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LIQUID CRYSTALS AS THE STATIONARY PHASE IN GAS CHROMATOGRAPHY

IV. EVALUATION OF THE COMBINATION OF A SEPARATION COLUMN AND AN ELECTRIC FIELD LIQUID CRYSTAL COLUMN

KATSUNORI WATABE*, TOSHIYUKI HOBO and SHIGETAKA SUZUKI

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158 (Japan)

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SUMMARY

The electric field-liquid crystal (EFLC) adsorption column described previously has been made shorter and located behind the glass capillary separation column, and the effects on the adsorption capacity, the reproducibility of adsorption, the utility of different stationary phases for the separation column and temperature programming of the separation column have been investigated. Several advantages, such as capability of selection of a suitable stationary phase and the possibility of temperature programming the separation column, were found. The combination of a temperature programmed high-performance separation column with a 4,4'-azoxydi-*n*-anisole EFLC column was applied successfully to the determination of aromatic hydrocarbons spiked in a vegetable oil fraction.

INTRODUCTION

In previous work¹⁻³ we found that when a direct current (d.c.) electric field is applied across a liquid crystal column, polar substances are selectively adsorbed on the column and are not eluted. This phenomenon takes place when the liquid crystal is in the nematic mesophase or is made nematic through the application of a d.c. electric field. Further, the amount adsorbed has a linear relationship with the dielectric constant of the sample molecule. Also, the amount adsorbed increases almost linearly with increasing field strength.

These phenomena were utilized for the determination of trace aromatic hydrocarbons in edible oil, coexisting oxygen-containing compounds, aldehydes, esters, etc., being eliminated by selective adsorption. As the aromatic hydrocarbons have low dielectric constants, they were not adsorbed. Even under a d.c. electric field, linear calibration graphs were obtained.

In this work, we made the electric field-liquid crystal (EFLC) column shorter and placed it behind the glass capillary separation column. The EFLC column was

used only as a selectively adsorbing column. The effect of the reduction of the EFLC column length on adsorption capacity and selectivity was investigated and several advantages were found.

EXPERIMENTAL

Materials

All chemicals used were of analytical-reagent grade, and each sample was injected into the gas chromatograph after dissolution in diethyl ether. 4,4'-Azoxydianisole (nematic mesophase in the temperature range 116–136°C) was obtained from Tokyo Chemical Industry (Tokyo, Japan), and PEG 20M and silicone DC 550 from Nishio Industry (Tokyo, Japan). Fine nickel wire (0.150 mm in diameter) for the inner electrode was purchased from Nippon Denkyu (Tokyo, Japan). Sealbest P-246, an electroconductive resin, for the outer electrode was obtained from Tokuriki Kagaku Institute (Kanagawa, Japan). Shrinkable PTFE tubing from Gasukuro Kogyo (Tokyo, Japan) was used for the column connections.

Gas chromatograph

A modified F & M Model 810 gas chromatograph equipped with a flame-ionization detector was used (Fig. 1). The modifications were as follows: a column connection system was used that afforded a glass capillary column of special configuration (Fig. 2a); a small oven was installed inside the main oven, which provided independent temperature control of the separation and adsorption columns; and the separation column and the EFLC column were connected by using two shrinkable PTFE tubes and a stainless-steel tube (1 mm O.D.) in between (Fig. 2b).

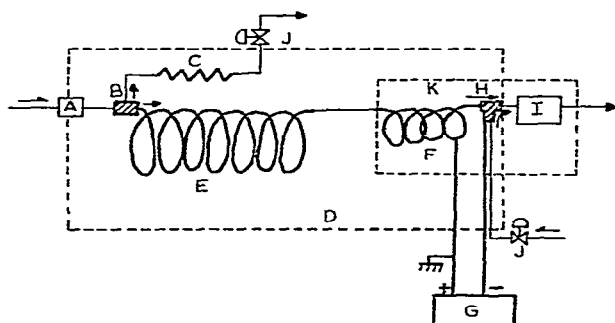


Fig. 1. Schematic diagram of apparatus. A = Injection port; B = splitter; C = resistor; D = oven; E = separation column; F = liquid crystal column with d.c. electric field applied; G = d.c. generator; H = column connector; I = flame-ionization detector; J = flow control valve; K = EFLC column oven.

EFLC column

The length of the EFLC column (0.35 mm I.D.) was varied in the range 1.5–30 m. The configuration and method of preparation of the EFLC column were described elsewhere¹.

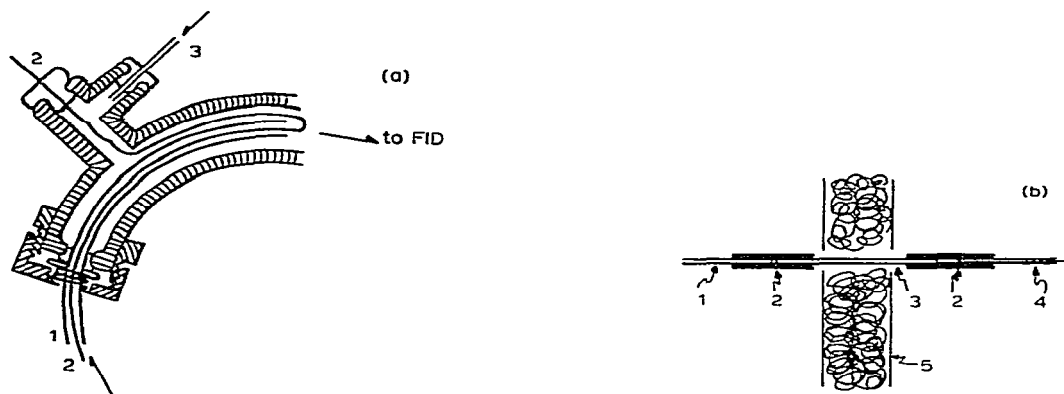


Fig. 2. (a) Column connection. 1 = Liquid crystal column with d.c. electric field applied; 2 = Ni wire; 3 = scavenger gas inlet. (b) Connection of separation column and liquid crystal column. 1 = Separation column; 2 = shrinkable PTFE tube; 3 = stainless-steel tube; 4 = liquid crystal column; 5 = adiabatic wall.

Separation column

A whisker wall open-tubular glass capillary column prepared as described by Schieke *et al.*⁴ was employed. The stationary phases used were 4,4'-azoxydianisole, PEG 20 M and silicone DC 550, with column lengths of 15, 15 and 30 m, respectively. All inner diameters were 0.35 mm.

d.c. generator

A high-voltage power supply for a photomultiplier (Hamamatsu TV, Model 1.5 k-M; Hamamatsu, Shizuoka, Japan) was used.

GC conditions

The temperatures of the injection port, detector and EFLC column were 170, 200 and 120°C, respectively, and that of the separation column was set at a suitable level for the separation of the samples. Pure nitrogen (99.999%) was used as the carrier gas at a flow-rate of *ca.* 1 ml/min.

Under these conditions, an appropriate d.c. voltage was applied. Before injection the EFLC column must be allowed to stand for 3–4 h, otherwise it is not possible to obtain reproducible results.

RESULTS AND DISCUSSION

Shortening of EFLC column

The effect of the length of the EFLC column on the amounts of aldehydes, ketones and esters adsorbed was investigated, with 4,4'-azoxydianisole (ADA) as the liquid stationary phase in both the separation column and the EFLC column. The length of the separation column was 15 m and the column temperatures were 120°C. Table I shows the dependence of the amounts of *n*-butyl acetate, diisopropyl ketone, 2-ethylhexylaldehyde, etc., adsorbed on the length of the EFLC column. The amounts adsorbed of all of the compounds investigated decreased as the length of the EFLC

TABLE I

EFFECT OF EFLC COLUMN LENGTH ON ADSORPTION

Separation column, 4,4'-azoxydianisole (15 m × 0.35 mm I.D.); column temperature, 120°C; EFLC column temperature, 120°C; applied potential, 50 V d.c. Results given are amounts adsorbed (nmol).

Compound	Column length (m)				
	1.5	2.5	3.0	5	30
<i>n</i> -Butyl acetate	0.11	0.25	0.31	0.76	8.0
Diisopropyl ketone	0.08	0.16	0.22	0.53	4.5
2-Ethylhexaldehyde	0.26	0.57	0.65	1.47	14.2
Phenylacetaldehyde	0.32	0.76	0.96	2.03	21.0
<i>n</i> -Hexaldehyde	0.35	0.87	1.08	2.64	27.6
<i>n</i> -Amyl acetate	0.10	0.22	0.32	0.68	6.9

column decreased. However, the relative amounts of any two compounds adsorbed was almost independent of the field strength and length of the EFLC column. Further, even in the shortest column (length 1.5 m) solutes with dielectric constants greater than 4 could be adsorbed completely when 1- μ l volumes of 0.2% solutions were injected.

Stationary phase in separation column

With ADA as the stationary phase for the EFLC column, different stationary phases were used for the separation column and the effects on adsorption capacity, retention indices and column efficiencies were studied. The adsorption capacities with three connecting modes are given in Table II. The amounts of each compound adsorbed in modes III and IV were slightly smaller than those in mode II. It is thought that the decrease in the amount adsorbed was caused by the bleeding of the different stationary phases used in the separation column. As the adsorption capacity of the ADA-EFLC column was still adequate, it was concluded that any stationary phase could be used for separation.

TABLE II

EFFECT OF STATIONARY PHASE IN SEPARATION COLUMN ON ADSORPTION

EFLC column, 4,4'-azoxydianisole/glass capillary (4 m × 0.35 mm I.D.; inner electrode, Ni wire; outer electrode, Sealbest P-246), at 120°C; applied potential, 150 V d.c. Results given are amounts adsorbed (nmol).

Compound	Mode*		
	II: ADA-ADA	III: PEG 20M-ADA	IV: DC550-ADA
<i>n</i> -Butyl acetate	1.12	1.03	0.98
Diisopropyl ketone	0.73	0.74	0.65
2-Ethylhexaldehyde	1.45	1.32	1.32
Phenylacetaldehyde	2.65	2.30	2.25
<i>n</i> -Hexaldehyde	3.24	3.01	2.97
<i>n</i> -Amyl acetate	0.97	0.96	0.95

* Mode I: ADA-EFLC column only. Separation column temperature: mode II, 120°C; mode III, 120°C; mode IV, 105°C.

Table III shows the variation of retention index with connection modes. The values in column A were obtained by using only the separation column and those in the B columns by using the connection modes. The presence of the EFLC column behind the separation column, as might be expected, gave different retention indices from those obtained by using only the separation column, except with mode II, in which the same stationary phase was utilized in both the separation and EFLC columns. In this experiment, the separation column was 5–15 times longer than the ADA–EFLC column, so the retention indices were close to those obtained by using the separation column only.

TABLE III
RETENTION INDICES AND COLUMN EFFICIENCIES

A, Separation column; B, separation column–EFLC column (B_{II} , B_{III} and B_{IV} correspond to modes II, III and IV, respectively).

Compound	Retention index					
	ADA*		PEG 20M*		Silicone DC550*	
	A	B_{II}	A	B_{III}	A	B_{IV}
Ethylbenzene	1072	1074	974	985	923	937
Diisopropyl ketone	1169	1173	1125	1140	1018	1005
<i>n</i> -Butyl acetate	1015	1013	912	932	848	857
2-Ethylhexaldehyde	1112	1109	1073	1078	919	909
<i>n</i> -Hexaldehyde	1157	1157	1145	1147	962	967
Ethyl isobutyl ketone	1061	1061	1005	1012	910	912
<i>n</i> -Amyl acetate	1112	1114	1009	1023	947	955
<i>m</i> -Chlorotoluene	1244	1238	1178	1180	—	—
Styrene	1174	1175	1045	1057	957	965
HETP (mm)	0.49	0.57	0.56	0.76	0.31	0.38

* Stationary phases in separation column. Separation column temperature: mode II, 120°C; mode III, 97°C; mode IV, 105°C.

In addition, as shown in Table III, it was possible to improve the separability of the system by dividing a long ADA column into a separation column and an EFLC column. In the previously reported mode of operation^{1–3} (mode I), the HETP values were as high as 1.0–1.5 cm and the number of theoretical plates attained using a 40-m column was only 2700–4000. In the new mode, the reduction of the column efficiency could be minimized by using an EFLC column.

Reproducibility of adsorption on the short EFLC column

The reproducibility of the adsorption of *tert*.-butyl, *sec*.-butyl, *n*-butyl and *n*-amyl acetate was studied, by using mode IV under 150 V d.c. The chromatograms of these esters obtained without an electric field are shown in Fig. 3a. The chromatograms shown in Fig. 3b, c and d were obtained with a 150-V electric field at the first, fifth and twentieth injections, respectively. The twentieth injection was performed 40 h after the first injection. Although the amounts of each compound adsorbed were different,

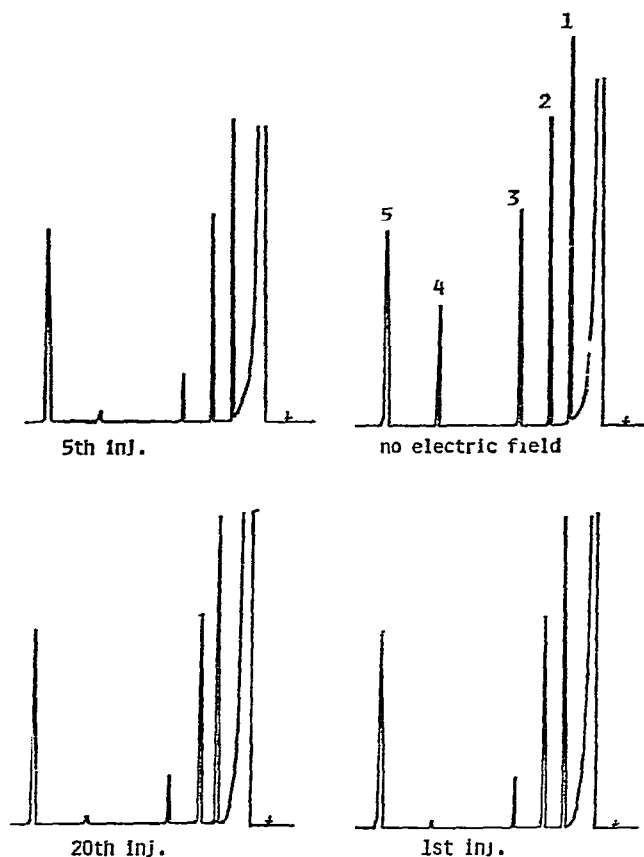


Fig 3. Repeatability check. 1 = *tert.*-Butyl acetate; 2 = *sec.*-butyl acetate; 3 = *n*-butyl acetate; 4 = *n*-amyl acetate; 5 = *n*-decane. Applied potential: 150 V d.c.

almost the same chromatograms could be obtained in any experiment, as can be seen in Fig. 3. Further, the shortened EFLC column also has a long life.

Temperature programming of separation column

In the previous work¹⁻³, the oven temperature had to be in the mesomorphic range. In this improved arrangement, the oven for EFLC column was installed separately, so any suitable separation column temperature could be chosen for the sample. Further, as the amount adsorbed should be independent of the separation column temperature, the separation temperature can be programmed, while keeping the EFLC column temperature constant.

A prepared sample consisting of *n*-hydrocarbons (C_6 - C_{15}), esters, ketones and aldehydes was run with temperature programming from 70 to 130°C in mode IV. The results are illustrated in Fig. 4. The chromatogram shown in Fig. 4a was obtained without applying an electric field to the EFLC column and Fig. 4b at 200 V d.c. It is clear that by applying the electric field the oxygen-containing compounds were eliminated and the peaks appearing were due only to hydrocarbons. The quantitative results were in good agreement with the known amounts spiked.

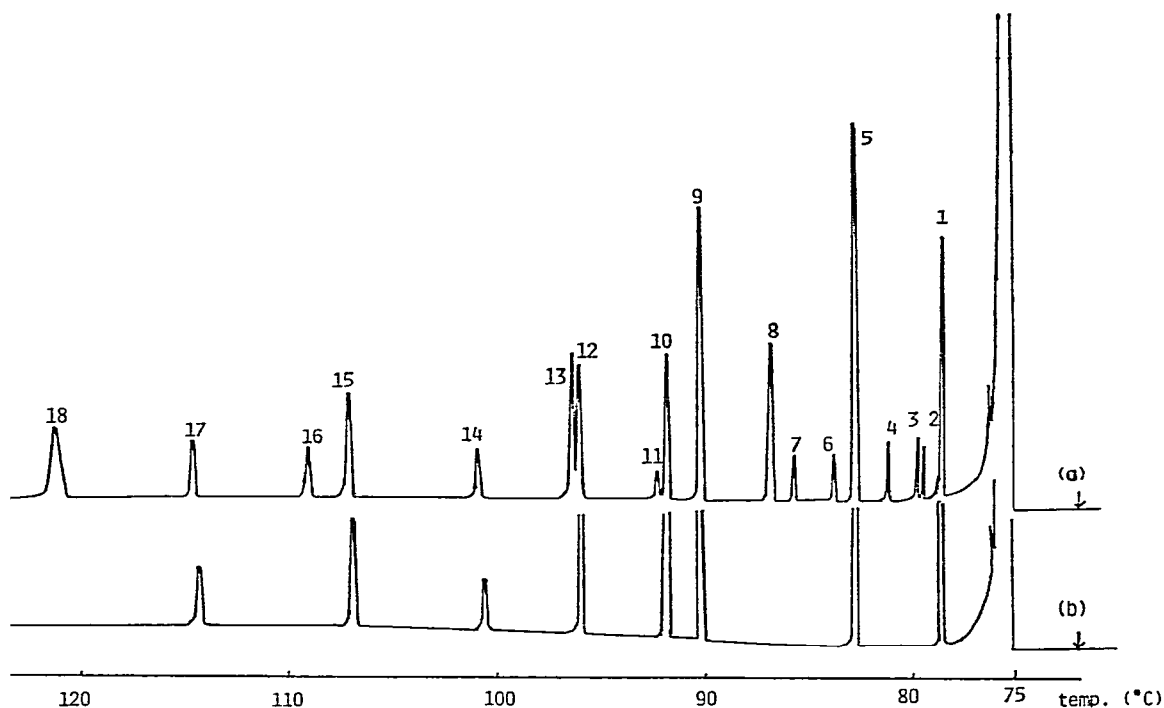


Fig. 4. Application to artificial mixture. (a) Without electric field; (b) with 250 V d c. applied. Peaks: 1 = *n*-C₇; 2 = *tert.*-butyl acetate; 3 = methyl isobutyrate; 4 = *sec.*-butyl acetate; 5 = *n*-C₈; 6 = isobutyl acetate; 7 = ethyl isobutyrate; 8 = *n*-butyl acetate; 9 = *n*-C₉; 10 = ethylbenzene; 11 = 2-ethylhexaldehyde; 12 = styrene; 13 = *n*-amyl acetate; 14 = *n*-C₁₀; 15 = α -methylstyrene; 16 = *n*-hexyl acetate; 17 = *n*-C₁₁; 18 = phenylacetaldehyde.

Application to analysis of edible oil

An edible oil was distilled up to 200°C, and the fraction obtained was spiked with ethylbenzene, styrene and α -methylstyrene then diluted with diethyl ether. A 1–2- μ l volume of the solution obtained was injected into the gas chromatograph.

The chromatograms shown in Fig. 5 were obtained by applying mode I, in which an ADA-EFLC column (40 m \times 0.35 mm I.D.) was used at 120°C. As shown in Fig. 5, good separations of trace amounts of aromatic hydrocarbons could not be achieved.

In contrast, the combination of a high-performance separation column with an ADA-EFLC column (mode IV) provided sharp, well resolved peaks, as shown in Fig. 6. Here, it was possible to separate the compounds of interest by programming the temperature of the separation column and the aromatic hydrocarbons could be eluted at suitable positions on the chromatogram. The quantitative results were in good agreement with the known amounts spiked.

CONCLUSIONS

Although the amounts of the compounds adsorbed decreased as the length of the EFLC column decreased the adsorption capacity of the shortened EFLC column

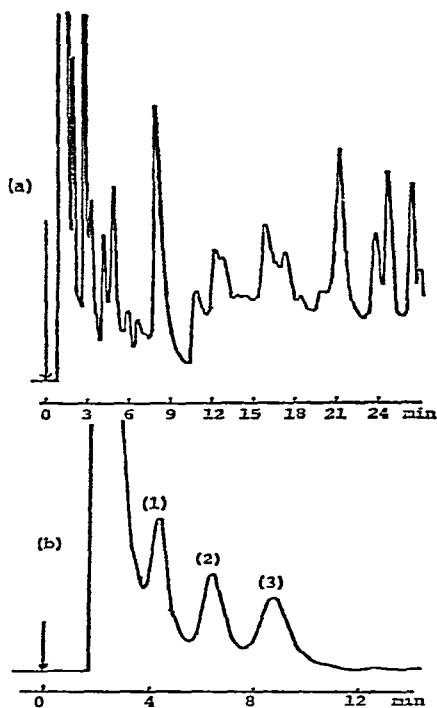


Fig. 5. Chromatograms of an edible oil fraction spiked with aromatic hydrocarbons. (a) Without electric field; (b) with 150 V d.c. applied. 4,4'-Azoxydianisole column (40 m \times 0.35 mm I.D. Ni wire) at 120°C; injection volume, 1 μ l. Peaks: 1 = Ethylbenzene; 2 = styrene; 3 = α -methylstyrene

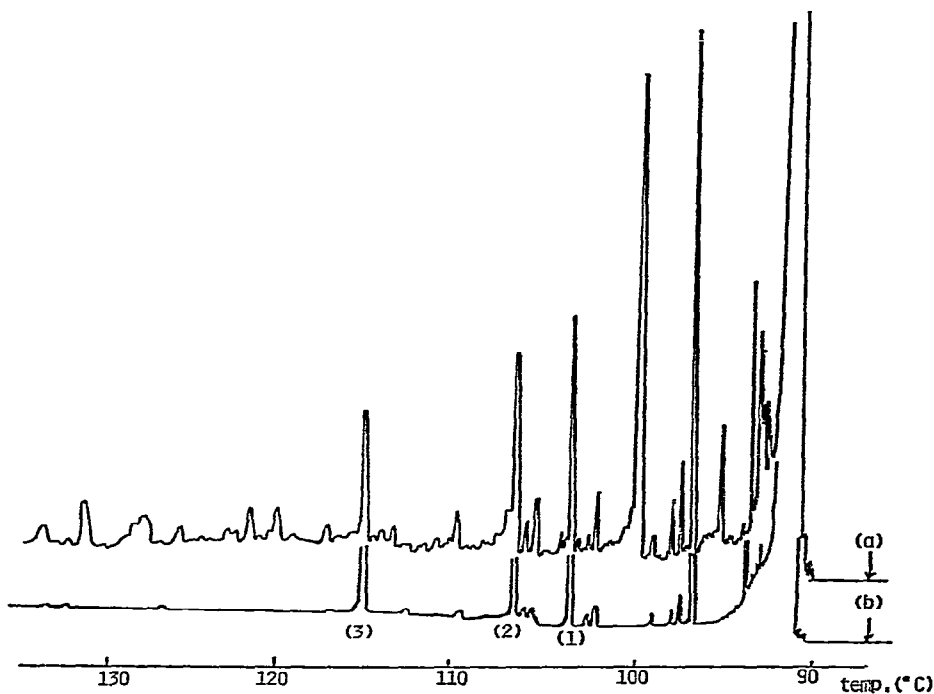


Fig. 6. Application to edible oil fraction. (a) Without electric field; (b) with 250 V d.c. applied, mode IV. Peaks: 1 = ethylbenzene; 2 = styrene; 3 = α -methylstyrene.

was still sufficient to adsorb the solutes when their dielectric constants were greater than 4.

The amounts of each compound adsorbed in modes II, III and IV were compared, and similar results were obtained. Any stationary phase could be used for the separation column.

Further, the shortened EFLC column showed sufficient reproducibility and lifetime for selective adsorption.

Installation of a separate oven for the EFLC column made the temperature of the separation column programmable, and this was applied successfully to the analysis of trace aromatic hydrocarbons in an edible oil. Oxygen-containing compounds were not observed on the chromatogram and sharp, well resolved peaks of aromatic hydrocarbons emerged at suitable positions.

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