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GAS CHROMATOGRAPHIC SEPARATION OF NAPHTHALENE AND BIPHENYL HOMOLOGUES ON CAPILLARY COLUMNS

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SUMMARY

Experimental conditions were investigated that would permit an optimal separation of methyl-, ethyl- and dimethylnaphthalenes, biphenyl, diphenylmethane, methylbiphenyls and acenaphthene to be obtained. Retention times were determined on efficient capillary columns prepared with the following stationary phases: SP 400, Reoplex 400, Amine 220, *p,p'*-azoxyphenetole, Bentone 34 mixed with didecyl phthalate and Ucon LB 550 X mixed with tris(cyanoethoxy)propane, and on a composite capillary column consisting of the last two columns, *i.e.*, Bentone 34 and didecyl phthalate plus Ucon LB 550 X and tris(cyanoethoxy)propane. The complete separation of all of the naphthalenes was obtained only on the last-mentioned composite column.

INTRODUCTION

The gas chromatographic separation of alkylnaphthalenes up to C_{12}, sometimes together with accompanying hydrocarbons, has been widely studied[1–17], but no procedure that permits the separation of all of the dimethylnaphthalenes on a single column from a single injection has been described however. The components that were not separated on a chromatographic column were identified by means of either spectral analysis[6,8] or analyses performed on two different columns[8–10].

The retention data published for the hydrocarbons in the present study were measured on conventional stationary phases of varying polarities[1,2,4–6,8,12,15], on adsorbents of both the first and second class according to Kiselev's classification[3,7,10,14,16] and on liquid crystals[9,11,13,17] in packed columns in most instances. Capillary columns[4,5,8,12,15] were used only with some of the conventional stationary phases (such as Apiezon L, DC 550, polyphenyl ether, polyethylene glycol adipate and Ucon 50 HB 2000). Even on capillary columns. the pairs of 2,6- and 2,7-dimethyl-

naphthalenes, 1,6- and 1,3-dimethylnaphthalenes and 1,4- and 2,3-dimethylnaphthalenes remained mostly unseparated. Adsorbents that showed steric effects[3,7,9–11,13,14,16,17] shifted the peaks of some of the unseparated pairs so that they could have been separated, but other pairs of peaks then appeared that were not separated. The above factors led to the assumption that a suitable combination of stationary phases together with a sufficient separation efficiency would make the complete separation of all of the dimethylnaphthalenes possible.

EXPERIMENTAL

Capillaries of soft (weak) glass with I.D. 0.25–0.28 mm were etched in the gaseous phase[18] and then coated by the dynamic method with a solution of the stationary phase of a suitable concentration. A 2% solution of phthalate and 2% Bentone 34 in benzene were used for the preparation of a mixed stationary phase. This mixture was agitated for several hours together with glass beads until a perfect dispersion was obtained[19] and the glass capillary was then coated with this dispersion. The capillary columns with conventional stationary phases, such as SP 400 silicone phase, Reoplex 400 polyester, Amine 220, a mixed phase containing Ucon LB 550 X and tris(cyanoethoxy)propane (85:15), and liquid crystals[20] of *p,p'*-azoxyphenetole, were prepared in the usual way. The characteristics of these columns are listed in Table I.

The measurements of the retention data were carried out in Fractovap Model C and Model 2100 instruments (Carlo Erba, Milan, Italy), equipped with flame-ionization detectors. The operating temperatures varied between 117° and 172°. A relatively high operating temperature, 172°, was used with the mixed phase of Bentone 34 and didecyl phthalate owing to its high capacity for all of the compounds chromatographed. With *p,p'*-azoxyphenetole the operating temperature of 141° was determined by the temperature range of the nematic interface.

Nitrogen was used as the carrier gas. Individual homologues of naphthalene and biphenyl were injected as solutions in cyclohexane.

RESULTS AND DISCUSSION

Retention times were determined for naphthalene, both of the methylnaphthalenes, ethylnaphthalenes and dimethylnaphthalenes on all of the capillary columns listed in Table I. The relative retention data (Table II) were calculated from retention times determined relative to that of naphthalene.

From the relative retention data, it can be seen that the same sequence is obtained for 1-methylnaphthalene and 2-methylnaphthalene on all of the stationary phases studied except *p,p'*-azoxyphenetole. The same applies to 1-ethylnaphthalene and 2-ethylnaphthalene. It is characteristic of these isomers that their separation numbers (according to Purnell), *S*, converge to 90,000 on all of the stationary phases studied, but on the columns packed with Bentone 34 and *p,p'*-azoxyphenetole they acquire substantially smaller values (*ca.* 8000).

The complete separation of all of the dimethylnaphthalenes was not obtained on any of the capillary columns. The pairs of 2,6- and 2,7-dimethylnaphthalenes, 1,3-, 1,6- and 1,7-dimethylnaphthalenes, and 1,4, 2,3- and 1,5-dimethylnaphthalenes, can

TABLE I

CHARACTERISTICS OF THE COLUMNS USED

Column No.	*Column length (m)*	*Stationary phase*	*No. of theoretical plates*	*Capacity ratio (for naphthalene)*
1	36	SP-400	160,000	2.6
2	62	Reoplex 400	174,000	4.1
3	23	Amine 220	68,000	2.6
4	44	Ucon + TCEP*	100,000	3.45
5	21	*p,p'*-azoxyphenetole	10,000	2.2
6	20	Bentone 34 + didecyl phthalate	54,000	3.8
7	64	composite columns 4 + 6	140,000	4.2

* TCEP = tris(cyanoethoxy)propane.

be separated only with difficulty on columns packed with the conventional stationary phases SP 400, Reoplex 400 and Amine 220. The separation of 2,6- and 2,7-dimethylnaphthalenes with a relative volatility of 1.015 and of 1,4- and 2,3-dimethyl naphthalenes is also difficult on the mixed phase containing Ucon LB 550 X plus tris(cyanoethoxy)propane. 1,5- and 1,6-dimethylnaphthalenes remain unseparated on the column coated with *p,p'*-azoxyohenetole; 1,3-, 1,4-, 1,2- and 1,5-dimethylnaphthalenes can be separated with difficulty on the mixed phase of Bentone 34 plus didecyl phthalate.

Combinations of the conventional stationary phases used in the capillary columns prepared, which might be effected by simple connection of capillary columns of appropriate lengths, did not lead to a substantial improvement in the separation of

TABLE II

RELATIVE RETENTION DATA FOR NAPHTHALENE HYDROCARBONS

Compound	*Column No.**						
	1	*2*	*3*	*4*	*5*	*6*	*7*
	Operating temperature (°C)						
	117	*120*	*127*	*128*	*141.5*	*172*	*140*
Naphthalene	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2-Methylnaphthalene	1.87	1.60	1.81	1.81	2.01	1.65	1.81
1-Methylnaphthalene	2.04	1.86	2.03	2.31	1.95	1.79	2.01
2-Ethylnaphthalene	3.17	2.39	2.95	2.92	2.70	2.40	2.85
1-Ethylnaphthalene	3.25	2.53	3.01	2.99	2.40	2.46	2.91
2,6-Dimethylnaphthalene	3.40	2.57	3.23	3.19	4.30	2.60	3.24
2,7-Dimethylnaphthalene	3.46	2.56	3.23	3.24	3.88	2.73	3.30
1,7-Dimethylnaphthalene	3.77	2.90	3.63	3.43	3.41	3.10	3.65
1,3-Dimethylnaphthalene	3.72	3.03	3.63	3.70	3.70	3.20	3.78
1,6-Dimethylnaphthalene	3.79	3.06	3.68	3.50	4.00	2.99	3.60
1,4-Dimethylnaphthalene	4.13	3.42	4.02	4.02	3.90	3.21	4.00
2,3-Dimethylnaphthalene	4.15	3.50	4.08	4.09	4.56	3.46	4.32
1,5-Dimethylnaphthalene	4.18	3.52	4.13	—	4.01	3.23	4.11
1,2-Dimethylnaphthalene	4.50	3.90	4.45	4.38	4.66	3.22	4.20
1,8-Dimethylnaphthalene	5.00	4.70	5.23	5.03	4.86	3.56	4.68

* As in Table I.

dimethylnaphthalenes as all of the compounds involved behaved almost identically on all of these stationary phases.

Graphical investigations of combinations of the conventional phases and *p,p'*-azoxyphenetole showed that the assumed possibility of separating all of the alkylnaphthalenes is valid and that the relative volatilities for the pairs of dimethylnaphthalenes, which were the most difficult to separate, are 1.010–1.018. A more favourable value (1.020) was found only in for the connection of *p,p'*-azoxyphenetole with Reoplex 400 in the ratio 1:1.

Combinations of the conventional phases with the column containing Bentone 34 plus didecyl phthalate showed the same relative volatilities and also varied between 1.010 and 1.019. The highest value was again obtained for a combination containing 40% of Reoplex 400.

In contrast, the combination of *p,p'*-azoxyphenetole with the mixed phase of Bentone 34 plus didecyl phthalate gave only limited possibilities of separating 1,4- and 1,3-dimethylnaphthalenes with a relative volatility of 1.010.

The combination of capillary columns with the mixed phases of Ucon LB 550 X plus tris(cyanoethoxy)propane and Bentone 34 plus didecyl phthalate gave the possibility of separating all of the dimethylnaphthalenes (Table II). The pair of 1,6- and 1,7-dimethylnaphthalenes with a relative volatility of 1.014 remained separable only with difficulty.

Using this combination of stationary phases for the analyses of alkylnaphthalene fractions in practice, the samples will contain, in addition to naphthalene homologues, also other aromatic hydrocarbons[1,5,8,12,15]. Therefore the retention times of biphenyl, diphenylmethane, three monomethylbiphenyls, acenaphthene and acenaphthylene were also determined. Their relative retention data are listed in Table III, and a comparison with the values in Table II shows that more exacting demands on the separation system will be necessary for the separation of biphenyl and 2-ethylnaphthalene ($S = 36{,}000$) only. The pairs of 1,8-dimethylnaphthalene and 3-methylbiphenyl, with relative retention times 4.67 and 4.68, and acenaphthene and 4-methylbiphenyl with values of 4.84 and 4.88, remained virtually unseparable. With tar fractions the problem is made simpler by the absence of 1,8-dimethylnaphthalene[5,8,21]. An example of a chromatogram obtained in practice is shown in Fig. 1.

TABLE III

RELATIVE RETENTION DATA FOR BIPHENYL DERIVATIVES, ACENAPHTHENE AND ACENAPHTHYLENE

Column No. 7 (see Table I) under the conditions described in Table II.

Compound	*Relative retention time**
2-Methylbiphenyl	2.19
Biphenyl	2.76
Diphenylmethane	3.13
3-Methylbiphenyl	4.67
4-Methylbiphenyl	4.88
Acenaphthene	4.84
Acenaphthylene	5.61

* Naphthalene = 1.00.

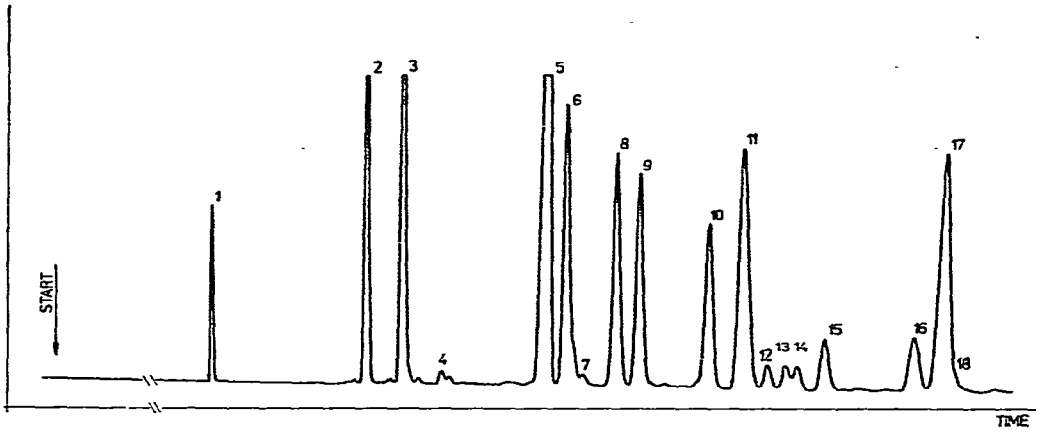

Fig. 1. Chromatogram of alkylnaphthalene fraction from coal tar. The column was coated with Bentone 34 and didecyl phthalate (50 : 50) and connected to column packed with Ucon LB 550 X and tris(cyanoethoxy)propane (85 : 15). Peaks: 1 = naphthalene; 2 = 2-methylnaphthalene; 3 = 1-methylnaphthalene; 4 = 2-methylbiphenyl; 5 = biphenyl; 6 = 2-ethylnaphthalene; 7 = 1-ethylnaphthalene; 8 = 2,6-dimethylnaphthalene; 9 = 2,7-dimethylnaphthalene; 10 = (1,6-dimethylnaphthalene), 1,7-dimethylnaphthalene; 11 = 1,3-dimethylnaphthalene; 12 = 1,4-dimethylnaphthalene; 13 = 1,5-dimethylnaphthalene; 14 = 1,2-dimethylnaphthalene; 15 = 2,3-dimethylnaphthalene; 16 = 3-methylbiphenyl (+ 1,8-dimethylnaphthalene); 17 = acenaphthene; 18 = 4-methylbiphenyl.

CONCLUSION

A separation system of capillary columns consisting of combinations of a conventional stationary phase [Reoplex 400 or a mixed phase containing Ucon LB 550 X plus tris(cyanoethoxy)propane] and a modified adsorbent (Bentone 34) or liquid crystals (*p,p'*-azoxyphenetole) permits the methyl-, ethyl- and dimethylnaphthalenes and most of the accompanying hydrocarbons to be separated.

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