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POLY(α -OLEFINS)—NOVEL NON-POLAR STATIONARY PHASES FOR GAS CHROMATOGRAPHY

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SUMMARY

Several special poly(α -olefinic) type polymers were characterized and evaluated as non-polar liquid phases for gas chromatography. In addition, a new non-polar stationary phase, produced by the catalytic hydrogenation of an Apiezon L grease is also described. These new phases have the advantage over squalane of a maximum operating temperature of 225° allowing preparation of non-polar wall-coated open-tubular columns exhibiting a much wider temperature range.

These polymers have desirable physical and chemical properties. Because of their structural configuration, they have the ability to coat glass surfaces with a uniform thin film.

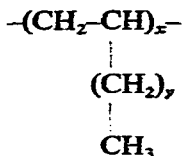
A limited number of applications indicate that capillary columns prepared with new phases provide very good separation of different functional group compounds and can separate structurally similar compounds such as Mirex and its metabolites.

INTRODUCTION

Today, at least 300 liquid phases are available for gas chromatographic (GC) use. The most popular types include silicone oils, polyesters and polyether glycols. However, only a few of the non-polar phases available possess enough of the qualities represented by squalane. Unfortunately, squalane suffers from the disadvantages discussed earlier¹. The choices in non-polar liquid phases are further limited by the quantity and types of materials marketed. An exception to this is the "tailor-made C₈₇-hydrocarbon", synthesized by Riedo *et al.*¹, which exhibits a significant degree of branching, has a molecular weight 1222 and a temperature limit of 250°. The synthesis of this compound, however, is complicated and this is reflected in the purchase price.

Among the higher-molecular-weight compounds, special polymers exist with intermediate structures between the branched and linear chained polymers. The macromolecules of these consist of long side chains of each monomer unit attached

to the polymer backbone with the aid of various chemical junctions. Their basic structure may be characterized by the following general formula:



where x may vary between 2-8 and $y = 3-16$.

The higher series of poly(α -olefins) which are similar in nature to these polymers were found to have advantageous properties as stationary phases in GC.

Although materials of this kind are classified as linear polymers, the specific and unique properties of the long side-chain make them desirable non-polar stationary liquid phases for capillary GC. They should be regarded as bulky, branched, comb-like, high-molecular-weight compounds having different physical and chemical properties than linear polymers.

Although silicone phases will probably continue to predominate for many analytical applications, there still exist those analyses where there are unsatisfactory separations due to lack of selectivity, thermal stability, working range or molecular weight distribution.

Recently, Vernon and Ogundipe² published their results and preparation of a non-polar Apiezon M produced by the catalytic hydrogenation of the grease. We also compared these results with the catalytic hydrogenation product of Apiezon L grease, which produced a highly stable, high-temperature, non-polar liquid phase suitable for glass capillary GC.

Even among researchers, there are varying views concerning the proper optimization of different liquid phases towards a difficult separation of certain pairs or groups of compounds. The difference in transfer of an analytical concentration of solute to the liquid phase must be regulated by means of a selective liquid film, as defined by their differences in Gibbs free energies, as recently discussed by Guiochon³. This formulation states clearly that more than half a dozen stationary phases are required, contrary to Verzele⁴. However, it may be correct that perhaps 90% of all applications can be performed on those six stationary phases, if all chromatographic conditions are optimized.

EXPERIMENTAL AND RESULTS

All experiments were performed on a Dani 3900 gas chromatograph using both flame-ionization (FID) and electron-capture detectors (ECD).

Preparation of Apiezon grease

Technical Apiezon L (Chromatographic Specialties, Brockville, Canada) is purified according to Jensen and Sundstrom⁵ on an aluminum oxide (neutral) column with *n*-hexane as eluent. A colorless wax is obtained. A 25-g amount of pre-purified Apiezon L and 10 g of freshly prepared palladium on carbon (5%) in 200 ml of *n*-hexane is hydrogenated at room temperature for 4 h with stirring and

using a hydrogen pressure of 5 atm. After removal of catalyst by filtration, the solvent is removed by rotary evaporation.

Residual unsaturation

The infrared (IR) spectra of Apiezon L, before hydrogenation, clearly show two moderate absorption maxima near 1670 cm^{-1} (*trans*-olefins) and 1650 cm^{-1} (*cis*-olefins). The hydrogenated Apiezon L showed only traces of residual unsaturation. Proton magnetic resonance (PMR) and ^{13}C -nuclear magnetic resonance (NMR) confirmed these data. Polyoctene-1 and Polydecene-1 were obtained from the Uniroyal Research Labs, Guelph, Canada. Table I lists physical properties of the poly(α -olefins).

TABLE I
PHYSICAL PROPERTIES OF POLY(α -OLEFINS) UNDER STUDY

Polymer	Polyoctene-1	Polydecene-1
Density (g/cm ³)	0.84	0.85
Viscosity (cSt) at 100°	64.3	12.9
Flash point	223°	293°

Size-exclusion chromatographic analysis (SEC)

Three samples containing polyoctene-1 (PAO-60), polydecene-1 (PAO-12) and hydrogenated Apiezon (AP-LH) have been characterized by means of SEC. A series of three porous silica columns (SE 100, 60, 60) and a flow-rate of 20 ml/min at room temperature were used. A volume of 0.5 ml of an 0.2% solution in chloroform was injected for profile analysis. SEC analysis was carried out using a DuPont 830 liquid chromatograph and an IR detector. The following conditions were employed: columns, SE 100, 60, 60; Slit, 1; Meter response, 40; wavelength, $3.4\ \mu\text{m}$; temperature, 20°; flow-rate, 2.0 ml/min; mobile phase, chloroform.

For the molecular-weight determination, SEC columns were calibrated with monodispersed polystyrene standards of known molecular weights. The calculation of molecular weight values from a SEC were performed from the following equations:

$$\bar{M}_w = \frac{\sum h_i M_i}{\sum h_i}; \bar{M}_n = \frac{\sum h_i (n_i) (M_i)}{\sum h_i N_i}; D = \frac{\bar{M}_w}{\bar{M}_n}$$

where h_i is the peak height (concentration) of the molecules in the i th molecular weight state; M_i is the molecular weight of the molecules in the i th molecular weight state; N is the molecular normalization factor.

TABLE II
MOLECULAR-WEIGHT DISTRIBUTION DATA FOR COMPOUNDS UNDER STUDY

Polymer	\bar{M}_w	\bar{M}_n	$D (M_w/M_n)$	Peak max.
PAO-60	690	605	1.14	573
PAO-12	602	495	1.22	560
AP-LH	1470	960	1.53	1200

The molecular-weight distribution values were calculated by means of a DuPont software program. From the SEC profile and the calibration curve, the \bar{M}_w , \bar{M}_n and D were calculated for each sample as given in Table II.

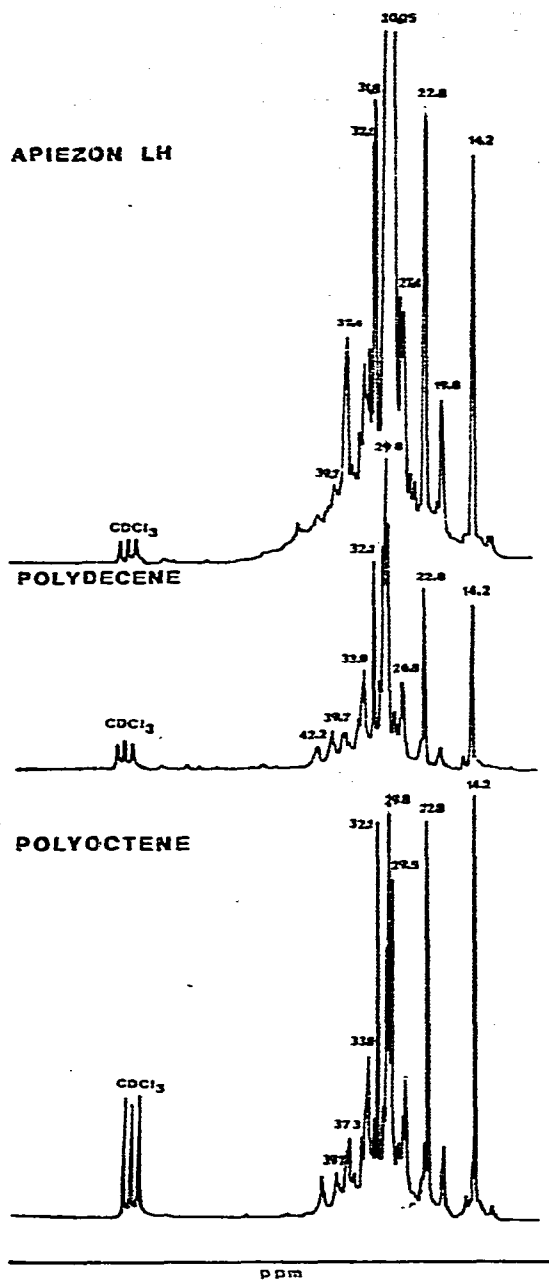


Fig. 1. ^{13}C -NMR spectra of polyoctene-1, polydecene-1 and hydrogenated Apiezon L.

¹³C-Nuclear and proton magnetic resonance data

These materials were further characterized by means of PMR and ¹³C-NMR spectra shown in Fig. 1. Experimentally, the chemical shifts of both the methyl and methylene groups in PAO-60 and PAO-12 occurred within a narrow range in the absence of β -substituents in the PMR spectra.

In spite of the apparent insensitivity in chemical shifts, careful examination of the characteristic signals assignable to the methyl group ($\delta = 0.88$) makes it possible to obtain considerable structural information from the spectra of paraffinic polymers. In combination with the ¹³C-NMR data, as outlined in Table III, no significant differences exist between a particular *n*-alkane and the corresponding polymer. ¹³C-NMR spectra support a saturated structure.

TABLE III

CHEMICAL SHIFTS IN ¹³C-NMR SPECTRA OF POLYMERS AND *n*-ALKANES

Compound	C-1	C-2	C-3	C-4	C-5	(-CH=)
<i>n</i> -Octane ⁶	14.1	23.0	32.4	29.7	—	—
PAO-60	14.2	22.8	32.1	29.8	—	—
<i>n</i> -Decane ⁶	14.1	23.0	32.4	29.9	30.3	—
PAO-12	14.2	22.8	32.1	29.8	30.2	29.5
AP-LH	14.2	22.8	32.1	29.8	30.05	—

Polymers of high stereoregularity yield spectra that can be interpreted in terms of single repetitive units, the chemical shifts of which reflect the average molecular environment of the monomer unit along the entire conformation of the chain. Even if the repeating monomer unit is of relatively simple structure, the problem of spectral interpretation is not unlike that encountered for *n*-alkanes.

Mass spectrometric (MS) characterization

The following mass spectra of three liquid phases are intended to aid the GC-MS operator in identifying characteristic fragment ions which may appear due to background bleed from the columns, (Fig. 2).

Chemical-ionization mass spectra of poly(α -olefins) by means of methane were obtained. The signals, with the time *versus* peak heights of the molecular ions for the various polymer unit lengths were integrated for constant temperature (250–300°), and ratios of the areas.

Composition of individual polymers is estimated in Table IV. There is considerable fragmentation (fragments are CH₂ apart), thus, it is quite uncertain how well these values reflect the actual proportion of polymer.

Thermogravimetric analysis

In Fig. 3, four thermograms of the two PAO samples, hydrogenated Apiezon L and C₈₇-hydrocarbon are given.

Data revealed that the materials were stable with a minimum of bleeding up to 240°; at 250°, 2% of C₈₇-hydrocarbon, 5% of PAO-60 and 3% of PAO-12 was lost; at 280°, over 15% C₈₇, PAO-60 and PAO-12 and only 4% AP-LH was lost

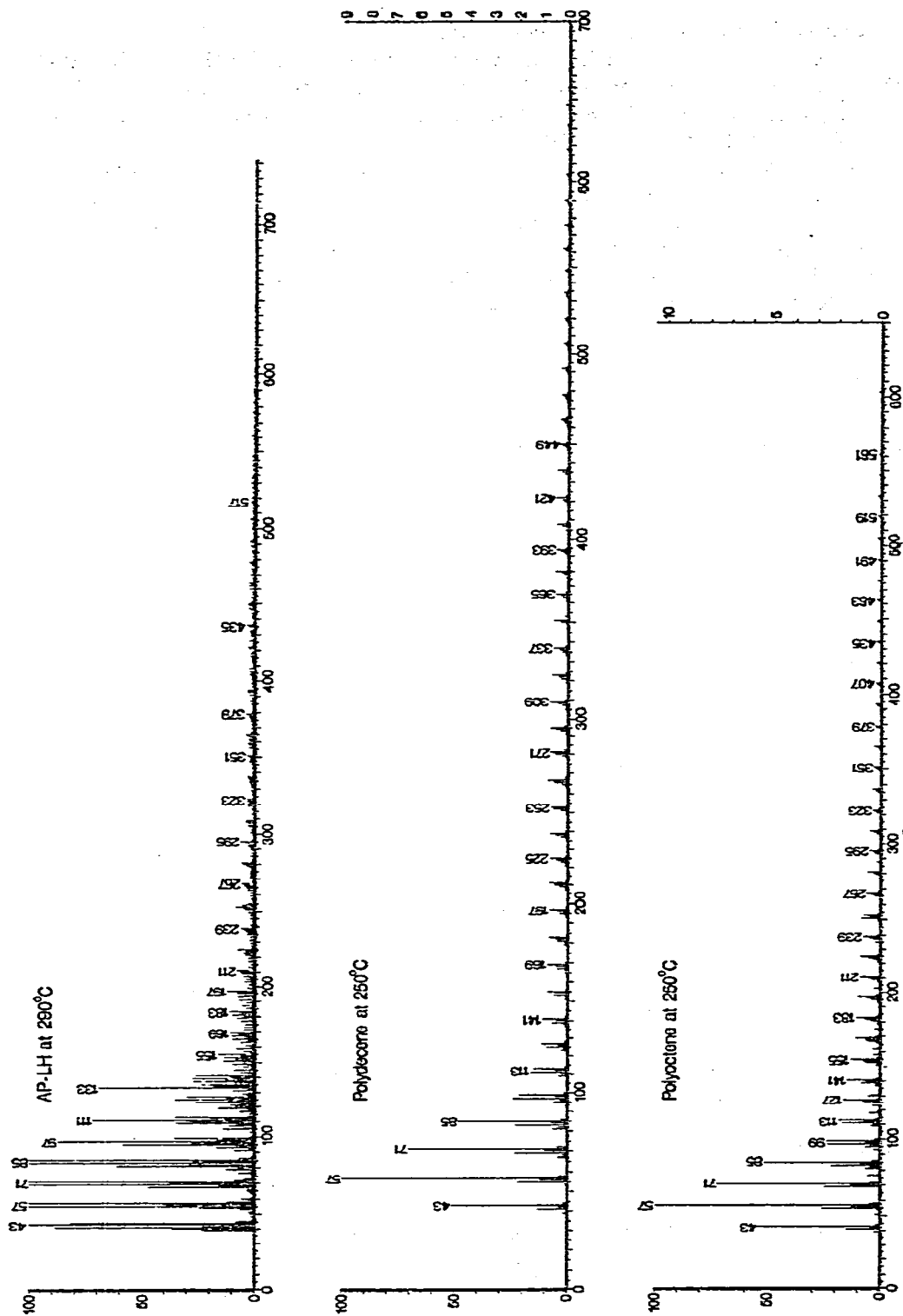


Fig. 2. Electron-impact mass spectra of poly(α -olefins) and hydrogenated Apiezon L obtained via a solid probe.

TABLE IV

ESTIMATED COMPOSITION OF INDIVIDUAL POLYMERS

	<i>Polyoctene-1, PAO-60 (%)</i>	<i>Polydecene-1, PAO-12 (%)</i>
Monomer	13.3 \pm 3.4	5.5 \pm 0.5
Dimer	27.2 \pm 0.1	11.8 \pm 0.4
Trimer	22.3 \pm 2.8	30.1 \pm 2.0
Tetramer	18.9 \pm 1.0	41.3 \pm 2.5
Pentamer	19.8 \pm 4.5	11.3 \pm 0.4
Hexamer	4.6 \pm 2.7	trace
Heptamer	trace	trace

from the column packing. It must be stressed that both PAO-60 and PAO-12 were not specially pre-treated but represent technical products as obtained.

Determination of McReynolds values

Determination of McReynolds values was performed on three packed columns using Chromosorb W HP. For polyoctene, 20% (w/w) of the liquid phase was

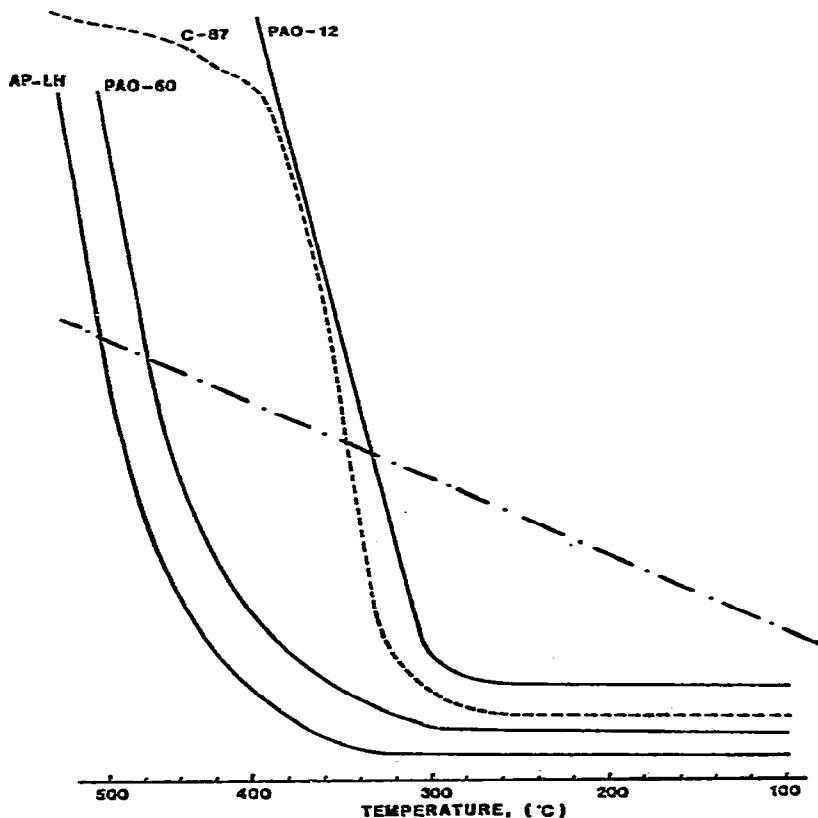


Fig. 3. Thermogravimetric analysis of poly(α -olefins), hydrogenated Apiezon L and C_{67} -hydrocarbon. (PAO-60 11.5 mg; PAO-12 10 mg; AP-LH 6.7 mg; C_{67} -hydrocarbon 4.95 mg; under nitrogen, programming rate 40°/min).

TABLE V
RETENTION INDICES AND RETENTION INDEX DIFFERENCES RELATIVE TO SQUALANE

Phase	Benzene	Butanol	2-Pentanone	1-Nitropropane	Pyridine	2-Methylpentanol	1-Isobutane	2-Octyne	Dioxane
Squalane	652	590	627	652	699	690	818	841	654
ΔI	0	0	0	0	0	0	0	0	0
AP-LH	665	599	630	664	731	692	825	—	—
ΔI	13	9	3	8	32	2	7	—	—
PAO-60	659	598	625	654	708	679	829	849	663
ΔI	7	8	-2	2	9	-11	8	8	9
PAO-12	657	585	627	654	702	684	829	845	660
ΔI	5	-5	0	2	3	-6	8	4	6
AP-L ¹¹⁴	687	627	651	700	770	—	—	—	—

employed. Polydecene as a liquid phase was coated over Chromosorb W HP with 25.8% and a hydrogenated Apiezon L concentration of 25% (w/w) on Chromosorb W HP was employed. The column lengths were 60 cm for each phase. All columns were properly conditioned and evaluated by a FID. Obtained values of the corresponding retention indices were calculated from three injections at 120°. They are listed in Table V. Squalane values were obtained from ref. 7.

Preparation of capillary columns

Two years ago, we described a method for the preparation of glass capillary columns where Pyrex glass has been used exclusively and, as an agent suitable for the formation of the whiskered surface (more precisely the filamentary crystals), ammonium hydrogen difluoride was employed^{8,9}. This treatment greatly reduced the catalytic activity of the boro-silicate surface. However, for low activity surface it is necessary to reduce remaining surface active sites by means of suitable deactivation. A suitable means of deactivating Pyrex glass is represented by the silylation, especially when non-polar liquid phases are to be used. We have been using a hexamethyldisilazane-trimethylchlorosilane mixture (5:1) as recommended by Novotny and Zlatkis¹⁰ and modified at our laboratory¹¹. Details will be published elsewhere in the near future.

All columns were coated by means of the mercury plug method¹⁴ using *n*-heptane solution (5%, w/v). Test chromatograms of the coated columns are presented in Fig. 4.

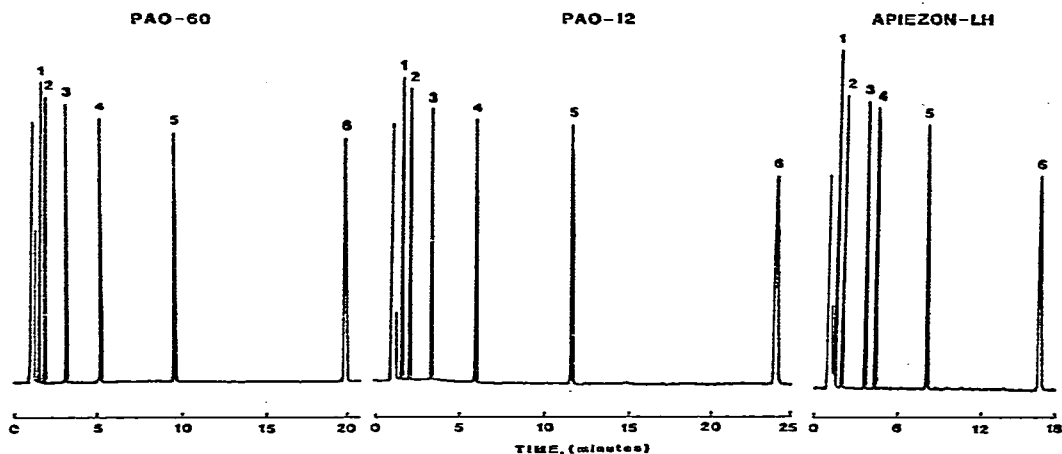


Fig. 4. Test chromatograms of three glass capillary columns. 1 = 1-Octanol; 2 = 5-nonanone; 3 = naphthalene; 4 = *n*-tridecane (C_{13}); 5 = *n*-tetradecane (C_{14}); 6 = *n*-pentadecane (C_{15}).

A check for "true neutrality", performed in terms of the quantitative procedure of Grob *et al.*¹² revealed a superior quality and neutrality reflected to acid/base properties. Although recommended by Grob *et al.*, our mixture did not contain all components suggested, because some were unavailable at our laboratory. Chromatograms are shown in Fig. 5.

Finally, all three columns were tested on the same sample for quantitative

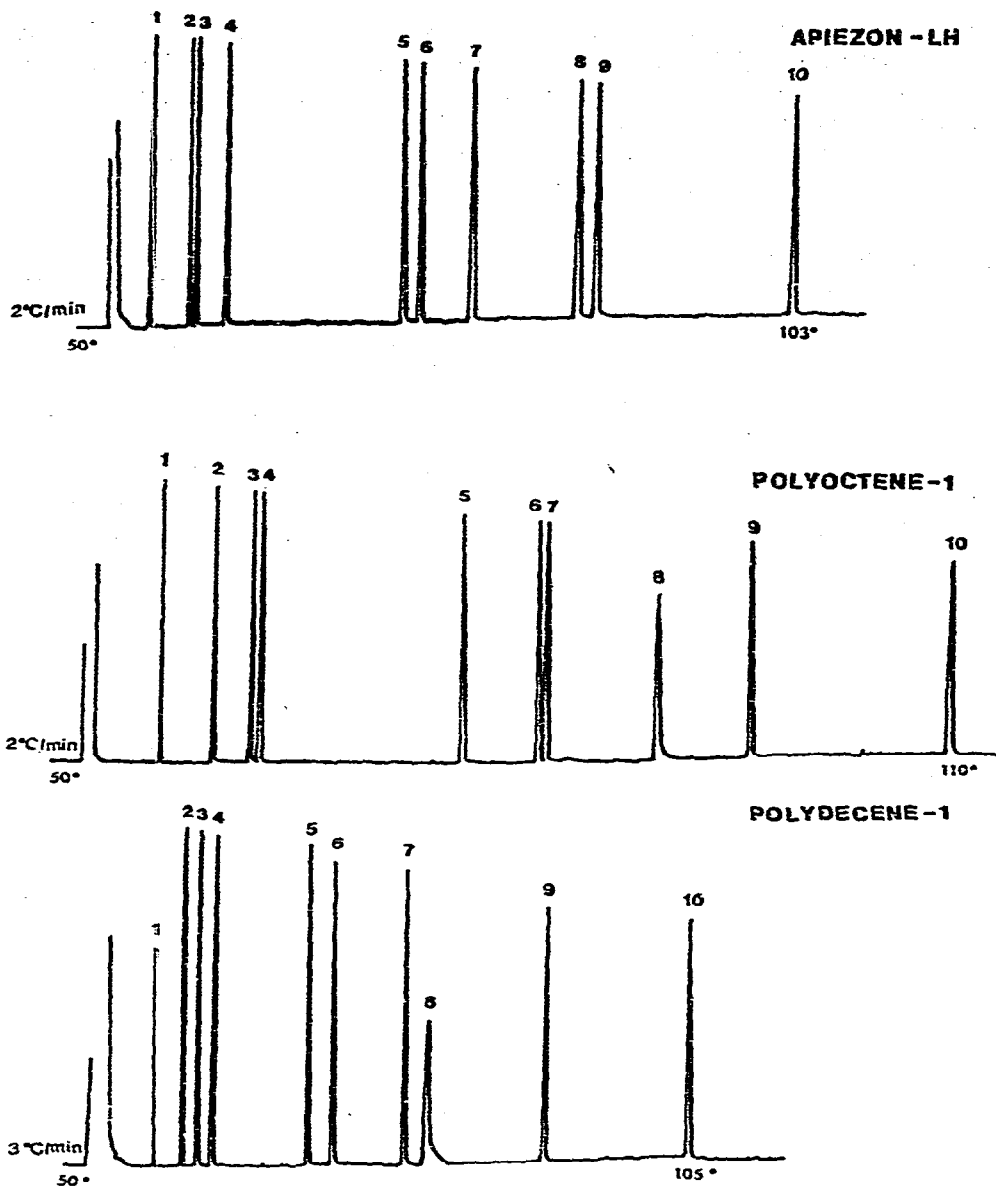


Fig. 5. Chromatograms showing neutrality of the columns. Helium as a carrier gas 25 cm/sec; Elution order: 1 = 1,3-propanediol (214°); 2 = C_{10} (174°); 3 = *i*-octanol (186°); 4 = 1-nonal (185°); 5 = C_{11} (196°); 6 = 2,6-DMP (203°); 7 = 2,6-DMA (215°); 8 = 2-ethyl hexanoic acid (228°); 9 = methyl decanoate (224°); 10 = methyl laureate (262° b.p.).

determination of Mirex and its metabolites using an electron capture detector in the modulated frequency mode. Chromatograms are shown in Fig. 6 and quantitative data in Table VI.

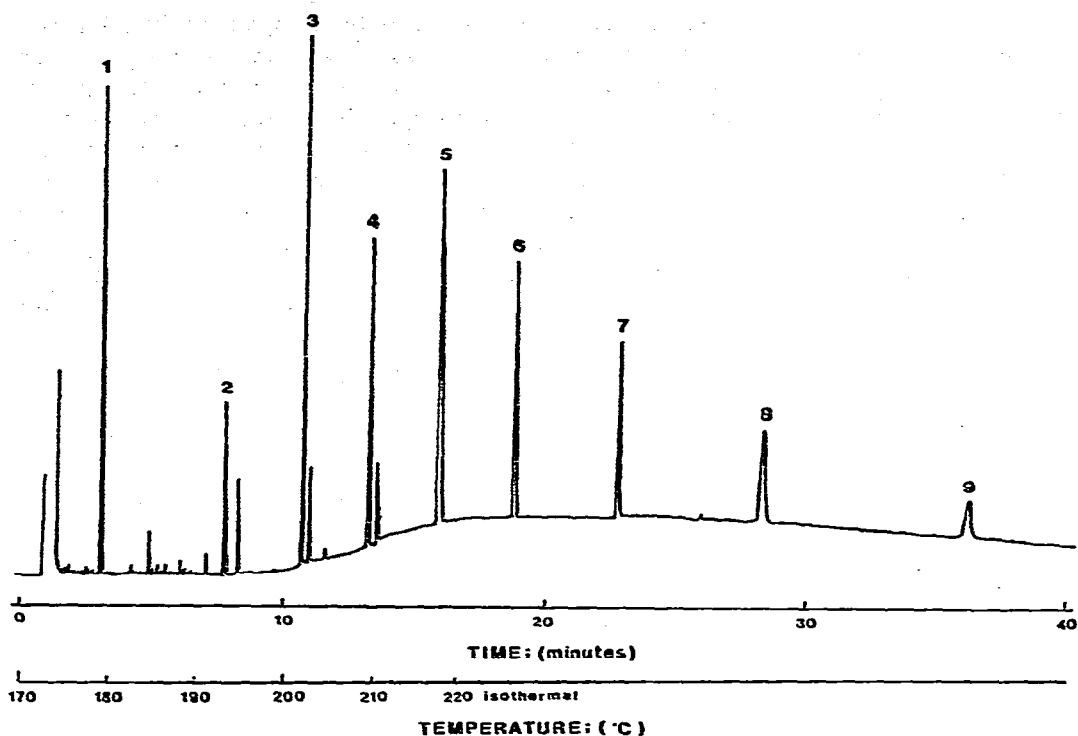


Fig. 6. Separation of Mirex and its metabolites on PAO-60 WCOT column by means of ECD. 1 = *trans*-Nonachlor; 2 = 2,8-dihydro-Mirex; 2a = 10,10-dihydro-Mirex; 3 = 8-hydro-Mirex; 4 = 10-hydro-Mirex; 5 = Mirex; 6, 7, 8 = phthalates; 9 = unknown.

DISCUSSION

Huber and Kováts¹⁵ have reported criteria for non-polar stationary phase which should have a molecular weight over 1200 and an upper operating temperature near 300°. We experienced that the temperature limit for C₃₇-hydrocarbon coated on a glass capillary surface is lower and due to the bleeding, cannot be used over 260°.

TABLE VI

COMPARISON OF QUANTITATIVE DATA FOR MIREX AND 8-MONOHYDRO-MIREX ON THREE COLUMNS

TV = true value/standard.

Mirex Amount injected (pg)	Amount recovered (pg)			8-Monohydro-Mirex Amount injected (pg)	Amount recovered (pg)		
	C-1	C-2	C-3		C-1	C-2	C-3
10.5	10.0	10.6	10.1	12.5	12.5	12.9	12.4
150.0	151.0	156.0	154.0	189.0	190.0	192.0	189.0
1046.0	1050.0	1050.0	1046.0	1250.0	1248.0	1253.0	1255.0

Poly(α -olefins), however, are commercially available and, as can be seen from Table IV, they consist primarily of a mixture containing tri-, tetra- and pentamers which, if pre-purified, could produce even better results than presented in this paper. We did not remove oligomers prior to coating of the capillary, however, work is under way to obtain a very narrow fraction of a specific polymer. The polyoctene-1 type phase looks very promising. Polyoctene-1 is a viscous liquid at room temperature and has not been obtained in crystalline form even at -30° . This fact makes it suitable to operate at subambient temperatures. The long term testing of both polyoctene-1 and polydecene-1 glass capillary columns shows that they are stable up to 210° . However, temperature programming over 200° causes substantial bleeding due to the oligomers present in the mixture.

It is evident that the well-known hydrocarbon grease, Apiezon L (after hydrogenation, which removes a substantial part of olefinic unsaturation) represents a suitable, relatively cheap and uniform product. This product is perhaps more like the proposed C_{87} hydrocarbon and its non-polar characteristics are even more pronounced than that of hydrogenated Apiezon M described by Vernon and Ogundipe². The material consists of branched aliphatic and olefinic compounds with molecular weights of about 1400. It spreads very easily on the glass surface and can be coated from *n*-hexane solution even as a 30% solution.

As can be seen, all three non-polar stationary phases represent relatively stable, well-defined solutes. They may be a good alternative to C_{87} -hydrocarbon and non-polar silicones and their thermal stability is only a little lower than for silicone oils. McReynolds' constants, as compared to the arbitrary zero values for squalane, show lower (negative) values for *n*-butanol, 2-methylpentanol and 2-pentanone. This phenomenon can be explained by the fact that even squalane may not be pure enough as discussed by Vernon and Ogundipe².

Column efficiencies expressed by their separation numbers (SN) show that: PAO-60 column exhibited $SN = 34$ for C_{13} - C_{14} at $k' = 4$ and 4500 theoretical plates (TP)/m for C_{14} ; PAO-12 column exhibited $SN = 28$ for C_{13} - C_{14} at $k' = 4.1$ and 3400 TP/m for C_{14} ; AP-L4 column exhibited $SN = 33$ for C_{13} - C_{14} at $k' = 4.0$ and 3450 TP/m for C_{14} .

The chromatogram in Fig. 6 illustrates the use of one of these columns applied to the separation of Mirex and its metabolites. Although this separation is not a difficult one, peak shapes and a complete separation can be achieved easily. The ECD trace is not affected by artifacts due to the aliphatic character of the phase. Quantitative results show that data obtained on all three columns are within the analytical error at picogram levels. There is no adsorption or a discrimination which could be attributed to the particular liquid phase.

In conclusion, the results given here have been confirmed by separations of many mixtures on the three columns at various temperatures. The initial study with poly(α -olefins) as stationary phases have shown some interesting results; particularly noteworthy are the McReynolds values which are lower than for "the most non-polar" squalane. These bulky polymers spread very easily on the glass surface and may be prepared in any desired molecular weight range. These polymers exhibit amorphous structure and their working range may be used from sub-ambient temperatures. Further, they are good solvents for hydrocarbons and even more polar materials. Because of their excellent wetting properties, they have yielded efficient glass capillary columns.

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