GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXX*. SEPARATION AND RETENTION INCREMENTS OF CHLORINATED SALICYLALDEHYDES (2-HYDROXYBENZALDEHYDES) ON LOW-POLARITY (SE-30) AND POLAR (OV-351) CAPILLARY COLUMNS

ILPO O. O. KORHONEN

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)

(Received March 30th, 1984)

SUMMARY

Low-polarity (SE-30) and polar (OV-351) capillary columns under isothermal or temperature-programmed conditions were used for the gas chromatographic separation of a mixture of salicylaldehyde and its chlorinated derivatives. All isomers are eluted as sharp peaks from SE-30, whereas on OV-351 tailing peaks were observed for the di- and polychloro isomers. The relative retention data for the compounds are given and the elution orders discussed. The retention indices and the retention index increments for each position of substitution are examined. The retention is maximized with the 3- and 3,4-, *i.e.*, *o*- and *o,m*-isomers with respect to the hydroxy group and minimized with the 4- and 4,6-isomers. The results are compared with those reported previously for other series of chlorinated aromatics, particularly with 4-hydroxybenzaldehydes.

INTRODUCTION

Previously, a series of studies to maximize the gas chromatographic (GC) separation of complex mixtures of various chlorinated aromatics, *viz.*, chlorinated phenols[1–3], catechols (1,2-dihydroxybenzenes)[1], benzenes[2], 4-hydroxybenzaldehydes[4], veratroles (1,2-dimethoxybenzenes)[5] and anisoles (methoxybenzenes)[6], and the acetate esters of chlorinated phenols[7,8], catechols[8], guaiacols (2-methoxyphenols)[8–10] and 4-hydroxybenzaldehydes[11], have been carried out in our laboratory, using temperature programming and capillary columns coated with low-polarity (SE-30, OV-101) and polar (Carbowax 20M, OV-351) stationary phases.

The retention indices and the retention index increments due to chlorine substitution have been examined, *e.g.*, with chlorinated phenyl acetates[12], benzenes[13], veratroles[5], 4-hydroxybenzaldehydes[4] and anisoles[6], and the effect of operating temperature on the values discussed.

---

* For Part XXIX, see ref. 3.

This paper describes a study of the retention data and the retention index increments for chlorinated salicylaldehydes on quartz capillary columns with low-polarity dimethyl polysiloxane (SE-30) and polar Carbowax–nitroterephthalic acid polymer (OV-351) as stationary phases. Isothermal operation at 140, 160 and 180°C and temperature programming from 100°C at 2, 6 and 10°C min^{-1} were used. The retention order of the isomers is discussed and the results are compared with those of the earlier observations with chlorinated aromatics, particularly with 4-hydroxy-benzaldehydes[4].

EXPERIMENTAL

Materials

Salicylaldehyde was a commercial product (Fluka, Buchs, Switzerland). Chlorinated salicylaldehydes were prepared from appropriate commercial chlorophenols (Fluka) applying the Reimer–Tiemann method[14].

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, 290°C; nitrogen carrier gas velocity for methane at 160°C, 16
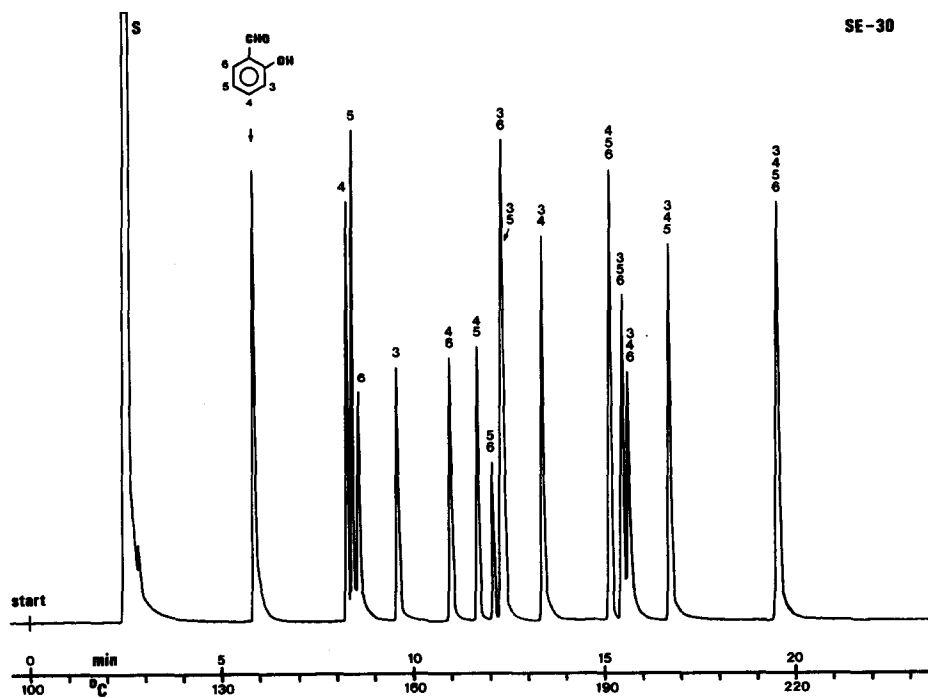

Fig. 1. Chromatogram of a mixture of salicylaldehyde and its chlorinated derivatives, separated on an SE-30 quartz capillary column with temperature programming from 100°C at 6°C min^{-1}. S = Solvent; the numbers indicate the chlorinated positions.

(SE-30) and 54 cm sec^{-1} (OV-351); splitting ratio, 1:30; and chart speed, 10 mm min^{-1}. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The column temperatures were as follows: isothermal at 140, 160 and 180°C; programmed from 100°C at 2, 6 and 10°C min^{-1} until elution of peaks had ceased.

The retention times were measured from the time of sample injection, a Hewlett-Packard Model 3390A reporting integrator being used. The Kováts retention indices were calculated off-line by using two appropriate n-alkanes, the dead volumes being determined by the injection of methane.

RESULTS AND DISCUSSION

A chromatogram of a mixture of salicylaldehyde and all its chlorinated derivatives, obtained on SE-30, is shown in Fig. 1. Only the peaks of the 3,6- and 3,5-dichloro isomers are overlapped, the polar components being eluted from the non-polar column without noticeable tailing of the peaks.

The polar column OV-351 proved to be unsuitable for the di- and polychlorosalicylaldehydes, the separation of a mixture of the mono- and dichloro isomers being presented in Fig. 2. The 4,6- and 6-isomers overlapped, and the 3,6- and 5,6-
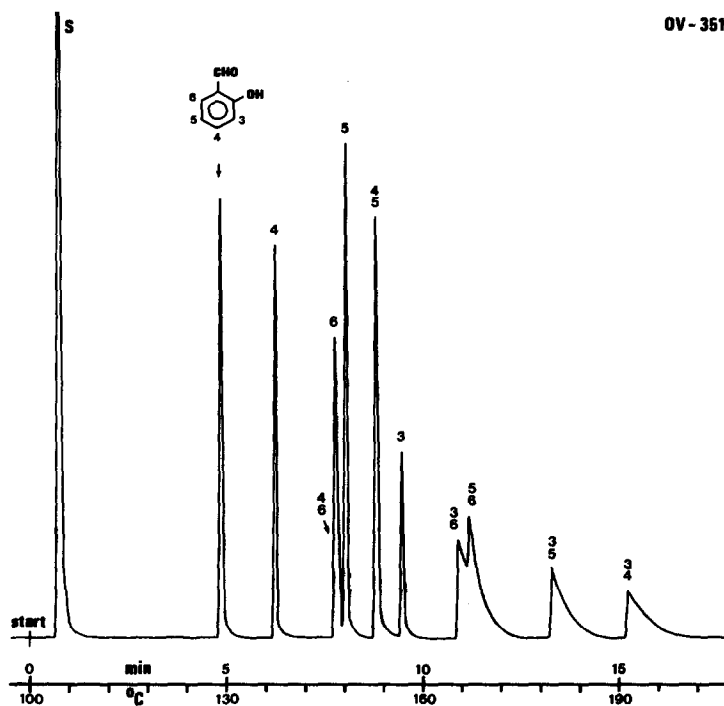

Fig. 2. Chromatogram of a mixture of salicylaldehyde and its mono- and dichloro isomers, separated on an OV-351 quartz capillary column with temperature programming from 100°C at 6°C min^{-1}. S = Solvent; the numbers indicate the chlorinated positions.

TABLE I

RELATIVE RETENTION TIMES FOR SALICYLALDEHYDE AND ITS CHLORINATED DERIV-
ATIVES, DETERMINED ON SE-30 AND OV-351 WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1 and 2.

Isomer	SE-30		OV-351			$\dfrac{RRT_{OV\text{-}351}{}^{\star\star}}{RRT_{SE\text{-}30}}$
	ART*	RRT*	ART*	RRT**	RRT***	
Salicylaldehyde	5.85	1.00	4.90	1.00	0.84	1.00
3-Cl	9.59	1.64	9.49	1.94	0.99	1.18
4-Cl	8.30	1.42	6.31	1.29	0.76	0.91
5-Cl	8.42	1.44	8.10	1.65	0.96	1.15
6-Cl	8.59	1.47	7.80	1.59	0.91	1.08
3,4-Di-Cl	13.40	2.29	15.22	3.11	1.14	1.36
3,5-Di-Cl	12.38	2.12	13.30	2.71	1.07	1.28
3,6-Di-Cl	12.32	2.11	10.92	2.23	0.89	1.06
4,5-Di-Cl	11.71	2.00	8.85	1.81	0.76	0.91
4,6-Di-Cl	10.99	1.88	7.73	1.58	0.70	0.84
5,6-Di-Cl	12.10	2.07	11.21	2.29	0.93	1.11
3,4,5-Tri-Cl	16.72	2.86				
3,4,6-Tri-Cl	15.62	2.67				
3,5,6-Tri-Cl	15.49	2.65				
4,5,6-Tri-Cl	15.19	2.60				
Tetra-Cl	19.55	3.34				

    * Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).
   ** Relative retention time for salicylaldehyde taken as 1.00.
 *** Relative retention time for the corresponding isomer on SE-30 taken as 1.00.

isomers were only partially separated. Enhanced peak tailing occurred with increas-
ing degree of chlorination, as previously found with chlorophenols on polar col-
umns[3]. In addition, the 3,4,5-trichloro and tetrachloro isomers showed no peaks on
OV-351.

The retention data, obtained on both columns under temperature-programmed
conditions as in Figs. 1 and 2, are presented in Table I. The values relative to sali-
cylaldehyde on SE-30 are in the range 1.42–3.34 and on OV-351 for the mono- and
dichloro isomers are in the range 1.29–3.11. Except for the 4-, 4,5- and 4,6-isomers,
higher relative retention times are observed on OV-351, the 3,4- and 4,6-isomers
showing the maximum and minimum ratios, respectively, between the columns used.

The retention indices of salicylaldehydes on both columns, determined at var-
ious temperatures, are presented in Tables II and III.

The isomers are eluted from the low-polarity column in order of their degree
of chlorination, as previously found for the acetate esters of chlorinated phenols[7,8,12],
catechols[8], guaiacols[8–10] and 4-hydroxybenzaldehydes[11] and chlorinated ben-
zenes[2,13], veratroles[5] and anisoles[6]. The retention index increases with increasing

column temperature, the elution order remaining unchanged. The value ΔI (20°C) varied in the range 10–41 retention index units (i.u.), the greatest change in I being found with the tetrachloro isomer. Generally lower values are observed with temperature programming, despite the higher elution temperatures of the isomers than with isothermal conditions (Table II). This is from a considerably lower initial temperature, and higher values with temperature programming are only observed for the tetrachloro isomer.

The monochloro isomers are eluted in the order 4- < 5- < 6- < 3-, the isolated isomers being eluted first. Based on earlier observations with other series of chlorinated aromatics[1–4], the lowest retention would be expected for the 3-, i.e., o-isomer with respect to the hydroxy group, this isomer being eluted even earlier than the parent component with catechols[1] and 4-hydroxybenzaldehydes[4]. The adjacent formyl group in salicylaldehydes, in contrast to the adjacent hydroxy group in catechols, seems to prevent the ortho-effect between the OH and Cl groups.

Judging from a relatively high retention enhancement observed for 2-chloro-4-hydroxybenzaldehyde[4], a higher retention time for the 6-, i.e., o-isomer with respect to the formyl group, would be expected. However, this isomer is eluted close together with the 4- and 5-isomers and clearly earlier than the 3-isomer (Figs. 1 and 3a). This is due to the adjacent hydroxy group, which obviously prevents the formation of

TABLE II

RETENTION INDICES FOR SALICYLALDEHYDE AND ITS CHLORINATED DERIVATIVES, DETERMINED ON SE-30 AT VARIOUS COLUMN TEMPERATURES

Isomer	Isothermal (°C)					Programmed from 100°C (°C min⁻¹)**					
	140	160	180	ΔI_1*	ΔI_2*	2	Et	6	Et	10	Et
Salicylaldehyde	1044	1062	1074	18	12	1021	114.1	1025	135.1	1031	152.8
3-Cl	1249	1264	1278	15	14	1228	128.8	1235	157.5	1244	179.1
4-Cl	1186	1201	1216	15	15	1162	123.2	1167	149.8	1178	170.5
5-Cl	1190	1206	1217	16	11	1169	123.8	1174	150.5	1184	171.2
6-Cl	1200	1214	1224	14	10	1177	124.4	1183	151.5	1190	172.0
3,4-Di-Cl	1413	1434	1451	21	17	1398	145.7	1419	180.4	1426	203.0
3,5-Di-Cl	1370	1388	1403	18	15	1355	141.2	1370	174.3	1377	196.6
3,6-Di-Cl	1368	1387	1403	19	16	1351	140.8	1367	173.9	1376	196.5
4,5-Di-Cl	1342	1358	1376	16	18	1323	137.9	1338	170.3	1343	192.1
4,6-Di-Cl	1311	1326	1344	15	18	1292	134.8	1304	165.9	1311	187.9
5,6-Di-Cl	1358	1376	1392	18	16	1342	139.8	1357	172.6	1359	194.2
3,4,5-Tri-Cl	1557	1577	1598	20	21	1555	162.8	1580	200.3	1593	224.4
3,4,6-Tri-Cl	1508	1529	1549	21	20	1502	157.0	1526	193.7	1535	217.3
3,5,6-Tri-Cl	1503	1522	1543	19	21	1496	156.3	1520	192.9	1526	216.1
4,5,6-Tri-Cl	1489	1510	1530	21	20	1481	154.7	1505	191.1	1514	214.6
Tetra-Cl	1681	1722	1737	41	15	1693	178.0	1724	217.3	1746	242.8

* $\Delta I_1 = I_{160°C} - I_{140°C}$; $\Delta I_2 = I_{180°C} - I_{160°C}$.

** Et = Elution temperature (°C).

TABLE III

RETENTION INDICES FOR SALICYLALDEHYDE AND ITS MONO- AND DICHLORO DERIVATIVES, DETERMINED ON OV-351 AT VARIOUS COLUMN TEMPERATURES

Isomer	Isothermal (°C)					Programmed from 100°C (°C min⁻¹)**						$\dfrac{I_{OV\text{-}351}}{I_{SE\text{-}30}}$ **	$I_{OV\text{-}351} - I_{SE\text{-}30}$ ***
	140	160	180	ΔI_1*	ΔI_2*	2	Et	6	Et	10	Et		
Salicylaldehyde	1751	1742	1699	−9	−43	1611	111.8	1620	129.4	1652	143.8	1.64	680
3-Cl	2066	2082	2112	16	30	1987	137.1	2009	156.9	2030	172.6	1.65	818
4-Cl	1834	1829	1814	−5	−15	1700	117.2	1721	137.9	1746	151.4	1.52	628
5-Cl	1965	1966	1969	1	3	1882	130.2	1886	148.6	1905	163.5	1.63	760
6-Cl	1944	1947	1948	3	1	1849	127.6	1852	146.8	1881	161.7	1.60	733
3,4-Di-Cl	2374	2426	2517	52	91	2355	158.1	2413	191.3	2459	207.9	1.69	992
3,5-Di-Cl	2272	2314	2399	42	85	2245	149.1	2303	179.8	2364	196.0	1.67	926
3,6-Di-Cl	2130	2160	2243	30	83	2072	139.0	2138	165.5	2167	182.0	1.56	773
4,5-Di-Cl	2020	2036	2054	16	18	1947	134.4	1952	153.1	1973	168.4	1.50	678
4,6-Di-Cl	1948	1957	1977	9	20	1835	126.6	1845	146.4	1878	161.5	1.48	631
5,6-Di-Cl	2179	2193	2251	14	58	2110	144.2	2165	167.3	2171	182.3	1.59	817

* $\Delta I_1 = I_{160°C} - I_{140°C}$; $\Delta I_2 = I_{180°C} - I_{160°C}$.

** Et = Elution temperature (°C).

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

intramolecular hydrogen bonding between the formyl proton and the adjacent chlorine substituent, this phenomenon being supposed to give rise to enhanced retention[4].

The retention behaviour of the di- and polychloro isomers generally follow that of the monochloro isomers. With the dichloro isomers the lowest retention is shown by the 4,6-isomer, where the chlorine substituents are isolated from each other, whereas enhanced retention occurred with the 4,5- and 5,6-isomers owing to the close proximity of the chlorine substituents. Almost equivalent retention is shown by the 3,6- and 3,5-isomers, the 3,4-isomer being eluted last.

The lowest retention observed for the 4,5,6-trichloro isomer is from the low retention of the 4,6- and 4,5-dichloro isomers, but a reversed elution sequence would be expected for the 3,5,6- and 3,4,6-isomers, corresponding to the order of the 4,6- and 5,6-isomers. On the other hand, the elution order which actually occurred is in accordance with that of the 3,5- and 3,4-isomers, the effect of the latter substituents being more pronounced.

An appreciable increased retention for the isomers is found on the more polar OV-351 stationary phase, as would be expected (Table III). As on SE-30, lower values are observed with temperature programming, the retention generally increasing with temperature. The value ΔI (20°C) varied in the range 1–91 i.u., being generally higher
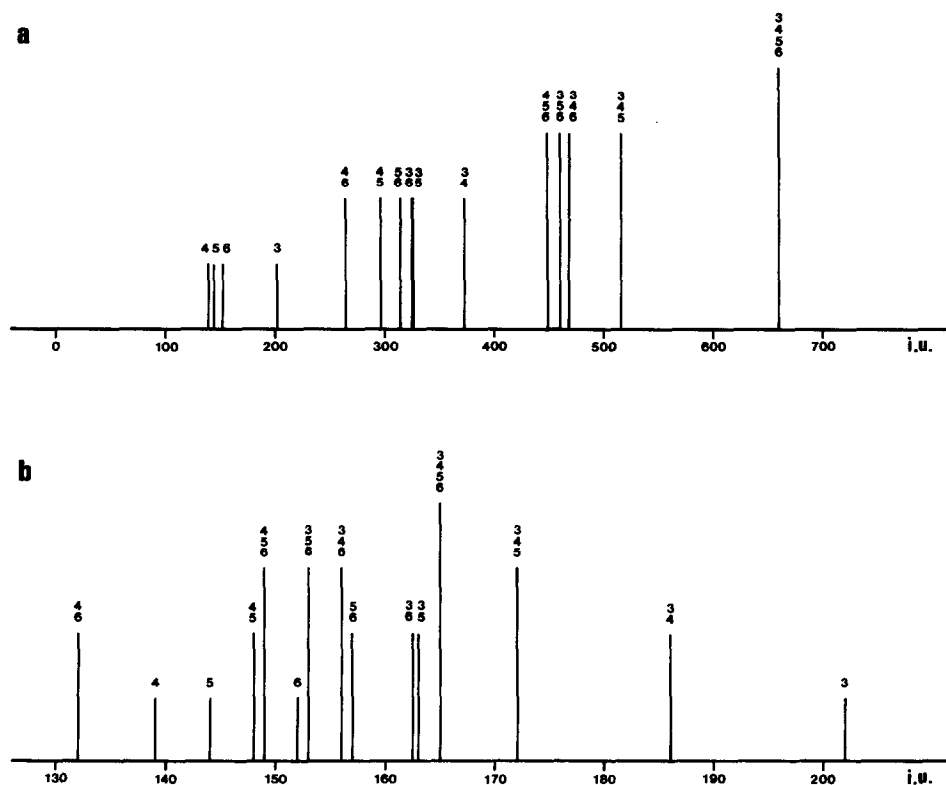

Fig. 3. Incremental effects due to the chlorine substituents, obtained on SE-30 at 160°C (Table IV). a, Total retention index increase; b, retention index increase per chlorine atom. i.u. = Retention index units; the numbers indicate the chlorinated positions.

I. O. O. KORHONEN

TABLE IV
INCREMENTAL EFFECTS OF CHLORINE SUBSTITUTION FOR SALICYLALDEHYDES ON SE-30

Isomer	Isothermal (°C)						Programmed from 100°C (°C min⁻¹)					
	140		160		180		2		6		10	
	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**
3-Cl	205	205	202	202	204	204	207	207	210	210	213	213
4-Cl	142	142	139	139	142	142	141	141	142	142	147	147
5-Cl	146	146	144	144	143	143	148	148	149	149	153	153
6-Cl	156	156	152	152	150	150	156	156	158	158	159	159
3,4-Di-Cl	369	185	372	186	377	189	377	189	394	197	395	198
3,5-Di-Cl	326	163	326	163	329	165	334	167	345	173	346	173
3,6-Di-Cl	324	162	325	163	329	165	330	165	342	171	345	173
4,5-Di-Cl	298	149	296	148	302	151	302	151	313	157	312	156
4,6-Di-Cl	267	134	264	132	270	135	271	136	279	140	280	140
5,6-Di-Cl	314	157	314	157	318	159	321	161	332	166	328	164
3,4,5-Tri-Cl	513	171	515	172	524	175	534	178	555	185	562	187
3,4,6-Tri-Cl	464	155	467	156	475	158	481	160	501	167	504	168
3,5,6-Tri-Cl	459	153	460	153	469	156	475	158	495	165	495	165
4,5,6-Tri-Cl	445	148	448	149	456	152	460	153	480	160	483	161
Tetra-Cl	637	159	660	165	653	163	672	168	699	175	715	179

* Total retention index increase.
** Retention index increase per chlorine atom.

than on SE-30. The isomers with highest retention showed the greatest variations (Table III). The parent and 4-isomers, *i.e.*, those with lowest retention, under isothermal conditions display the opposite trend, the greatest reduction in $\Delta I(20°C)$ of 43 i.u. being found with the parent component (Table III).

The elution order of the 6- and 5-isomers is reversed, the retention of the 4-isomer being increased less and that of the 3-isomer more than of the other two isomers (Table III). Of the dichloro compounds, the 5,6-isomer has a higher retention than the 3,6-isomer, and the 4,6-isomer is usually eluted earlier than the 6- and 5-isomers, the 4,5-isomer appearing earlier than the 3-isomer.

The incremental effects of chlorine substitution, obtained on SE-30 and OV-351 at various column temperatures, are presented in Tables IV and V, and Figs. 3 and 4 show the incremental effects at 160°C. The effect of an additional chlorine atom on both columns at 160°C is shown in Table VI.

It is evident that with both phases the incremental disparities generally increase with temperature, the effect being more pronounced on OV-351, particularly under isothermal conditions (Table V). As a consequence of the elution of the compounds in order of their degree of chlorination, the incremental increases on SE-30 are relatively constant at the same levels of substitution, whereas on OV-351 the variations are noticeably greater.

The retention increase per chlorine atom on SE-30 and OV-351 at 160°C varied in the ranges 132–202 (Fig. 3b) and 87–342 i.u. (Fig. 4b). The greatest enhancement on both columns is shown by the 3-, *i.e.*, *o*-isomer with respect to the hydroxy group, even if on OV-351 the highest increase sometimes occurred with the 3,4-isomer, this isomer exhibiting the greatest disparity between the columns used (Table V). With further substitution, the isomers exhibiting highest retention, *viz.*, 3- → 3,4- → 3,4,5- → 3,4,5,6-isomers, show on SE-30 decreasing enhancements in the series 202 → 186 → 172 → 165 i.u.

The isomers exhibiting the lowest retention, *viz.*, 4- → 4,6- → 4,5,6 → 3,4,5,6-isomers, show on SE-30 enhancements per chlorine atom of 139 → 132 → 149 → 165 i.u., *i.e.*, a reduction of 7 i.u. for the 4,6-isomer is observed. On OV-351, however, the 4-isomer showed the lowest increase of 87 i.u., this being enhanced to 108 i.u. by the 4,6-isomer. The 4-isomer had the minimum ratio (0.63) and subtraction (− 52 i.u.) between the retention enhancements on the low-polarity and polar columns used (Table V).

As evident from Table VI, where the total retention index increase due to an additional chlorine atom is shown, the greatest retention enhancements on SE-30 are found with the series 4- → 3,4- (233 i.u.), 4,5- → 3,4,5- (219 i.u.) and 4,5,6- → 3,4,5,6- (212 i.u.), whereas the series 6- → 4,6- (112 i.u.), 3,4- → 3,4,6- (95 i.u.) and 3,4,5- → 3,4,5,6- (145 i.u.) show the lowest increases. On the polar column the maximum and minimum enhancements for the series 4- → 3,4- (597 i.u.) and 6- → 4,6- (10 i.u.) observed, are higher and lower, respectively, than on SE-30, these series showing the greatest disparities between the columns, *viz.*, 364 and -102 i.u. (Table VI).

By comparing the retention behaviour of 2- and 4-hydroxybenzaldehydes[4], it becomes apparent that all mono-(2-OH) isomers appeared earlier than the first 3-(4-OH) isomer eluted, all di-(2-OH) isomers before all di-(4-OH) isomers, two lower tri-(2-OH) isomers before the 2-(4-OH) isomer and the tetra-(2-OH) isomer earlier than the 2,6-(4-OH) isomer, the elution sequence being shown below with *o*- being
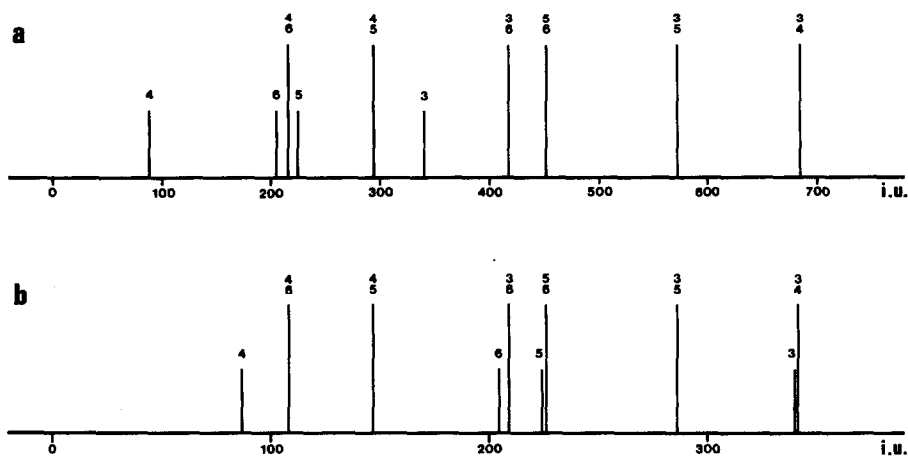
TABLE V

INCREMENTAL EFFECTS OF CHLORINE SUBSTITUTION FOR MONO- AND DICHLORI-
NATED SALICYLALDEHYDES ON OV-351

Isomer	Isothermal (°C)					
	140		160		180	
	$\Sigma \Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma \Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma \Delta I_{nCl}$*	ΔI_{1Cl}**
3-Cl	315	315	340	340	413	413
4-Cl	83	83	87	87	115	115
5-Cl	214	214	224	224	270	270
6-Cl	193	193	205	205	249	249
3,4-Di-Cl	623	312	684	342	818	409
3,5-Di-Cl	521	261	572	286	700	350
3,6-Di-Cl	379	190	418	209	544	272
4,5-Di-Cl	269	135	294	147	355	178
4,6-Di-Cl	197	99	215	108	278	139
5,6-Di-Cl	428	214	451	226	552	276

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

Fig. 4. Incremental effects due to the chlorine substitution, obtained on OV-351 at 160°C (Table V). Details as in Fig. 3.

Programmed from 100°C (°C min⁻¹)						$\dfrac{I_{OV\text{-}351}}{I_{SE\text{-}30}}$***	$I_{OV*351} - I_{SE*30}$***
2		6		10			
$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**	$\Sigma\Delta I_{nCl}$*	ΔI_{1Cl}**		
376	376	389	389	378	378	1.68	138
89	89	101	101	94	94	0.63	−52
271	271	266	266	253	253	1.56	80
238	238	232	232	229	229	1.35	53
744	372	793	397	807	404	1.84	156
634	317	683	342	712	356	1.75	123
461	231	518	259	515	258	1.28	46
336	168	332	166	321	161	0.99	− 1
224	112	225	113	226	113	0.82	−24
499	250	545	273	519	260	1.44	69

the *ortho-*, *i.e.*, 2-hydroxy isomer and *p-* the *para-*, *i.e.*, 4-hydroxy isomer:

$o < o\text{-}4 < o\text{-}5 < o\text{-}6 < o\text{-}3 < p\text{-}3 < p < o\text{-}4,6 < o\text{-}4,5 < o\text{-}5,6 < o\text{-}3,6 \leqslant o\text{-}3,5 < o\text{-}3,4 < p\text{-}2,5 < p\text{-}2,3 \leqslant p\text{-}3,5 < o\text{-}4,5,6 < o\text{-}3,5,6 \leqslant p\text{-}2 < o\text{-}3,4,6 < o\text{-}3,4,5 < p\text{-}2,3,5 < p\text{-}2,3,6 < o\text{-}\text{tetra} < p\text{-}2,6 < p\text{-}\text{tetra}$

A summary of the retention indices and the retention index increments of these two series are shown in Table VII. The enhanced retentions observed for the 2-hydroxy isomer with respect to phenol[4] and benzaldehyde[4] are 98 and 84 i.u., whereas the 4-hydroxy isomer[4] showed corresponding enhancements of 356 and 342 i.u., respectively. Owing to the considerable high difference (258 i.u.) between the retention indices of the parent components, except for the 2- and 2,6-isomers, the chlorinated (4-OH)-isomers show lower retention increments than the (2-OH)-isomers.

Although the comparison between the various chlorinated isomers of these two series may not be sensible owing to the different positions of the ring substituents, it should be mentioned that the *o*-isomers with respect to the CHO group, *i.e.*, the 6-(2-OH) and 2-(4-OH) isomers, show enhancements of 152 and 204 i.u. and the *o*-isomers relative to the OH group, *i.e.*, the 3-(2-OH) and 3-(4-OH) isomers show enhancements of 202 and − 29 i.u., respectively. With the *o,o′*-isomers, relative to the CHO and OH groups, *i.e.*, the 3,6-(2-OH) and 2,3-(4-OH) or 2,5-(4-OH) isomers, the increases observed are 325, 143 and 129 i.u., respectively. The tetra-(4-OH) isomer shows a value 98 i.u. higher than the corresponding (2-OH)-isomer, the retention enhancement of the latter being 160 i.u., however.

TABLE VI

INCREMENTAL EFFECT OF AN ADDITIONAL CHLORINE ATOM INTRODUCED INTO SALICYLAL-
DEHYDE AND ITS CHLORINATED DERIVATIVES, OBTAINED ON SE-30 AND OV-351 AT 160°C

Lower isomer with nCl, n = 0–3	Higher isomer with (n+1) Cl, n = 0–3								
	3-Cl 3,4-Di-Cl 3,4,5-Tri-Cl Tetra-Cl			4-Cl 3,5-Di-Cl 3,4,6-Tri-Cl			5-Cl 3,6-Di-Cl 3,5,6-Tri-Cl		
	SE-30	OV-351		SE-30	OV-351		SE-30	OV-351	
	$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}
Parent	202	340	138	139	87	−52	144	224	80
3-Cl	170	344	174	124	232	108	123	78	−45
4-Cl	233	597	364	–	–	–	–	–	–
5-Cl	–	–	–	182	348	166	–	–	–
6-Cl	–	–	–	–	–	–	173	213	40
3,4-Di-Cl	143			95			–		
3,5-Di-Cl	189			–			134		
3,6-Di-Cl	–			142			135		
4,5-Di-Cl	219			–			–		
4,6-Di-Cl	–			203			–		
5,6-Di-Cl	–			–			146		
3,4,5-Tri-Cl	145								
3,4,6-Tri-Cl	193								
3,5,6-Tri-Cl	200								
4,5,6-Tri-Cl	212								

* Total retention index increase due to an additional chlorine atom, i.e., $\Sigma\Delta I = \Delta I_{(n+1)Cl} - \Delta I_{nCl}$.
** $\Delta I = \Sigma\Delta I_{OV-351} - \Sigma\Delta I_{SE-30}$.

TABLE VII

SUMMARY OF RETENTION INDICES AND RETENTION INDEX INCREMENTS OF 2- AND
4-HYDROXYBENZALDEHYDES, OBTAINED ON SE-30 AT 160°C

Isomer	2-Hydroxybenzaldehyde*		4-Hydroxybenzaldehyde**	
	I	ΔI^{***}	I	ΔI^{***}
Parent	1062		1320	
Mono-Cl	1201–1264	139–202	1291, 1524	−29, 204
Di-Cl	1326–1434	264–372	1449–1753	129–433
Tri-Cl	1510–1577	448–515	1632, 1651	312, 331
Tetra-Cl	1722	660	1820	500

* From Tables II and IV.
** From ref. 4.
*** Total retention index increase.

6-Cl 4,5-Di-Cl 4,5,6-Tri-Cl			4,6-Di-Cl			5,6-Di-Cl		
SE-30	OV-351		SE-30	OV-351		SE-30	OV-351	
$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}	$\Sigma\Delta I^*$	$\Sigma\Delta I^*$	ΔI^{**}
152	205	53						
—	—	—	—	—	—	—	—	—
157	207	50	125	128	3	—	—	—
152	70	−82	—	—	—	170	227	57
—	—	—	112	10	−102	162	246	84
—								
—								
—								
152								
184								
134								

CONCLUSIONS

The present and earlier[4] results show that chlorinated hydroxybenzaldehydes can be analysed as free components on a capillary column with low-polarity dimethyl polysiloxane (SE-30) as stationary phase. A capillary column coated with polar Carbowax–nitroterephthalic acid polymer (OV-351) is suitable only for the lower chlorinated isomers. The 3,6- and 3,5-isomers which overlap on SE-30 can be separated on OV-351, but owing to the peak tailing, these isomers should be analysed on polar columns as their more volatile derivatives, as with the other di- and polychloro isomers.

ACKNOWLEDGEMENTS

REFERENCES

1 I. O. O. Korhonen and J. Knuutinen, *Chromatographia*, 17 (1983) 154.
2 I. O. O. Korhonen, *Chromatographia*, 17 (1983) 195.
3 I. O. O. Korhonen, *J. Chromatogr.*, in press.
4 I. O. O. Korhonen and J. Knuutinen, *J. Chromatogr.*, 292 (1984) 345.
5 I. O. O. Korhonen, J. Knuutinen and R. Jääskeläinen, *J. Chromatogr.*, 287 (1984) 293.
6 I. O. O. Korhonen, *J. Chromatogr.*, 294 (1984) 99.
7 I. O. O. Korhonen and J. Knuutinen, *J. Chromatogr.*, 256 (1983) 135.
8 J. Knuutinen and I. O. O. Korhonen, *J. Chromatogr.*, 257 (1983) 127.
9 J. Knuutinen and E. Kolehmainen, *Chromatographia*, 15 (1982) 707.
10 J. Knuutinen, *J. Chromatogr.*, 248 (1982) 289.
11 J. Knuutinen, E. Kolehmainen, J. Tarhanen, J. Salovaara and M. Lahtiperä, *Chromatographia*, 15 (1982) 364.
12 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 257 (1983) 267.
13 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 265 (1983) 323.
14 C. Postmus, Jr., I. A. Kaye, C. A. Graig and R. S. Matthews, *J. Org. Chem.*, 29 (1964) 2693.