CHROM. 3329

Separation of biphenyl and the terphenyls by gas–solid chromatography on graphitized carbon black and on Chromosorb coated with caesium chloride

Much attention has been paid to the gas chromatographic separation of the polyphenyls which are important moderator coolants for atomic reactors. A mixture of biphenyl and the polyphenyls has been separated, at higher temperatures, on Chromosorb coated with Apiezon L, Carbowax or silicone oil[1–3]. Eutectic mixtures of potassium and silver nitrates[4] or of K, Na and Li nitrates[5] have also been used. The latter are more stable at higher temperatures. Very good results have been obtained with sorbents modified[6–8] with inorganic salts such as LiCl, CsCl, $CaCl_2$ and K_3PO_4, which gave successful separations of the terphenyls and quaterphenyls up to hexaphenyls. Thus, gas–liquid chromatography has been replaced by chromatography on a modified sorbent surface. Other authors[9–11] have separated the polyphenyls by chromatography on columns packed with a mixture of Bentone 34 and 10% silicone grease or with 3% Apiezon L on Celite.

TABLE I

EXPERIMENTAL CONDITIONS

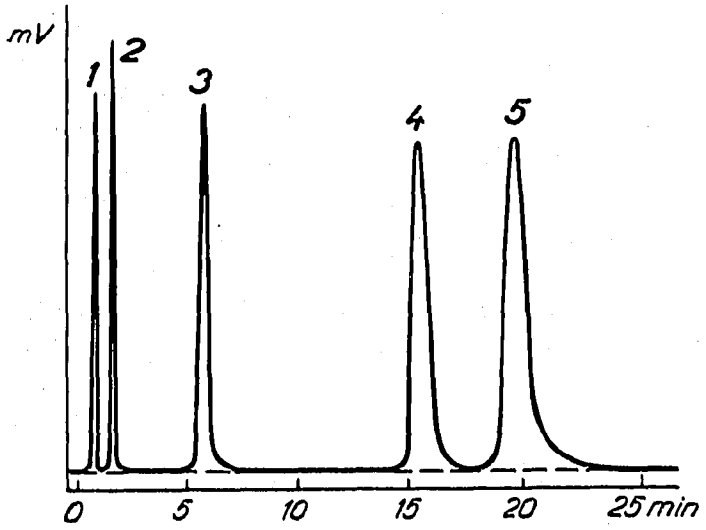
Instrument type	Carlo Erba C	Perkin Elmer F-11
Detector	FID	FID
Sensitivity	16–256 × 10	10–100 ×
Column dimensions	100 cm; diameter 5 mm	60 cm; diameter 1 mm
Adsorbent	Chromosorb P, 15% CsCl	Graphitized carbon black
Particle size	80–100 mesh	0.075–0.1 mm
Temperature of:		
column	230°, 251°, 270°, 300°	380°, 390°, 400°
sampling point	335°	400°
detector	340°	400°
Carrier gas	Nitrogen	Nitrogen
Flow rate at 25°, ml/min	48.8	1.7
Specific area, m^2/g	—	7.6

In the present paper (*cf.* ref. 12) we have separated a mixture of benzene, biphenyl and all the terphenyls by gas–solid chromatography using graphitized carbon black which proved to be a suitable adsorbent for this analysis. The surface of graphitized carbon black as studied by KISELEV[13], reveals non-specific properties and permits the separation of a mixture of the polyphenyls on a short column.

Experimental

Separation was performed (Table I) with an F 11 gas chromatograph (Perkin-Elmer, Beaconsfield, Great Britain) and with the Carlo Erba instrument, Model C (Milan, Italy). The graphitized carbon black used was a Sterling MT 3100 specimen produced by Cabot (Cambridge, Mass., U.S.A.). The total specific area was determined by adsorption of krypton at the temperature of liquid nitrogen.

The samples were injected with a Hamilton 1 μl microsyringe (Whittier, Calif., U.S.A.). The results of the separation are illustrated in Fig. 1.



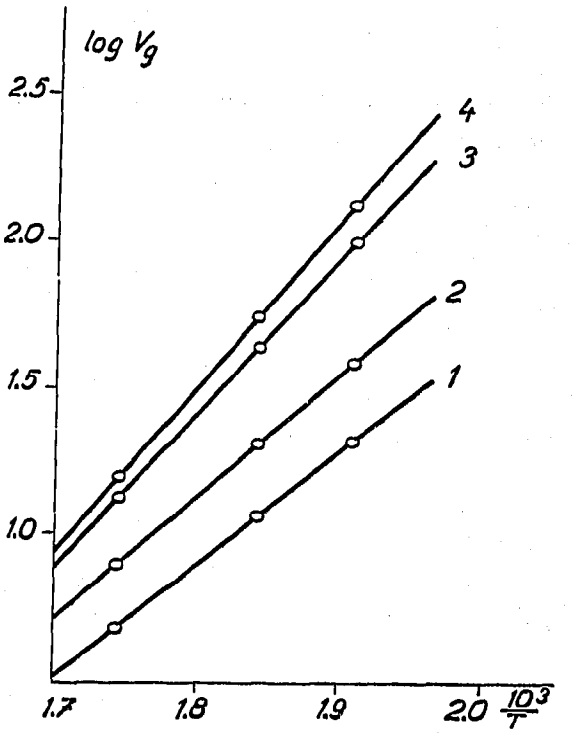


Fig. 1. Chromatogram of the mixture of polyphenyls on caesium chloride modified Chromosorb P. 1 = Solvent; 2 = biphenyl; 3 = *o*-terphenyl; 4 = *m*-terphenyl; 5 = *p*-terphenyl.

Fig. 2. The isosters of biphenyl and the terphenyls on Chromosorb P modified with caesium chloride at temperatures ranging from 230° to 300°. 1 = Biphenyl; 2 = *o*-terphenyl; 3 = *m*-terphenyl; 4 = *p*-terphenyl.

The peaks obtained in the separation on Chromosorb P coated with 10% CsCl at 230° or 251° are not very symmetrical. At the above temperatures, *o*-terphenyl tails and at 270° *m*-terphenyl also tails, but the time of analysis is favourable (Table II).

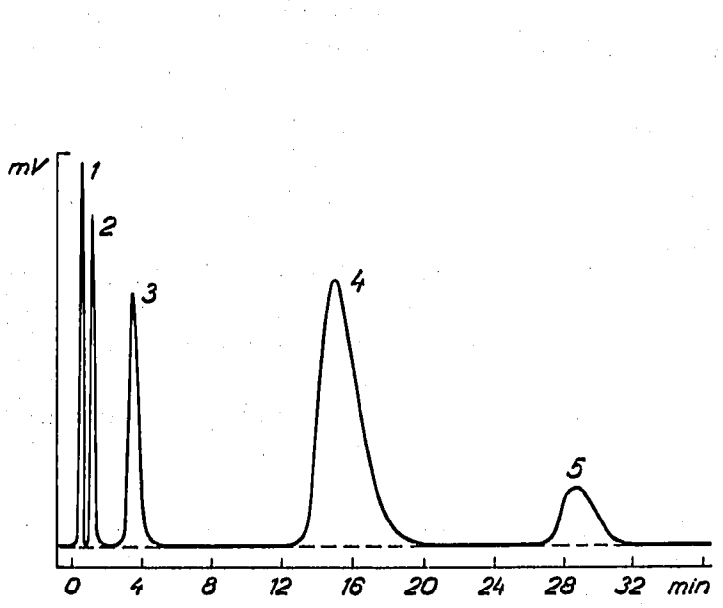
On the basis of these measurements, the course of the isosters of the components chromatographed was plotted for the column packed with CsCl on Chromosorb P, as log V_g against $1/T$. The plot is shown in Fig. 2.

These data were used for expressing the heats of adsorption of the aromatic hydrocarbons of the biphenyl series. The best separation was achieved at 270° to 300°.

TABLE II

SPECIFIC RETENTION VOLUMES FOR THE COMPONENTS ON CAESIUM CHLORIDE MODIFIED COLUMN PACKING AT VARIOUS TEMPERATURES

Component	V_g				ΔH_a
	230°	*251°*	*270°*	*300°*	
Biphenyl	—	20.9	11.5	4.91	17.8
o-Terphenyl	86.0	38.9	20.6	8.10	19.4
m-Terphenyl	196	99.8	42.8	13.5	24.6
p-Terphenyl	336	133	54.4	15.7	26.3



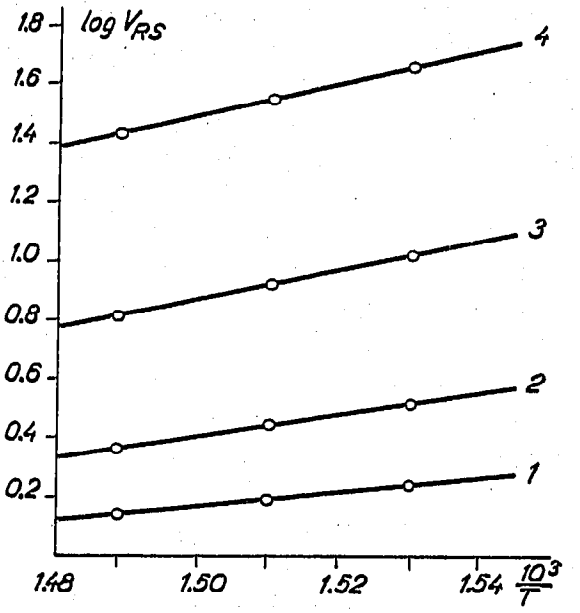


Fig. 3. Chromatogram of the mixture of polyphenyls on graphitized carbon black. 1 = Benzene; 2 = biphenyl; 3 = *o*-terphenyl; 4 = *m*-terphenyl; 5 = *p*-terphenyl.

Fig. 4. The isosters of biphenyl and the terphenyls on graphitized carbon black over the temperature range 380–400°. 1 = Benzene; 2 = biphenyl; 3 = *o*-terphenyl; 4 = *m*-terphenyl.

The separation of biphenyl and the terphenyls on graphitized carbon black is illustrated in Fig. 3. The peaks are symmetrical at 390°, but *meta*- and *para*-terphenyls can be seen to tail. The strong dispersion interaction with graphitized carbon black is reflected in longer retention times even when a comparatively high temperature of the chromatographic column is chosen.

The absolute retention volumes for the individual components at two different temperatures are listed in Table III, which was prepared by performing calculations according to ref. 14.

The isosters of the components are shown in Fig. 4.

Discussion

The order of elution of the components from the column packed with graphitized carbon black can be interpreted on the basis of the structure of these molecules.

TABLE III

ABSOLUTE RETENTION VOLUMES V_{RS} (V_R PER m^2 OF ADSORBENT AREA) OF THE COMPONENTS ON GRAPHITIZED CARBON BLACK AT VARIOUS TEMPERATURES

Component	V_{RS}		$\log V_{RS}$		ΔH_a
	380°	*400°*	*380°*	*400°*	
Benzene	1.74	1.39	0.240	0.1432	10.7
Biphenyl	5.40	2.31	0.513	0.3638	16.6
o-Terphenyl	10.4	6.08	1.016	0.8100	22.8
m-Terphenyl	46.2	26.4	1.665	1.4214	27.0
p-Terphenyl	—	—	—	—	—

The separation is considerably influenced by non-specific interactions of the sorbate with the sorbent, independent of local distribution of electron density over the nuclei of the polyphenyls.

The spherical configuration of the *o*-terphenyl molecule permits less of a dispersion interaction with an edge or plane of the graphitized carbon black surface than does *m*-terphenyl, which interacts to a still lesser degree with the carbon black surface than *p*-terphenyl. The retention volume of *p*-terphenyl, which is relatively large as compared with that of *m*-terphenyl, suggests that the interaction of *p*-terphenyl with the surface of graphitized carbon black occurs between the surface and the flat phenyl nuclei. The separation of the polyphenyls on Chromosorb P coated with 10% CsCl is most advantageous at 270° or at higher temperatures, where isothermal conditions can be maintained. The symmetry of the peaks is improved with increasing temperature and at 300° all of the components in question will be well separated in 4 min, whilst highly symmetrical peaks are obtained.

The heats of adsorption agree well with previous data for benzene. The value of —10.7 kcal/mole measured for benzene by gas chromatography agrees well with —10.3 kcal/mole measured by a static method[14].

A comparison of the heats of adsorption obtained on graphitized carbon black and on Chromosorb P coated with caesium chloride for the terphenyls, shows that the heats of adsorption on graphitized carbon black are higher. This probably depends on the dispersion forces which, for a non-specific adsorbent, are stronger than those encountered with caesium chloride where the principle of separation is not yet known.

The heats of adsorption obtained in the above manner are valuable because they were actually measured, since calorimeters suitable for the determination of these values, are unobtainable on purely constructional grounds. The values obtained are of sufficient accuracy for the usual measurements performed in catalysis and chemical engineering.

Conclusions

Graphitized carbon black can be used for the analytical separation of polyphenyls in a gas–solid system. Molecules having like carbon numbers, *e.g.* the terphenyls, manifest the influence of their geometrical configuration. The heats of adsorption can be used to predict the spatial configuration of such molecules.

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1 N. M. HUTCHINSON AND L. E. BARDNER, *IDO Report No. 16869, Org. Reactor Technol. Final. Progr. Rep.* 1962-31, (1963).
2 R. T. KEEN, R. A. BAXTER, B. H. J. GERCKE AND W. L. ORR, *Atomic Inter. NAA-SR-4355* (1962).
3 B. J. GUDZINOWICZ AND E. R. SMITH, *Detroit Anal. Chem. Conf., 8th, 1960.*
4 W. W. WEST, *AEC Report TID 17508*, 1962.

5 J. WEISS, C. H. COLLINS, J. SUCHER AND N. CARCIELLO, *Ind. Eng. Chem. Prod. Res. Develop.*, 3 (1964) 73.
6 P. W. SOLOMON, *Anal. Chem.*, 36 (1964) 476.
7 P. S. HUDSON, W. M. HUTCHINSON, B. B. REGIER, A. J. MOFFAT AND R. A. MENGELLAMP, *IDO Report No. 16830, Org. Reactor Technol. Quart. Rept.*, July 1962.
8 L. B. YEATTS, Jr., D. N. HESS, H. F. MCDUFFIE AND W. T. RAINEY, Jr., *US-AEC ORNL-3602, TID-4500.*
9 B. VERSINO, F. GEISS AND G. BARBERO, *Z. Anal. Chem.*, 201 (1964) 20.
10 F. GEISS AND H. LAURENT, *Nuclear Congress, Vienna, May 1966.*
11 J. M. VERGNAUD, *J. Chromatog.*, 27 (1967) 54.
12 F. ONUŠKA, *Thesis*, Univerzita J. E. Purkyně, Brno, 1967.
13 L. D. BELYAKOVA, A. V. KISELEV AND N. V. KAVALEVA, *Anal. Chem.*, 36 (1964) 1517.
14 A. V. KISELEV, E. A. PASKONOVA, R. S. PETROVA AND K. D. ŠČERBAKOVA, *Zh. Fiz. Khim.*, 38 (1964) 84.

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CHROM. 3366

Essential oils and their constituents

Part XLI. Identification of sesquiterpene hydrocarbons in oil of opoponax*

In a paper from this laboratory the occurrence of isomeric bisabolenes in oil of opoponax has been reported[2]. A personal communication, received since, claiming the presence of only α-santalene and α-bisabolene in this oil[3] prompted us to re-examine our samples following column and gas chromatographic purification.

Fig. 1 shows the gas chromatogram of the sesquiterpene fraction as originally recorded employing the silicone nitrile XE-60 column[2]. Four fractions corresponding

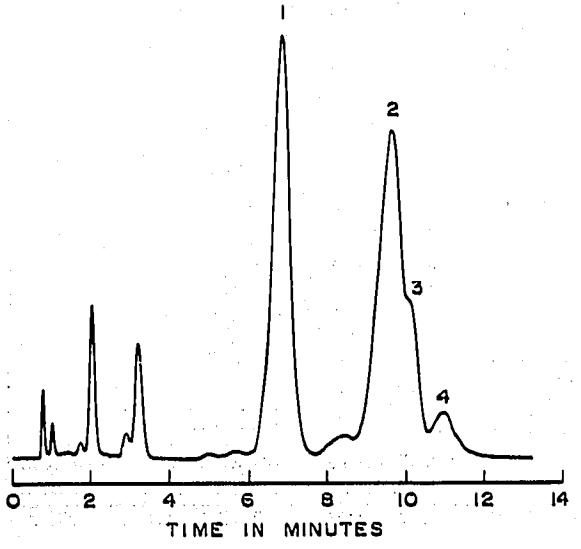

Fig. 1. Gas chromatogram of the sesquiterpene fraction of oil of opoponax.

* For the previous paper, see ref. 1.