

STATIONARY PHASE FOR GAS CHROMATOGRAPHY IV. NITRI- LATED POLYCHLORINE n-ALKANES SEPARATED FROM KERO- SENE BY SUCCESSIVE UREA ADDUCTION, (NPCAK) PHASE

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ABSTRACT

A stationary phase was prepared by nitration of polychlorinated n-alkanes, which were separated from kerosene by successive urea adduction. Chromatographic characteristics of the phase were investigated, separation capacity and column efficiency were demonstrated. Mc-Reynolds' constants were determined.

INTRODUCTION

PCAK stationary phase manifested better chromatographic properties than PCK phase (Obalı, 1988). By changing the chemical structure of this phase i.e. by adding new functional groups, chromatographic characteristics can be altered. Substitution of nitrile group only to primary carbons was attempted first by using phase transfer catalysis (Mcintosh, 1978). The results were not satisfactory. Then substitution reaction was carried out by using dimethyl sulfoxide as solvent (Friedman and Shechter, 1960), secondary chlorides also reacted to give nitriles.

This new phase was attained proton acceptor and donor properties and successfully used in the separations of compounds displaying these properties such as acids and alcohols. Increased interaction of the phase with support resulted better coating of the support by the phase in which better separations were achieved at temperature programmed works.

EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents were general laboratory or analytical grade. Kerosene was obtained from Orta Ana-

doğu Rafinerisi (Kırıkkale-Ankara-Turkey) which was distilled from Kirkuk origin crudes. Specifications were B.P. range 152°–242° in which 20% distills 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 Inc. (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 Chromatographic separation conditions are given in the figure captions.

n-Alkanes mixture separated from kerosene by successive urea adduction was chlorinated equivalent amount to carbon number of n-alkanes mixture which was described in previous article heading "Stationary Phase for Gas Chromatography II." (Obalı, 1988). By chlorination of 15 g urea adducted n-alkanes mixture 51.3 g product was obtained. Reaction of polychlorinated n-alkanes which are separated from kerosene by urea adduction, with sodium cyanide: Polychlorinated n-alkanes (15 g 26.7 mmol.) dissolved in dimethyl sulfoxide (23 ml dried over silicagel) was added in 10–15 min to a rapidly stirred partially soluble mixture of sodium cyanide (16.6 g, 339 mmol dried at 110° overnight) in dimethyl sulfoxide (60 ml dried over silicagel) at 20°. The temperature of the mixture rose rapidly and was kept at $60 \pm 5^\circ$ by cooling with water when necessary for 6 h. During the reaction the mixture became more fluid, and insoluble salts more crystalline. When the reaction was apparently complete at the end of 6 h the dark brown reaction mixture was cooled, diluted with water to a volume of ca. 300 ml and extracted with diethyl ether (3x60 ml.) The brown ether extract was washed with 6N hydrochloric acid (to hydrolyze the small amount of noxious isocyanide) and several times with saturated sodium chloride solution and dried over silicagel overnight. After removal of great portion of ether by distillation under vacuum, the viscous liquid was poured on a watch glass and was put under a I.R. lamp to evaporate last portions of ether. Product was brown coloured semi glassy which would not flow at room temperature.

Column packing containing 7% (w/w) of nitrilated polychlorine n-alkanes separated from kerosene by successive urea adduction (NPCAK) on Chromosorbs 750 (100–120 mesh) was prepared by using the rotary evaporator technique and T.H.F. as solvent. The air dried packing was resieved to insure proper particle size. 1/8 in. 2m. stainless steel column was cleaned by toluene, methylene chloride acetone repeatedly dried at 120° in the oven and filled with prepared packing by gravity and gentle vibration by the aid of an electrical vibrator. Packed column was coiled in the appropriate shape of the instrument oven and with temperature programming conditioned over night at 150° max (50° 30 min after to 150° at 5°C 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 chromatographic condition 1 μ l 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

Attempts to nitrillate polychlorinated n-alkanes separated from kerosene by successive urea adduction by using phase transfer catalyst were unsuccessful. At low temperatures no reaction was occurred, at elevated temperature, black tarry product was obtained. Nitrillation by using dimethyl sulfoxide as solvent was successful at low temperature long reaction times. IR spectra of reactant polychlorinated n-alkanes of kerosene and nitrilated product were given in Figure 1. Sharp characteristic C=N stretching frequency is seen at 2260–2240 cm⁻¹ while characteristic C-Cl stretching vibration of polychlorinated compound appeared at low frequencies 800–700 cm⁻¹ is decreased and broadened. This indicates the increase of the molecule size during nitrilation by side reactions i.e. dimerization of olefinic products of elimination reaction.

7% (w/w) NPCAK coated column has 1050 plates per meter. It is calculated for n-undecane which is not particularly high, reflects the mechanical stability of the support. Gas hold up times (t_M) at different temperatures used in finding adjusted retention times (t'_R) from

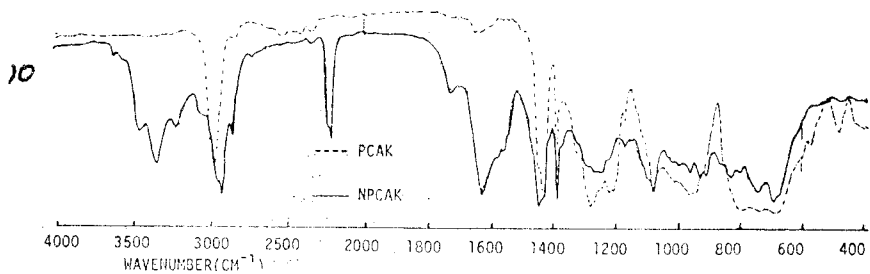


Figure 1. Infrared spectra of polychlorinated n-alkanes separated from kerosene, by successive urea adduction (PCAK) and nitrillated product (NPCAK). By coating on KBr pressed disc. Scan mode 5 min.

chromatographic data were calculated from three successive n-alkanes retention times by Peterson and Hirsch (1959) method. (Smith. et.al. 1985) In its simplest terms retention in gas-liquid chromatography is governed primarily by the vapor pressure of the sample and the strength of solute-solvent interactions experienced by the sample in the stationary phase. Gas phase interactions can reasonably be assumed to be negligible compared to liquid phase interactions, the fact that a solute exhibits different retention for different liquid phases is explained by the capacity of the solute to enter into intermolecular interactions with the liquid phase to different extents. Individual interactions have been estimated by the formal procedure proposed by Rohrschneider (1959) and McReynolds' (1970). In contemporary practice to define a stationary phase McReynolds' constants are being used commonly by commercial and scientific sources. For NPCAK stationary phase these constants are summarized in Table I. To make a comparison also constants of PCAK (polychlorinated n-alkanes separated from kerosene) phase are given because NPCAK is prepared from PCAK phase. Some approachy may be done on the behaviour of NPCAK phase. In the liquid phase the intermolecular forces of importance are mainly dispersion, induction, orientation and donor-acceptor comple-

Table I. Summary of McReynolds' Constants Data and Capacity Ratio for NPCAK.

	X'	Y'	Z'	U'	S'	J
NPCAK	162	351	339	366	455	159
PCAK	143	219	519	433	521	787
k	2.3	5.8	7.0	10.7	27.5	7.3

$$t_M(\text{cal}) = 16 \text{ sec}$$

xation. High Y' constant indicates that orientation properties of this phase with both proton donor and proton acceptor capabilities are effective in intermolecular interactions with solute. Carboxylic acids which are proton donors can be separated effectively by this phase in Figure 2. Acetic, propanoic, butanoic acids are separated at 100° with retention indices 968 i.u., 1067 i.u., 1159 i.u., respectively. Even aromatic acidic isomers can be separated. In Figure 3 separation of cresols are given ($I_{o-Cresol} = 1403$ i.u., $I_{p-Cresol} = 1473$ i.u.) and in Figure 4 separation of nitrotoluenes are given ($I_{o-NT} = 1566$ i.u., $I_{p-NT} = 1631$ i.u.), both separations are at 140° . As it is pointed out proton acceptor functional groups such as alcohols can be separated also by this phase. In Figure 5 separation of 1-Pentanol ($I = 1051$ i.u.) from 2-Pentanol ($I = 954$ i.u.) isomer at 90° is given. As it is seen Y' , Z' , U' constants are in the same order and they are moderately high. Separation of esters defined by Z' constant are also achieved. In Figure 6 temperature programmed separation of acetate esters is given ($I(TPGC)_{Me\cdot Ac} = 731$ i.u., $I(TPGC)_{Et\cdot Ac} = 831$ i.u., $I(TPGC)_{Pr\cdot Ac} = 904$ i.u., $I(TPGC)_{Bu\cdot Ac} = 1012$ i.u.). As it is seen from this chromatogram, peak symmetry is identical at elevated temperatures with the lower temperature peaks, this shows the interaction of this stationary phase is strong enough with support material causing no uncoated support surface at high temperatures.

Repeated water injections are changing the retention characteristics, while some McReynolds' constants value increasing few units, such as S' and Y' the others are decreased as U' . This is probably because of hydrolysis of nitrile groups.

CONCLUSION

NPCA-K phase is a moderately polar stationary phase. It is very capable in the separation of compounds which have proton acceptor and proton donor properties. Because of nitrile groups, NPCA-K phase chemical stability is not as much as PCA-K phase. But its coating ability of the support is excellent that can be used in temperature programmed separations without peak distortions. NPCA-K phase is sensitive to water, so care must be taken in the separation of aqueous mixtures.

TIME	AREA
41	66 1
79	11024 S
137	2664 S
252	15969

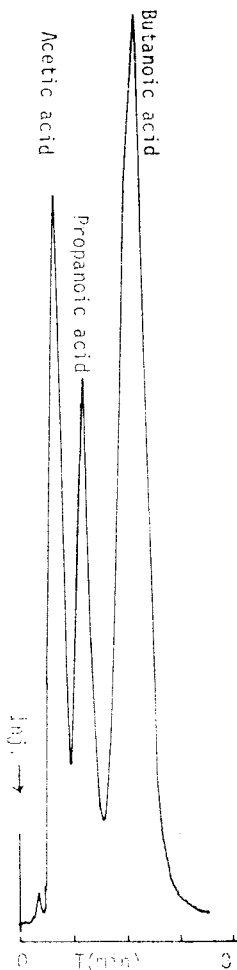


Figure 2. Separation of carboxylic acids at 100° with nitrogen carrier gas flow rate 30 ml min^{-1} $t_M(\text{cal}) = 18 \text{ sec}$.

TIME	AREA
97	7270
205	4580
296	8493

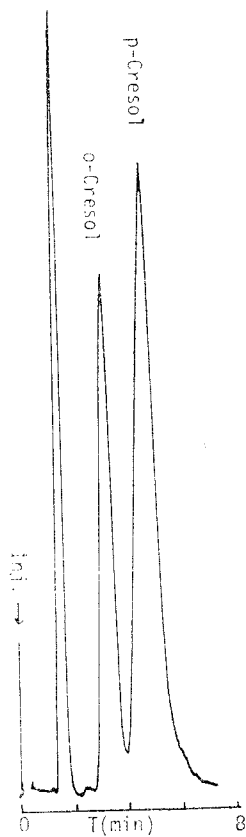


Figure 3. Separation of cresols at 140° with nitrogen carrier gas flow rate 30 ml min^{-1} $t_M(\text{cal}) = 15 \text{ sec}$.

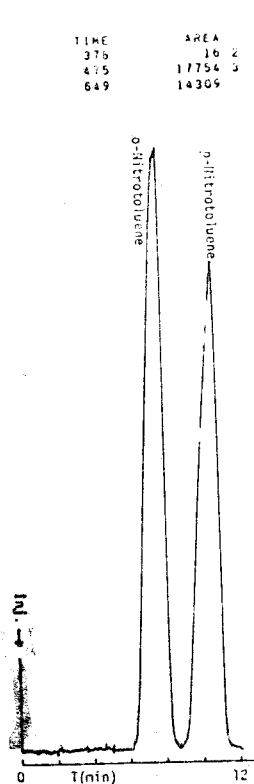


Figure 4. Separation of Nitrotoluenes at 140° with nitrogen carrier gas flow rate 30 ml min^{-1}
 $t_M(\text{cal}) = 15 \text{ sec.}$

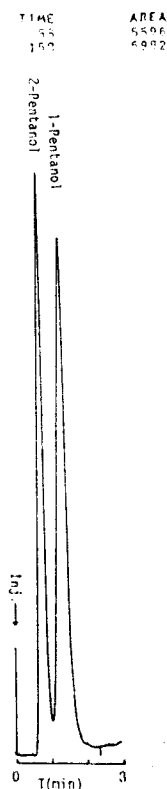


Figure 5. Separation of isomer alcohols at 90° with nitrogen carrier gas flow rate 30 ml min^{-1}
 $t_M(\text{cal}) = 19 \text{ sec.}$

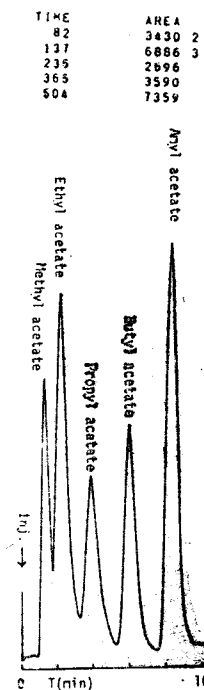


Figure 6. Separation of Acetate esters. Temperature programm 40° – 100° at $8^{\circ}\text{C min}^{-1}$ with nitrogen carrier gas flow rate 30 ml min^{-1} .

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