

STATIONARY PHASE FOR GAS CROMATOGRAPHY II POLYCHLORINATED n-ALKANES SEPARATED FROM KEROSENE BY UREA ADDUCTION (PÇAK) PHASE.

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ABSTRACT

A stationary phase was prepared by equivalent chlorination according to carbon number of n-alkanes mixture separated from kerosene by successive urea adduction. Gas chromatographic characteristics were examined in comparison with polychlorinated kerosene, the separation ability and column efficiency were demonstrated in the separation of halogenated isomers McReynolds' constants were given.

INTRODUCTION

Separations in gas-liquid chromatography occur because of selective interactions between the sample and the liquid phase. All components have essentially the same residence time in the gas phase. Thus, many liquids have been evaluated as stationary phases for gas chromatography but only a few of these can be described as having unique separation properties. In general, there exists a large number of stationary phases having nearly identical separation properties. From which a small number can be identified as preferred phases, characteristic of all others. Recently we have described the properties of polychlorinated kerosene as stationary phase for gas chromatography (Obali, 1988) which imparts support deactivation, enabling acidic compounds to be analyzed at low concentrations and compared to nonchlorinated phases of similar polarity, the retention of organic compounds is generally lower enabling chromatographic separations achieved at lower temperatures.

Main drawback of polychlorinated kerosene phase was "column bleeding" at elevated temperatures. First attempt to overcome this situation was changing the composition of kerosene.

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 % distills in the range 152°–167°, $D_{22} = 0.7826$. 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.

Aromatic and unsaturated components of kerosene were separated by treating at 60° for 2 h with 40 % con. sulfuric acid. By four successive urea adduction in reactant / urea ratios of 1.6, 1.0, 0.6, 0.6; 99.8 % pure n-alkanes mixture of kerosene was obtained and dried over silica-gel. The composition of the urea adduct was determined by gas chromatographic quantitative analysis using 15 % Squalane column. FID. detector relative sensitivity data for n-alkanes was obtained from literature (Dietz, 1967). Analysis was repeated six times by temperature programming from 60°–140° at 4°C min⁻¹ rating.

15 g urea adducted kerosene was put in a temperature control jacketed glass reactor and chlorine was bubbled, after a short induction period chlorination was started and hydrogen chloride was evolved. During the first 90 min temperature was at 20° and raised to 90° gradually as the viscosity of the chlorinated product increased. Chlorination was continued until total weight of the product reached to 51.3 g (1 chlorine per carbon). Product was cleaned from dissolved hydrogen chloride and chlorine by keeping under reduced pressure at 150° for 30 min. Product was colourless glassy semi-solid which would not flow at room temperature.

Column packings containing 7 % (w/w) polychlorinated urea adducted kerosene (PCAK) and squalane on Chromosorb 750 were

prepared by using 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 with toluene, methylene chloride and acetone repeatedly. Dried at 120° and filled with prepared packings by gravity and gentle vibration of an electrical vibrator. Packed columns were coiled and with temperature programming conditioned overnight 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 chromatographic condition 1 ml 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

By successive urea adduction n-alkanes in kerosene were separated from unadducted portion at 99.8 % (w) purity but the ratios of n-alkanes were differed that of the kerosene while higher n-alkanes ratio increased lowers were decreased in the adduct. The result of GC quantitative analysis of n-alkanes mixture was given in Table 1. The average molecular weight of-n-alkanes mixture is 164.273 and carbon number of this hypothetical n-alkane is 11.568. In the chlorination of n-alkanes mixture for one mole of alkane 11.568 moles chlorine were introduced to the molecule (it is equivalent chlorination to carbon atoms of alkanes).

Table 1. The n-Alkanes Composition of Final Urea Adduct of Kerosene.

n-Alkanes	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	Total
Weight %	0.048	2.429	16.666	30.989	28.931	13.841	3.537	1.075	0.360	99.887
MW _{xw} %	0.055	3.115	23.714	48.442	49.284	27.382	9.002	2.284	0.995	164.273

Average molecular weight of n-alkanes mixture: 164.273

IR spectra of n-alkanes mixture separated from kerosene by urea adduction and polychlorinated product (PCK) of this mixture were given in Figure 1. It is seen that C-H stretching of CH₂ groups in alkanes (2900-2950 cm⁻¹) decreased and shift to high frequency in the polychlorinated product while characteristic C-Cl stretching vibrations are appeared at 800-700 cm⁻¹.

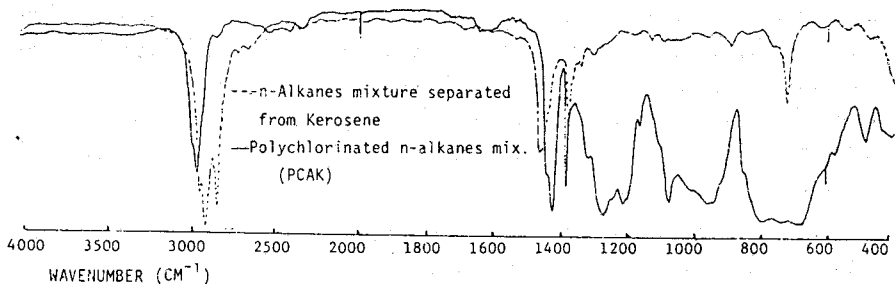


Figure 1. Infrared spectra of n-alkanes mixture separated from kerosene by successive urea adduction and polychlorinated product of this mixture (PCAK). By coating on KBr disc. Scan mode 5min.

7 % (w/w) polychlorinated n-alkanes separated from kerosene (PCAK) coated column had 1180 plate number per meter which was calculated for decanal, was not particularly high. This reflects the mechanical stability of the support.

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 PCAK and PCK (Polychlorinated kerosene which was discussed in the previous article, Obali, 1988) phases these values were summarized in Table 2. Several trends may be noted. First, except benzene and butanol the absolute retention of the test probes is substantially higher on PCAK than PCK phase. As would be anticipated, the McReynolds' constants characterize the PCAK phase being more polar than PCK. Especially high Z' and S' values indicates more dipole orientation properties with strong proton acceptor capabilities. This was shown in Figure 2. in the

Table 2. Summary of McReynolds Constants Data of PCAK and PCK phases and Capacity Ratio for PCAK phase.

	X'	Y'	Z'	U'	S'	J
PCAK	143	219	519	433	521	787
PCK	161	228	263	316	280	151
k	1.89	2.16	3.79	1.84	8.42	7.84

t_M calculated = 19 sec.

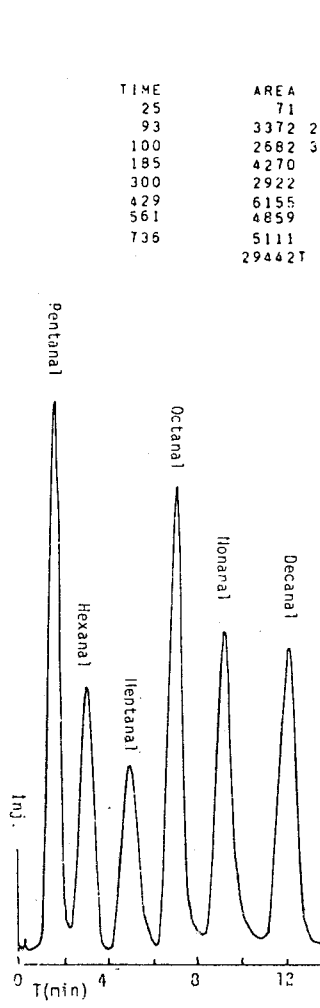


Figure 2. Separation of C₅-C₁₀ n-aldehydes. Temp. Prog. 75°-140° at 8°C min⁻¹ with nitrogen carrier gas flow rate 30 ml min⁻¹

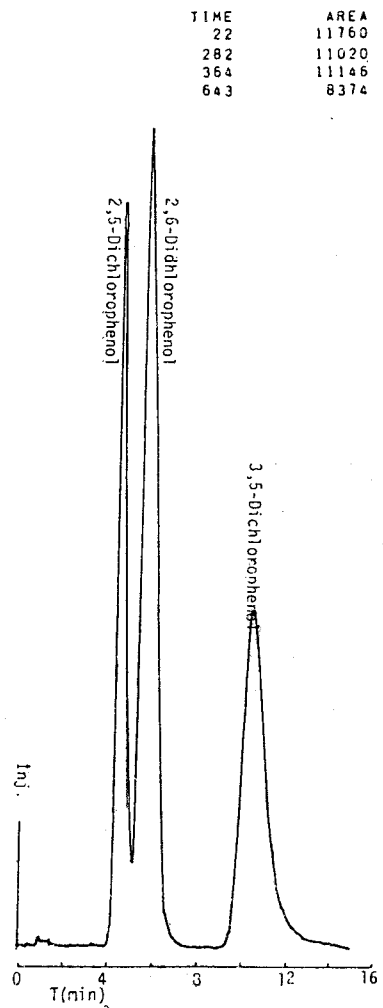


Figure 3. Separation of dichlorophenols at 140° with nitrogen carrier gas flow rate 30 ml min⁻¹, t_M (cal.) = 18 sec.

separation of aldehydes in which no column bleeding was observed in temperature programmed separation. This indicates the PCAK phase thermal stability. Symmetry in the higher aldehydes peak at elevated temperature and no "ghost" peak observation indicates no contraction of the phase film, exposing bare support surface. Very high J' value of PCAK contrary to PCK phase indicates chlorocarbon chain is contributed effectively in the separation of halogenated compounds. It was made feasible to separate isomers having identical or very near melting and boiling points. As it is seen in Figure 3. 3,4-dichlorophenol (I (140°) = 1518 i.u.), 2,6-dichlorophenol (I (140°) = 1415 i.u.) and 2,5-dichlorophenol (I (140°) = 1368 i.u.) were separated from each other. Also acidic isomers can be separated on this phase. Figure 4. shows the separation of 3-nitrotoluene (I (140°) = 1452 i.u.) from 2-nitrotoluene (I (140°) = 1401 i.u.). The separation of underivatized carboxylic acids is a particularly severe test of the support deactivating properties of the phase. Figure. 4 shows the separation of 3-chloropropanoic acid (I (125°) = 1157 i.u.) from 2-chloropropanoic acid (I (125°) = 1071 i.u.). 7 % PCAK column was completely unaffected by repeated injection of water. No preconditioning of the packing with injections of water was necessary to obtain reproducible peak areas. Also no "ghosting" of components was observed when injections of water were made subsequent to sample injections.

CONCLUSION

Polychlorinated kerosene as a stationary phase is possessed the property of deactivation solid support enabling the separation of highly active organic compounds like halogenated acids but the main drawback was column bleeding at elevated temperatures. To overcome this problem n-alkanes part separated by urea adduction and chlorinated. This new stationary phase PCAK is displayed better chromatographic properties in the separation of halogenated isomers and column bleeding.

TIME	AREA
23	8
31	86
124	4454
337	4003
447	4835
	13386T

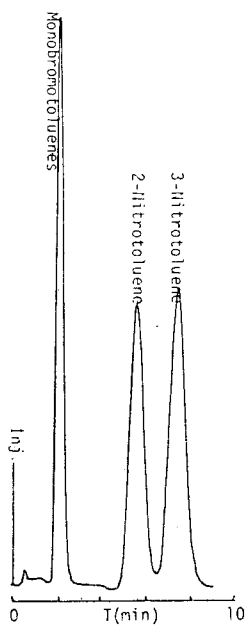


Figure 4. Separation of nitrotoluenes at 140° with $N_2 = 30 \text{ ml min}^{-1}$ t_M (cal) = 18 sec.

TIME	AREA
42	108
103	2801
169	5721

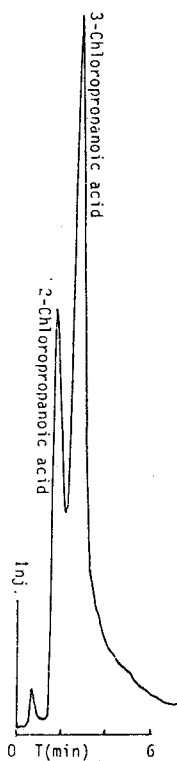


Figure 5. Separation of chloropropanoic acids at 126° with $N_2 = 30 \text{ ml min}^{-1}$ t_M (cal) = 19 sec.

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