Two Alkyl Resorcarenes as New Stationary Phases for Isomer Separation by GC

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Two resorcarene derivatives were synthesized and used as a new kind of capillary gas chromatography stationary phase. The results showed that they have high efficiency, medium polarity and excellent selectivity for isomers of industrial chemicals such as substituted benzenes. In the separation of naphthalene and analogs, the strong retention ability was observed. The thermal stability of the new stationary phases are approximately 240 ℃.

Calixarenes have been the focus of the supramolecular-chemistry since the structure of p-tert-butylcalixarene was reported by A. Zinke and E. Ziegler.[1] As a typical host-compound, they can form inclusion compound with many metal ions and organic molecules.[2-4] Recently, some calixarenes have been used as gas chromatography stationary phase.[5-7] Resorcarenes, the similar cavity structure compound, are also typical host-compound.[8-10] They have been reported as pseudo-stationary phases in electrokinetic chromatography (EKC).[11] In this paper, two alkyl resorcarenes derivatives (as showed in graphical abstract) were synthesized by alkylated reaction and successfully used as high-resolution GC stationary phase.

Fused silica capillary (0.25 mm i.d., Yong Nian Optical Fibre Factory, Hebei, China) was treated by sodium chloride deposition method.[12] Columns were statically coated stationary phase (I) and dynamically coated stationary phase (II) in dichloromethane, Then columns were conditioned at 220 ℃ for 6h. The column evaluation was carried out on a SP-3700 Gas Chromatograph (Beijing Analytical Instrument Factory, Beijing, China) equipped with a flame ionization detector (FID). Carrier gas was nitrogen.

Table 1 lists the column efficiency of two alkyl resorcarene derivatives capillary columns. Both stationary phases possess high efficiency and fine reproducibility. It shows that statically coated columns have better efficiency than dynamically coated columns because static coating can produce more even and smooth film. Grob test mixture are well separated and have nearly symmetrical peaks. Furthermore, naphthalene eluted after 2,6-dimethylaniline (DMA) on both stationary phases. It means that two stationary phases have special retention ability for naphthalene. McReynolds' constant (ΔI) (120 ℃) were 194 for stationary phase (I) and 223 for stationary phase (II).

Some isomers of substituted benzene were well separated on both stationary phases, such as chlorotoluene, bromotoluene, nitrochlorobenzene, nitrobromobenzene, nitrotoluene, cresol, dimethoxybenzene, and xylenol. But for two same groups substituted isomers, such as dichlorobenzene, dibromobenzene, xylene, and toluidine, the m- and p- isomer can be separated

Table 1. Chromatographic properties of the alkyl resorcarene columns at 120 ℃

SP[a]	No.	Dimension (m × mm)	Coating style	Flow rate (cm/s)	Dodecane (k)[b]	Dodecane (n)[c]
I	1#	12.2 × 0.25	statically	14.5	3.13	3660
	2#	18.7 × 0.25	statically	13.5	3.13	3680
	3#	21.5 × 0.25	statically	14.3	3.33	2890
II	4#	10.5 × 0.25	dynamically	15.4	1.92	2550
	5#	21.0 × 0.25	dynamically	16.7	1.83	2230

[a] Stationary Phase. [b] Capacity factor. [c] Theoretical plate number/m.

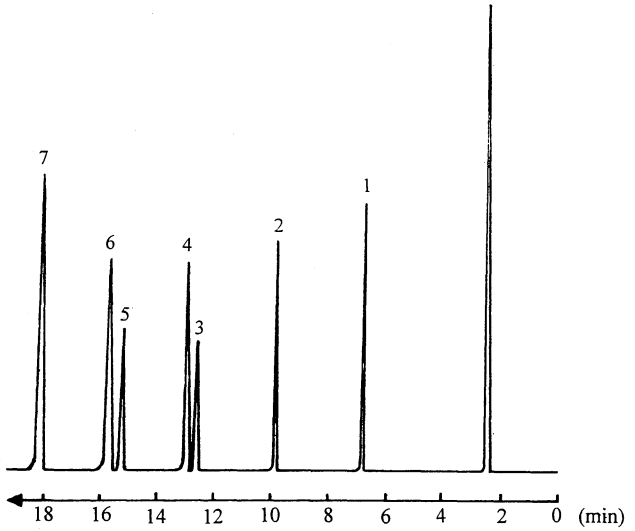

Figure 1. The separation chromatogram of xylenol isomers and phenol on 3# column at 140 ℃. N_2 linear veleocity: 14.3 cm/s. Peaks : 1=phenol; 2=2,6-xylenol; 3=2,5-xylenol; 4=2,4-xylenol; 5=3,5-xylenol; 6=2,3-ylenol; 7=3,4-xylenol.

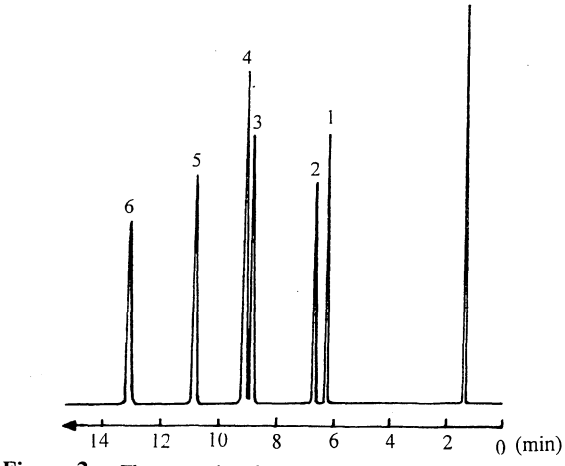

Figure 2. The separation chromatogram of dinitrotoluene (DNT) isomers on 5# column at 190 ℃. N_2 carrier linear veleocity: 26.9cm/s. Peaks: 1=2,6-DNT; 2=2,5-DNT; 3=2,3-DNT; 4=2,4-DNT; 5=3,5-DNT; 6=3,4-DNT.

slightly or not on both stationary phases. It was considered that the same substituted group will cause less polarity difference than different substituted group.

Two typical separation chromatograms are showed. Xylenol isomers and phenol, which are important industrial materials, are baseline separated on 3# column at 140 ℃ (Figure 1). Figure 2 is the dinitrotoluene (DNT) isomers separation chromatogram on 5# column at 190 ℃.

Two resorcarene derivatives show a good film-formation ability and possess high efficiency as a new kind of stationary phase for high-resolution GC. These stationary phases have excellent separation ability for alkanes, alkanols, phenols, disubstituted benzenes and aromatic hydrocarbons.

References and Notes

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