COMMUNICATIONS

STATIONARY PHASE FOR GAS CHROMATOGRAPHY I
POLYCHLORINATED KEROSENE (PCK) PHASE

by

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ABSTRACT

The polychlorinated kerosene (PCK) is a useful medium-polar staticnary phase with a usable temperature range from ~40°to 150° and imparts an unusually high degree of support deactivation enabling nitro compounds, aldehydes, carboxylic acids to be analyzed at low concentrations. McReynolds constants are given.

INTRODUCTION

The principles of gas chromatography (GC) were first suggested by Martin and Synge (1941) and later advanced by James and Martin (1952). With the advent of the technique, the separation of very closely related compounds was made possible. In order to achieve these separations, column technology has been and continues to be of prime importance, in as much as the column is the heart of the chromatographic system. In its evolution the chromatographic column has changed from a system of rather low efficiency to high efficiencies, to one in which the resolution of isomers are possible. Broadly speaking, columns may be divided into two subcategories, the open-tubular or capillary systems and packed-bed systems. Packed colups continue to be used and without question serve many useful purposes especially in high volume preparative separations and crude synthetic reactions mixture separations in organic research laboratories. Chief advantages of packed columns are sample ruggedness, ease of preparation and low cost. Today's problem is focused on separation of isomers. Modified kerosene derivatives are potent to show such property in the separations.

For this reason a programmed investigation is started for the preparation of kerosene originated, chemically modified stationary phases.

Kerosene is the middle range fraction of crude petroleum and its main components are branched chain hydrocarbons and n-alkanes with lesser amounts of unsaturated and aromatic compounds, the ratio of which vary according to the origin. This indefinite composition is the main drawback. But in GC column technology a lot of such commercial produtcs are being used succesfully for decades. As an example fluorinated surfactants of which their chemical structures are propriotory information have been introduced by Poole and Dhanesar (1983). They have unique properties as a stationary phase.

In the fist part of this study, we have investigated chlorinated kerosene. There are about 700 to 1000 liquid phases which have been mentioned in the literature and most firms dealing in GC supplies now list about 100 to 200. This multitude of liquid phases is best arranged on a scale of chromatographic selectivity by using a scheme first suggested by Rohrschneider (1957) and further improved by Mc Reynolds (1970). Both the Rohrschneider and McReynolds'values (I_R, inappropriately termed "constants") are the differences between Kováts (1958) retention indices for carefully selected test compounds determined on any GC liquid phase and on a reference liquid phase; squalane. Slightly different test compounds and different temperatures, 100° vs. 120° are used in determining Rohrschneider and McReynolds constants. Determination of Kováts indices is based upon a plot of the linear relationship between the logaritms of the adjusted retention time (t'_R) and the carbon number of a homologous series of n-alkanes at constant temperature on a GC column. The Kováts indices for normal alkanes are by definition 100 times the carbon number.

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°, $D_{22} = 0.7826$. 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.

Kerosene (15 g) was put in a temperature control jacketed glass reactor and chlorine was bubled from the inlet tube with a sintered glass plate at its lower end. After short induction period chlorination was started and hydrogen chloride was evolved. During the first 90 min temperature was kept at 20° and raised to 90° gradually, as the viscosity of the chlorinated product increased. Chlorination was continued until the product had increased in weight by 51.3 g. Product was cleaned from dissolved hydrogen chloride and chlorine by keeping under reduced pressure at 150° for 30 min. Product was light strawcolored glassy semisolid which would not flow at ambient temperature.

Column packings containing 7 % (w/w) of polychlorinated kerosene (PCK) 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 130° max with nitrogen carrier gas flow rate of 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.

Number of theoretical plates (n) of the column for a given solute is determined from (Ettre 1977).

$$n = 5.545 \ (t_R / w_h)^2 \qquad\qquad (1)$$

Number of theoretical plates per meter is n / L. Where (t_R) is the retention time of solute, (w_h) is peak width of the solute at half height. (L) is the column length in meter.

Gas hold up time (air peak) (t_M) of the column for a given temperature is determined from (Peterson, Hirsch, 1959).

$$t_M = t_{R2} - \frac{x_3 \cdot x_2}{x_3 - x_1} \quad \text{where,} \tag{2}$$

$$x_3 = t_{R3} - t_{R2}, \qquad x_1 = t_{R2} - t_{R1}$$

Where t_{R1}, t_{R2}, t_{R3} are retention times of three subsequent members of the homologous series which are equidistant in their carbon number.

The retention index of a solute on a stationary phase at a specified column temperature ($I_s{}^{st.ph.}$ (T)) is determined from the adjusted retention times (t'_R) using the standard procedure Kovátz (1958).

$$I_s{}^{st.ph.} (T) = 100z + 100 \frac{\log t'_{Ri} - \log t'_{Rz}}{\log t'_{R(z+1)} - \log t'_{Rz}} \quad \text{i.u.} \tag{3}$$

Where t'_{Ri} is the adjusted retention time of the compound of interest, $t_{R(z+1)}$, t'_{Rz} are the adjusted retention times of two bracketing n-alkanes with the carbon numbers z and z+1.

The retention index in temperature-programmed separation is determined from the equation of Van den Dool and Kratz (1963).

$$I (TPGC)_s{}^{st.ph.} = 100z + 100n \frac{t_{Ri} - t_{Rz}}{t_{R(z+n)} - t_{Rz}} \quad \text{i.u.} \tag{4}$$

Where i refers to the substance of interest, n is the difference in the carbon numbers of the two bracketing n-alkanes z is the carbon number of smaller bracketing n-alkanes.

McReynolds (1970) constants are determined by subtracting the retention index for the test probe on squalane from that of the test probe on any other liquid phase of interest.

$$\triangle I_R = I_R{}^{test\ phase} - I_R{}^{squalane} \tag{5}$$

The higher the value of the McReynolds constants the more the chromatographic polarity or selectivity of the phase.

RESULTS AND DISCUSSION

IR spectra of kerosene and polychlorinated kerosene (PCK) were given in Figure 1. It is seen that C-H stretching of CH_2 groups in kerosene (2900–2950 cm^{-1}) decreased or dissapeared in PCK, while characteristic C-Cl strecthing vibrations were appeared at 800–700 cm^{-1} in PCK.
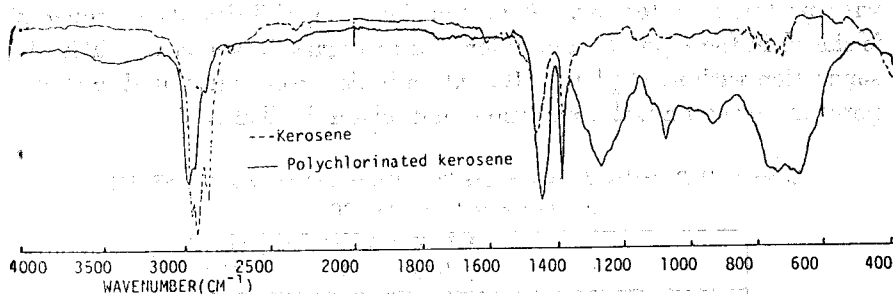

Figure 1. Infrared spectra of kerosene and polychlorinated kerosene, kerosene spectra in 0.05 mm. thickness liquid cell with KBr window, polychlorinated kerosene on KBr disc. Scan mode 5 min.

7 % (w / w) PCK coated packing having 1900 plates per meter (calculated for n-tridecane) (Figure 2.) was prepared by standard procedures and without any particular difficulties. Although the plate count is not particularly high the value quoted reflect the mechanical stability of the support rather than undesirable coating characteristics of the phase (Cander, 1979). Similar values were obtained for the squalane which was used for the determination of McReynolds' constants, prepared with the same batch of support, coated and packed in an identical manner. Gas gold up times (t_M) used in retention index calculations were determined from three succesive n-alkanes retention times by using the method of Peterson and Hirsch (1959). (Brian, Kersten, et. al, 1987).

The McReynolds' values for PCK were given in Table 1. On the basis of these values PCK could be described as a moderately polar phase. As it is seen, chlorocarbon chain is not likely to contribute additional separation to halogenated compounds because J' value is nearly the same with the Silicon Ge SR 119 phase; this was shown in Figure

3. In the separation of butyl bromide isomers, where only tert-butyl bromide was separated from n-butyl bromide, not the others. Retention indices were found It_{t-BuBr}^{PCK} (50) = 715 i.u., I_{n-BuBr}^{PCK} (50) = 845 i.u. respectively.

In terms of their McReynolds' constants the Silicone GE SR 119 phase is closest among generally available stationary phases in matching the properties of PCK, although 42 i.u. difference exist in Z' value; see Table 1. This shows that PCK phase contributes orientation properties with proton acceptor but not proton doner capabilities. This property is shown in the separation of aldehydes in Figure 4., which is a difficult separation with most phases. Retention indices were calculated for temperature programmed separation and given in Table 2.

Table 1. McReynolds. Constants for PCK Phase and Silicone GE SR 119*
and Capacity Ratios for PCK.

		PCK (i.u)	GE SR 119 (i.u)	Capacity ratio (k)
ΔI Benzene	(X')	161	166	2.24
ΔI Butanol	(Y')	228	238	2.35
ΔI 2– Pentanon	(Z')	263	221	4.05
ΔI 1– Nitroprcpane	(U')	216	314	7.70
ΔI Pyridine	(S')	280	299	7.76
ΔI 1– Iod butane	(J')	151	158	7.18

t_M calculated for 120° = 16 sec.

*From McReynolds. (1970) publication.

Table 2. Calculated I (TPGC)PCK of n-Aldehydes Temperature
Programming from 75° to 140° at 8° C min⁻¹.

Compound	I(TPGC)PCK i.u.
n-Butanol	826
n-Pentanal	896
n-Hexanal	994
n-Heptanal	1084
n-Octanal	1178
n-Nonatal	1285
n-Decanal	1383

S' value is 19 i.u. less than Silicon Ge SR 119 phase. This indicates the less acidic character of the phase. Y' value is 10 i.u. less which indicates less basicity (Burns, Hawkes 1977). So PCK phase is more neutral than silicon Ge SR 119. This was best shown in the separation of chlorinated propanoic acid isomers in Figure 5, with the retention
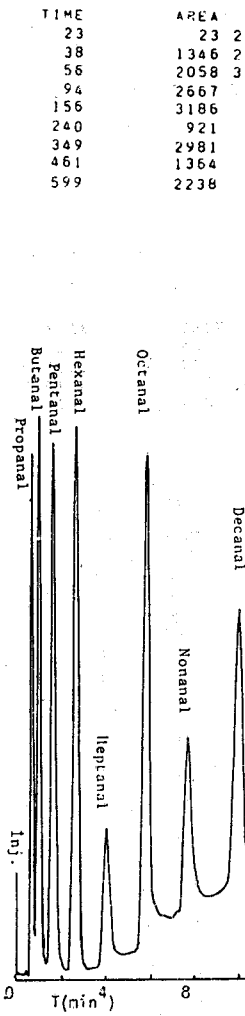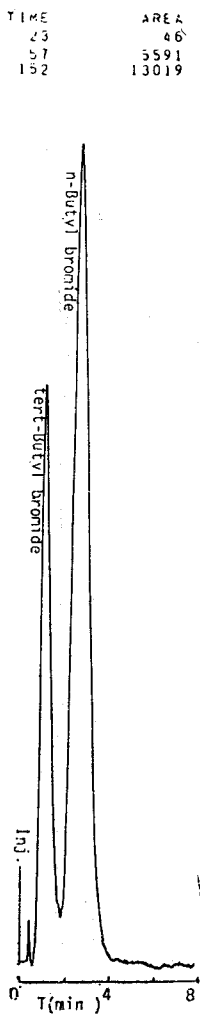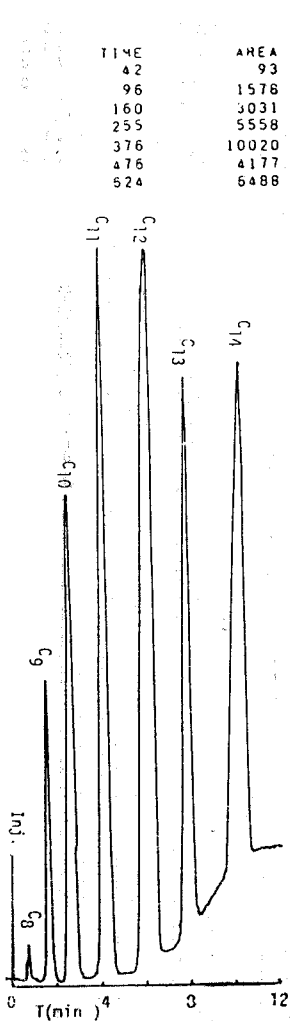
Figure 2. Test chromatogram, illustrating column efficiency. Test mixture C₂-C₁₂ n-alkanes. Temp. Prog. 75°-140° at 8°C min⁻¹ with nitrogen carries gas flow rate 30 ml. min⁻¹.

Figure 3. Separation of butyl bromides at 50°, with nitrogen carrier gas flow rate 30 ml. min⁻¹.

Figure 4. Separation of C₃-C₁₀ n-aldehydes Temp. Prog. 75°-140° at 8°C min⁻ with nitrogen carrier gas flow rate 30 ml. min⁻¹.

TIME | AREA
.23 | 18 2
.30 | 17 2
41 | 9 3
59 | 52
95 | 3730
293 | 8271
397 | 7233 2

TIME | AREA
59 | 23 2
93 | 2652 3
294 | 7501
456 | 8108

TIME | AREA
36 | 37 2
57 | 716 2
114 | 4715 3
219 | 5833

2-Nitrotoluene
3-Nitrotoluene
2-Nitrotoluene
Monobromotoluenes
4-Nitrotoluene
Monobromotoluenes
Inj.

3-Chloropropanoic acid
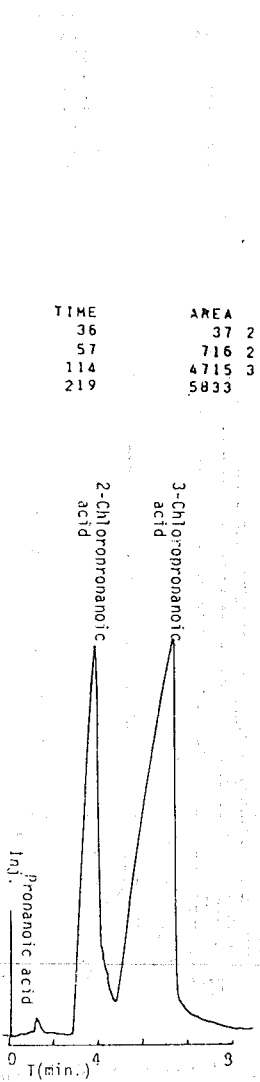2-Chloropropanoic acid
Propanoic acid
Inj.

T(min.)

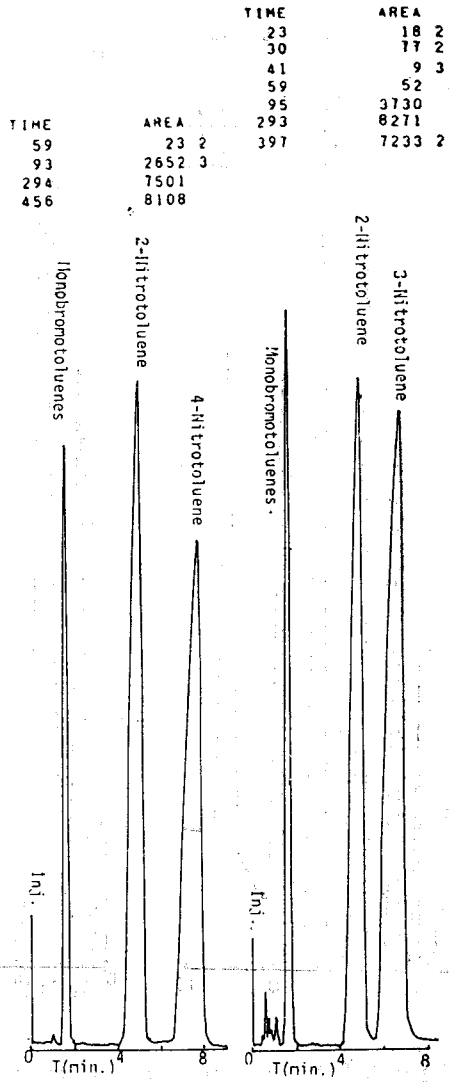Figure 5. Separation of chloropropanoic acids at 120°. N_2 = 30 ml. min^{-1}. t_M (cal. .) = 16 sec.

Figure 6. Separation of nitrotoluenes at 140° with nitrogen carrier gas flow rate 30 ml. min^{-1} t_M (cal.) = 15 sec.

indices $I_{2-ClPrAc}^{PCK}$ (120) = 1124 i.u., $I_{3-ClPrAc}^{PCK}$ (120) = 1235 i.u. res-

pectively, and in the separation of nitrotoluenes, but not in haloto-

luenes in Figure 6. with the retention indices I_{2-NT}^{PCK} (140) = 1511 i.u.

I_{3-NT}^{PCK} (140) = 1569 i.u. I_{3-NT}^{PCK} = 1595 i.u. respectively. After five times

repeated separations no change in retention indices was observed. So
there is no interaction between strong acids and phase, this increases
the useful life time of the phase.

Retention on PCK phase is therefore a combination of selective
interactions between the polar functional groups of the solute and
phase which is largely independent of the presence of chlorine, except
perhaps for some modification due to the inductive effect of chlorine
and diminished retention due to the weak dispersive interactions occur-
ing between the solute and the chlorocarbons of the phase.

As it is seen in Figures 2 and 4 at elevated temperatures there exists
column bleeding, which shows PCK is not producing a very stable film
at elevated temperatures. This we attribute to the poor support wetting
characteristics of PCK.

As it is seen in chromatographic separations of PCK there is no
tailing and even very small quantities of samples are separated. This
imparts high degree of support deactivation and as a result no interac-
tion between solute and support is observed.

PCK column 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 distilled water are made
subsequent to the sample injections.

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