

CHROM. 9624

HYDROCARBON STATIONARY PHASES FOR GAS-LIQUID CHROMATOGRAPHY

F. VERNON and C. O. E. OGUNDIPE

The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancs. (Great Britain)

(Received July 9th, 1976)

SUMMARY

For the use of squalane as a standard stationary phase in gas-liquid chromatography, a preliminary clean-up step is suggested where the squalane, in a paraffin solvent, is passed successively through columns of activated carbon and alumina. A new standard non-polar stationary phase, produced by the catalytic hydrogenation of an Apiezon grease, is described. It has the advantage over squalane of a maximum operating temperature of 200°, allowing column polarities at high temperature to be evaluated.

INTRODUCTION

The polarity of a stationary phase, as defined by Rohrschneider¹, using the Kováts retention index system², and later by McReynolds³ is based on the retention of various substances on the phase compared with their retentions on squalane. Although generally accepted as the standard non-polar phase, squalane suffers from the obvious disadvantage that, due to its volatility, it cannot be used at temperatures above 120°. Huber and Kováts⁴ have stated that the molecular weight (MW) of a hydrocarbon to be used as a stationary phase should be higher than 1100, as the upper temperature limit for such a hydrocarbon would be around 300°. McReynolds has evaluated squalane, hexatriacontane, nujol, mineral oil, liquid paraffin, and Convoil-20 as paraffin hydrocarbon stationary phases, but they all have average MWs which are too low, all lying in the MW range of 400–900. In an earlier study on aromatic hydrocarbons as stationary phases⁵, the behaviour of polystyrene and polybenzyl was compared with Apiezon L as a standard phase. The Apiezon greases have a sufficiently high MW to ensure thermal stability but their high degree of unsaturation will mean that retention parameters on Apiezon columns will depend upon the origin and nature of the stationary phase. It was therefore decided that an attempt to hydrogenate completely a sample of Apiezon grease would be undertaken. Average MWs, determined by differential vapour pressure determination, on samples of Apiezon L and M greases gave values of 3,970 and 2,340, respectively, consequently Apiezon M was chosen for the work.

It would be pointless to introduce a new standard stationary phase at this stage if such a phase rendered obsolete the enormous amount of data collected using squalane. As several papers^{3,4} have demonstrated the dependence of the retention index (I) on the MW of the stationary phase, I values on such a new phase are highly likely to be higher than those obtained on squalane and a close comparison of the two, using the McReynolds system, is necessary to prove their interchangeability. During the study of squalane, it became apparent that I values far higher than those given by McReynolds were being obtained. The impurities in commercially available squalane and their effects upon I are also the subject of this paper, which claims that hydrogenated Apiezon M is a suitable material for standard stationary phase preparation and has the advantage of a max. operating temperature of 200°.

EXPERIMENTAL

All experiments were made on a Pye 104 gas-liquid chromatograph with flame ionization detector. The degree of hydrogenation of Apiezon grease was determined by UV spectrophotometry using a Unicam S.P. 800 spectrophotometer.

Hydrogenation of Apiezon grease—recommended method

10 g of Apiezon M and 5 g of freshly prepared Raney nickel catalyst in 200 ml of cyclohexane are hydrogenated at 260° for 24 h with stirring and using a hydrogen pressure of 100 atm. After removal of catalyst by filtration, the solvent is removed by rotary evaporation.

Degree of residual unsaturation

The UV spectra of both Apiezon L and M show clearly defined max. at 238 and 260 nm, being the absorbance max. of olefinic and aromatic unsaturation, respectively. Measurement of absorbances at these two wavelengths, (a) of a suitably diluted sample of the Apiezon M in cyclohexane, and (b) of the hydrogenation solution after removal of catalyst and re-adjustment of solution volume to 200 ml, will give the percentages of residual unsaturation of each type directly.

Clean-up procedure for commercial squalane

5 g of squalane are dissolved in 100 ml of petroleum ether (b. p. 60–80°). The solution is passed first through a column (15 × 1 cm I.D.) of activated carbon, then through a column (30 × 1 cm I.D.) of activated alumina. The columns are washed with a further 50 ml of petroleum ether (b.p. 60–80°) and the bulked solution is evaporated using a rotary evaporator.

I of benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine were determined on the hydrocarbon columns at a temperature of 120° and a 20% loading of stationary phase. I of *n*-butylbenzene, benzyl alcohol, acetophenone, nitrobenzene, and aniline were determined at 180° column temperature.

RESULTS AND DISCUSSION

From MW determinations on the Apiezon greases, Apiezon M—MW 2340—was selected as being sufficiently above the min. value of 1100 recommended by

Huber and Kováts⁴ to ensure thermal stability. After hydrogenation, and the rehydrogenation necessary to bring residual olefinic and aromatic unsaturation down to values below 2%, the average MW of the product was found to be 2,680. Addition of hydrogen cannot account for such a large increase and it has been assumed that the increase is mainly due to the removal of low-molecular-weight material during the prolonged rotary evaporation treatment when the material, as a thin film, was subjected to high vacuum and a temperature of 100°.

Initial attempts to hydrogenate the grease involved the use of a catalyst consisting of active nickel in kieselguhr⁶ but the residual unsaturation with this catalyst was very high (see Table I). Conditions under which Apiezon L had already been hydrogenated⁷, involving the use of an active nickel catalyst prepared from Raney nickel alloy, were used on Apiezon M and, with increase in catalyst concentration and hydrogenation time, the product described in Tables I-III was produced with residual olefinic unsaturation and aromatic unsaturation percentages of 1.6 and 1.2, respectively.

TABLE I
HYDROGENATION OF APIEZON M

No.	Hydrogenation conditions	Percentage residual unsaturation	
		Olefinic	Aromatic
1	Ni-kieselguhr (30%) 260°, 100 atm H ₂ , 12 h	44	29
2	Raney Ni (25%) 260°, 100 atm H ₂ , 12 h	29	22
3	Rehydrogenation of No. 2 Raney Ni (50%) 260°, 100 atm H ₂ , 24 h	1.6	1.2

Thermogravimetric analysis of 20% Apiezon M hydrogenated (Apiezon MH) on silylated Celite conditioned at 100° revealed that the material is stable to 180°, whilst a similar column packing conditioned at 200° was subsequently stable at this temperature, and at 250° 3% of the phase was lost from the column packing.

From Table II, it can be seen from a comparison of the data on the two commercial squalane samples and McReynolds' values, that the squalanes are impure. Particularly high values are obtained for *I* of 1-butanol, indicating that the impurity is electron donating in character although high values for the electron donor compounds indicate electron acceptor properties on the squalane. The possibilities are that some squalene is present and that oxidation producing some ketone compound has occurred. The nature of these impurities is not, however, important. What matters is that these squalane samples, obtained at different times from different suppliers of materials for gas-liquid chromatography, should give *I* values showing such wide variation from the generally accepted values. Treatment of the second commercial sample by activated carbon and alumina can be seen to have reduced the variation to what may be considered as tolerable limits although this itself is debatable. The question which now arises is: How much work has been published giving polarity

data where the workers have assumed that their squalane was pure material? Chemical analysis will be of no help in this situation, where a little impurity goes a long way, however, a careful scrutiny of *I* on squalane of both the Rohrschneider and McReynolds compounds is urged. The clean-up procedure for squalane suggested here should be adopted as routine when working with this phase.

The *I* values on Apiezon MH, given in Table II, are higher than the value for purified squalane given by McReynolds and others. This is believed to be a stationary phase MW effect however, rather than retention due to residual unsaturation in the grease. Huber and Kováts have given theoretical max. for *I* of the McReynolds compounds on a paraffin hydrocarbon of infinite MW. These values are included in Table II and it may be seen that the corresponding values for Apiezon MH are slightly lower or equal to the max. values. From the work of Huber and Kováts, it has been possible to approximate *I* of the McReynolds compounds on a stationary phase of MW 2,700, the value obtained for Apiezon MH. These values are also included in Table II and the close relationship between them and the experimental values on Apiezon MH is apparent. This grease is therefore strictly analogous to squalane in its retention behaviour, slight increases in *I* values being attributable to the MW of the phase.

TABLE II
RETENTION INDICES (*I*) OF THE McREYNOLDS COMPOUNDS AT 120°

Stationary phase	<i>I</i>				
	Benzene	1-Butanol	Pentanone	Nitropropane	Pyridine
Commercial squalane (1st sample)	769	740	694	659	757
Commercial squalane (2nd sample)	678	720	690	740	820
Purified squalane (2nd sample)	651	607	632	678	716
Squalane (McReynolds' values ³)	653	590	627	652	699
Infinite MW hydrocarbon (theoretical from ref. 4)	684	602	635	669	736
Hydrocarbon, MW 2,700 (theoretical from ref. 4)	678	597	632	665	730
Apiezon M hydrogenated	671	599	632	667	736
Apiezon L	687	627	651	700	770

Table III lists the *I* values for the aromatic compounds suggested as high temperature standard substances in earlier work⁵, a column temperature of 180° having been selected as a reference. Values are given for retention data on the four Apiezon greases L, M, T, and W and it can be seen that the polarity of the greases increases in this order. Each of the greases had been hydrogenated under comparable conditions (Table I No. 2), and the lowering of *I* upon hydrogenation is clearly seen although the so-called hydrogenated greases in Table III in fact contained approximately 20% of residual unsaturation. The effects of hydrogenation under similar conditions upon the retention properties of the greases are quite unusual. Thus Apiezon T shows the smallest decreases in *I*, except for benzyl alcohol, where hydrogenation causes the largest decrease— ΔI being 110 units. Apiezon W shows the largest decrease for the electron donor acetophenone, ΔI on hydrogenation of this

grease, at 87 units, being twice the values obtained on Apiezon M and L. Finally, the comparatively small decreases for ΔI of aniline on M, T, and W are not in accordance with the large decrease of 80 units for this substance on hydrogenated Apiezon L.

It may be seen from Table III that the min. values for all retention data are obtained on Apiezon MH as would be expected. These values could be taken as the non-polar standards for the five substances at 180°. An interesting comparison is that made between Apiezon MH and polyethylene, where the MW effect of the stationary phase will be at a max. The values on polyethylene then must represent values on an infinite MW saturated phase, and, for the four substances containing a functional group, give increments of approximately 40 units over the values on Apiezon MH.

TABLE III

RETENTION INDICES (*I*) ON THE APIEZON GREASES, HYDROGENATED APIEZON GREASES, AND LINEAR POLYETHYLENE AT 180°

Stationary phase	<i>I</i>				
	<i>n</i> -Butylbenzene	Benzyl alcohol	Acetophenone	Nitrobenzene	Aniline
<i>Commercial greases</i>					
Apiezon L	1099	1120	1141	1147	1065
M	1098	1085	1123	1143	1000
T	1104	1176	1124	1156	1029
W	1144	1219	1297	1306	1117
<i>Hydrogenated greases</i>					
Apiezon L	1085	1041	1093	1128	985
M (Table I, No. 2)	1086	1036	1083	1112	988
T	1097	1067	1115	1150	1011
W	1130	1142	1210	1261	1101
<i>Rehydrogenated greases</i>					
Apiezon MH (Table I, No. 3)	1083	1032	1053	1105	986
Polyethylene	1095	1071	1096	1139	1001

Apiezon M grease may therefore be hydrogenated comparatively easily to procedure a stationary phase with reduced retention values. The *I* values obtained on such a phase compare closely with values obtained on squalane at 120° and on polyethylene at 180°. Apiezon MH grease, therefore, offers the means of obtaining standard values for column polarity evaluation without the temperature limits imposed by squalane. The new phase is stable initially to 180° but, after a conditioning period at the temperature, may be used successfully at 200°.

REFERENCES

- 1 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
- 2 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 3 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 4 G. A. Huber and E. Kováts, *Anal. Chem.*, 45 (1973) 1155.
- 5 F. Vernon and E. A. K. Yacoub, *J. Chromatogr.*, 86 (1973) 17.
- 6 J. Wicklatz, in E. M. Fettes (Editor), *Chemical Reactions of Polymers*, Interscience, New York, 1964, p. 173.
- 7 E. A. K. Yacoub, *M.Sc. Thesis*, Salford, 1973.