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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXVIII*. CAPILLARY COLUMN STUDIES OF CHLORINATED ANISOLES

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SUMMARY

All nineteen ring-substituted chloroanisoles were separated on non-polar (SE-30) and polar (OV-351) capillary columns under various temperature-programmed and isothermal conditions. The relative retention data for the isomers were examined, together with the retention indices and the increments of retention indices for each position of chlorine substitution. The retention order of the compounds is discussed and the results are compared with those reported earlier for chloroanisoles and chlorinated phenyl acetates.

INTRODUCTION

Chlorinated anisoles have been subject of many recent investigations and their determination in various environmental samples has been reported, *e.g.*, in mushroom-house air[1], chlorophenol metabolites[2–5], wine with cork taint[6,7], musty taint in broiler chickens[8–10], soil and fish[11,12], oysters[13], chicken tissues[14], soy oil[15] and industrial and municipal wastewater effluents[12,16]. Although the use of both packed and capillary columns with polar and non-polar stationary phases has been reported, only a few chloroanisole isomers, *viz.*, the polychloro isomers, have been analysed. There are few papers dealing with the systematic gas chromatographic (GC) study of all ring-substituted chloroanisoles[17], and retention and relative retention data for all isomers and retention indices of the components have not been reported.

As a continuation of our research programme on the GC retention behaviour of the compounds formed, *e.g.*, in pulp bleaching or by biomethylation of chlorophenolic compounds[18,19], this paper gives the results for all nineteen ring-substituted chloroanisoles. The isomers were separated on non-polar (SE-30) and polar (OV-351) capillary columns under various temperature-programmed and isothermal operating conditions. The relative retention data for the components are given, with the retention indices and the increments of the retention indices for each position of

* For Part XXVII, see ref. 19.

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chlorine substitution. The elution order of the isomers is compared with that reported earlier for chloroanisoles and chlorinated phenyl acetates.

EXPERIMENTAL

Samples

Anisole was a commercial product (Fluka, Buchs, Switzerland). Chlorinated anisoles were obtained from the corresponding chlorophenols (Fluka) by methylation with dimethyl sulphate[20]. The purity of the isomers was checked by GC and their structures were verified by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS). The retention sequence of the compounds was checked by GC–MS using non-polar and polar capillary columns with suitable operating conditions. The components that overlapped were chromatographed separately.

TABLE I

PHYSICAL PROPERTIES AND RETENTION DATA FOR ANISOLE AND ITS CHLORINATED DERIVATIVES, OBTAINED ON SE-30 AND OV-351 WITH TEMPERATURE PROGRAMMING FROM 100°C AT 6°C min^{-1}

Conditions as in Figs. 1 and 3.

Isomer	*B.p.** (°C/mmHg)	*M.p.** (°C)	*Column*				
			SE-30		*OV-351*		
			*ART***	*RRT****	*ART***	*RRT****	*RRT§*
Anisole	155	–	4.58	1.00	4.85	1.00	1.06
2-Cl	196	–	7.39	1.61	8.82	1.82	1.19
3-Cl	194	–	7.09	1.55	7.83	1.61	1.10
4-Cl	198	−18	7.24	1.58	8.19	1.69	1.13
2,3-Di-Cl	–	31	11.29	2.47	13.33	2.75	1.18
2,4-Di-Cl	229	29	10.58	2.31	12.08	2.49	1.14
2,5-Di-Cl	226/752	24	10.39	2.27	11.89	2.45	1.14
2,6-Di-Cl	105/20	10	9.02	1.97	9.29	1.92	1.03
3,4-Di-Cl	202	−8	10.73	2.34	11.98	2.47	1.12
3,5-Di-Cl	–	40	9.94	2.17	10.29	2.12	1.04
2,3,4-Tri-Cl	–	70	15.15	3.31	17.38	3.58	1.15
2,3,5-Tri-Cl	–	82	14.12	3.08	15.20	3.13	1.08
2,3,6-Tri-Cl	228/756	45	12.58	2.75	12.71	2.62	1.01
2,4,5-Tri-Cl	254/742	78	14.03	3.06	15.10	3.11	1.08
2,4,6-Tri-Cl	236/758	65	11.73	2.56	10.85	2.24	0.92
3,4,5-Tri-Cl	258	63	14.42	3.15	15.10	3.11	1.05
2,3,4,5-Tetra-Cl	–	83	18.36	4.01	19.82	4.09	1.08
2,3,4,6-Tetra-Cl	–	64	15.88	3.47	14.96	3.08	0.94
2,3,5,6-Tetra-Cl	–	89	15.81	3.45	14.96	3.08	0.95
Penta-Cl	–	108	19.90	4.34	18.84	3.88	0.95

* From refs. 22–26.

** Absolute retention times (min) were measured from sample injection (Figs. 1 and 3).

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

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

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 following operating conditions: injection and flame-ionization detection (FID) temperatures, 275°C; carrier gas (nitrogen) flow-rate, 1 ml min^{-1}; splitting ratio, 1:30; and chart speed, 10 mm min^{-1}. The columns used were (i) a vitreous-silica wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), coated with non-polar SE-30 stationary phase and supplied by SGE (North Melbourne, Australia), and (ii) a fused-silica WCOT column (25 m × 0.32 mm I.D.), coated with polar OV-351 stationary phase and supplied by Orion Analytica (Espoo, Finland). The column temperature was programmed from 100°C at 2, 4, 6, 8 and 10°C min^{-1} until the elution of peaks had ceased, the isothermal data being recorded at 140, 160 and 180°C.

The retention times were measured from the time of sample injection, the dead volume being determined by injection of methane. The Kováts retention indices were calculated off-line as described earlier[21].

TABLE II

RETENTION INDICES (*I*) FOR ANISOLE AND ITS CHLORINATED DERIVATIVES, DETERMINED ON SE-30 AT VARIOUS COLUMN TEMPERATURES

Isomer	*Column temperature*					
	Isothermal at			*Programmed from 100°C at*		
	140°C	*160°C*	*180°C*	*2°C min^{-1}*	*6°C min^{-1}*	*10°C min^{-1}*
Anisole	887	880	900	907	906	908
2-Cl	1097	1099	1108	1093	1099	1102
3-Cl	1080	1085	1092	1072	1081	1084
4-Cl	1090	1094	1108	1082	1090	1093
2,3-Di-Cl	1298	1309	1322	1287	1299	1306
2,4-Di-Cl	1265	1272	1282	1253	1263	1269
2,5-Di-Cl	1256	1264	1273	1244	1254	1260
2,6-Di-Cl	1190	1198	1215	1174	1185	1192
3,4-Di-Cl	1275	1285	1298	1259	1271	1281
3,5-Di-Cl	1236	1243	1254	1222	1232	1238
2,3,4-Tri-Cl	1476	1488	1501	1469	1484	1494
2,3,5-Tri-Cl	1428	1437	1452	1418	1433	1440
2,3,6-Tri-Cl	1358	1371	1388	1344	1359	1370
2,4,5-Tri-Cl	1423	1433	1447	1415	1429	1436
2,4,6-Tri-Cl	1319	1333	1350	1305	1319	1327
3,4,5-Tri-Cl	1441	1454	1470	1431	1448	1457
2,3,4,5-Tetra-Cl	1618	1633	1649	1620	1644	1660
2,3,4,6-Tetra-Cl	1506	1520	1538	1500	1520	1530
2,3,5,6-Tetra-Cl	1504	1518	1536	1497	1516	1529
Penta-Cl	1681	1699	1721	1690	1724	1741

TABLE III

RETENTION INDICES (I) FOR ANISOLE AND ITS CHLORINATED DERIVATIVES, DETERMINED ON OV-351 AT VARIOUS COLUMN TEMPERATURES

Isomer	*Column temperature*						$\frac{I_{OV\text{-}351}}{I_{SE\text{-}30}}$*	$I_{OV\text{-}351} - I_{SE\text{-}30}$*
	Isothermal at			*Programmed from 100°C at*				
	140°C	*160°C*	*180°C*	*2°C min⁻¹*	*6°C min⁻¹*	*10°C min⁻¹*		
Anisole	1375	1373	1331	1342	1344	1349	1.56	493
2-Cl	1689	1690	1684	1650	1657	1674	1.54	591
3-Cl	1623	1628	1618	1582	1588	1604	1.50	543
4-Cl	1648	1656	1645	1607	1613	1630	1.51	562
2,3-Di-Cl	1957	1977	1985	1933	1945	1951	1.51	668
2,4-Di-Cl	1885	1905	1902	1857	1868	1869	1.50	633
2,5-Di-Cl	1874	1892	1886	1845	1857	1857	1.50	628
2,6-Di-Cl	1720	1732	1733	1676	1690	1706	1.45	534
3,4-Di-Cl	1878	1899	1900	1846	1862	1864	1.48	614
3,5-Di-Cl	1780	1800	1798	1744	1757	1770	1.45	557
2,3,4-Tri-Cl	2182	2204	2225	2176	2202	2212	1.48	716
2,3,5-Tri-Cl	2067	2085	2098	2047	2060	2065	1.45	648
2,3,6-Tri-Cl	1918	1943	1952	1887	1906	1909	1.42	572
2,4,5-Tri-Cl	2061	2080	2097	2042	2054	2062	1.45	647
2,4,6-Tri-Cl	1813	1837	1842	1775	1794	1805	1.38	504
3,4,5-Tri-Cl	2061	2080	2097	2042	2054	2062	1.43	626
2,3,4,5-Tetra-Cl	2319	2340	2367	2336	2362	2369	1.43	707
2,3,4,6-Tetra-Cl	2044	2071	2094	2020	2046	2055	1.36	551
2,3,5,6-Tetra-Cl	2044	2071	2094	2021	2046	2055	1.36	553
Penta-Cl	2245	2279	2313	2257	2298	2315	1.34	580

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

RESULTS AND DISCUSSION

The absolute and relative retention data obtained on non-polar and polar capillary columns with temperature programming, together with the boiling points of the anisole isomers, are given in Table I. The retention indices for the compounds are presented in Tables II and III, and the incremental effects of chlorine substitution are shown in Tables IV and V. Table VI illustrates the incremental effect of an additional chlorine atom introduced into the anisole isomers.

The chromatogram obtained on SE-30 with temperature programming (Fig. 1) shows only one overlap for a mixture of 20 components, *i.e.*, the peaks of the 2,3,5,6- and 2,3,4,6-tetrachloro isomers. Fig. 2 shows that the isomers were partially separated at 140 and 160°C and with a slow temperature programming rate or a low enough initial temperature. The retention order of the individual isomers is the same as reported previously on glass capillary columns coated with non-polar OV-101, SE-54, OV-17 and $C_{87}H_{176}$ stationary phases[17]. The last phase separated all 19 chloroanisoles; also, the tetrachloro isomer pair overlapped on the other columns, but the lower chlorinated isomers were resolved on this hydrocarbon liquid phase with some difficulty[17].

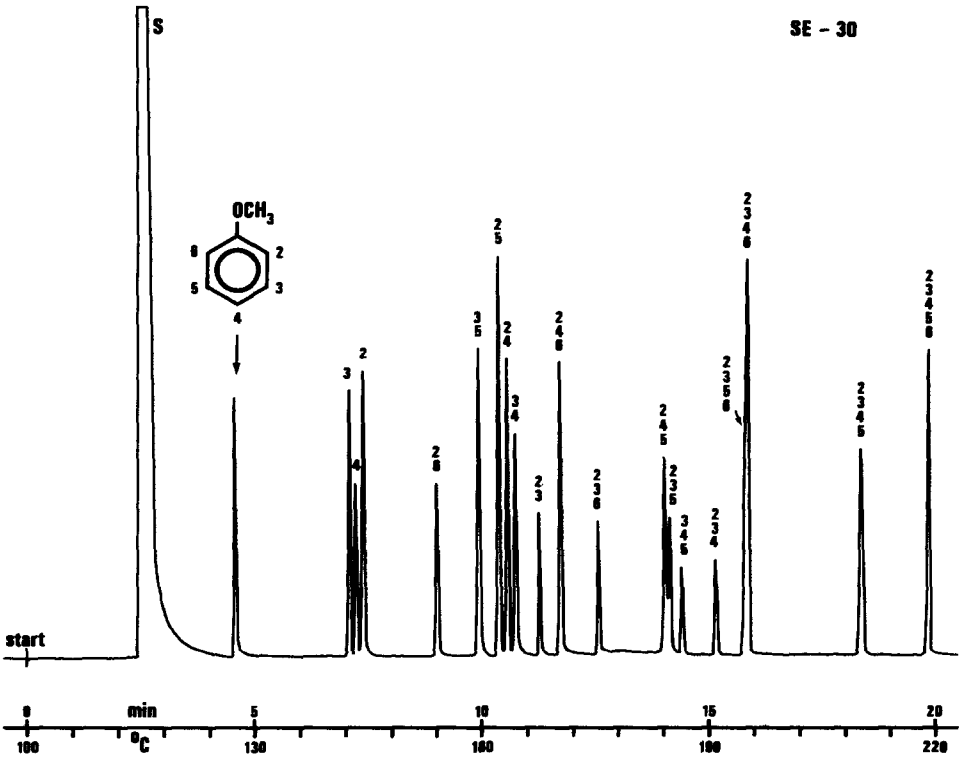


Fig. 1. Chromatogram of a mixture of anisole and its chlorinated derivatives, obtained on SE-30 with temperature programming from 100°C at 6°C min^{-1} until the elution of peaks had ceased. S = Solvent; the peak numbers indicate the positions of chlorination.

TABLE IV

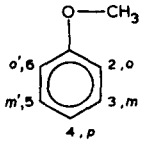
INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION ON SE-30

Anisole isomer	*Column temperature*					
	Isothermal at					
	140°C		*160°C*		*180°C*	
	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**
2-Cl	210	210	219	219	208	208
3-Cl	193	193	205	205	192	192
4-Cl	203	203	214	214	208	208
2,3-Di-Cl	411	206	429	215	422	211
2,4-Di-Cl	378	189	392	196	382	191
2,5-Di-Cl	369	185	384	192	373	187
2,6-Di-Cl	303	152	318	159	315	158
3,4-Di-Cl	388	194	405	203	398	199
3,5-Di-Cl	349	175	363	182	354	177
2,3,4-Tri-Cl	589	196	608	203	601	200
2,3,5-Tri-Cl	541	180	557	186	552	184
2,3,6-Tri-Cl	471	157	491	164	488	163
2,4,5-Tri-Cl	536	179	553	184	547	182
2,4,6-Tri-Cl	432	144	453	151	450	150
3,4,5-Tri-Cl	554	185	574	191	570	190
2,3,4,5-Tetra-Cl	731	183	753	188	749	187
2,3,4,6-Tetra-Cl	619	155	640	160	638	160
2,3,5,6-Tetra-Cl	617	154	638	160	636	159
Penta-Cl	794	159	819	164	821	164

* Total retention index increase.

** Retention index increase per chlorine atom.

The structure of the anisole isomers is shown below, the numbers or symbols used indicating the chlorinated positions with respect to the methoxy group, with *ortho* as *o* and *o'*, *meta* as *m* and *m'* and *para* as *p*.



The data obtained on SE-30 (Tables I, II, IV and VI) show that the isomers are eluted in the order of the degree of chlorination, and that with all components the retention, relative to *n*-alkanes, generally increases with increasing column temperature, the retention sequence remaining unchanged.

The monochloro isomers are eluted in the order 3- (*m*-), 4- (*p*-) and 2- (*o*-) isomer, the retention sequence not following the order of the boiling points of the

Programmed from 100°C at					
2°C min^{-1}		*6°C min*$^{-1}$		*10°C min*$^{-1}$	
$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**
186	186	193	193	194	194
165	165	175	175	176	176
175	175	184	184	185	185
380	190	393	197	398	199
346	173	357	179	361	181
337	169	348	174	352	176
267	134	279	140	284	142
352	176	365	183	373	187
315	158	326	163	330	165
562	187	578	193	586	195
511	170	527	176	532	177
437	146	453	151	462	154
508	169	523	174	528	176
398	133	413	138	419	140
524	175	542	181	549	183
713	178	738	185	752	188
593	148	614	154	622	156
590	148	610	153	621	155
783	157	818	164	833	167

isomers (194, 198 and 196°C, respectively). This is due to the adjacent *o*-chloro substituent, which obviously gives rise to steric inhibition of resonance and hinders the free rotation of the methoxy group[18,19], leading to enhanced retention of the *o*-isomer also on a non-polar stationary phase. As reported previously, 2-chlorophenol[27,28] and the corresponding acetate ester[29–31] are eluted earlier than the other monochloro isomers on SE-30.

With the dichloroanisoles the lowest retention is shown by the 2,6- (*o,o'*-) isomer followed by the other symmetrical isomer, *i.e.*, the 3,5- (*m,m'*-) isomer. Enhanced retention occurred with the 2,5- (*o,m'*-) and 2,4- (*o,p*-) isomers, where the chlorine substituents are at isolated positions with respect to each other. Owing to some reinforcement of the polar effects by the close proximity of the chlorine substituents, the vicinal 3,4- (*m,p*-) and 2,3- (*o,m*-) isomers are eluted last. As with the monochlorinated anisoles, the dichloro isomers are not eluted according to their boiling points, as also are the trichloro isomers (Table I).

The retention orders observed for the tri- and tetrachloro isomers follow com-

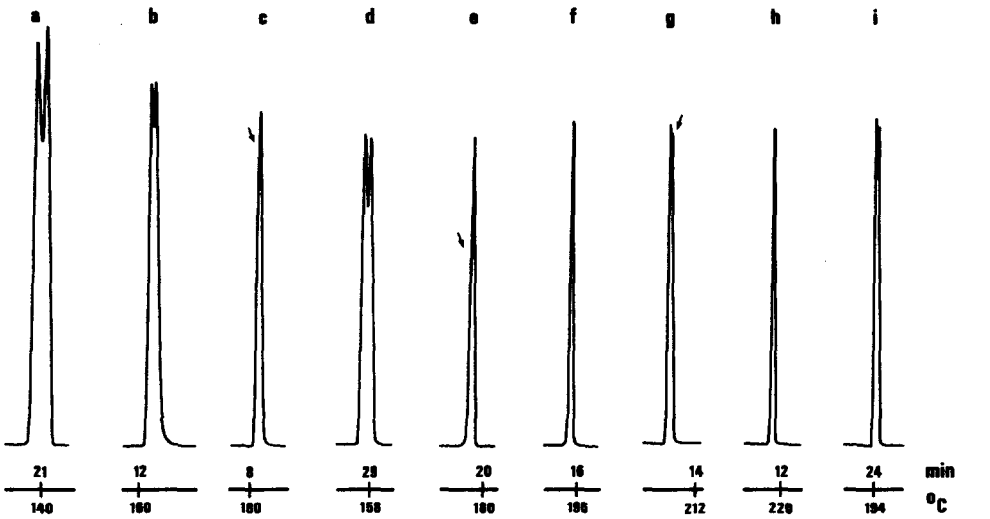


Fig. 2. Separation of the 2,3,5,6- and 2,3,4,6-tetrachloro isomers on SE-30. Operating conditions: isothermal at (a) 140, (b) 160 and (c) 180°C; programmed from 100°C at (d) 2, (e) 4, (f) 6, (g) 8 and (h) 10°C min^{-1}; programmed from 50°C at (i) 6°C min^{-1}. The 2,3,5,6-isomer is always eluted first.

pletely the behaviour of the lower isomers, the retention sequences being *o,o',p* < *o,o',m* < *o,p,m'* < *o,m,m'* < *m,m',p* < *o,m,p* and *o,o',m,m'* ⩽ *o,o',m,p* < *o,m,m',p*. The pentachloro isomer, as expected, is eluted last on the non-polar column.

A poorer resolution of the components occurred on the polar OV-351 column, the 2,3,4,6- and 2,3,5,6- and the 2,4,5- and 3,4,5- isomers overlapping in spite of the various operating conditions used. Several partially resolved peaks were also observed, as shown in Fig. 3.

The use of polar columns for analysing chlorinated anisoles has received little attention in the literature[14,17]. Gee *et al.*[14] separated the higher chlorinated isomers (tri- to pentachloro) on packed columns coated with Carbowax 20M and Apiezon L stationary phases. The elution sequence observed on Carbowax 20M is nearly the same as in this work, although on OV-351 two reversed elution orders between the isomers occurred, *viz.*, (i) the overlapping tetrachloro isomer pair eluted earlier than the 2,4,5- (*o,p,m'*-) isomer and (ii) the 3,4,5- (*m,m',p*-) isomer appeared earlier than the 2,3,5- (*o,m,m'*-) isomer. These disparities are due to the close proximity of the boiling points of the isomers and to the different columns with different operating conditions. It would have been of great interest to examine the retention sequence observed previously for sixteen chloroanisoles (di- to pentachloro) on Carbowax 20M capillary column by Farrell[17], but owing to the lack of retention data and to the poor chromatograms presented, this was impracticable. However, the tetrachloro isomer pair seems to have overlapped, as on OV-351.

The data obtained on the polar column given in Tables I, III, V and VI show the retention enhancement for the isomers. The elution sequence of the monochloro

isomers remains unchanged, but the isomers are eluted further away from each other than on SE-30 (*cf.*, Figs. 1 and 3). The reverse retention order occurred with the 3,4- (*m,p*-) and 2,4- (*o,p*-) and the 3,4,5- (*m,m',p*-) and 2,3,5- (*o,m,m'*-) isomers. Additional disparities between the columns found are due to the *o,o'*-substitution, *viz.*, (i) the 2,4,6- (*o,o',p*-) and 2,3,6- (*o,o',m*-) isomers eluted between the dichloro isomers, (ii) the 2,3,4,6- (*o,o',m,p*-) and 2,3,5,6- (*o,o',m,m'*-) isomers appeared earlier than most trichloro isomers and (iii) the penta- and 2,3,4,5- (*o,m,m',p*-) isomers eluted in the reverse order.

The relatively higher retention increase observed for the *o*-isomers on a polar column supports the assumption of the steric effect mentioned above[18,19]. The reduction or relatively small enhancement of the retention of the *o,o'*-isomers indicates that this phenomenon is prevented owing to the competing chlorine atoms. This gives rise to reverse elution orders on OV-351, as the polar and steric effects are maximized on the polar stationary phases.

The incremental effects of chlorine substitution on SE-30 and OV-351 are shown in Tables IV and V and in Figs. 4 and 5, respectively. Table VI shows the incremental effect of an additional chlorine atom, introduced into the anisole isomers, on both columns at 160°C.

The incremental disparities generally increase with increasing column temperature, even if the maximum effects are shown on SE-30 at 160°C (Table IV). The

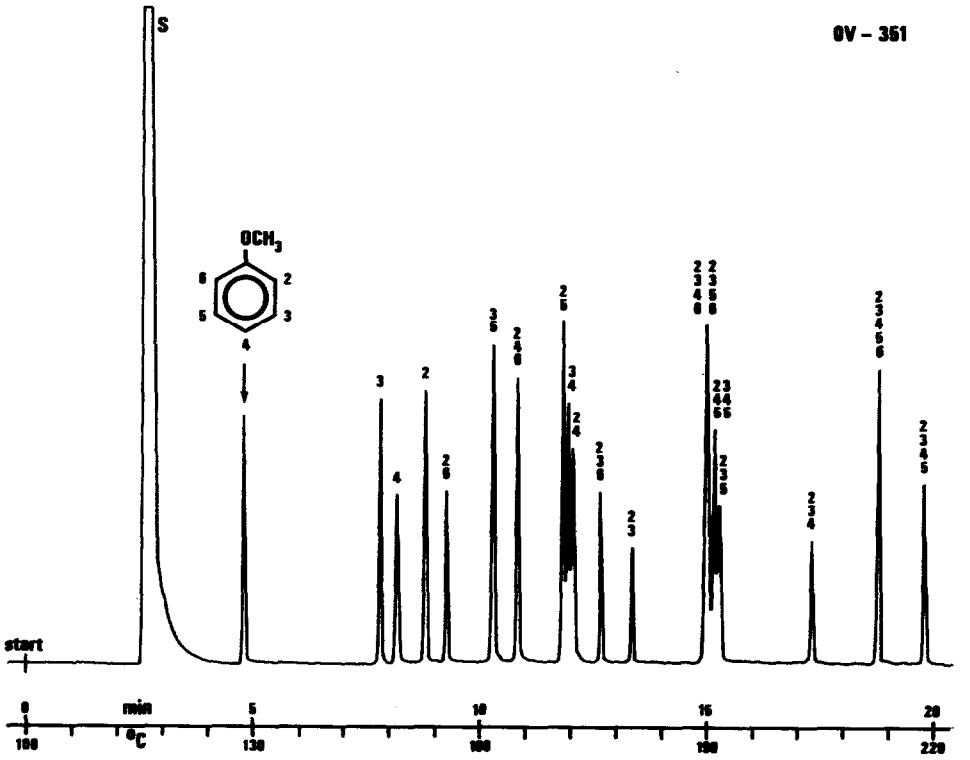


Fig. 3. Chromatogram of the same mixture as in Fig. 1, obtained on OV-351 using the same operating conditions.

TABLE V

INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION ON OV-351

Anisole isomer	*Column temperature*					
	Isothermal at					
	140°C		*160°C*		*180°C*	
	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**
2-Cl	314	314	317	317	353	353
3-Cl	248	248	255	255	287	287
4-Cl	273	273	283	283	314	314
2,3-Di-Cl	582	291	604	302	654	327
2,4-Di-Cl	510	255	532	266	571	286
2,5-Di-Cl	499	250	519	260	555	278
2,6-Di-Cl	345	173	359	180	402	201
3,4-Di-Cl	503	252	526	263	569	285
3,5-Di-Cl	405	203	427	214	467	234
2,3,4-Tri-Cl	807	269	831	277	894	298
2,3,5-Tri-Cl	692	231	712	237	767	256
2,3,6-Tri-Cl	543	181	570	190	621	207
2,4,5-Tri-Cl	686	229	707	236	766	255
2,4,6-Tri-Cl	438	146	464	155	511	170
3,4,5-Tri-Cl	686	229	707	236	766	255
2,3,4,5-Tetra-Cl	944	236	967	242	1036	259
2,3,4,6-Tetra-Cl	669	167	698	175	763	191
2,3,5,6-Tetra-Cl	669	167	698	175	763	191
Penta-Cl	870	174	906	181	982	196

* Total retention index increase.
** Retention index increase per chlorine atom.
*** Determined at 160°C; for values on SE-30, see Table IV.

variation is more pronounced on a polar column, particularly with increasing degree of chlorination (Table V).

The highest retention increments on both columns are shown by the 2- (*o*-) isomer, *viz.*, at 160°C on SE-30 219 retention index units (i.u.) and on OV-351 317 i.u., the ratio (1.45) given in Table V constituting the greatest disparity between the columns used. With further substitution, *e.g.*, the isomers with the highest retentions, *i.e.*, 2- (*o*-) → 2,3- (*o,m*-) → 2,3,4- (*o,m,p*-) → 2,3,4,5- (*o,m,m',p*-) → 2,3,4,5,6- (*o,o',m,m',p*-), on SE-30 show retention index increases per chlorine atom of 219 → 215 → 203 → 188 → 164 i.u., respectively (Table IV) and on OV-351 of 317 → 302 → 277 → 242 → 181 i.u., respectively (Table V). From the data in Table VI, where the effect of an additional chlorine atom is shown, the same series on SE-30 shows total retention index increases of 219 → 210 → 179 → 145 → 66 i.u. and on OV-351 of 317 → 287 → 227 → 136 → −61 i.u., respectively.

The lowest retention increment occurs with the 2,4,6- (*o,o',p*-) isomer, showing

Programmed from 100°C at						$\frac{\Delta I_{OV\text{-}351}^{***}}{\Delta I_{SE\text{-}30}}$	$\Delta I_{OV\text{-}351} - I_{SE\text{-}30}^{***}$
2°C min^{-1}		*6°C min*$^{-1}$		*10°C min*$^{-1}$			
$\Sigma\Delta I_{nCl}^{*}$	$\Sigma\Delta I_{1Cl}^{**}$	$\Sigma\Delta I_{nCl}^{*}$	ΔI_{1Cl}^{**}	$\Sigma\Delta I_{nCl}^{*}$	ΔI_{1Cl}^{**}		
308	308	313	313	325	325	1.45	98
240	240	244	244	255	255	1.24	50
265	265	269	269	281	281	1.32	69
591	296	601	301	602	301	1.41	175
515	258	524	262	520	260	1.36	140
503	252	513	257	508	254	1.35	135
334	167	346	173	357	179	1.13	41
504	252	518	259	515	258	1.30	121
402	201	413	207	421	211	1.18	64
834	278	858	286	863	288	1.37	223
705	235	716	239	716	239	1.28	155
545	182	562	187	560	187	1.16	79
700	233	710	237	713	238	1.28	154
433	144	450	150	456	152	1.02	11
700	233	710	237	713	238	1.23	133
994	249	1018	255	1020	255	1.28	214
678	170	702	176	706	177	1.09	58
698	170	702	176	706	177	1.09	60
915	183	954	191	966	193	1.11	87

increments for a chlorine atom of 151 and 155 i.u. at 160°C on SE-30 and OV-351, respectively. These increments give the minimum ratio (1.02) between the columns (Table V). The 2- (*o*-) → 2,6- (*o,o'*-) → 2,4,6- (*o,o',p*-) isomers show increases for a chlorine atom of 219 → 159 → 151 i.u. on SE-30 and 317 → 180 → 155 i.u. on OV-351. As is evident from Table VI, the same series on SE-30 and OV-351 gives total retention index increases of 219 → 99 → 135 and 317 → 42 → 105 i.u., respectively.

As would be expected, enhanced retention occurred on SE-30 on introducing an additional chlorine atom into the anisoles, *viz.*, the components are eluted in order of their degree of chlorination. The highest increase of 224 i.u. is observed with the 3- (*m*-) → 2,3- (*o,m*-) isomers, *i.e.*, 205 → 429 i.u., whereas the 2,3,4- (*o,m,p*-) → 2,3,4,6- (*o,o',m,p*-) isomers show an increase of only 32 i.u., *i.e.*, 608 → 640 i.u. (Table VI). On OV-351, however, six series show reduced retentions, the reduction being highest (−133 i.u.) with the 2,3,4- (*o,m,p*-) → 2,3,4,6- (*o,o',m,p*-) isomers, *i.e.*, 831 → 698 i.u. The greatest enhancement, of 255 → 604 i.u., occurred with the 3- (*m*-)

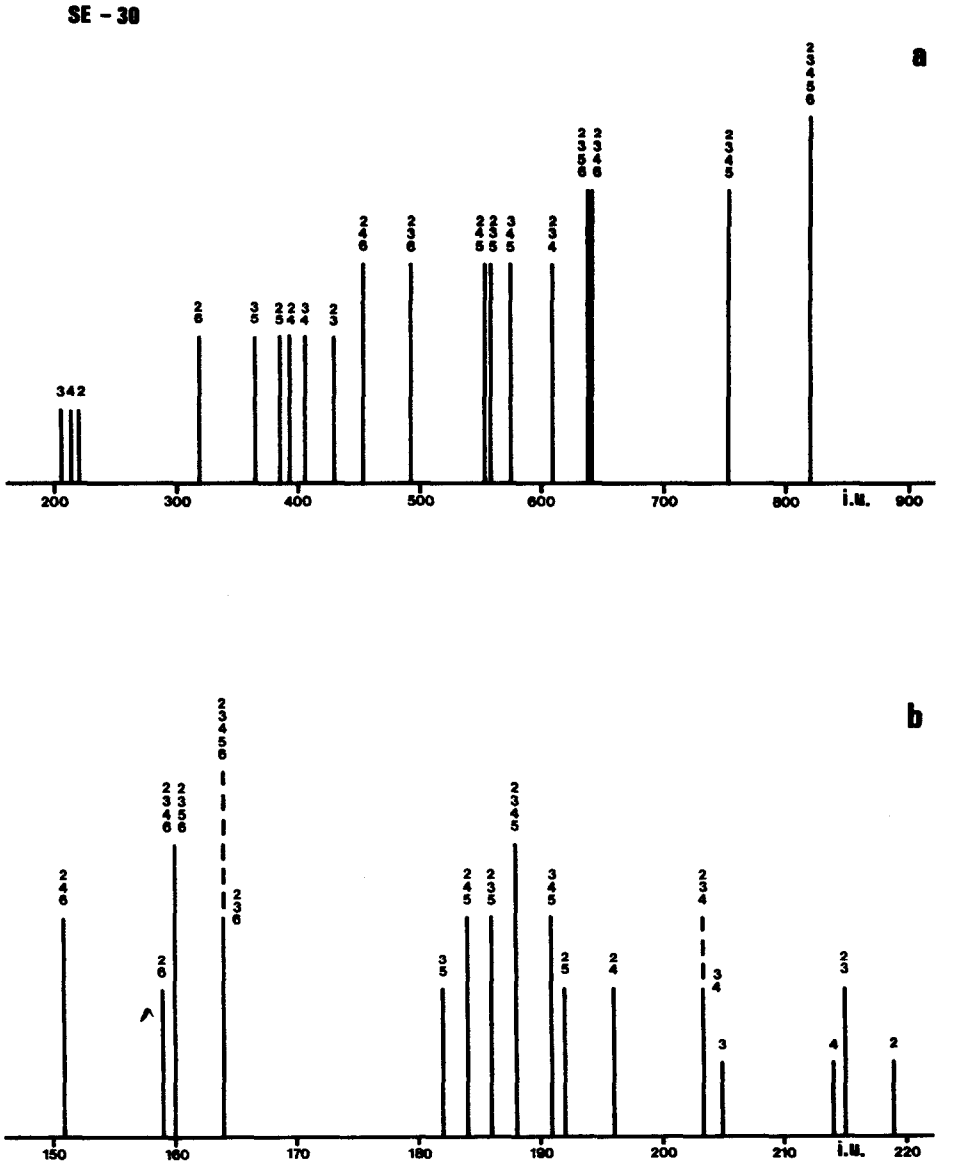


Fig. 4. Incremental effects of chlorine substitution, obtained on SE-30 at 160°C. (a) Total retention index increase; (b) retention index increase per chlorine atom. The numbers indicate the positions of chlorination.

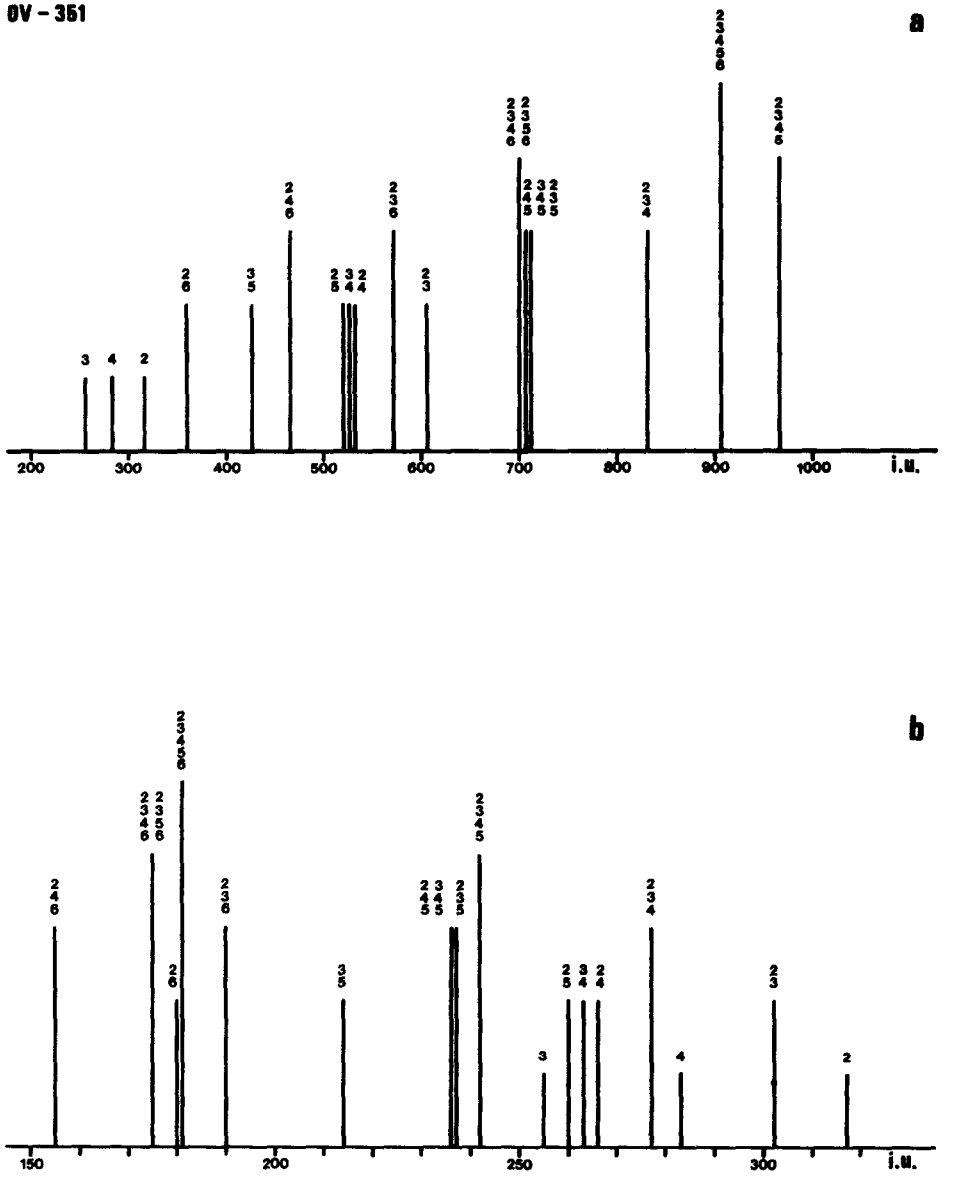


Fig. 5. Incremental effects of chlorine substitution as in Fig. 4, obtained on OV-351 at 160°C.

TABLE VI

INCREMENTAL EFFECT OF AN ADDITIONAL CHLORINE ATOM INTRODUCED INTO THE ANISOLE ISOMERS, DETERMINED ON SE-30 AND OV-351 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		*OV-351*		*SE-30*		*OV-351*		*SE-30*		*OV-351*	
	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}
Anisole	219	219	317	317	205	205	255	255	214	214	283	283
2-Cl	210	−4	287	−15	173	−23	215	−51	165	−27	202	−57
3-Cl	224	10	349	47	—	—	—	—	179	−13	264	5
4-Cl	—	—	—	—	178	−18	249	−17	—	—	—	—
2,3-Di-Cl	179	−12	227	−25	128	−29	108	−65	62	−51	−34	−112
2,4-Di-Cl	216	7	299	11	—	—	—	—	—	—	—	—
2,5-Di-Cl	—	—	—	—	173	−6	193	−23	107	−28	51	−70
2,6-Di-Cl	—	—	—	—	—	—	—	—	173	5	211	10
3,4-Di-Cl	203	0	305	14	—	—	—	—	—	—	—	—
3,5-Di-Cl	—	—	—	—	194	4	285	23	—	—	—	—
2,3,4-Tri-Cl	145	−15	136	−35	32	−43	−133	−102	—	—	—	—
2,3,5-Tri-Cl	196	2	255	5	—	—	—	—	81	−26	−14	−62
2,3,6-Tri-Cl	—	—	—	—	149	−4	128	−15	147	−4	128	−15
2,4,5-Tri-Cl	200	4	260	6	87	−24	−9	−61	—	—	—	—
2,4,6-Tri-Cl	—	—	—	—	187	9	234	20	—	—	—	—
3,4,5-Tri-Cl	179	−3	260	6	—	—	—	—	—	—	—	—
2,3,4,5-Tetra-Cl	66	−24	−61	−61								
2,3,4,6-Tetra-Cl	179	4	208	6								
2,3,5,6-Tetra-Cl	181	4	208	6								

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

→ 2,3- (*o,m*-) isomers, the increase of 349 i.u. observed being 125 i.u. higher than the corresponding increase on SE-30 (Table VI).

The retention index ratios on the two columns determined at 160°C are shown in Table V and Fig. 6a. As shown, the polar effects are maximal with the 2- (*o*-), 2,3- (*o,m*-), 2,3,4- (*o,m,p*-) and 2,3,4,5- (*o,m,m',p*-) isomers, *i.e.*, with the isomers having *o*-substitution with adjacent chlorine atoms.

Table VI and Fig. 6b show the subtraction of the non-polar contributions, obtained at 160°C. The enhanced retention of the various isomers is greatest with the 2,3,4- (*o,m,p*-) and 2,3,4,5- (*o,m,m',p*-) isomers, *viz.*, 223 and 214 i.u., respectively. The minimum value of 11 i.u. is observed for the 2,4,6- (*o,o',p*-) isomer, this isomer being one of the three that have lower retention times on OV-351 than on SE-30 (Table I).

The correlation between the retention indices of the chlorinated phenyl acetates and anisoles on both columns is shown in Table VII. Bearing in mind the retention

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		*OV-351*		*SE-30*		*OV-351*		*SE-30*		*OV-351*	
$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	ΔI^{**}
99	−60	42	−137	—	—	—	—	—	—	—	—
—	—	—	—	200	−2	271	8	158	−23	172	−41
—	—	—	—	191	−11	243	−20	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
161	−12	175	−30	61	−45	−68	−111	—	—	—	—
169	−8	188	−24	—	—	—	—	—	—	—	—
—	—	—	—	135	−8	105	−25	—	—	—	—
148	−19	181	−27	—	—	—	—	169	−12	181	−27
—	—	—	—	—	—	—	—	211	9	280	22

sequence obtained previously on SE-30 for the chlorinated phenyl acetates[29–31], the following disparities relative to chloroanisoles were found: (i) the monochloro isomers were eluted in the order 2- (*o*-), 3- (*m*-) and 4- (*p*-) isomer, (ii) the 2,4- (*o,p*-) and 2,5- (*o,m'*-) isomers appeared earlier than the 3,5- (*m,m'*-) isomer and some compound pairs eluted in the reverse order, *viz.*, (iii) the 2,3- (*o,m*-) and 3,4- (*m,p*-) isomers, (iv) the 2,3,5- (*o,m,m'*-) and 2,4,5- (*o,p,m'*-) isomers and (v) the 2,3,4- (*o,m,p*-) and 3,4,5- (*m,m',p*-) isomers. The retention order of the higher chlorinated phenyl acetates[29–31] and the corresponding anisoles remained unaltered on SE-30.

With the polar phase the order of elution of the isomers is greatly influenced by the compound structures. This can clearly be seen over ten reverse retention sequences occurring between the isomeric phenyl acetates and anisoles on OV-351 (Table VII).

With one exception, *i.e.*, the 2,3,4,5- (*o,m,m',p*-) isomers on OV-351, anisole is eluted earlier than the corresponding phenyl acetate. The disparities vary on SE-30 from 37 to 128 i.u. and on OV-351 from −7 to 260 i.u., the parent isomers giving the greatest differences (Table VII).

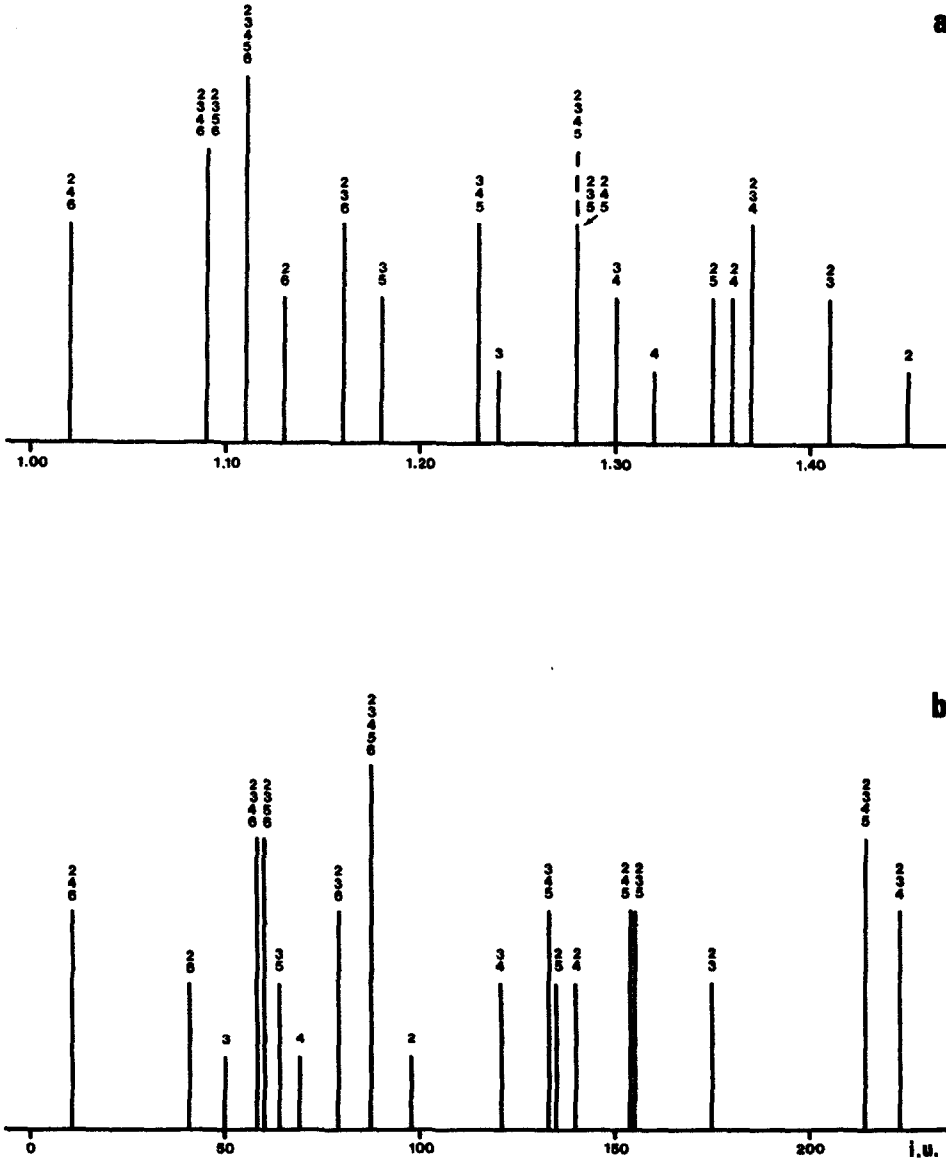


Fig. 6. (a) Ratio of the incremental effects on the columns used, *i.e.*, $\Delta I_{OV\text{-}351} / \Delta I_{SE\text{-}30}$, determined at 160°C (Table V). (b) Subtraction of the non-polar contributions of the incremental effects, *i.e.*, $\Delta I_{OV\text{-}351} - \Delta I_{SE\text{-}30}$, determined at 160°C (Table V).

TABLE VII

CORRELATION BETWEEN RETENTION INDICES (*I*) OF CHLORINATED PHENYL ACETATES AND CHLOROANISOLES ON SE-30 AND OV-351 AT 160°C

Isomer	*Column*							
	SE-30				*OV-351*			
	*Phenyl acetate (P)**	*Anisole (A)*	I_P/I_A	I_P-I_A	*Phenyl acetate (P)**	*Anisole (A)*	I_P/I_A	I_P-I_A
Parent	1008	880	1.15	128	1633	1373	1.19	260
2-Cl	1173	1099	1.07	74	1829	1690	1.08	139
3-Cl	1198	1085	1.10	113	1848	1628	1.14	220
4-Cl	1203	1094	1.10	109	1870	1656	1.13	214
2,3-Di-Cl	1350	1309	1.03	41	2052	1977	1.04	75
2,4-Di-Cl	1317	1272	1.04	45	1986	1905	1.04	81
2,5-Di-Cl	1317	1264	1.04	53	1986	1892	1.05	94
2,6-Di-Cl	1296	1198	1.08	98	1971	1732	1.14	239
3,4-Di-Cl	1377	1285	1.07	92	2072	1899	1.09	173
3,5-Di-Cl	1334	1243	1.07	91	1964	1800	1.09	164
2,3,4-Tri-Cl	1525	1488	1.02	37	2233	2204	1.01	29
2,3,5-Tri-Cl	1476	1437	1.03	39	2117	2085	1.02	32
2,3,6-Tri-Cl	1463	1371	1.07	92	2139	1943	1.10	196
2,4,5-Tri-Cl	1481	1433	1.03	48	2133	2080	1.03	53
2,4,6-Tri-Cl	1420	1333	1.07	87	2035	1837	1.11	198
3,4,5-Tri-Cl	1543	1454	1.06	89	2215	2080	1.06	135
2,3,4,5-Tetra-Cl	1679	1633	1.03	46	2333	2340	1.00	−7
2,3,4,6-Tetra-Cl	1617	1520	1.06	97	2236	2071	1.08	165
2,3,5,6-Tetra-Cl	1612	1518	1.06	94	2225	2071	1.07	154
Penta-Cl	1808	1699	1.06	109	2401	2279	1.05	122

* From ref. 31.

CONCLUSIONS

The results show that the use of a non-polar column is to be recommended for the analysis of chloroanisole isomers, a polar column being more suitable only for the monochloro isomers. The tetrachloro isomers that overlapped on both columns can be partially separated on SE-30 with optimal operating conditions but, as reported earlier[17], the separation of these isomers is complete on a suitable non-polar $C_{87}H_{176}$ liquid hydrocarbon stationary phase[32,33].

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