Notes

CHROM. 5472

Gas–solid chromatography on modified alumina stationary phases

I. Behaviour of aromatic hydrocarbons

Gas–solid chromatography (GSC) has certain characteristics which make it a more attractive separation technique than gas–liquid chromatography (GLC) for some systems. The work of GIDDINGS[1] laid the basis for a theoretical treatment of GSC in which the coefficient of adsorption–desorption exchange, C_k, is much smaller than the resistance to mass transfer in the liquid phase term, C_L, which it replaces in the van Deemter equation, and hence better resolution is obtained. Also, the adsorbents in GSC have a far greater selectivity than inactive supports coated with liquid stationary phases. The advantages of GSC over GLC in terms of high column temperature operation are obvious. SCOTT[2] has written an extensive review on the potentialities of GSC.

Owing to the concave curvature of the isotherm in GSC, chromatographic peaks usually exhibit severe tailing effects[3] and, as the curvature of adsorption isotherms is dependent on the molecular weight of the sample component, GSC has been restricted mainly to gas analysis. Sample size is another factor in tailing of chromatographic peaks and, until the development of highly sensitive detectors, column overloading has been a major contributary factor to peak tailing.

With the development of modified stationary phases, peak tailing has been greatly reduced, SCOTT[4] obtaining symmetrical peaks for paraffins up to C_{36} on a sodium hydroxide-modified alumina stationary phase, whilst MOFFAT AND SOLOMON[5] separated polyphenyls on a column of firebrick impregnated with lithium chloride.

This paper describes the use of a sodium chloride-impregnated, sodium hydroxide-modified alumina stationary phase for the separation of polycyclic aromatic hydrocarbons. The column performance for alkylbenzenes is also described in terms of their KOVATS[6] retention indices and the temperature coefficients are compared with values obtained by SAHA AND MITRA[7] and by SOJAK AND HRIVNAK[8] on GLC columns. The possibility of using GSC for the analysis of heavy oil and anthracene oil fractions from coal tar distillation is indicated.

Experimental

A Pye series 104 gas chromatograph with a flame ionization detector was used throughout. The column was 0.45 m × 0.32 mm I.D., copper tubing packed with 6.5 g of modified alumina, 80–100 mesh. The stationary phase was 50 g of chromatography grade alumina, type 0, slurried with a solution of 0.5 g of sodium hydroxide and 5 g of sodium chloride in 50 ml of water. The slurry was dried at 400° for 24 h, crushed, sieved, and the 80–100 mesh fraction used for column packing. All retention times were determined directly with a stop-clock, corrected retention times being calculated by the ratio method of PETERSON AND HIRSCH[9] using n-paraffin peaks.

The carrier gas (nitrogen) flow rate was maintained at 30 ml/min for the work on alkyl benzenes and at 60 ml/min for the polycyclic hydrocarbons. Internal calibration was by addition of appropriate n-alkanes to all samples.
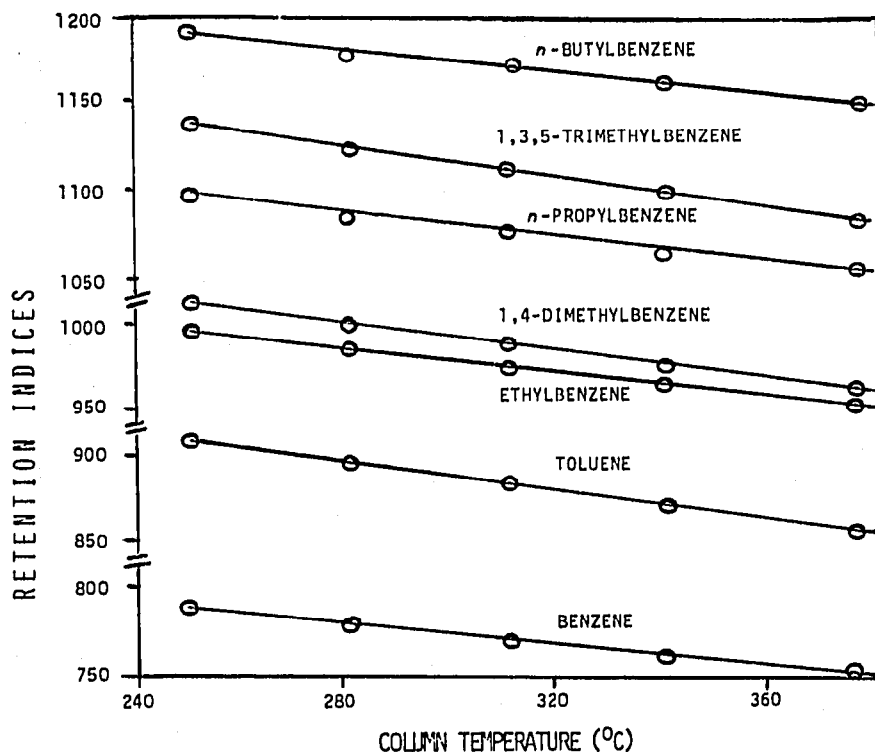
Fig. 1. Plot of retention index against column temperature for aromatic hydrocarbons.

Results

The retention data and calculated chromatographic parameters are given in Fig. 1 and Table I for benzene and alkylbenzenes, and in Fig. 2 and Table II for polycyclic hydrocarbons. The column efficiencies and height equivalent to a theoretical plate (HETP) values, from the benzene peak, over a range of temperatures are given in Table III from which, by extrapolation, the standard efficiency (benzene at 80°) was found to be 160 theoretical plates with an HETP value of 0.23 cm.

Discussion

The alkylbenzenes appear to fall into two distinct series. The first, benzene–

TABLE I

GSC RETENTION INDICES (I) FOR C_6–C_{10} AROMATIC HYDROCARBONS

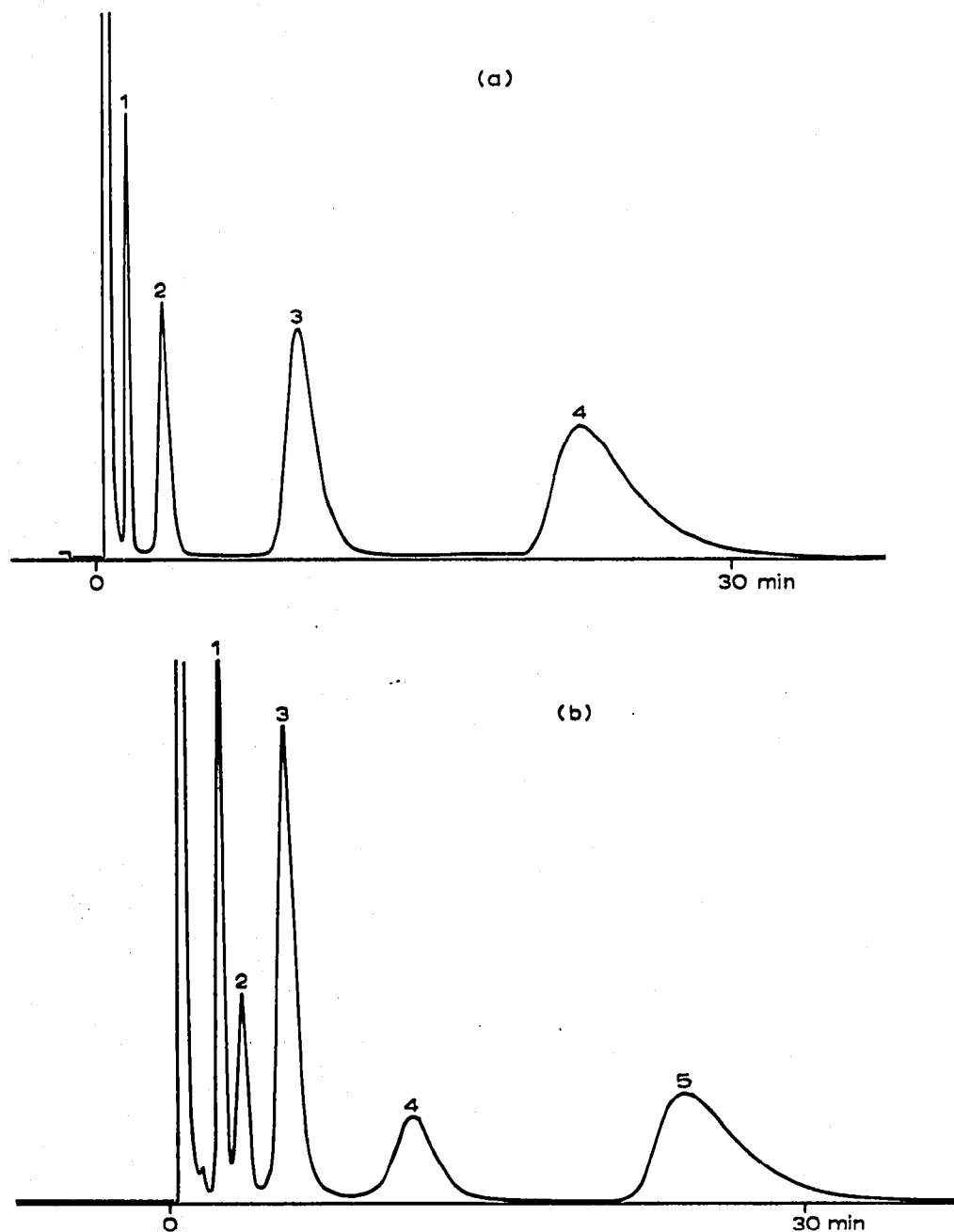| Hydrocarbon	I			$\triangle I/°C$
	$250°$	$300°$	$350°$	
Benzene	790	774	759	—0.31
Toluene	910	890	869	—0.41
p-Xylene	1012	993	973	—0.39
1,3,5-Trimethylbenzene	1139	1117	1097	—0.42
Ethylbenzene	995	979	964	—0.31
n-Propylbenzene	1098	1082	1066	—0.32
n-Butylbenzene	1192	1176	1161	—0.31

Fig. 2. Gas–solid chromatograms of polycyclic hydrocarbons. (a), 1 = naphthalene; 2 = acenaphthene; 3 = phenanthrene; 4 = pyrene. (b), 1 = biphenyl; 2 = acenaphthylene; 3 = fluorene; 4 = anthracene; 5 = fluoranthrene.

trimethylbenzene, entails substitution of successive methyl groups into the aromatic ring. This series shows an average increment of retention index, ΔI, of 114 for ring substitution of –CH$_3$ whereas the second series, benzene–n-butylbenzene, after the anomalous first two members, shows the expected increment of 100 when the side chain is lengthened by –CH$_2$–. BARK AND CLARKE[12], working with n-alkylphenols and GLC columns, found that the theoretical increment of 100 was not reached until the chain length exceeded four carbon atoms. Whether this is a fundamental

TABLE II

GSC RETENTION INDICES (I) FOR POLYCYCLIC HYDROCARBONS AT 400°

Hydrocarbon	b.p. (°C)	I
Naphthalene	218	1342
Biphenyl	254	1507
Acenaphthene	278	1555
Acenaphthylene	—	1600
Fluorene	295	1732
Phenanthrene	340	1878
Anthracene	354	1935
Pyrene	260/60 mm Hg	2123
Fluoranthrene	250/60 mm Hg	2138

difference between GSC and GLC or whether an electronic effect due to the presence of the phenolic group is the predominating factor is not known, but the latter seems more likely.

The difference between the polymethylbenzene series and the monosubstituted alkylbenzene series is apparent when the temperature coefficients of the retention indices are considered. Toluene, as would be expected, falls into the first series, the temperature coefficients of which are —0.4, whereas the monoalkylbenzenes, from ethylbenzene, have a temperature coefficient of —0.3. It is of interest to note that the coefficients are negative, whereas the GLC coefficients[7,8] are positive.

The conclusions drawn by SAHA AND MITRA[7], that the temperature coefficients for aromatic compounds are characteristic, would indicate that GLC is not as specific as GSC for discriminating between the different structures of polymethylbenzenes and mono-n-alkylbenzenes. It is intuitively apparent that differences are to be expected; for instance, if we consider an extreme case, one wonders whether SAHA AND MITRA would have classified dodecylbenzene as aromatic or as paraffinic.

The values of the retention indices extrapolated to comparable temperatures give, in the case of benzene, for instance, a value of 843. Comparison with the values of 650 and 985 for squalane and PEG400, respectively, as given by SOJAK AND HRIVNAK[8], leads to the conclusion that the modified alumina may be regarded as a "semi-polar" stationary phase with quite a high degree of interaction between the phase and the delocalised electrons of the benzene. Values[7] for benzene of 650 and 980 for SE-30 and PEG400, respectively, mean that the alumina phase is considerably more "polar" than silicone oil.

The efficiency of the GSC column is seen from Table III to be highly temperature-dependent, the number of theoretical plates being calculated for the benzene

TABLE III

COLUMN EFFICIENCIES CALCULATED FROM THE BENZENE PEAK

Temperature (°C)	Theoretical plates	HETP (cm)
200	230	0.20
250	250	0.18
300	284	0.16

peak at 80°. A value of 160 theoretical plates is obtained by extrapolation, as this temperature is too low for the column to function. However, it should be noted that the assumption has been made that the values for retention index against temperature lie on the asymptotic slope of the hyperbola down to 80°, and this may or may not be the case although DUCROS[10] has shown that for the usual working temperature range of GLC columns, the values do lie on the asymptotic slope and the relationship may be regarded as linear.

Table III shows that the efficiency increases markedly with temperature and, in the working temperature range, n is of the order of 280 theoretical plates.

Fig. 2 shows chromatograms obtained for nine polycyclic hydrocarbons with their retention indices given in Table II. It may be seen that their retention is in order of their boiling points[11] with the exceptions of pyrene and fluoranthrene where the elution order is reversed. From Fig. 2, it is obvious that chromatographic separation of high-boiling aromatic hydrocarbons is quite feasible by GSC with the production of symmetrical peaks for hydrocarbons the boiling points of which are as high as 350°. This technique should lend itself, with advantage, to the analysis of the high-boiling fractions from coal-tar distillation, analyses involving pyrene and fluoranthrene being completed within 30 min when a column temperature of 400° is used. It would seem that the limitation to such separations would be catalytic oxidation and breakdown of hydrocarbons by the stationary phase at high temperature, but there was no evidence of this at the temperatures used here.

Chemistry Department, Sheffield Polytechnic,   F. VERNON[*]
Sheffield, Yorks (Great Britain)

1 J. C. GIDDINGS, *Anal. Chem.*, 36 (1964) 1170.
2 C. G. SCOTT, *J. Gas Chromatogr.*, 4 (1966) 4.
3 J. TRANCHANT, *Practical Manual of Gas Chromatography*, Elsevier, Amsterdam, 1969, pp. 121 and 224.
4 C. G. SCOTT, in M. VAN SWEENEY (Editor), *Gas Chromatography*, Butterworth, London, 1962.
5 H. J. MOFFAT AND P. W. SOLOMON, *AEC Res. Dev. Rep., Reactor Technol.*, 1961.
6 E. KOVATS, *Helv. Chim. Acta*, 41 (1958) 1915.
7 N. C. SAHA AND G. D. MITRA, *J. Chromatogr. Sci.*, 8 (1970) 84.
8 L. SOJAK AND J. HRIVNAK, *Ropa Uhlie*, 11 (1969) 364.
9 M. L. PETERSON AND J. HIRSCH, *J. Lipid Res.*, 1 (1959) 132.
10 M. DUCROS, *Thèse*, Paris, 1962.
11 L. F. FIESER AND M. FIESER, *Organic Chemistry*, Reinhold, Princeton, 1956, p. 528.
12 L. S. BARK AND K. F. CLARKE, *J. Chromatogr.*, 48 (1970) 418.

---

* Present address: Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancs., Great Britain.