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Note

Gas–liquid chromatographic analyses

XXIX*. Separation of free chlorophenol isomers on non-polar and polar quartz capillary columns

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Phenolic compounds occurring in the environment are of widespread origin, *viz.*, introduced directly as industrial effluents and indirectly as transformation products from natural and synthetic chemicals.

Owing to their high polarities and low vapour pressures, chlorinated phenols have generally been analysed by gas chromatography (GC) as their more volatile derivatives, such as methyl[1–3], ethyl[4–7], 2,4-dinitrophenyl[8] and silyl[9–12] ethers, and heptafluorobutanoic acid[13,14] and acetic acid[15–22] esters. As derivatization often involves toxic reagents and complicates the method, thus increasing the possibility of error, chlorophenols have been analysed also as free components. Packed columns, with a wide range of polar[10,23–33] and non-polar[23,26,27,29–31] stationary phases, have been tested. However, little attention has been paid to the use of capillary columns. Our previous work[34,35] reported the first detailed GC data for all chlorophenol isomers, separated on a low-polarity SE-30 quartz capillary column.

This paper reports the retention behaviour of all chlorinated phenols, extending the previous studies with chlorinated aromatics[3,36,37]. Separations were carried out on SE-30, FFAP and OV-351 quartz capillary columns with temperature programming and isothermal operation. The retention data relative to phenol and the compounds on SE-30 are given and the elution order of the isomers is discussed. The results are compared with those of earlier studies[10,23–35].

EXPERIMENTAL

Materials

Phenol and chlorophenols were commercial products (Fluka, Buchs, Switzerland), and were used without further purification. The mixture used contained an appropriate amount of each isomer for the sensitivity of the flame-ionization detector, the amount increasing with increasing degree of chlorination.

* For Part XXVIII, see ref. 3.

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Methods

A Perkin-Elmer Sigma 3 gas chromatograph with the following operating conditions was used: injection and flame-ionization detection (FID) temperatures, 275°C; splitting ratio, 1:20; chart speed, 10 mm min^{-1}. The columns used were: (i) a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.); (ii) a vitreous silica FFAP WCOT column (25 m × 0.35 mm I.D.), both supplied by SGE (North Melbourne, Australia); (iii) a fused silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). Nitrogen was used as the carrier gas with flow-rates at 160°C of 16 (SE-30), 48 (FFAP) and 54 cm sec^{-1} (OV-351). The column temperature was programmed from 100 to 260°C (SE-30) and to 230°C (FFAP and OV-351) at 6°C min^{-1} and maintained at 230°C on polar columns until elution of peaks had ceased. The isothermal data were obtained at 160°C.

RESULTS AND DISCUSSION

Chromatograms of a mixture of chlorophenols are shown in Figs. 1 and 2, obtained with temperature programming on SE-30 and FFAP, respectively. The corresponding retention data, together with physical properties of the compounds, are given in Table I. The isothermal data are presented in Table II.

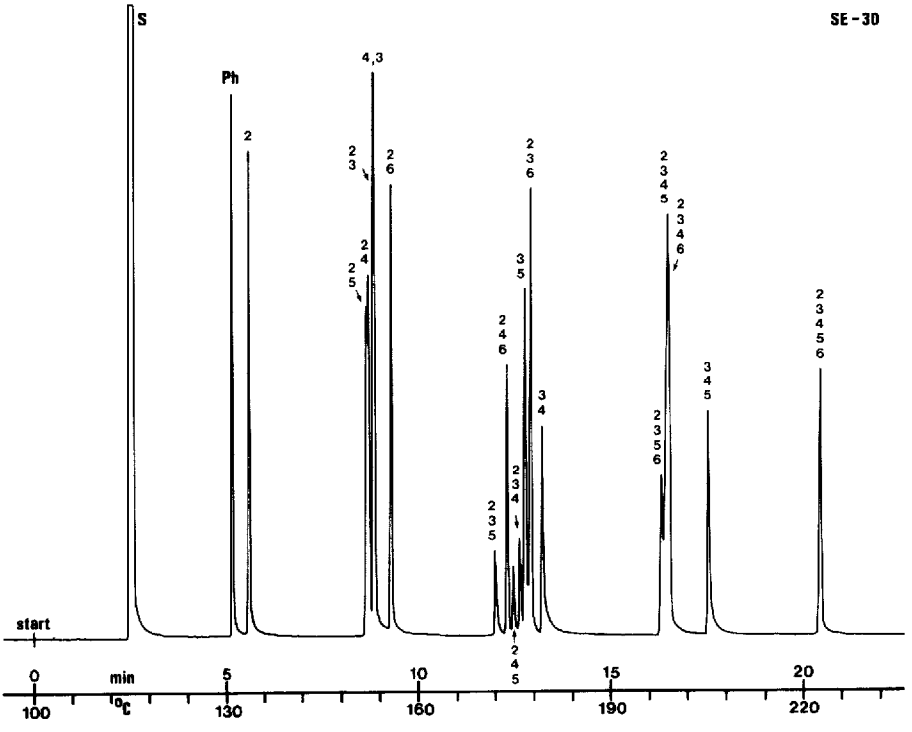

Fig. 1. Chromatogram of a mixture of chlorophenols obtained on an SE-30 quartz capillary column with temperature programming from 100°C at 6°C min^{-1} until elution of peaks had ceased. S = Solvent; Ph = phenol. The numbers indicate the chlorinated positions.

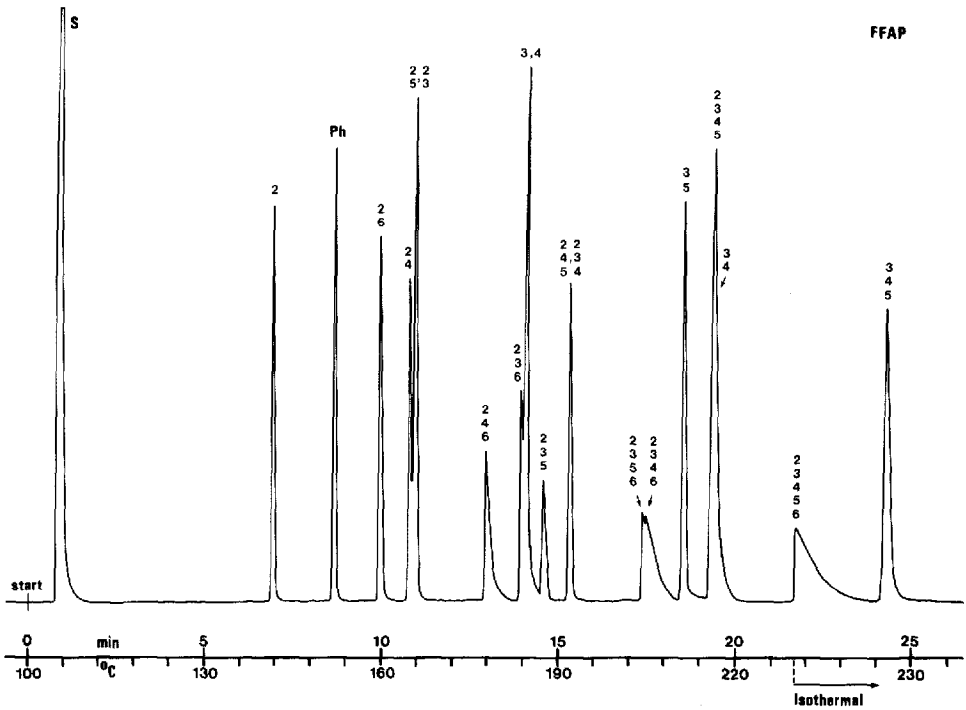

Fig. 2. Chromatogram of the same mixture as in Fig. 1, obtained on an FFAP quartz capillary column. Temperature programme from 100 to 230°C at 6°C min^{-1} and then isothermal at 230°C until elution of peaks had ceased.

The 3- and 4-chloro isomers overlap on SE-30 (Fig. 1), whereas the di- and trichloro isomers are resolved, except for partial overlapping of the 2,5- and 2,4-dichloro isomers. A poor separation was obtained for the tetrachloro isomers, *viz.*, the 2,3,5,6- and 2,3,4,5-isomers partially overlap and the 2,3,4,5- and 2,3,4,6- isomers are nearly coincident.

A change in the operating temperature gives rise to alterations in the elution on SE-30 (Table II), due to the close proximity of the boiling points of the isomers (Table I). The elution sequence on SE-30 obtained in this work is in good accord with found earlier on non-polar packed columns[23,27,29,30] (Table III), although one divergant result has been reported, *viz.*, the 4-chloro isomer is eluted from SE-30 later than the 2,4,5-trichloro isomer[27].

Much poorer resolution of the mixture was obtained on polar columns (Fig. 2). As shown, five compound pairs overlapped, *viz.*, (i) the 2,5- and 2,3-dichloro, (ii) 3- and 4-chloro, (iii) 2,4,5- and 2,3,4-trichloro, (iv) 2,3,5,6- and 2,3,4,6-tetrachloro, and (v) 2,3,4,5-tetrachloro and 3,4-dichloro isomers. In addition, the 2,4-dichloro and 2,3,6-trichloro isomers were only partially resolved from the other isomers (Fig. 2). The elution order of the components remained unaltered under various operating conditions (Table I). The polar columns gave broadened and tailing peaks for all *o,o'* isomers, *i.e.*, the 2,6-dichloro, 2,4,6- and 2,3,6-trichloro, 2,3,5,6- and 2,3,4,6-tetrachloro and pentachloro isomers, the tailing being more pronounced with increasing

TABLE I

PHYSICAL PROPERTIES AND RETENTION DATA FOR CHLORINATED PHENOLS, SEPARATED ON SE-30, FFAP AND OV-351 CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1 and 2.

Isomer	*B.p.** (°C^{mmHg})	*M.p.** (°C)	*SE-30*		*FFAP*			*OV-351*		
			*ART***	*RRT****	*ART***	*RRT****	*RRT*§	*ART***	*RRT****	*RRT*§
Phenol	181.75^{760}	43	5.14	1.00	8.60	1.00	1.67	9.16	1.00	1.78
2-Cl	174.9^{760}	9	5.58	1.09	6.89	0.80	1.23	7.71	0.84	1.38
3-Cl	214^{760}	33	8.85	1.72	14.08	1.64	1.59	14.02	1.53	1.58
4-Cl	219.75	43–44	8.84	1.72	14.10	1.64	1.60	14.03	1.53	1.59
2,3-Di-Cl	–	57–59	8.81	1.71	10.95	1.27	1.24	11.20	1.22	1.27
2,4-Di-Cl	210^{760}	45	8.69	1.69	10.78	1.25	1.24	11.06	1.21	1.27
2,5-Di-Cl	211^{744}	59	8.64	1.68	10.93	1.27	1.27	11.20	1.22	1.30
2,6-Di-Cl	219–220^{740}	68–69	9.30	1.81	9.91	1.15	1.07	10.29	1.12	1.11
3,4-Di-Cl	253.5^{767}	68	13.22	2.57	19.46	2.26	1.47	19.21	2.10	1.45
3,5-Di-Cl	233^{757}	68	12.79	2.49	18.60	2.16	1.45	18.36	2.00	1.44
2,3,4-Tri-Cl	sub	83.5	12.62	2.46	15.36	1.79	1.22	15.21	1.66	1.21
2,3,5-Tri-Cl	248–249^{250}	62	11.98	2.33	14.60	1.70	1.22	14.43	1.58	1.20
2,3,6-Tri-Cl	–	58	12.92	2.51	13.99	1.63	1.08	13.82	1.51	1.07
2,4,5-Tri-Cl	244–248^{746}	68–70.5	12.46	2.42	15.32	1.78	1.23	15.19	1.66	1.22
2,4,6-Tri-Cl	246^{760}	69.5	12.31	2.39	13.00	1.51	1.06	12.93	1.41	1.05
3,4,5-Tri-Cl	271–277^{746}	101	17.52	3.41	24.27	2.82	1.39	23.59	2.58	1.35
2,3,4,5-Tetra-Cl	sub	116–117	16.50	3.21	19.42	2.26	1.18	19.15	2.09	1.16
2,3,4,6-Tetra-Cl	150^{15}	70	16.52	3.21	17.43	2.03	1.06	17.11	1.87	1.04
2,3,5,6-Tetra-Cl	–	115	16.31	3.17	17.36	2.02	1.06	17.08	1.86	1.05
Penta-Cl	309–310^{754}	174	20.48	3.98	21.72	2.53	1.06	20.56	2.24	1.00

* From ref. 38.

** Absolute retention times were measured from sample injection (*e.g.*, Figs. 1 and 2).

*** Relative retention time for phenol taken as 1.00.

§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

TABLE II

RETENTION DATA FOR CHLORINATED PHENOLS, SEPARATED ON SE-30 AND FFAP CAPILLARY COLUMNS AT 160°C

Isomer	*SE-30*		*FFAP*		
	*ART**	*RRT***	*ART**	*RRT***	*RRT****
Phenol	3.35	1.00	2.90	1.00	0.87
2-Cl	3.58	1.07	2.06	0.71	0.58
3-Cl	4.61	1.38	9.56	3.30	2.07
4-Cl	4.61	1.38	9.56	3.30	2.07
2,3-Di-Cl	4.81	1.44	4.71	1.62	0.98
2,4-Di-Cl	4.72	1.41	4.58	1.58	0.97
2,5-Di-Cl	4.72	1.41	4.71	1.62	1.00
2,6-Di-Cl	5.02	1.50	3.86	1.33	0.77
3,4-Di-Cl	7.87	2.35	35.80	12.34	4.55
3,5-Di-Cl	7.80	2.33	28.95	9.98	3.71
2,3,4-Tri-Cl	7.55	2.25	12.82	4.42	1.70
2,3,5-Tri-Cl	6.81	2.03	10.70	3.69	1.57
2,3,6-Tri-Cl	7.35	2.19	9.46	3.26	1.29
2,4,5-Tri-Cl	7.39	2.21	12.80	4.41	1.73
2,4,6-Tri-Cl	7.19	2.15	7.51	2.59	1.04
3,4,5-Tri-Cl	15.65	4.67	110.50	38.10	7.06
2,3,4,5-Tetra-Cl	13.02	3.89	35.65	12.29	2.74
2,3,4,6-Tetra-Cl	13.11	3.91	18.51	6.38	1.41
2,3,5,6-Tetra-Cl	12.76	3.81	18.45	6.36	1.45
Penta-Cl	25.79	7.70	50.20	17.31	1.95

* Absolute retention times were measured from sample injection.
** Relative retention time for phenol taken as 1.00.
*** Relative retention time for the corresponding compound on SE-30 taken as 1.00.

degree of chlorination. It has been reported[24] that the addition of a small amount (1.7%) of phosphoric acid to the polar stationary phase Carbowax 20M eliminated tailing and sharpened peaks significantly, whereas too much H_3PO_4 (3.4%) drastically reduced retention volumes and the resolution was lost.

The retention sequence on the polar capillary columns generally follows that reported previously on packed columns (Table III), but the comparison is not strictly valid as the separation of all isomers was not carried out earlier. Edgerton and Moseman[28] used support bonded and double support bonded polyester column packings for the separation of all sixteen Cl_2–Cl_5 chlorophenols. The 2,3,5- and 2,3,6-trichloro isomers are eluted on DEGS, SB-DEGS and DSB-DEGS in reversed order to those on FFAP and OV-351, the greatest disparity between the columns being found with the 3,4,5-trichloro isomer, however. The latter isomer is eluted on packed columns between the 3,5-dichloro and 2,3,4,5-tetrachloro isomers instead of its last elution on FFAP and OV-351. The reversed retention orders for the isomers are more pronounced on SB-BDS stationary phase[28] as compared with those obtained in this work on the capillary columns (Table III).

On SE-30 with temperature programming all isomers had higher retention times, relative to phenol, than on FFAP (Fig. 3), whereas with isothermal operation

TABLE III

RETENTION SEQUENCE OF THE CHLOROPHENOL ISOMERS ON SEVERAL NON-POLAR AND POLAR STATIONARY PHASES

Column	*Temperature (°C)*	*Compound**	*Ref.*
Silicone oil 200	175	Ph, 2, 4 + 24, 26, 246	23
5% SE-30	200	Ph + 2, 24 + 25, 26, 246, 245, 4, 35, 2345	27
3% SE-30	Unknown	24, 4, 3, 26, 246, 245, 35	29
10% Apiezon L	200	Ph, 2, 4, 24, 26, 246, 2346, Penta	30
SE-30 capillary column	160	Ph, 2, 4 + 3, 24 + 25, 23, 26, 235, 246, 236, 245, 234, 35, 34, 2356, 2345, 2346, 345, Penta	**
SE-30 capillary column	100 to 260/ 6°C min^{-1}	Ph, 2, 25, 24, 23, 4, 3, 26, 235, 246, 245, 234, 35, 236, 34, 2356, 2345, 2346, 345, Penta	**
5% Cyanosilicone GE XE-60	150	2, 26, 24, 25, 3, 4, 245, 34	10
Diisodecyl phthalate	175	2 + Ph, 24 + 26, 4, 246	23
20% Carbowax 20M + 1.7% H_3PO_4	220	2, Ph, 26, 24, 23 + 25, 246, 4, 245, 2346, Penta	24
15% Carbowax 20M + 2% H_3PO_4	170	2, 26, 24 + 25, 246, 245, 2346, Penta	25
15% EGA + 2% H_3PO_4	165	2, 26 + 24 + 25, 246, 245, 2346, Penta	25
15% DEGS + 2% H_3PO_4	155	2, 26, 24 + 25, 246, 245, 2346, Penta	25
10% EGM + 2% H_3PO_4	155	2, 26, 24 + 25, 246, 245, 2346, Penta	25
15% EGS + 2% H_3PO_4	165	2, 26 + 24 + 25, 246, 245, 2346, Penta	25
15% DEGS	200	2, Ph, 24 + 25, 26, 4, 246	27
25% Carbowax 20M	200	2, Ph, 26, 24 + 25, 246, 4, 245, 2345, 35	27
5% DEGS	180	26, 24, 25, 23, 246, 235, 236, 245, 234, 2356, 2346, 35, 345, 2345, 34, Penta	28
SB-DEGS	155	26, 24, 25, 23, 246, 235, 236, 245, 234, 2356, 2346, 35, 345, 2345, 34	28
DSB-DEGS	170	26, 24 + 25, 23, 246, 235, 236, 245, 234, 2356, 2346, 35, 345, 2345, 34, Penta	28
SB-BDS	190	26 + 24, 25 + 23, 246 + 235, 234, 245, 236, 35, 34, 2345, 2346, 345, 2356	28
3% OV-225	Unknown	24, 26, 3, 4, 246, 245, 35	29
3% NGA	Unknown	26, 24, 4, 3, 246, 245, 35	29
5% DEGS + 1% H_3PO_4	160	2, Ph, 26, 24, 246, 4, 2346, Penta	30
20% Silicone KF-53***	140	25 + 24, 23, 26, 35, 34	32
20% Dibenzo-18-crown-6***	140	26, 25, 24, 23, 35, 34	32
20% Sodium dodecylbenzenesulphonate***	140	26, 25, 24, 23, 35, 34	33
FFAP and OV-351 capillary columns	160	2, Ph, 26, 24, 25 + 23, 246, 236, 3 + 4, 235, 245, 234, 2356, 2346, 35, 2345, 34, Penta, 345	**

* In order of increasing retention; Ph = phenol. The numbers indicate the chlorinated positions.

** Present work.

*** Same order occurred on several other stationary phases.

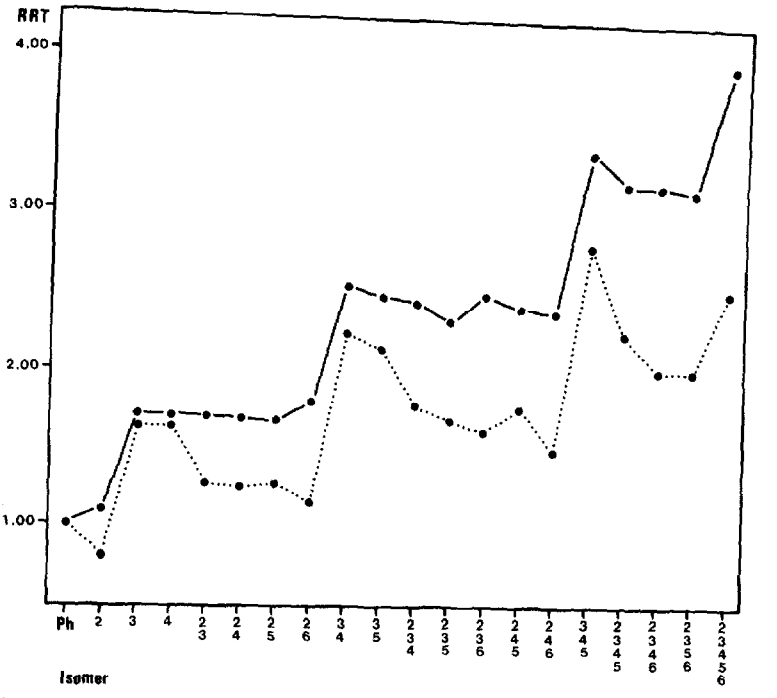

Fig. 3. Relative retention times (RRTs) for chlorinated phenols (the numbers indicate the chlorinated positions), determined on SE-30 (●——●) and FFAP (● · · · ●) with temperature programming. Relative retention time for phenol (Ph) taken as 1.00 (Table I). Conditions as in Figs. 1 and 2.

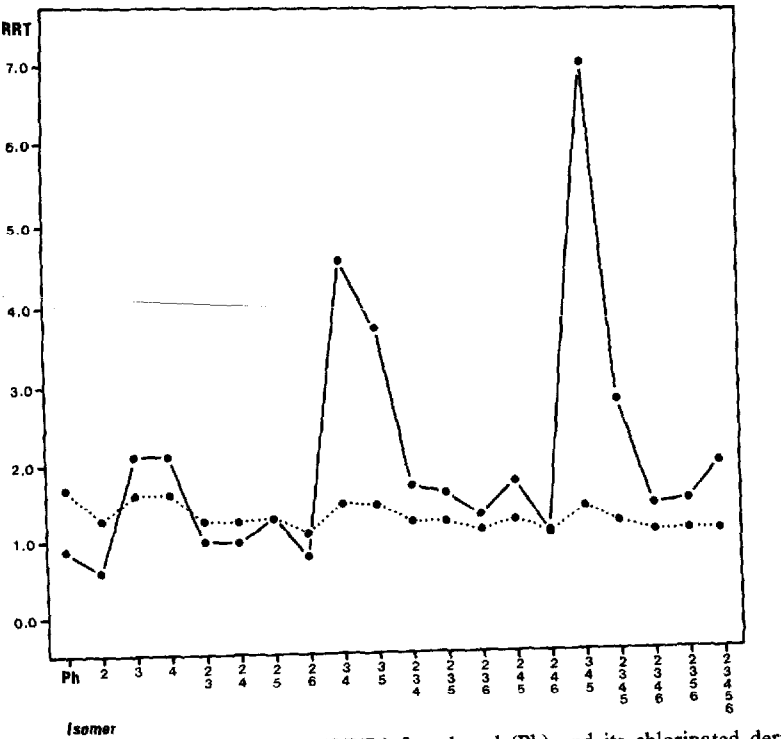

Fig. 4. Relative retention times (RRTs) for phenol (Ph) and its chlorinated derivatives (the numbers indicate the chlorinated positions), determined on FFAP at 160°C (●——●) and with temperature programming (● · · · ●). Relative retention time for the corresponding isomer on SE-30 taken as 1.00 (Tables

only the 2-chloro and 2,6-dichloro isomers showed the same trend (Table II). The difference between the polar columns is negligible, OV-351 giving lower retention times, except for the 2-chloro isomer (Table I). As expected, the disparity between the columns used is greatest with the *m*- and *p*-isomers, being maximal with the 3,4,5-trichloro isomer, where the polar effects are maximized. Owing to the *ortho*-effect[39], the differences shown by the *o,o'*-isomers are minimal. All disparities observed are more pronounced under isothermal conditions (Fig. 4), as expected.

CONCLUSIONS

The 3- and 4-chlorophenols overlap on both columns used, as they do also on packed columns[10,29]. The di- and trichloro isomers are resolvable on SE-30, whereas on polar columns one compound pairs overlap. Excellent separation for the dichloro isomers has been reported on a polar packed column with sodium dodecylbenzenesulphonate as liquid phase[33], whereas the complete resolution of all trichloro isomers has not yet been achieved on packed columns[28]. Whereas the tetrachloro isomers overlapped on capillary columns, they can be separated on support bonded and double support bonded polyester column packings; however, DSB-DEGS allowed only the elution of pentachlorophenol[28].

The earlier results show that the chlorophenol isomers which overlapped in GLC can usually be separated by using a suitable high-performance liquid chromatographic (HPLC) technique[27,40,41].

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