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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXXI*. RETENTION INCREMENTS OF ISOMERIC CHLOROPHENOLS ON LOW-POLARITY (SE-30) AND POLAR (FFAP) CAPILLARY COLUMNS

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SUMMARY

Isothermal and temperature-programmed capillary gas chromatography of isomeric chlorophenols has been studied on SE-30 and FFAP stationary phases at various temperatures. Unlike FFAP, a change in temperature on SE-30 gives rise to changes the retention sequence of some individual isomers. Retention index measurements and the retention index increments for each position of chlorine substitution are discussed. The results are compared with those of earlier studies with chlorophenols and their derivatives, *viz.*, chlorinated phenyl acetates and anisoles.

INTRODUCTION

Gas chromatography (GC) of isomeric chlorophenols, either as free components or as suitable derivatives, has been widely investigated using, most frequently, packed columns with several polar and low-polar stationary phases[1]. The use of capillary columns and GC analysis of all chlorophenol isomers have received little attention, however[1–3].

Although the retention times, relative retention times or retention ratios have been variously reported, only the paper by Grzybowski *et al.*[4] shows the retention indices for some chlorophenols, *viz.*, the 3-, 4-, 2,4-, 2,6-, 3,5-, 2,4,5- and 2,4,6-isomers, determined on glass columns packed with SE-30, OV-225 or NGA.

The effect on the retention of increasing chlorine substitution has not been reported, and this work shows the incremental effect in terms of retention indices on a low-polarity (SE-30) and a polar (FFAP) quartz capillary column under various isothermal and temperature-programmed conditions; the work extends our previous studies of the GC retention behaviour of chlorinated aromatics[5]. The results are compared with those reported earlier for chlorophenols[4] and their derivatives, *viz.*, chlorinated phenyl acetates[6] and anisoles[7].

* For Part XXX, see ref. 5.

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EXPERIMENTAL

Materials

Phenol and chlorophenols were commercial products (Fluka, Buchs, Switzerland), and were used without further purification.

Commercial mixtures of *n*-alkanes were obtained from different sources.

Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the operating conditions reported previously[1]. The quartz capillary columns used were obtained from SGE (North Melbourne, Australia). The column temperature was programmed from 100°C to 260°C (SE-30) and 230°C (FFAP) at 2, 6 and 10°C min^{-1} and held on FFAP at 230°C until elution of peaks had ceased. The isothermal data were recorded at 140, 160, 180 and 200°C.

All retention times were measured from the time of sample injection, the Kováts retention indices being calculated off-line using two appropriate *n*-alkanes. The dead volumes under isothermal temperatures were determined by the injection of methane.

The mixtures of chlorophenols and *n*-alkanes were chromatographed at each temperature one after the other, whereas the isomers overlapped were analysed separately together with appropriate *n*-alkanes.

RESULTS AND DISCUSSION

Table I shows that the operating temperature for SE-30 caused changes in the retention sequence of some individual chlorophenol isomers; the corresponding effect had not been seen previously with other series of chlorinated aromatics[5]. With an increase in temperature from 140 to 180°C, the reduction in retention of the 2,3,6-isomer is more pronounced than that of the other related isomers. In addition, the retention order for the 3,4- and 3,5-isomers was reversed at high temperature. With temperature-programming the greatest effects are shown by the lower retention isomers, *viz.*, at an increased programming rate, the 2,4- and 2,5-isomers and the 4- and 3- and 2,3-isomers appeared in reversed order, as also did the 2,3,6- and 3,5-isomers. The 4- and 3-isomers are eluted more frequently later with temperature-programming than the 2,4-, 2,5- and 2,3-isomers[1], in contrast to the isothermal operation. This is due to the increased interaction between the *m*- and *p*-monochlorinated isomers and the liquid phase, which is greatly affected by an increase in temperature[8].

The elution sequence of isomeric chlorophenols obtained on a polar column remained unaltered under various conditions; the changes relative to the low-polar column are shown in Table I.

The retention indices for the components, determined on SE-30 under various conditions, are shown in Table II. The isomers are not eluted in the order of their degree of chlorination, as generally occurred on low-polar columns with other series of chlorinated aromatics[5]; the 3,5-, 3,4- and 3,4,5-isomers are different in this respect (Table I). The retention generally increased with temperature, the variations ΔI/20°C and ΔI/4°C min^{-1} lying in the ranges from -14 to 23 and from -1 to 34 retention index units (i.u.), respectively. The temperature-programmed experiments more frequently showed lower disparities, as is evident from Table II.

TABLE I

EFFECT OF COLUMN TEMPERATURE ON RETENTION SEQUENCE OF CHLOROPHENOLS ON SE-30 AND FFAP CAPILLARY COLUMNS

Retention	*SE-30*						*FFAP**
	Column temperature						
	Isothermal (°C)			*Programmed from 100°C (°C min^{-1})*			
	140	*160*	*180*	*2*	*6*	*10*	
Increasing** ↓	Phenol	Phenol	Phenol	Phenol	Phenol	Phenol	2
	2	2	2	2	2	2	Phenol
	4 }	4 }	4 }	24	25	25	26
	3 }	3 }	3 }	25	24	24	24
	24 }	24 }	24 }	23	23	4 }	25 }
	25 }	25 }	25 }	4	4 }	3 }	23 }
	23	23	23	3	3 }	23	246
	26	26	26	26	26	26	236
	235	235	235	235	235	235	3 }
	246	246	236	246	246	246	4 }
	245	236	246	245	245	245	235
	234	245	245	234	234	234	245 }
	236	234	234	236	35	35	234 }
	35	35	34	35	236	236	2356
	34	34	35	34	34	34	2346
	2356	2356	2356	2356	2356	2356	35
	2345	2345	2345	2345	2345	2345	2345 }
	2346	2346	2346	2346	2346	2346	34 }
	345	345	345	345	345	345	Penta
	Penta	Penta	Penta	Penta	Penta	Penta	345

* The retention order is unchanged under various conditions.
** } = Overlapping.

A predictably increased retention for the isomers is observed on a more polar FFAP stationary phase (Table III). The ratio $I_{FFAP}/I_{SE\text{-}30}$, determined at 160°C, lies in the range 1.64–2.15, the penta- and parent-isomers giving the lower and upper limit values, respectively. The difference between the non-polar contributions, *i.e.*, $I_{FFAP} - I_{SE\text{-}30}$, varies between 875 and 1441 i.u., the 2- and 3,4,5-isomers showing a minimum and maximum disparity between the columns, respectively. The increased retention with temperature is not so pronounced as on SE-30, the variations ΔI/20°C and ΔI/4°C min^{-1} being in the ranges from −54 to 47 and from −8 to 75 i.u., both larger than on SE-30.

Table IV shows that the retention indices determined previously[4] for some chlorophenols on a packed column with SE-30 as stationary phase, are in good agreement with the values obtained on an SE-30 capillary column in this work. The variation lies in the range from −33 to 11 i.u., the 3- and 4-isomers showing the greatest disparities. The polar columns, however, unexpectedly show great variations, the retention indices obtained on the more polar FFAP (2546, ref. 9) capillary column being 354–474 and 210–348 i.u. higher than on OV-225 (1819, ref. 4) and NGA (1849,

TABLE II

RETENTION INDICES FOR CHLOROPHENOLS ON SE-30 AT VARIOUS COLUMN TEMPERATURES

Compound	*Column (SE-30) temperature*									
	Isothermal (°C)					*Programmed from 100°C (°C min^{-1})*				
	140	*160*	*180*	ΔI_1*	ΔI_2**	*2*	*6*	*10*	ΔI_1*	ΔI_2**
Phenol	943	929	932	−14	3	944	946	945	2	−1
2-Cl	987	991	1000	4	9	975	979	987	4	8
3-Cl	1159	1157	1161	−2	4	1165	1167	1169	2	2
4-Cl	1158	1157	1161	−1	4	1165	1167	1169	2	2
2,3-Di-Cl	1169	1180	1188	11	8	1155	1165	1173	10	8
2,4-Di-Cl	1160	1170	1181	10	11	1147	1158	1168	11	10
2,5-Di-Cl	1162	1170	1181	8	11	1149	1156	1166	7	10
2,6-Di-Cl	1189	1200	1214	11	14	1179	1190	1198	11	8
3,4-Di-Cl	1374	1378	1384	4	6	1383	1382	1391	−1	9
3,5-Di-Cl	1358	1375	1392	17	17	1362	1362	1367	0	5
2,3,4-Tri-Cl	1345	1363	1380	18	17	1340	1354	1364	14	10
2,3,5-Tri-Cl	1317	1327	1347	10	20	1313	1323	1334	10	11
2,3,6-Tri-Cl	1352	1354	1359	2	5	1353	1368	1378	15	10
2,4,5-Tri-Cl	1338	1356	1370	18	14	1335	1346	1359	11	13
2,4,6-Tri-Cl	1331	1346	1360	15	14	1327	1339	1349	12	10
3,4,5-Tri-Cl	1584	1587	1595	3	8	1590	1596	1597	6	1
2,3,4,5-Tetra-Cl	1517	1536	1558	19	22	1521	1545	1552	24	7
2,3,4,6-Tetra-Cl	1519	1538	1559	19	21	1523	1546	1552	23	6
2,3,5,6-Tetra-Cl	1511	1530	1551	19	21	1515	1536	1545	21	9
Penta-Cl	1700	1720	1743	20	23	1719	1753	1762	34	9

* $\Delta I_1 = I_{160°C} - I_{140°C}$; $I_{6°C\ min^{-1}} - I_{2°C\ min^{-1}}$.
** $\Delta I_2 = I_{180°C} - I_{160°C}$; $I_{10°C\ min^{-1}} - I_{6°C\ min^{-1}}$.

ref. 4), respectively, with the McReynolds polarities of the stationary phases given in parentheses. The increased retention observed on FFAP is due to its high polarity, whereas the variation (119–169 i.u.) between the two packed columns is due to the different properties of stationary phases, *viz.*, OV-225 (3-cyanopropyl methylpolysiloxane) was found to exhibit electron-withdrawing properties, whereas NGA (polyneopentyl glycol adipate) was an electron-donor at equal polarity[4].

The incremental effects of chlorine substitution, obtained on both columns at three isothermal temperatures, are given in Table V, the corresponding effect of an additional chlorine atom determined at 160°C being shown in Table VI. The retention sequences of the isomers, with the retention increments obtained on SE-30 and FFAP at 160°C, are illustrated in Figs. 1 and 2, respectively.

Examining the data in Table V, it is evident that the incremental effects on both columns increase with temperature. The ratio between the polar and low-polar column varied from −2.16 (2-isomer) to 1.63 (3-, 4- and 3,4-isomers), the difference

TABLE III

RETENTION INDICES FOR CHLOROPHENOLS ON FFAP AT VARIOUS COLUMN TEMPERATURES

Compound	*Column (FFAP) temperature*									$\frac{I_{FFAP}}{I_{SE\text{-}30}}$ ***	$I_{FFAP} - I_{SE\text{-}30}$ ***
	Isothermal (°C)					*Programmed from 100°C (°C min^{-1})*					
	160	*180*	*200*	ΔI_1*	ΔI_2**	*2*	*6*	*10*	ΔI_1*	ΔI_2**	
Phenol	2000	1971	1957	−29	−14	1950	1942	1962	−8	20	2.15	1071
2-Cl	1866	1812	1800	−54	−12	1764	1771	1820	7	49	1.88	875
3-Cl	2371	2371	2380	0	9	2333	2350	2364	17	14	2.05	1214
4-Cl	2371	2371	2380	0	9	2335	2352	2364	17	12	2.05	1214
2,3-Di-Cl	2160	2143	2152	−17	9	2107	2117	2131	10	14	1.83	980
2,4-Di-Cl	2151	2131	2145	−20	14	2096	2104	2120	8	16	1.84	981
2,5-Di-Cl	2160	2143	2152	−17	9	2105	2115	2131	10	16	1.85	990
2,6-Di-Cl	2097	2081	2083	−16	2	2032	2038	2061	6	23	1.75	897
3,4-Di-Cl	2731	2752	2777	21	25	2737	2767	2774	30	7	1.98	1353
3,5-Di-Cl	2675	2691	2713	16	22	2670	2700	2707	30	7	1.95	1300
2,3,4-Tri-Cl	2453	2460	2476	7	16	2424	2447	2458	23	11	1.80	1090
2,3,5-Tri-Cl	2403	2403	2410	0	7	2368	2389	2399	21	10	1.81	1076
2,3,6-Tri-Cl	2368	2361	2376	−7	15	2319	2343	2359	24	16	1.75	1014
2,4,5-Tri-Cl	2453	2460	2476	7	16	2420	2444	2458	24	14	1.81	1097
2,4,6-Tri-Cl	2301	2306	2321	5	15	2247	2270	2284	23	14	1.71	955
3,4,5-Tri-Cl	3028	3075	3112	47	37	3077	3120	3140	43	20	1.91	1441
2,3,4,5-Tetra-Cl	2730	2751	2776	21	25	2733	2763	2774	30	11	1.78	1194
2,3,4,6-Tetra-Cl	2554	2573	2615	19	42	2602	2609	2620	7	11	1.66	1016
2,3,5,6-Tetra-Cl	2553	2573	2615	20	42	2598	2603	2620	5	17	1.67	1023
Penta-Cl	2821	2848	2885	27	37	2855	2930	2942	75	12	1.64	1101

* $\Delta I_1 = I_{180°C} - I_{160°C}$; $I_{6°C\ min^{-1}} - I_{2°C\ min^{-1}}$.

** $\Delta I_2 = I_{200°C} - I_{180°C}$; $I_{10°C\ min^{-1}} - I_{6°C\ min^{-1}}$.

*** Determined at 160°C; for retention indices on SE-30, see Table II.

TABLE IV

CORRELATION BETWEEN RETENTION INDICES OF SOME CHLOROPHENOLS ON PACKED AND CAPILLARY COLUMNS COATED WITH LOW-POLAR AND NON-POLAR STATIONARY PHASES

Isomer	*Column*								
	*Packed**	*Capillary***		*Packed**		*Capillary***			
	SE-30	*SE-30*		*OV-225*	*NGA*	*FFAP*			
	I	*I*	ΔI_1***	*I*	*I*	*I*	ΔI_2§	ΔI_3§§	ΔI_4§§§
3-Cl	1194	1161	−33	1911	2061	2371	150	460	310
4-Cl	1192	1161	−31	1922	2058	2371	136	449	313
2,4-Di-Cl	1183	1181	−2	1708	1877	2131	169	423	254
2,6-Di-Cl	1206	1214	8	1727	1871	2081	144	354	210
3,5-Di-Cl	1391	1392	1	2217	2343	2691	126	474	348
2,4,5-Tri-Cl	1362	1370	8	2039	2158	2460	119	421	302
2,4,6-Tri-Cl	1349	1360	11	1928	2067	2306	139	378	239

* From ref. 4; the operating temperature is unknown.
** Present work at 180°C (Tables II and III).
*** $\Delta I_1 = I_{\text{capillary SE-30}} - I_{\text{packed SE-30}}$.
§ $\Delta I_2 = I_{\text{NGA}} - I_{\text{OV-225}}$.
§§ $\Delta I_3 = I_{\text{FFAP}} - I_{\text{OV-225}}$.
§§§ $\Delta I_4 = I_{\text{FFAP}} - I_{\text{NGA}}$.

being in the range from −196 (2-isomer) to 370 (3,4,5-isomer) i.u., both determined at 160°C.

Figs. 1b and 2b show that the increases of the retention index per chlorine atom fall on both columns into three general groups, *viz.* (a) the *o*-isomer, (b) the other *o*-isomers, and (c) the *m*- and *p*-isomers. The *o*-isomer shows a retention enhancement of 62 i.u. on SE-30 and, owing to the *ortho*-effect, a reduction of −134 i.u. on FFAP. With other *o*-isomers the enhancement observed is in the ranges 121–158 i.u. (SE-30) and 49–183 i.u. (FFAP). The highest retention increments are shown by the *m*- and *p*-isomers, *viz.*, 219–228 i.u. on SE-30 and 338–371 i.u. on FFAP. With both columns the incremental effect of a single chlorine atom is greatest, decreasing slightly with further *m*- or *p*-substitution (Figs. 1 and 2).

The data in Table VI indicate that an additional chlorine atom introduced into chlorophenols with different levels of substitution shows on SE-30 the greatest retention enhancements with the following series: 3- and 4- → 3,4- (221 i.u.), 3,5- → 3,4,5- (212 i.u.), 2,3,5- → 2,3,4,5- (209 i.u.) and 2,3,5,6- → penta- (190 i.u.). The lowest increments are shown by the 3- → 2,5- and 4- → 2,4- (13 i.u.), 3,5 → 2,3,5- (−48 i.u.), 3,4,5- → 2,3,4,5- (−51 i.u.) and 2,3,4,6 → penta- (182 i.u.) isomers. On FFAP the 3- and 4- → 3,4- (360 i.u.), 3,5- → 3,4,5- (353 i.u.), 2,3,5- → 2,3,4,5- (327 i.u.) and 2,3,5,6- → penta (268 i.u.) isomers show the largest enhancements; the smallest are observed with the 4- → 2,4- (−220 i.u.), 3,4- → 2,3,4- or 2,4,5- (−278 i.u.), 3,4,5- → 2,3,4,5- (−298 i.u.) and 2,3,4,5- → penta- (91 i.u.) isomers. The greatest disparities between the columns are shown by the 3,5- → 3,4,5-isomers (141 i.u.) and 3,4- → 2,3,4-isomers (−263 i.u.), as is evident from Table VI.

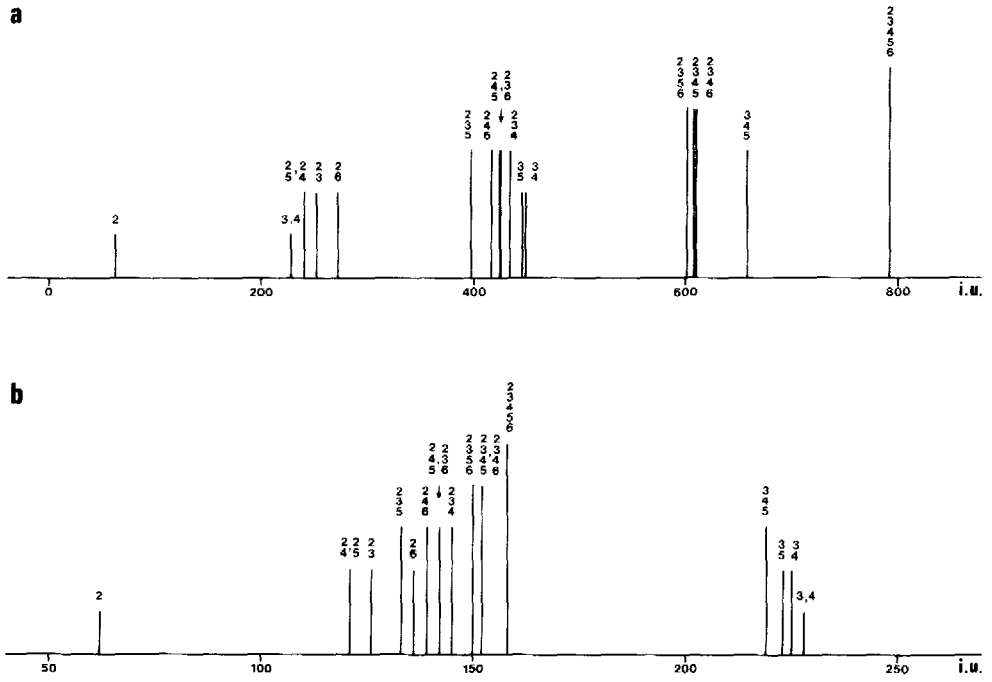

Fig. 1. Incremental effects of chlorine substitution with chlorophenols on SE-30 at 160°C. (a) Total retention index increase; (b) retention index increase per chlorine atom; i.u. = retention index units; the numbers indicate the positions of chlorination.

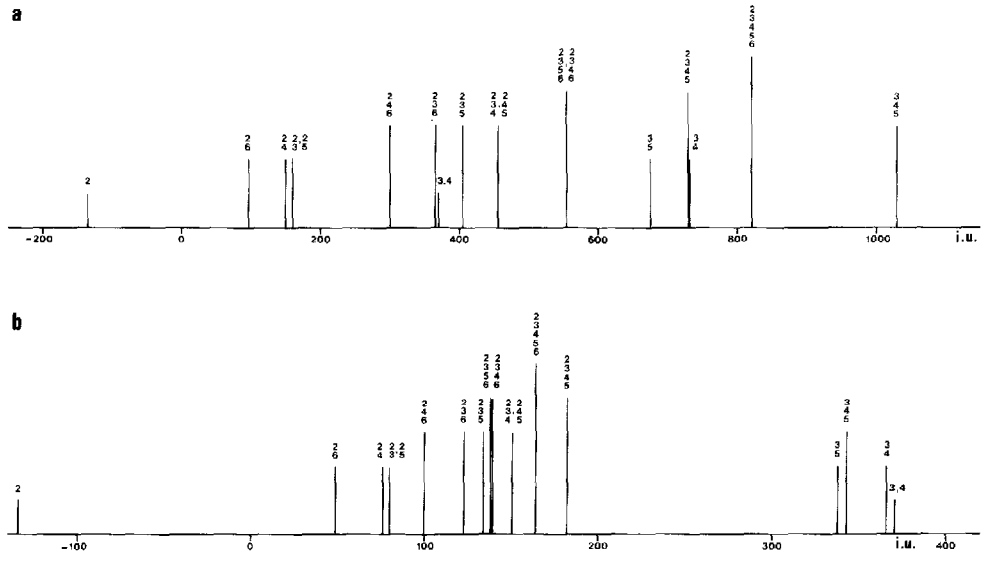

Fig. 2. Incremental effects of chlorine substitution with chlorophenols on FFAP at 160°C. (a) Total retention index increase; (b) retention index increase per chlorine atom; i.u. = retention index units; the numbers indicate the positions of chlorination.

TABLE V

INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION ON SE-30 AND FFAP AT ISOTHERMAL COLUMN TEMPERATURES

Isomer	*Column*						
	SE-30						*FFAP*
	140°C		*160°C*		*180°C*		*160°C*
	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$
2-Cl	44	44	62	62	68	68	−134
3-Cl	216	216	228	228	229	229	371
4-Cl	215	215	228	228	229	229	371
2,3-Di-Cl	226	113	251	126	256	128	160
2,4,-Di-Cl	217	109	241	121	249	125	151
2,5-Di-Cl	219	110	241	121	249	125	160
2,6-Di-Cl	246	123	271	136	282	141	97
3,4-Di-Cl	431	216	449	225	452	226	731
3,5-Di-Cl	415	208	446	223	460	230	675
2,3,4-Tri-Cl	402	134	434	145	448	149	453
2,3,5-Tri-Cl	374	125	398	133	415	138	403
2,3,6-Tri-Cl	409	136	425	142	427	142	368
2,4,5-Tri-Cl	395	132	427	142	438	146	453
2,4,6-Tri-Cl	388	129	417	139	428	143	301
3,4,5-Tri-Cl	641	214	658	219	663	221	1028
2,3,4,5-Tetra-Cl	574	144	607	152	626	157	730
2,3,4,6-Tetra-Cl	576	144	609	152	627	157	554
2,3,5,6-Tetra-Cl	568	142	601	150	619	155	553
Penta-Cl	757	151	791	158	811	162	821

* Total retention index increase.
** Retention index increase per chlorine atom.
*** Determined at 160°C.

The retention sequences of isomeric chlorophenols and their derivatives, *viz.*, chlorinated phenyl acetates[6] and anisoles[7], are shown in Table VII. Correlations between retention indices and increments of retention indices of these three series are shown in Tables VIII and IX and in Fig. 3.

On SE-30, the derivatives of chlorophenols are eluted in the order of their degree of chlorination; however, this is not so on FFAP, where the elution sequence is much more influenced by the structures of the components. Owing to the *ortho*-effect, this tendency is greatest with phenols and decreases with increasing size of the ring-substituent, *i.e.*, anisole > phenyl acetate (Table VII).

Examination of the retention behaviour of phenols and phenyl acetates shows that on SE-30 the retention increases with derivatization, except for the 3,4-, 3,5- and 3,4,5-isomers. The ratio $I_{\text{phenol}}/I_{\text{phenyl acetate}}$ lies in the range 0.84–1.03, the difference $I_{\text{phenol}} - I_{\text{phenyl acetate}}$ being between −182 and 44 i.u. The variation between the

	180°C		200°C		$\frac{\Delta I_{FFAP}}{\Delta I_{SE\text{-}30}}$***	$\Delta I_{FFAP} - \Delta I_{SE\text{-}30}$***
ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**		
−134	−159	−159	−157	−157	−2.16	−196
371	400	400	423	423	1.63	143
371	400	400	423	423	1.63	143
80	172	86	195	98	0.64	−91
76	160	80	188	94	0.63	−90
80	172	86	195	98	0.66	−81
49	110	55	126	63	0.36	−174
366	781	391	820	410	1.63	282
338	720	360	756	378	1.51	229
151	489	163	519	173	1.04	19
134	432	144	453	151	1.01	5
123	390	130	419	140	0.87	−57
151	489	163	519	173	1.06	26
100	335	112	364	121	0.72	−116
343	1104	368	1155	385	1.56	370
183	780	195	819	205	1.20	123
139	602	151	658	165	0.91	−55
138	602	151	658	165	0.92	−48
164	877	175	928	186	1.04	30

retention index increments is greater, *viz.*, $\Delta I_{\text{phenol}}/\Delta I_{\text{phenyl acetate}}$ is 0.38–1.37 and $\Delta I_{\text{phenol}}/\Delta I_{\text{phenyl acetate}}$ is from −103 to 123 i.u. (Table IX).

On a polar column the retention is reducing with derivatization, *i.e.*, $I_{\text{phenol}}/I_{\text{phenyl acetate}}$ lies in the range 1.02–1.37 and $I_{\text{phenol}} - I_{\text{phenyl acetate}}$ between 37 and 813 i.u., the 2- and 3,4,5-isomers showing the limit values (Fig. 3). Owing to the retention time of phenol being 367 i.u. higher than that of phenyl acetate, the retention increments observed for chlorophenols are more frequently lower, the ratio and the difference being in the ranges from −0.68 to 2.04 and from −330 to 446 i.u., respectively (Table IX).

As a consequence of the smaller size of the ring-substituent, the retention indices of chlorinated anisoles are lower on both columns than those of chlorinated phenyl acetates, except for the 2,3,4,5-isomer on a polar column[7]. Chloroanisoles always show higher retention index increments than chlorinated phenyl acetates, as

TABLE VI

INCREMENTAL EFFECT OF AN ADDITIONAL CHLORINE ATOM INTRODUCED INTO THE PHENOL ISOMERS, DETERMINED ON SE-30 AND FFAP AT 160°C

Lower isomer with nCl, n = 0–4	*Higher isomer with (n + 1) Cl, n = 0–4*								
	2-Cl *2,3-Di-Cl* *2,3,4-Tri-Cl* *2,3,4,5-Tetra-Cl* *Penta-Cl*			*3-Cl* *2,4-Di-Cl* *2,3,5-Tri-Cl* *2,3,4,6-Tetra-Cl*			*4-Cl* *2,5-Di-Cl* *2,3,6-Tri-Cl* *2,3,5,6-Tetra-Cl*		
	SE-30	*FFAP*		*SE-30*	*FFAP*		*SE-30*	*FFAP*	
	$\Sigma\Delta I$*	$\Sigma\Delta I$*	ΔI**	$\Sigma\Delta I$*	$\Sigma\Delta I$*	ΔI**	$\Sigma\Delta I$*	$\Sigma\Delta I$*	ΔI**
Phenol	62	−134	−196	228	371	143	228	371	143
2-Cl	189	294	105	179	285	106	179	294	115
3-Cl	23	−211	−234	–	–	–	13	−211	−224
4-Cl	–	–	–	13	−220	−233	–	–	–
2,3-Di-Cl	183	293	110	147	243	96	174	208	34
2,4-Di-Cl	193	302	109	–	–	–	–	–	–
2,5-Di-Cl	–	–	–	157	243	86	184	208	24
2,6-Di-Cl	–	–	–	–	–	–	154	271	117
3,4-Di-Cl	−15	−278	−263	–	–	–	–	–	–
3,5-Di-Cl	–	–	–	−48	−272	−224	–	–	–
2,3,4-Tri-Cl	173	277	104	175	101	−74	–	–	–
2,3,5-Tri-Cl	209	327	118	–	–	–	203	150	−53
2,3,6-Tri-Cl	–	–	–	184	186	2	176	185	9
2,4,5-Tri-Cl	180	277	97	182	101	−81	–	–	–
2,4,6-Tri-Cl	–	–	–	192	253	61	–	–	–
3,4,5-Tri-Cl	−51	−298	−247	–	–	–	–	–	–
2,3,4,5-Tetra-Cl	184	91	−93						
2,3,4,6-Tetra-Cl	182	267	85						
2,3,5,6-Tetra-Cl	190	268	78						

* Total retention index increase due to an additional chlorine atom, *viz.*, $\Sigma\Delta I = \Delta I_{(n+1)Cl} - \Delta I_{nCl}$.

** $\Delta I = \Sigma\Delta I_{FFAP} - \Sigma\Delta I_{SE\text{-}30}$.

2,6-Di-Cl *2,4,5-Tri-Cl*			*3,4-Di-Cl* *2,4,6-Tri-Cl*			*3,5-Di-Cl* *3,4,5-Tri-Cl*		
SE-30	*FFAP*		*SE-30*	*FFAP*		*SE-30*	*FFAP*	
$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}
209	231	22	–	–	–	–	–	–
–	–	–	221	360	139	218	304	86
–	–	–	221	360	139	–	–	–
–	–	–	–	–	–	–	–	–
186	302	116	176	150	−26	–	–	–
186	293	107	–	–	–	–	–	–
–	–	–	146	204	58	–	–	–
−22	−278	−256	–	–	–	209	297	88
–	–	–	–	–	–	212	353	141

TABLE VII

RETENTION SEQUENCE OF CHLORINATED PHENOLS, PHENYL ACETATES AND ANISOLES ON LOW-POLAR AND POLAR CAPILLARY COLUMNS AT 160°C

Retention	*Column*					
	Low-polar (SE-30)			*Polar (FFAP or OV-351)*		
	*Phenol**	*Phenyl acetate***	*Anisole****	*Phenol**	*Phenyl acetate***	*Anisole****
	Parent	Parent	Parent	2	Parent	Parent
	2	2	3	Parent	2	3
	4 }	3	4	26	3	4
	3 }	4	2	24	4	2
	24 }	26	26	25 }	35	26
	25 }	24 }	35	23 }	26	35
	23	25 }	25	246	24 }	246
	26	35	24	236	25 }	25
	235	23	34	3 }	246	34
	246	34	23	4 }	23	24
	236	246	246	235	34	236
	245	236	236	245 }	235	23
	234	235	245	234 }	245	2346 }
	35	245	235	2356	236	2356 }
	34	234	345	2346	345	245 }
	2356	345	234	35	2356	345 }
	2345	2356	2356	2345	234	235
	2346	2346	2346	34	2346	234
	345	2345	2345	Penta	2345	Penta
Increasing§	Penta	Penta	Penta	345	Penta	2345

* Present work.
** From ref. 6.
*** From ref. 7.
§ } = Overlapping.

is evident from lower $\Delta I_{\text{phenol}}/\Delta I_{\text{anisole}}$ and $\Delta I_{\text{phenol}} - \Delta I_{\text{anisole}}$ values given in Tables VIII and IX. A retention enhancement on SE-30 arising from the derivatization is not as pronounced with anisoles as with phenyl acetates; the parent-, 3-, 4-, 2,6-, 3,4-, 3,5-, 2,4,6-, 3,4,5-, 2,3,4,6-, 2,3,5,6- and penta-isomers all show reduced retentions relative to the corresponding phenols (Table VIII and Fig. 3). The greatest enhancement of 129 i.u. is observed for the 2,3-isomer, whereas the 3,4,5-isomer showed the greatest reduction of 133 i.u. On a polar column, the enhanced retention is in the range 176–948 i.u., the 2- and 3,4,5-isomers showing the limit values, respectively.

As a summary of the retention behaviour of the three series studied, it is evident that with both non-polar and polar columns the incremental effect of a single chlorine atom is greatest, *viz.*, with 4-chlorophenyl acetate[6], 195 (SE-30) and 237 (OV-351) i.u.; 2-chloroanisole[7], 219 (SE-30) and 317 (OV-351) i.u.; and 3- and 4-chlorophenol, 228 (SE-30) and 371 (FFAP) i.u. (Table V). The lowest retention increments are shown by 2,4,6-trichlorophenyl acetate[6], 137 (SE-30) and 134 (OV-351) i.u.; 2,4,6-trichloroanisole[7], 151 (SE-30) and 155 (OV-351) i.u.; and 2-chlorophenol, 62 (SE-30) and −134 (FFAP) i.u. (Table V).

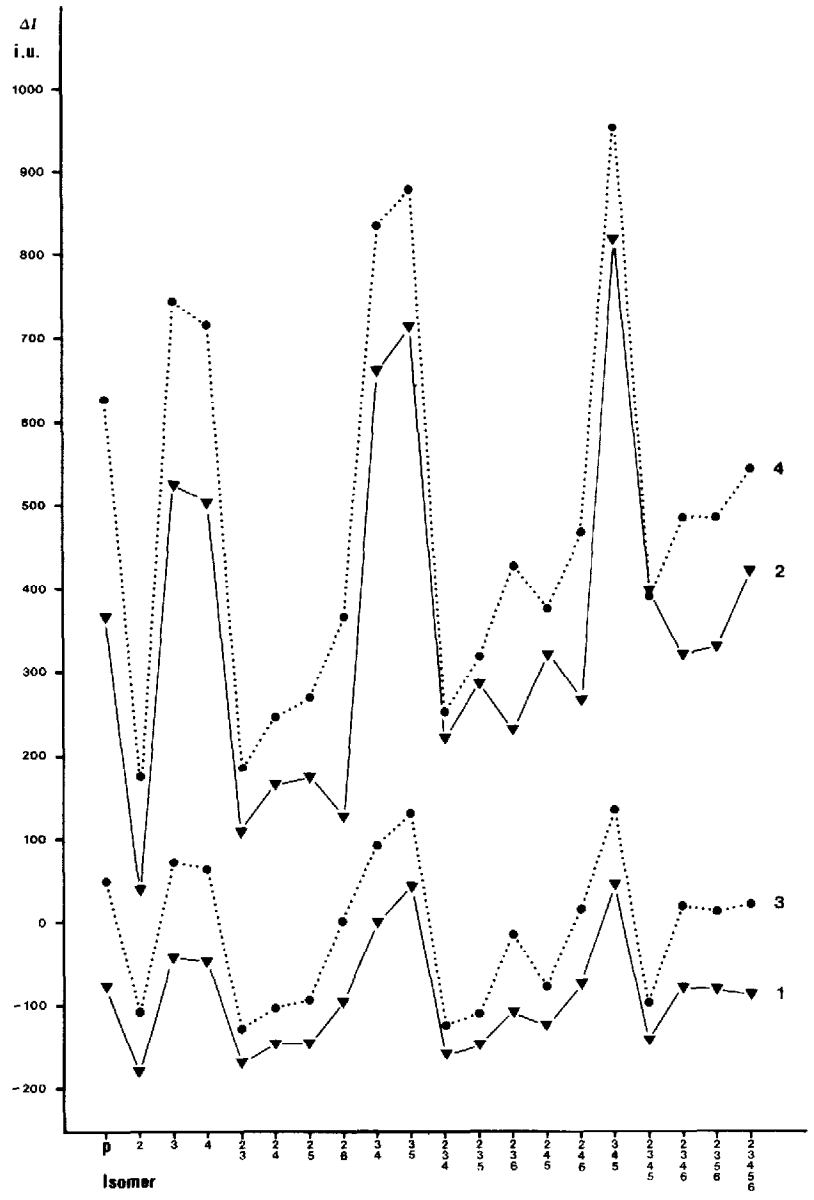

Fig. 3. Differences of retention indices of chlorinated phenols (Ph), and phenyl acetates (PhAc) and anisoles (A), determined at 160°C (Table VIII). $I_{Ph(SE-30)} - I_{PhAc(SE-30)}$, curve 1; $I_{Ph(FFAP)} - I_{PhAc(OV-351)}$, curve 2; $I_{Ph(SE-30)} - I_{A(SE-30)}$, curve 3; $I_{Ph(FFAP)} - I_{A(OV-351)}$, curve 4; i.u. = retention index units; p = parent component; the numbers indicate the positions of chlorination.

TABLE VIII

RATIO AND DIFFERENCE OF RETENTION INDICES AND INCREMENTAL EFFECTS OF CHLORINATED PHENOLS AND THEIR DERIVATIVES, *viz.*, PHENYL ACETATES AND ANISOLES, DETERMINED ON LOW-POLAR AND POLAR STATIONARY PHASES AT 160°C

Isomer	*Column*					
	Low-polar (SE-30)					
	Ph/PhAc***		*Ph*/A****		*Ph* − PhAc***	
	I	*ΔI*	*I*	*ΔI*	*I*	*ΔI*
Parent	0.92		1.06		−79	
2-Cl	0.84	0.38	0.90	0.28	−182	−103
3-Cl	0.97	1.20	1.07	1.11	−41	38
4-Cl	0.96	1.17	1.06	1.07	−46	33
2,3-Di-Cl	0.87	0.73	0.90	0.59	−170	−91
2,4-Di-Cl	0.89	0.78	0.92	0.61	−147	−68
2,5-Di-Cl	0.89	0.78	0.93	0.63	−147	−68
2,6-Di-Cl	0.93	0.94	1.00	0.85	−96	−17
3,4-Di-Cl	1.00	1.22	1.07	1.11	1	80
3,5-Di-Cl	1.03	1.37	1.11	1.23	41	120
2,3,4-Tri-Cl	0.89	0.84	0.92	0.71	−162	−83
2,3,5-Tri-Cl	0.90	0.85	0.92	0.71	−149	−70
2,3,6-Tri-Cl	0.93	0.93	0.99	0.87	−109	−30
2,4,5-Tri-Cl	0.92	0.90	0.95	0.77	−125	−46
2,4,6-Tri-Cl	0.95	1.01	1.01	0.92	−74	5
3,4,5-Tri-Cl	1.03	1.23	1.09	1.15	44	123
2,3,4,5-Tetra-Cl	0.91	0.90	0.94	0.81	−143	−64
2,3,4,6-Tetra-Cl	0.95	1.00	1.01	0.95	−79	0
2,3,5,6-Tetra-Cl	0.95	1.00	1.01	0.94	−82	−3
Penta-Cl	0.95	0.99	1.01	0.97	−88	−9

* For retention indices (*I*) and increments (*ΔI*) of chlorinated phenols (Ph), see Tables II, III and V.
** For retention indices (*I*) and increments (*ΔI*) of chlorinated phenyl acetates (PhAc), see ref. 6.
*** For retention indices (*I*) and increments (*ΔI*) of chlorinated anisoles (A), see ref. 7.

Polar (OV-351 or FFAP)									
Ph − A****		*Ph*/PhAc***		*Ph*/A****		*Ph* − PhAc***		*Ph* − A****	
I	*ΔI*	*I*	*ΔI*	*I*	*ΔI*	*I*	*ΔI*	*I*	*ΔI*
49		1.22		1.46		367		627	
−108	−157	1.02	−0.68	1.10	−0.42	37	−330	176	−451
72	23	1.28	1.73	1.46	1.45	523	156	743	116
63	14	1.27	1.57	1.43	1.31	501	134	715	88
−129	−178	1.05	0.38	1.09	0.26	108	−259	183	−444
−102	−151	1.08	0.43	1.13	0.28	165	−202	246	−381
−94	−143	1.09	0.45	1.14	0.31	174	−193	268	−359
2	−47	1.06	0.29	1.21	0.27	126	−241	365	−262
93	44	1.32	1.67	1.44	1.39	659	292	832	205
132	83	1.36	2.04	1.49	1.58	711	344	875	248
−125	−174	1.10	0.76	1.11	0.55	220	−147	249	−378
−110	−159	1.14	0.83	1.15	0.57	286	−81	318	−309
−17	−66	1.11	0.73	1.22	0.65	229	−138	425	−202
−77	−126	1.15	0.91	1.18	0.64	320	−47	373	−254
13	−36	1.13	0.75	1.25	0.65	266	−101	464	−163
133	84	1.37	1.77	1.46	1.45	813	446	948	321
−97	−146	1.17	1.04	1.17	0.75	397	30	390	−237
18	−31	1.14	0.92	1.23	0.79	318	−49	483	−144
12	−37	1.15	0.93	1.23	0.79	328	−39	482	−145
21	−28	1.17	1.07	1.24	0.91	420	53	542	−85

TABLE IX

SUMMARY OF VALUES PRESENTED IN TABLE VIII

Ratio or difference	*Column*			
	Low-polar (SE-30)		*Polar (OV-351 or FFAP)*	
	I	*ΔI*	*I*	*ΔI*
Ph*/PhAc**	0.84–1.03	0.38–1.37	1.02–1.37	−0.68 to 2.04
Ph*/A***	0.90–1.11	0.28–1.23	1.09–1.49	−0.42 to 1.58
Ph* − PhAc**	−182 to 44	−103 to 123	37–813	−330 to 446
Ph* − A***	−129 to 133	−178 to 84	176–948	−451 to 321

*,**,*** As in Table VIII.

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