

## Notes

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CHROM. 5056

### Gas chromatographic separation of methylphenols on tricresylphosphates using open tubular columns

Gas chromatography is widely employed for analysis of mixtures of phenol, cresols and xylenols used as starting materials for phenol-formaldehyde polycondensates as well as for analysis of final resins by pyrolysis obtaining phenols of related composition as the raw material used<sup>1-3</sup>. Various types of liquid phases have been proposed for gas chromatographic analysis of methylphenols. Phosphates, especially tri(2,4-xylenyl)phosphate and tricresylphosphate belong to the most selective liquid phases for methylphenols<sup>1, 2, 4-7</sup>. The relatively good separation of some methylphenols on tricresylphosphate as the liquid phase<sup>8,9</sup> prompted us to study the selectivity of pure triortho- (TOCP), trimeta- (TMCP), and tripara-cresylphosphate (TPCP) towards phenol, cresols and xylenols using open tubular columns.

#### *Experimental*

*Apparatus.* A Fractovap Model GI (Carlo Erba, Milan) gas chromatograph equipped with a flame ionisation detector was used for these studies. Nitrogen was used as the carrier gas. The stainless-steel open tubular columns were 20 m long, and had an I.D. of 0.01 in.

*Chemicals.* Methylphenols were obtained commercially from Caolite and Chem. Products, London, and from Aldrich Chem. Comp., Wisc. Individual tricresylphosphates were prepared from pure cresols (in the purity of 98-99 %, by gas chromatography) with the reaction of POCl<sub>3</sub>.

*Column preparation.* The plug method was used. Columns were coated with a solution (0.3-0.5 ml) of the liquid phase (95 mg) and orthophosphoric acid (5 mg, 85 w/w) in acetone (1.0 ml). Prior to use the columns were conditioned at 120° for 3 h under carrier gas flow.

#### *Results and discussion*

The net retention times of phenol, cresols and xylenols relative to 3-methylphenol on TOCP, TMCP and TPCP at a temperature of 120° are given in Table I. As could be expected from the literature, 2,6-dimethylphenol and phenol, 3- and 4-methylphenol, and 2,4- and 2,5-dimethylphenol are the critical pairs of the 10-component mixture. It is evident from Table I that the column with TPCP allows the best separation for closely related compounds. Only poor resolution for all pairs was obtained on TOCP. The pair of 2,6-dimethylphenol and phenol is best resolved on the column with TMCP while 2,4- and 2,5-dimethylphenol is only poorly resolved on this column.

The elution order of phenol and 2,6-dimethylphenol (steric hindrance) indicates

TABLE I

THE NET RETENTION RELATIVE TIMES OF PHENOL, CRESOLS AND XYLENOLS AT 120°

No.	Compound	TOCP	TMCP	TPCP	TPP
1	2,6-Dimethylphenol	0.57	0.54	0.55	0.56
2	Phenol	0.59	0.60	0.58	0.61
3	2-Methylphenol	0.71	0.71	0.69	0.69
4	4-Methylphenol	0.93	0.93	0.92	0.94
5	3-Methylphenol	1.00	1.00	1.00	1.00
6	2,4-Dimethylphenol	1.11	1.10	1.10	1.07
7	2,5-Dimethylphenol	1.16	1.15	1.16	1.11
8	2,3-Dimethylphenol	1.46	1.43	1.45	1.41
9	3,5-Dimethylphenol	1.68	1.65	1.71	1.65
10	3,4-Dimethylphenol	1.92	1.92	1.94	1.92

that hydrogen bonds between phenols and the liquid phase play a part in the separation. The stronger the hydrogen bond the better the separation of this pair on polar liquid phases. It seems from this observation that the relative polarity of the liquid phases increases in order of TOCP, TPCP and TMCP, which is in agreement with the polarity effects of the methyl group in benzene nuclei. (The relatively poorer hydrogen bond on TOCP towards TPCP can be attributed to sterical hindrance.) For comparison, in Table I are also included the net retention times on triphenylphosphate (TPP). The elution sequence of the other phenols is in the order of their boiling points. The effect of the operating temperature on relative retention times at temperatures of 100, 110, 120 and 130° is illustrated in Figs. 1-3. As can be seen, the temperature changes only slightly affect the separations.

A chromatogram of a mixture of phenol, cresols and xylenols using TPCP as

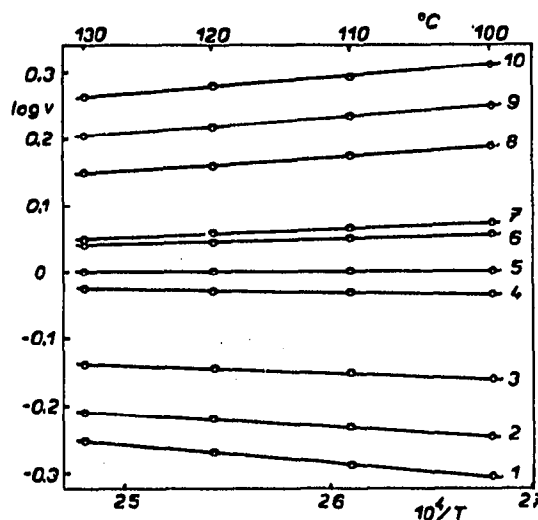
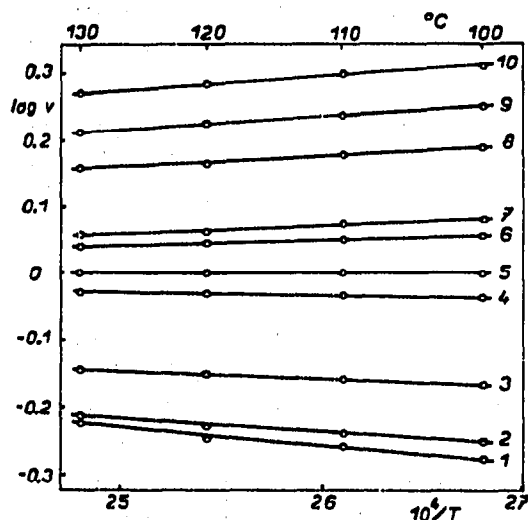


Fig. 1. Variation of the logarithm of relative retention  $\times \log v$  of phenol and methylphenols on TOCP column with change of temperatures (No. identification in Table I).

Fig. 2. Variation of the logarithm of relative retention  $\times \log v$  of phenol and methylphenols on TMCP column with change of temperatures (No. identification in Table I).

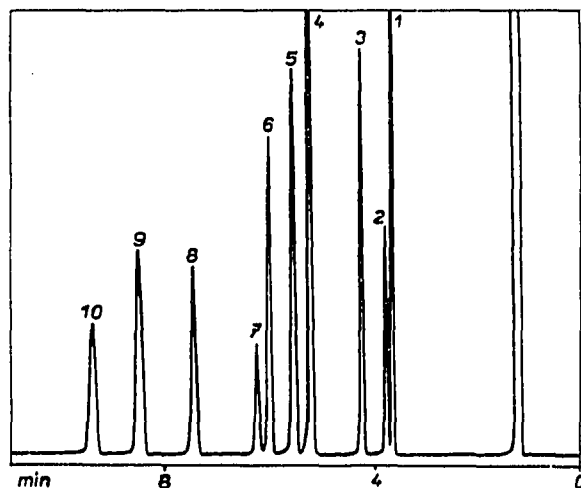
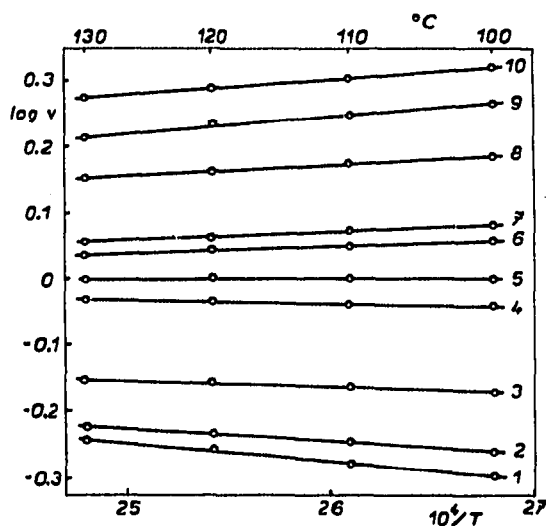


Fig. 3. Variation of the logarithm of relative retention  $\times \log v$  of phenol and methylphenols on TPCP column with change of temperatures (No. identification in Table I).

Fig. 4. Gas chromatogram of phenol and methylphenols on TPCP liquid phase at 130° (See peak names, Table I).

the liquid phase is illustrated in Fig. 4. The high efficiency of the open tubular column and the good selectivity of the liquid phase used allowed a complete separation of the 10 compounds in less than 10 min. This column had a good thermal stability up to 135°. The undesirable effect of the metallic wall of the column usually resulting in tailing was eliminated by addition of phosphoric acid to the liquid phase<sup>10</sup>.

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- 1 S. T. PRESTON, *A Guide to the Analysis of Phenols by Gas Chromatography*, Polyscience, Evanston, Ill., 1966.
- 2 J. ZULAICA AND G. GUIOCHON, *J. Polymer. Sci.*, 4 (1966) 567.
- 3 C. LANDAULT AND G. GUIOCHON, *Anal. Chem.*, 39 (1967) 713.
- 4 V. T. BROOKS, *Chem. and Ind. (London)*, (1959) 1317.
- 5 A. R. PATERSON, in H. J. NOEBELS, R. F. WALL AND N. BRENNER (Editors), *Gas Chromatography, Instr. Soc. Amer. Symposium, June 1959*, Academic Press, 1961, pp. 323-326.
- 6 E. D. BARBER, E. SAWICKY AND S. P. MCPHERSON, *Anal. Chem.*, 36 (1964) 2442.
- 7 E. R. ADLARD AND G. W. ROBERTS, *J. Inst. Petrol*, 51 (1965) 376.
- 8 H. ROTZSCHE, in M. VAN SWAAY (Editor), *Gas Chromatography*, Butterworths, London, 1963 pp. 117-121.
- 9 J. HRIVŇÁK AND J. MACÁK, *Anal. Chem.*, in press.
- 10 J. HRIVŇÁK, *J. Chromatog. Sci.*, 8 (1970) 602.

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