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STATIONARY PHASE FOR GAS CHROMATOGRAPHY III. POLYCHLORINATED UREA UNADDUCTED KEROSENE (PCUK) PHASE

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ABSTRACT

A stationary phase was prepared by polychlorination of urea unadducted kerosene part. Chromatographic characteristics of the phase were examined in comparison with chlorinated kerosene and chlorinated urea adducted kerosene. Separation capacity and column efficiency were demonstrated and McReynolds' phase constants were determined.

INTRODUCTION

As a stationary phase polychlorinated kerosene was possessed the property of deactivation solid support enabling the separation of highly polar organic compounds without tailing, and chlorocarbon chain was not contributing additional separation for halogenated compounds. The main drawback of this phase was elution at elevated temperatures. (M. Obalı 1988) To change the chromatographic character of the phase, another phase was prepared by chlorination of n-alkanes mixture separated from kerosene. Halogenated isomers was separated better by the latter phase. What was left from kerosene after the separation of n-alkanes was another substrat for a different stationary phase.

This new substrat of kerosene contained only 14.4% n-alkanes which was not possible to separate by urea adduction, the rest, was branched chain alkanes because aromatic and unsaturated part had been also removed. This phase attained high degree of branching of carbon chain. Generally the higher the degree of branching results in the lower thermal stability and the higher selectivity, because of hydrogen atoms, attached to the tertiary carbon atoms in the hydrocarbon chain. To make a comparison, urea unadducted kerosene part will be chlorinated same amount as urea adducted kerosene and the chromatographic properties of this new stationary phase will be investigated. The results are presented herein.

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. GmbH. (Switzerland).

Infrared spestra 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 Minigratot in series with a 1 mv input sensitivity Perkin Elmer Model 54 linear Recorder. Chromatographic separation conditions are given in the figure captions.

Aromatic and unsaturated components of kerosene were separated by treatment with with 40% (w.) con. sulfuric acid at 60° for 2 h. To remove n-alkanes, urea adduction was performed with excess urea, at seventh successsive adduction no precipitation of n-alkanes urea adduct was observed. (Obalı 1989) The liquid phase was washed two times with hot water to remove dissolved urea, dried over silicagel and analyzed with gas chromatography using 15 % squalane column. F.I.D. detector relative sensitivitiy data for n-alkanes was obtained from literature (Dietz, 1967). Analysis was repeated several times by temperature programming from 60° to 140° at 4 °C min^{-1}.

15 g urea unadducted kerosene was put in a temperature control jacketed glass reactor and chlorine was bubbled. After short induction period (apr. 5 min) chlorination was started and was ceased when the total weight of the product reached to 51.3 g (This is the same amount in the previous publication (M. Obalı 1988) Chlorination temperature was kept at 20° first hour and raised to 90° gradually as the viscosity of the product increased. Dissolved hydrochloric acid, formed during reaction and uncreated chlorine was expelled by leaving the product

under reduced pressure at 150°. Product was light yellow coloured glassy semisolid which would not flow at room temperature.

Column packing containing 7% (w/w) of polychlorinated urea unadducted kerosene (PCUK) and squalene on Chromosorb 750 (100–120 mesh) were prepared by using conventional rotary evaporator technique and toluene as solvent. The air-dried packings were resieved to insure proper particle size. 1/8 in. 2 m. stainless steel columns were cleaned by toluene, methylene chloride, acetone repeatedly dried at 120° and filled with the prepared packings by gravity and gentle vibration by the aid of electrical vibrator. Packed columns were coiled in the appropriate shape of the instrument oven and with temperature programming conditioned over night 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

Aromatic and unsaturated aliphatic components of kerosene were removed totally by the reaction with sulfuric acid, but n-alkanes removal was achieved partially by successive urea adduction in excess urea, after seventh urea adduction no precipitation of the adduct was occured. So it was the maximum amount of n-alkanes that could be removed by urea adduction from kerosene. The results of GC quantitative analysis of urea unaddacted kerosene was given in Table I. In calculation all branched alkanes FID relative responces were assumed identical. 14.4 % of n-alkanes were remained in unadducted kerosene. This mixture was chlorinated until the same ratio of weight increase

Table I. The n-Alkanes Remained in unadducted Kerosene.

n-Alkanes	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
Weight % Σ n-C %	0.603 14.485	3.955	4.000	2.792	1.100	0.976	0.414

as urea adducted kerosene was attained. That was 3.43 (chlorinated product /urea unadducted kerosene (w /w)).

IR spectra of unadducted kerosene and chlorinated product (PCUK) which was used as stationary phase were given in Figure 1. It is seen that C–H stretching of methylene groups in alkanes (2900–2800 cm^{-1}) is decreased in the polychlorinated product while characteristic C–Cl strecthing vibration is appeared at 800–700 cm^{-1}. The spectrum of polychlorinated product has shown differences in 1200–1000 cm^{-1} region than polychlorinated n-alkanes of kerosene published in previous paper (Obalı 1988) This is due to chlorination of branched centers of the molecules.

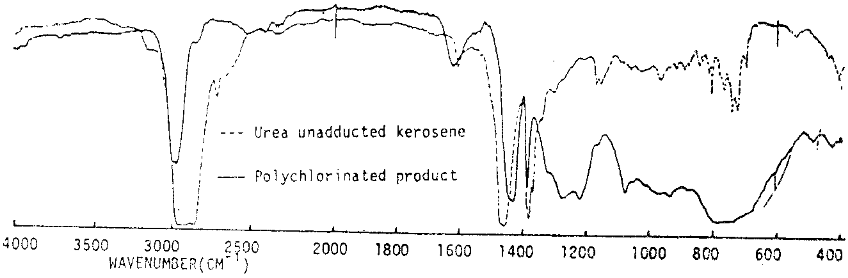

Figure 1. Infrared spectra of urea unadducted kerosene and its polychlorinated product. Both KBr pressed disc coating. Scan mode 5 min.

7% (w /w) polychlorinated urea unadducted kerosene (PCUK) coated column has 900–1100 calculated theoretical plates per meter for the separation of octanol and dodecan respectively column's lower efficiency than polychlorinated kerosene column is because of increased percent of branched chain centers in the stationary phase which are acted as active sites and decrease the liquid film coating properties especially at elevated temperatures. This is seen in the temperature programmed chromatogram of n-alcohols in Figure 2. As the temperature increases symmetry of the peaks are reduced. Gas hold up times (t_M), used in Retention Index calculations were calculated from three successive n-alkanes retention times by Peterson and Hirsch (1959) method.

The polarity and selectivity of a stationary phase can be characterized by its McReynolds' constants values. Ettre (1974). For PCUK

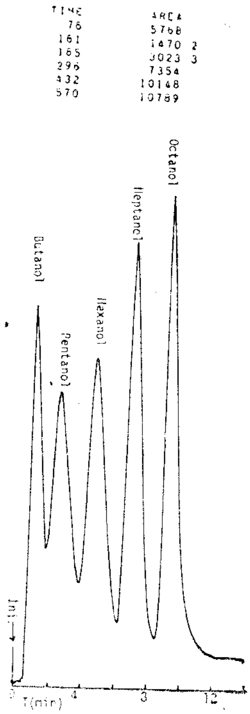

Figure 2. Chromatogram of C_4–C_8 alcohols Temperaure program 50° to 120° at 8°C min^{-1} with nitrogen carrier gas flow rate 30 ml min^{-1}.

and previously discussed PCAK and PCK (Obalı 1988) phases. These values are summarized in Table II. Several trends may be noted. Smaller X′ value indicates interastion of PCUK phase with aromatic and unsaturated compounds is weaker than PCAK and much weaker than PCK phase. But high U′ value indicates strong dipole orientation properties, that is nitro compounds are retarded strongly by this phase.

Table II. Summary of McReynolds′ Constants Data and Capacity Ratio for PCUK Phase.

	X′	Y′	Z′	U′	S′	J
PCUK	116	206	510	578	524	788
PCAK	143	219	519	433	521	787
PCK	161	228	263	316	280	151
k	1.16	1.50	2.72	4.83	6.56	6.00

t'_M(cal). = 18 sec.

As an example nitrotoluene isomers can be separated, despite they are aromatic. This separation is given in Figure 3. (I_{2-NT} (140°) = 1440 i.u., I_{3-NT} (140°) = 1493 i.u., I_{4-NT} (140°) = 1520 i.u.

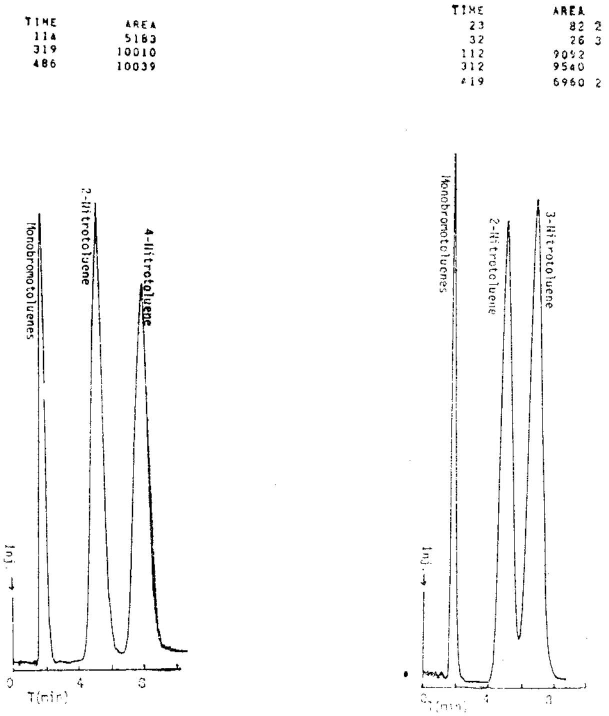

Figure 3. Separation of Nitrotoluenes at 140° with nitrogen carrier gas flow rate 30 ml min^{-1} $t_M(cal) = 17$ sec.

Very high J value emphasizes the existance of strong dipole orientation properties of the phase; so it is possible to separate halogenated compounds, better aliphatic ones, with this phase. Z′ value also 250 i.u higher than PCK phase so we can separated ethers, carbonyls, epoxides, esters better by using PCUK phase. Separation of esters is given in Figure 4 at 80°. ($I_{Et \cdot Ac} = 771$ i.u., $I_{Bu \cdot Ac} = 973$ i.u., $I_{Amy \cdot Ac} = 1068$ i.u.).

Repeated water injections are changing the some retention characteristics Y′, S′, values increases several units and this change increases from 50° to 90° and change in peak areas also observed. This

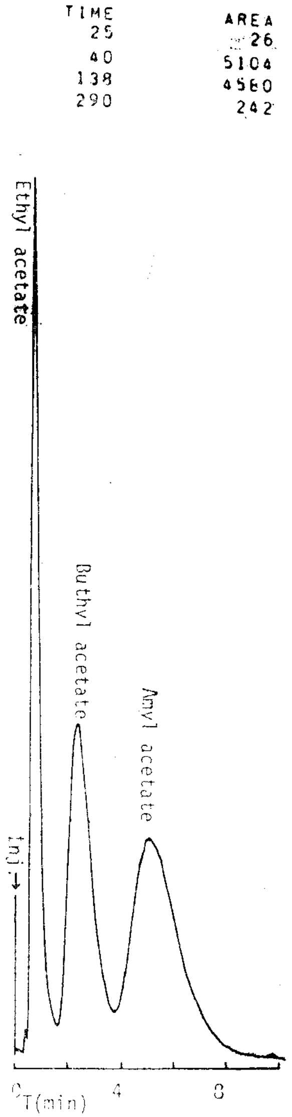

Figure 4. Separation of Alkyl acetates at 80° with nitrogen carrier gas flow rate 30 ml min^{-1} $t_M(cal)$ = 20 sec.

points out that there is liquid phase contractions on the support surface leaving active zones causing interfacial interactions.

CONCLUSION

PCUK phase is shown to function as a medium polar stationary phase for gas chromatography. Especially useful in the separation of aliphatic halogen compounds because of unusual high J value. But the interaction is not so strong with solid phase and phase contraction is observed at elevated temperatures.

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