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Note

Analysis of low-boiling isomers of phenols by gas chromatography

ASIT BHATTACHARJEE and A. BHAUMIK
Central Fuel Research Institute, P.O. FRI, Dhanbad, Bihar (India)
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The complete analysis of the low-boiling isomers of phenols by gas chromatography on conventional packed columns has not been achieved so far owing to the excessive peak tailing caused by non-linear adsorption on the solid support on the one hand and the lack of a suitable single stationary phase on the other. Although peak tailing has been eliminated in some instances by converting the phenols into their methyl[1,2] or silyl ethers[3], such procedures are cumbersome and time consuming. In order to overcome the difficulty of using a single stationary phase, Janak and Komers[4] and Kolšek and Matičič[5] suggested the use of two different stationary phases, based on their studies on a number of polar and non-polar phases. The selection of a suitable pair of stationary phases is also important as it is essential that a pair of components that overlap completely on one of the phases should be completely resolved on the other phase, and *vice versa*; partial overlapping or partial separation may lead to erroneous results. Unfortunately, no pair of stationary phases studied by previous workers[4,5] satisfy the above requirements so far as the complete separation of *m*- and *p*-cresol and 2,4- and 2,5-xylenol in particular is concerned.

We have found a pair of stationary phases that overcomes peak tailing appreciably without the need to convert the phenols into their methyl or silyl ethers and facilitates the almost complete separation of all of the peaks. Several 10-component mixtures of phenols containing phenol, three cresols and six xylenols have been analysed on this pair of stationary phases with acceptable accuracy.

EXPERIMENTAL

Equipment

A Perkin-Elmer 810 gas chromatograph fitted with a flame-ionization detector and a Honeywell 1-mV recorder was used. Experiments were carried out on a stainless-steel column (6 ft. × 1/8 in. O.D.) with nitrogen as the carrier gas (flow-rate 30 ml/min). The packing materials for the following two columns were prepared by slurrying the stationary phases with the support in a water–methanol mixture (column I) and in a chloroform–methanol mixture (column II) followed by removal of the solvents by heating: column I, 40% rubidium benzenesulphonate + 2% Carbowax 20M + 2% ascorbic acid on Chromosorb P (60–80 mesh); column II, 12% Apiezon L + 0.5% Carbowax 20M + 1% ascorbic acid on Chromosorb W (60–80 mesh. acid washed). Prior to analysis, column I was activated at 175° for 1 h or longer

until there was a complete separation of *m*- and *p*-cresol at 150°. Column II was pre-conditioned at 160° for 1 h under a flow of nitrogen.

Chemicals

The following pure grade chemicals were used: phenol (BDH, Poole, Great Britain), o-cresol (E. Merck, Darmstadt, G.F.R.), m-cresol (BDH), p-cresol (Naarden, Naarden, The Netherlands), 2,6-xylenol (BDH, recrystallised from cyclohexane), 2,4-, 2,5-, 2,3-, 3,5- and 3,4-xylenol (BDH) and ascorbic acid (BDH).

RESULTS AND DISCUSSION

In a previous study, it was shown that rubidium benzenesulphonate[6] modified with Carbowax 20M and ascorbic acid[7] (column I) was an excellent stationary phase for the separation of cresols and xylenols. All the six xylenols are separated on this phase at a column temperature of 150°. A mixture of 10 phenols containing phenol, three cresols and six xylenols is separated into seven peaks with the order of elution 2,6-xylenol, *o*-cresol, phenol + 2,5-xylenol, *m*-cresol + 2,3-xylenol, *p*-cresol + 2,4-xylenol, 3,5-xylenol, 3,4-xylenol.

Apiezon L grease, one of the most widely used non-polar stationary phases, has the major disadvantage that it causes peak tailing of polar compounds such as phenols. In some instances[1–3], peak-symmetry has been achieved by converting the phenols into their alkyl or silyl ethers. In this study, peak tailing of all compounds except phenol has been successfully eliminated by using Apiezon L modified with 0.5% Carbowax 20M and 1% ascorbic acid (column II) without altering the order of elution obtained on an unmodified Apiezon L column. Carbowax 20M and ascorbic acid when used individually with Apiezon L, however, failed to overcome tailing appreciably. On this column, at a column temperature of 135°, a mixture of 10 phenols was also separated into seven distinct peaks with the following order of elution: phenol, *o*-cresol, *m*-cresol + *p*-cresol, 2,6-xylenol, 2,4-xylenol + 2,5-xylenol, 2,3-xylenol + 3,5-xylenol, 3,4-xylenol.

It can be seen from the orders of elution of the phenols that no two particular

TABLE I

ANALYSIS OF SYNTHETIC MIXTURES OF PHENOLS USING COLUMNS I AND II AT 150° AND 135°, RESPECTIVELY

The figure quoted are percentages by weight.

Compound	*Mixture 1*		*Mixture 2*		*Mixture 3*		*Mixture 4*	
	Found	*Present*	*Found*	*Present*	*Found*	*Present*	*Found*	*Present*
Phenol	6.8	6.8	5.2	5.2	4.8	5.2	5.7	5.7
o-Cresol	15.0	15.8	4.5	4.8	4.4	4.7	8.4	8.4
m-Cresol	8.9	9.6	29.0	29.3	39.7	40.7	39.1	39.7
p-Cresol	18.7	18.7	25.0	23.6	14.0	13.3	6.9	6.8
2,6-Xylenol	5.8	5.7	1.3	1.3	4.4	4.3	6.1	6.2
2,4-Xylenol	5.6	5.5	4.3	4.4	5.0	4.1	6.1	4.8
2,5-Xylenol	16.7	15.7	4.9	5.5	5.6	5.2	9.5	9.4
2,3-Xylenol	3.4	2.8	4.1	4.6	6.7	6.7	4.1	3.6
3,5-Xylenol	7.3	7.2	6.1	5.7	5.4	5.3	8.2	8.5
3,4-Xylenol	12.2	12.2	15.5	15.6	10.4	10.5	6.3	6.9

phenols are eluted together from both columns. The pairs *m*- and *p*-cresol, 2,4- and 2,5-xylenol and 2,3- and 3,5-xylenol, which overlap on column II, are completely resolved on column I. These characteristic elution patterns led us to study the analysis of mixtures of low-boiling isomers of phenols on these two phases. Several synthetic mixtures have been analysed using these two columns and the results were satisfactory (Table I). Figs. 1 and 2 show the chromatograms of synthetic mixture 1 on columns I and column II, respectively. The relative retention times of the phenols on both phases are presented in Table II.

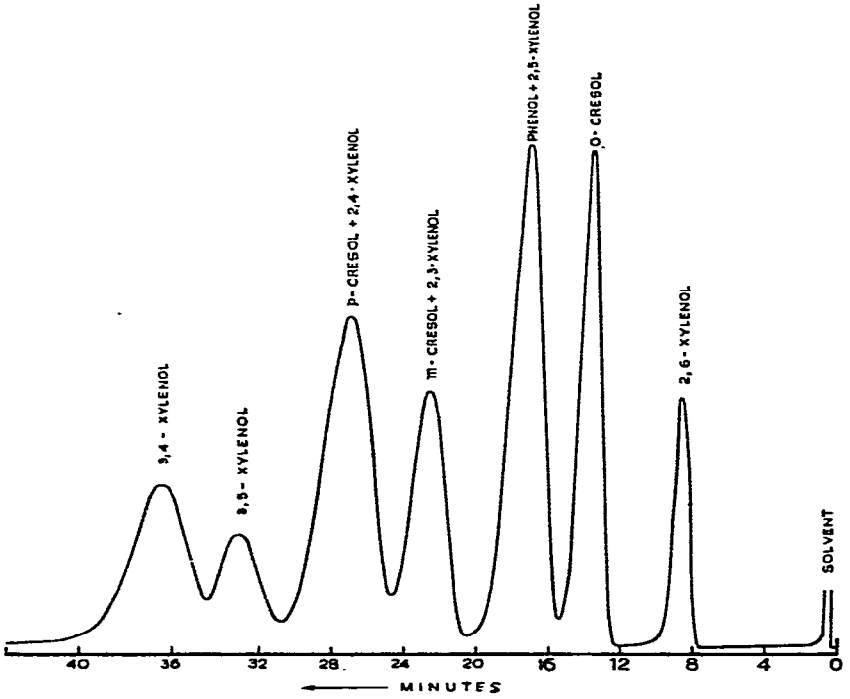

Fig. 1. Chromatogram of synthetic mixture 1 (Table I) on column I at 150°.

TABLE II

RELATIVE RETENTION TIMES OF PHENOLS

Compound	*Boiling point (°C)*	*Relative retention time on column I (150°)*	*Relative retention time on column II (135°)*
Phenol	181.7	1.00	1.00
o-Cresol	190.8	0.82	1.37
m-Cresol	202.1	1.32	1.61
p-Cresol	201.5	1.60	1.58
2,6-Xylenol	200.6	0.51	1.91
2,4-Xylenol	211.3	1.55	2.30
2,5-Xylenol	211.5	1.01	2.30
2,3-Xylenol	217.1	1.31	2.78
3,5-Xylenol	221.0	1.90	2.71
3,4-Xylenol	227.0	2.18	3.14

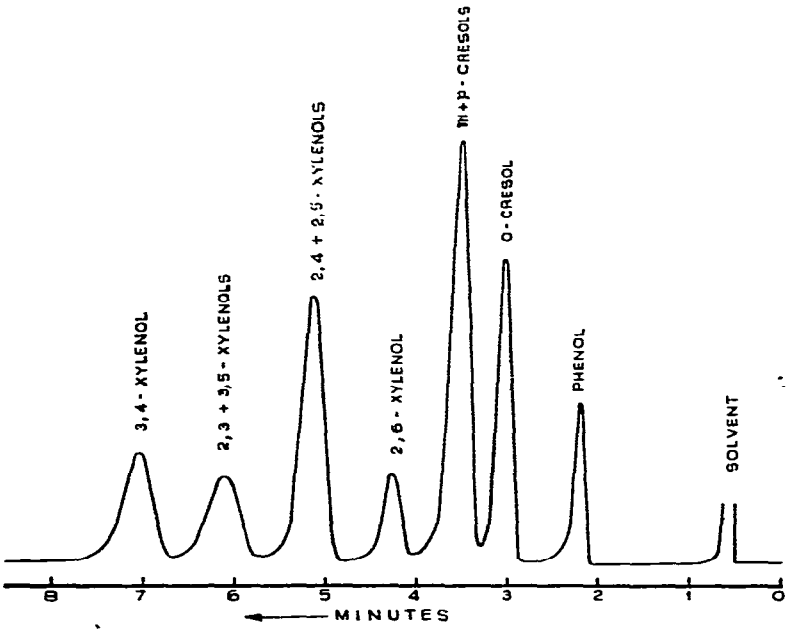

Fig. 2. Chromatogram of synthetic mixture 1 (Table I) on column II at 135°.

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