-1}.

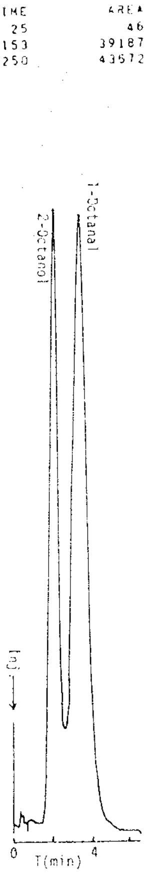
point out that the level of PPCAK phase deactivation property, of the support is significantly high.

Phenolic hydrogens play role in some critical separations by their hydrogen bonding properties. These type of interactions are important in the separation of some isomers as in the separation of octanol isomers (Figure 7).



TIME	AREA
146	4191
237	1004
378	5606
536	5117
704	5568
871	5737
1033	831

Figure 6. Separation of C_6–C_{12} n-aldehydes. Temperature program 80°–190° at 5 °C min^{-1} with nitrogen carrier gas flow rate 30 ml min^{-1}.



TIME	AREA
25	46
153	39187
250	43572

Figure 7. Separation of 1–Octanol from 2–Octanol at 120°, with nitrogen carrier gas flow rate 30 ml min^{-1}.

PPCAK phase is completely unaffected by repeated injections of water. No preconditioning, of the packing with injection of water is necessary to obtain reproducible peak areas. Also no "ghosting" of components is observed when injections of distilled water are made subsequent to sample injections. Thus, PPCAK phase appears to be a feasible alternative to the porous polymers and carbon supports which are utilized for samples with aqueous matrices (Supelco 1976).

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