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GAS-LIQUID CHROMATOGRAPHIC ANALYSES

XLIII*. RETENTION INCREMENTS FOR 2-CHLORO-, 2,2-DICHLORO- AND 2,2,2-TRICHLOROETHYL ESTERS OF ALIPHATIC C₂–C₂₀ *n*-ALKANOIC ACIDS ON SE-30 AND OV-351 CAPILLARY COLUMNS

ILPO O. O. KORHONEN

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

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SUMMARY

The Kováts retention indices for ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of aliphatic C₂–C₂₀ *n*-alkanoic acids were determined on a low-polarity (SE-30) and a highly polar (OV-351) capillary column at different temperatures. The increments in retention indices for the methylene groups and chlorine atoms are examined and discussed, and the results compared with those from earlier studies with corresponding aliphatic and aromatic esters.

INTRODUCTION

Previous gas chromatographic (GC) studies of the haloalkyl esters involved the retention behaviour of the chloromethyl esters of aliphatic C₂–C₂₀ *n*-alkanoic acids¹, *n*-C₃–C₁₂^{2,3} and C₅⁴ alkanolic and monochloroalkanoic acids, chloroalkyl esters of acetic^{5,6} and chloroacetic acids⁷, 2-haloethyl esters of lower alkanolic acids¹, *n*-C₃–C₁₂^{2,3} and C₅⁴ alkanolic and monochloroalkanoic acids, chloroalkyl GC separations of a mixture of ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of aliphatic C₂–C₂₀ *n*-alkanoic acids¹² and of benzoic and monochlorobenzoic acids¹³ were reported on low-polarity (SE-30) and highly polar (OV-351) capillary columns. The Kováts retention indices and the retention index increments for the chlorine substituents both on the acyl and alkyl chains of the aromatic esters¹³ were examined and discussed.

This work extends the earlier studies by determining the Kováts retention indices for ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of aliphatic C₂–C₂₀ *n*-alkanoic acids on SE-30 and OV-351 capillary columns at different temperatures. The retention index increments, determined based on data obtained with temperature programming, show the effects of the methylene groups and the various chlorine atoms. The results are compared with those reported previously for

* For Part XLII, see I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 328 (1985) 325.

various aliphatic 2-chloroethyl and 2,2,2-trichloroethyl esters on OV-101, SE-54, SP-400 and SP-1000 stationary phases by Komárek *et al.*⁸⁻¹⁰. Comparisons are also made with data for the corresponding esters of benzoic and monochlorobenzoic acids¹³. The retention indices of the aliphatic ω -chlorinated ethyl esters on the polar capillary columns have not been reported previously and the retention indices for the aliphatic 2,2-dichloroethyl esters are generally lacking.

EXPERIMENTAL

Materials

Ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of aliphatic C₂-C₂₀ *n*-alkanoic acids were prepared as described earlier¹². Mixtures of *n*-alkanes were obtained from different commercial 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; nitrogen (SE-30) and hydrogen (OV-351) carrier gas flow-rates for methane at 160°C, 14.0 and 46.3 cm sec⁻¹, respectively; splitting ratio, 1:25; chart speed, 10 mm min⁻¹. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 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 temperature was programmed from 100 to 320°C (SE-30) and from 100 to 230°C (OV-351) at 6°C min⁻¹ and on OV-351 was held at 230°C until elution of peaks had ceased. The isothermal data were obtained at the temperatures shown in Tables I and II.

The retention times were measured from the time of sample injection with a Hewlett-Packard Model 3390A reporting integrator. The Kováts retention indices were calculated off-line by using two appropriate adjacent *n*-alkanes as described earlier¹⁴. The dead volumes were determined by the injection of methane.

Each of the four groups of esters and *n*-alkanes were chromatographed separately in turn.

RESULTS AND DISCUSSION

The retention indices of the ethyl and ω -chloroethyl esters studied determined on a low-polarity (SE-30) and a highly polar (OV-351) capillary column at different temperatures are presented in Tables I and II, respectively. Fig. 1 shows the retention index plots for the four series of esters, obtained on the two columns with temperature programming.

The separation of a mixture of all 76 individual esters studied was previously examined on SE-30 and OV-351 with temperature programming¹² and it is evident that the elution order reported for the compounds is practically the same on the two columns under the various isothermal conditions used.

The data in Tables I and II show that it is especially useful to analyse complex mixtures of compounds with a wide range of chain lengths using temperature programming, *viz.*, all the compounds can be analysed in the same experiment, the analysis time being thus reduced enormously and the retention indices observed are nearly identical with those found under isothermal conditions (Tables I and II).

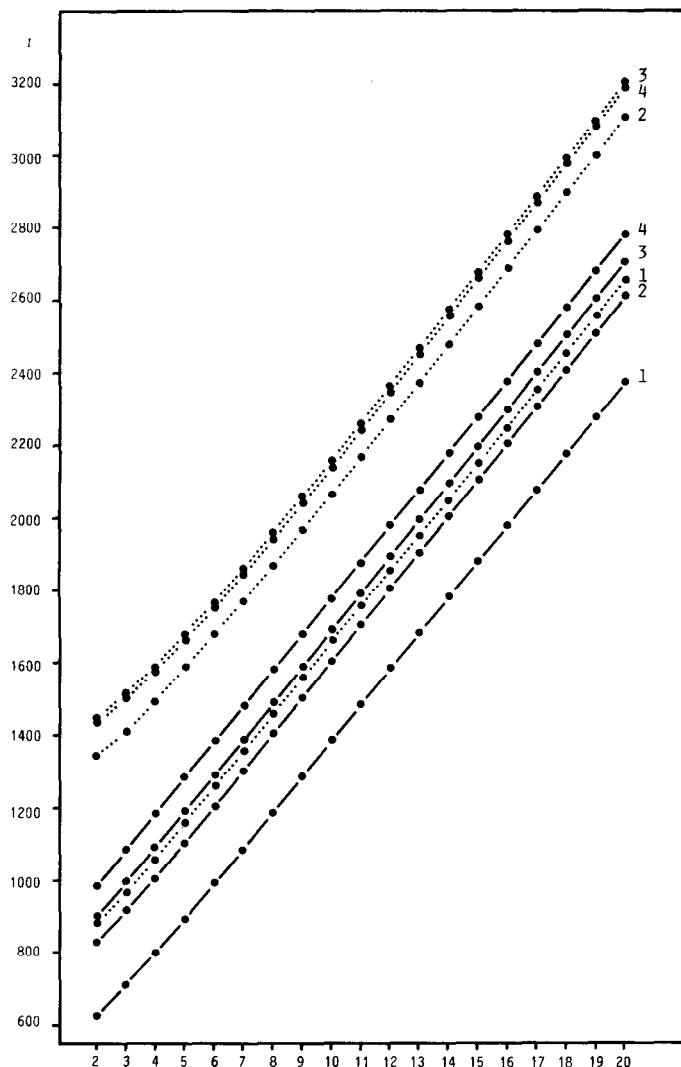


Fig. 1. Plots showing retentions of ethyl (curve 1), 2-chloroethyl (curve 2), 2,2-dichloroethyl (curve 3) and 2,2,2-trichloroethyl (curve 4) esters of aliphatic C_2 - C_{20} n -alkanoic acids, analysed on SE-30 (●—●) and OV-351 (●.....●) capillary columns with temperature programming (Tables I and II). I = Retention index units (i.u.). Numbers on abscissa indicate the chain length of the n -acid.

The retention indices on SE-30 (Table I) are in good accord with those reported previously by Komárek *et al.* on low-polarity SP-400⁸ and OV-101⁹ glass capillary columns for the three homologous series, *i.e.*, ethyl, 2-chloroethyl and 2,2,2-trichloroethyl esters of aliphatic C_2 - C_{10} n -alkanoic acids.

The increased retentions that occurred on the highly polar OV-351 capillary column are shown in Table II and particularly in Table III, where a comparison between the retention behaviour of the esters on SE-30 and OV-351, based on data

TABLE I

RETENTION INDICES FOR ETHYL AND ω -CHLOROETHYL ESTERS OF ALIPHATIC C₂-C₂₀ *n*-ALKANOIC ACIDS, OBTAINED ON AN SE-30 CAPILLARY COLUMN AT DIFFERENT TEMPERATURES

Chain length of ester of <i>n</i> -acid	Column temperature								
	Programmed* (°C)	E.t.* (°C)	140°C	160°C	180°C	200°C	220°C	240°C	260°C
<i>Ethyl ester</i>									
C ₂	624	118	655	700	760	—	—	—	—
C ₃	712	120	707	739	788	—	—	—	—
C ₄	800	122	796	806	846	910	—	—	—
C ₅	893	126	883	896	913	950	980	—	—
C ₆	993	132	979	989	1000	1023	1031	1082	—
C ₇	1088	140	1077	1081	1096	1119	1116	1134	—
C ₈	1190	150	1176	1178	1187	1193	1218	1219	1099
C ₉	1288	161	1274	1277	1284	1284	1304	1314	1209
C ₁₀	1386	173	1376	1378	1380	1385	1400	1405	1320
C ₁₁	1483	185	1476	1477	1478	1479	1493	1500	1446
C ₁₂	1581	197	1576	1578	1578	1577	1588	1594	1549
C ₁₃	1681	208	1677	1676	1676	1678	1689	1693	1667
C ₁₄	1779	219	1777	1777	1777	1779	1787	1788	1766
C ₁₅	1878	230	—	1876	1876	1879	1884	1887	1867
C ₁₆	1978	241	—	1976	1976	1979	1982	1983	1973
C ₁₇	2077	251	—	—	2074	2078	2082	2083	2073
C ₁₈	2177	260	—	—	2175	2179	2183	2179	2175
C ₁₉	2277	270	—	—	—	2278	2282	2281	2277
C ₂₀	2379	278	—	—	—	2378	2383	2382	2378
<i>2-Chloroethyl ester</i>									
C ₂	828	123	816	828	846	—	—	—	—
C ₃	916	127	903	909	920	950	961	1027	—
C ₄	1004	133	990	976	1010	1023	1031	1100	—
C ₅	1103	142	1090	1086	1109	1119	1126	1174	—
C ₆	1203	152	1192	1187	1202	1207	1218	1262	1108
C ₇	1302	163	1292	1290	1300	1305	1313	1345	1230
C ₈	1401	175	1391	1392	1399	1400	1406	1430	1350
C ₉	1500	187	1492	1493	1497	1497	1505	1526	1477
C ₁₀	1600	199	1591	1593	1596	1596	1604	1622	1600
C ₁₁	1701	211	1693	1693	1697	1699	1712	1725	1693
C ₁₂	1801	222	1792	1793	1797	1800	1808	1815	1797
C ₁₃	1902	233	—	1893	1896	1903	1907	1915	1902
C ₁₄	2004	243	—	1994	1996	2002	2004	2011	2009
C ₁₅	2105	253	—	—	2094	2102	2107	2112	2107
C ₁₆	2207	263	—	—	2196	2202	2207	2212	2210
C ₁₇	2308	272	—	—	—	2302	2309	2315	2312
C ₁₈	2411	281	—	—	—	2403	2409	2414	2412
C ₁₉	2513	290	—	—	—	—	2510	2515	2511
C ₂₀	2614	298	—	—	—	—	2611	2616	2612
<i>2,2-Dichloroethyl ester</i>									
C ₂	899	126	892	911	919	942	977	—	—
C ₃	997	133	988	989	991	1010	1035	—	—
C ₄	1092	140	1080	1081	1089	1105	1126	1123	1098
C ₅	1191	151	1178	1184	1180	1200	1224	1219	1201

TABLE I (continued)

Chain length of ester of <i>n</i> -acid	Column temperature								
	Programmed* (°C)	E.t.* (°C)	140°C	160°C	180°C	200°C	220°C	240°C	260°C
C ₆	1289	161	1278	1282	1283	1297	1318	1314	1300
C ₇	1388	173	1378	1381	1384	1392	1412	1405	1392
C ₈	1486	185	1477	1483	1486	1490	1502	1500	1494
C ₉	1588	197	1577	1583	1586	1587	1600	1597	1609
C ₁₀	1689	209	1678	1681	1685	1690	1701	1704	1711
C ₁₁	1790	221	1778	1781	1785	1791	1799	1800	1809
C ₁₂	1891	231	—	1880	1884	1893	1899	1905	1909
C ₁₃	1993	242	—	1981	1986	1992	1998	2003	2014
C ₁₄	2095	252	—	—	2082	2092	2100	2106	2115
C ₁₅	2197	262	—	—	2184	2193	2201	2202	2214
C ₁₆	2301	272	—	—	—	2293	2301	2305	2315
C ₁₇	2405	281	—	—	—	2395	2402	2406	2413
C ₁₈	2507	290	—	—	—	—	2503	2508	2512
C ₁₉	2608	298	—	—	—	—	2603	2608	2612
C ₂₀	2708	306	—	—	—	—	2704	2709	2715
<i>2,2,2-Trichloroethyl ester</i>									
C ₂	988	131	974	978	991	999	—	—	—
C ₃	1087	140	1078	1080	1089	1094	1101	1100	—
C ₄	1185	150	1180	1183	1191	1207	1218	1219	1166
C ₅	1286	161	1278	1277	1284	1289	1309	1318	1288
C ₆	1384	173	1378	1376	1378	1379	1390	1400	1384
C ₇	1482	185	1478	1477	1477	1478	1479	1484	1484
C ₈	1579	196	1578	1577	1578	1574	1577	1574	1574
C ₉	1678	208	1679	1676	1678	1674	1675	1680	1678
C ₁₀	1776	219	1778	1776	1778	1776	1779	1780	1779
C ₁₁	1875	230	—	1875	1877	1877	1876	1878	1879
C ₁₂	1977	240	—	1976	1977	1977	1974	1976	1981
C ₁₃	2074	250	—	—	2074	2077	2076	2077	2079
C ₁₄	2175	260	—	—	2175	2177	2177	2176	2177
C ₁₅	2274	269	—	—	—	2276	2278	2278	2277
C ₁₆	2376	279	—	—	—	2377	2378	2379	2378
C ₁₇	2481	287	—	—	—	—	2474	2482	2486
C ₁₈	2582	296	—	—	—	—	2575	2583	2588
C ₁₉	2685	304	—	—	—	—	2676	2683	2690
C ₂₀	2785	312	—	—	—	—	2776	2783	2790

* From 100 to 325°C at 6°C min⁻¹; E.t. = elution temperature.

obtained with temperature programming, is presented. The enhancements for the ethyl esters are in the range 257–279 retention index units (i.u.), those for the mono-, di- and trichloroethyl esters being higher, *i.e.*, in the ranges 465–513, 468–548 and 361–450 i.u., respectively (Table III). The trends in the enhancements for the isomeric aliphatic esters are the same as previously found with the corresponding aromatic esters¹³.

The retention indices for ethanol and all ω -chlorinated ethanols were previously examined¹⁵ on the same columns as in the present work, and it is evident that on the low-polarity SE-30 column the retention always increases upon replace-

TABLE II

RETENTION INDICES FOR ETHYL AND ω -CHLOROETHYL ESTERS OF ALIPHATIC C₂-C₂₀ n-ALKANOIC ACIDS, OBTAINED ON AN OV-351 CAPILLARY COLUMN AT DIFFERENT TEMPERATURES

Chain length of ester of n-acid	Column temperature							
	Programmed*	E.t.* (°C)	120°C	140°C	160°C	180°C	200°C	220°C
<i>Ethyl ester</i>								
C ₂	892	105	—	—	—	—	—	—
C ₃	970	106	910	—	—	—	—	—
C ₄	1057	107	1025	1051	—	—	—	—
C ₅	1160	108	1125	1159	1113	—	—	—
C ₆	1261	110	1231	1267	1220	—	—	—
C ₇	1360	113	1328	1375	1325	1369	—	—
C ₈	1461	118	1442	1477	1437	1458	—	—
C ₉	1563	125	1548	1579	1538	1580	1531	—
C ₁₀	1665	132	1647	1668	1639	1678	1636	—
C ₁₁	1754	140	1744	1763	1739	1775	1740	1757
C ₁₂	1850	148	1842	1860	1840	1874	1846	1873
C ₁₃	1946	157	1941	1955	1940	1966	1948	1986
C ₁₄	2046	166	2041	2053	2043	2063	2055	2077
C ₁₅	2148	176	2140	2150	2146	2159	2157	2172
C ₁₆	2246	185	2240	2248	2245	2259	2257	2273
C ₁₇	2349	194	2342	2348	2343	2359	2357	2370
C ₁₈	2451	203	—	2446	2444	2459	2458	2467
C ₁₉	2553	211	—	2547	2547	2563	2559	2565
C ₂₀	2657	220	—	2649	2649	2662	2660	2664
<i>2-Chloroethyl ester</i>								
C ₂	1341	113	1313	1365	1331	1370	—	—
C ₃	1409	115	1378	1426	1391	1432	—	—
C ₄	1493	120	1473	1510	1467	1510	—	—
C ₅	1586	126	1569	1598	1560	1603	—	—
C ₆	1678	134	1665	1687	1664	1701	1685	—
C ₇	1770	142	1761	1779	1765	1797	1783	—
C ₈	1869	150	1859	1876	1863	1895	1884	1900
C ₉	1965	159	1957	1973	1963	1995	1983	2001
C ₁₀	2068	168	2058	2071	2064	2087	2080	2101
C ₁₁	2169	178	2158	2168	2168	2182	2181	2200
C ₁₂	2272	187	2259	2268	2266	2282	2283	2301
C ₁₃	2373	196	2361	2368	2365	2383	2386	2399
C ₁₄	2478	205	—	2469	2469	2488	2487	2500
C ₁₅	2584	214	—	2571	2572	2590	2591	2599
C ₁₆	2690	222	—	2672	2675	2691	2692	2701
C ₁₇	2791	230	—	—	2777	2792	2794	2801
C ₁₈	2900	230	—	—	2881	2895	2897	2904
C ₁₉	3003	230	—	—	—	2997	2999	3009
C ₂₀	3108	230	—	—	—	3100	3102	3111
<i>2,2-Dichloroethyl ester</i>								
C ₂	1447	117	1426	1465	1451	1480	—	—
C ₃	1513	121	1495	1527	1513	1545	—	—
C ₄	1588	126	1569	1598	1583	1617	—	—

TABLE II (continued)

Chain length of ester of <i>n</i> -acid	Column temperature							
	Programmed*	E.t.* (°C)	120°C	140°C	160°C	180°C	200°C	220°C
C ₅	1678	133	1660	1685	1669	1705	1657	—
C ₆	1765	141	1754	1775	1758	1797	1756	—
C ₇	1860	149	1850	1869	1852	1886	1854	1900
C ₈	1956	158	1946	1963	1952	1982	1963	2001
C ₉	2056	167	2046	2061	2055	2078	2072	2100
C ₁₀	2158	177	2146	2158	2157	2175	2175	2197
C ₁₁	2260	186	2245	2256	2255	2274	2275	2294
C ₁₂	2363	195	2348	2357	2354	2373	2378	2392
C ₁₃	2467	204	—	2456	2457	2476	2479	2491
C ₁₄	2573	213	—	2558	2560	2579	2581	2590
C ₁₅	2679	222	—	2659	2663	2680	2682	2692
C ₁₆	2780	230	—	—	2765	2781	2785	2792
C ₁₇	2888	230	—	—	2868	2884	2887	2895
C ₁₈	2992	230	—	—	—	2985	2988	2999
C ₁₉	3096	230	—	—	—	3087	3091	3101
C ₂₀	3199	230	—	—	—	3189	3194	3203
<i>2,2,2-Trichloroethyl ester</i>								
C ₂	1438	117	1422	1441	1432	1470	—	—
C ₃	1503	120	1484	1504	1494	1532	—	—
C ₄	1573	125	1559	1580	1560	1600	—	—
C ₅	1661	132	1645	1668	1647	1688	1655	—
C ₆	1750	139	1738	1761	1739	1784	1753	—
C ₇	1843	148	1832	1854	1840	1874	1850	1898
C ₈	1940	157	1928	1948	1938	1966	1956	1997
C ₉	2039	166	2026	2045	2040	2065	2058	2090
C ₁₀	2142	175	2126	2140	2144	2160	2163	2183
C ₁₁	2244	185	2224	2237	2240	2260	2264	2281
C ₁₂	2349	194	2326	2337	2338	2360	2365	2386
C ₁₃	2452	203	—	2436	2440	2462	2467	2485
C ₁₄	2558	212	—	2537	2544	2565	2568	2582
C ₁₅	2666	221	—	2638	2646	2664	2670	2682
C ₁₆	2767	229	—	—	2747	2766	2772	2783
C ₁₇	2873	230	—	—	2849	2867	2873	2883
C ₁₈	2980	230	—	—	—	2969	2975	2988
C ₁₉	3084	230	—	—	—	3070	3077	3089
C ₂₀	3191	230	—	—	—	3172	3179	3192

* From 100 to 230°C at 6°C min⁻¹, then at 230°C until elution of peaks had ceased; E.t. = elution temperature.

ment of the OH group with the much larger RCOO group, as expected. For the lowest esters, *i.e.*, ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl acetates, the enhancements are 192, 205, 161 and 145 i.u., respectively, based on data obtained with temperature programming. On the highly polar OV-351 stationary phase, where the polar effects are much more significant, the corresponding acetate esters show lower retentions than the alcohols, *viz.*, the reductions observed are -26, -45, -163 and -270 i.u., respectively. The relative mobility of the esters increases

TABLE III

COMPARISON BETWEEN THE RETENTION BEHAVIOUR OF THE ESTERS STUDIED ON SE-30 (TABLE I) AND OV-351 (TABLE II), BASED ON DATA OBTAINED WITH TEMPERATURE PROGRAMMING

$$R = I_{OV-351}/I_{SE-30}; S = I_{OV-351} - I_{SE-30}.$$

Chain length of <i>n</i> -acid	Ethyl		2-Chloroethyl		2,2-Dichloroethyl		2,2,2-Trichloroethyl	
	R	S	R	S	R	S	R	S
C ₂	1.43	268	1.62	513	1.64	548	1.46	450
C ₃	1.36	258	1.54	493	1.52	516	1.38	416
C ₄	1.32	257	1.49	489	1.45	496	1.33	388
C ₅	1.30	267	1.44	483	1.41	487	1.29	375
C ₆	1.27	268	1.39	475	1.37	476	1.26	366
C ₇	1.25	272	1.36	468	1.34	472	1.24	361
C ₈	1.23	271	1.33	468	1.32	470	1.23	361
C ₉	1.21	275	1.31	465	1.29	468	1.22	361
C ₁₀	1.20	279	1.29	468	1.28	469	1.21	366
C ₁₁	1.18	271	1.28	468	1.26	470	1.20	369
C ₁₂	1.17	269	1.26	471	1.25	472	1.19	372
C ₁₃	1.16	265	1.25	471	1.24	474	1.18	378
C ₁₄	1.15	267	1.24	474	1.23	478	1.18	383
C ₁₅	1.14	270	1.23	479	1.22	482	1.17	392
C ₁₆	1.14	268	1.22	483	1.21	479	1.16	391
C ₁₇	1.13	272	1.21	483	1.20	483	1.16	392
C ₁₈	1.13	274	1.20	489	1.19	485	1.15	398
C ₁₉	1.12	276	1.19	490	1.19	488	1.15	399
C ₂₀	1.12	278	1.19	494	1.18	491	1.15	406

TABLE IV

INFLUENCE OF THE STATIONARY PHASE POLARITY ON THE RETENTION INDICES (*I*) OF ALIPHATIC AND AROMATIC ESTERS HAVING THE SAME NUMBER OF CARBON ATOMS

Compound	Formula	SE-30		OV-351		OV-351 - SE-30	
		<i>I</i> *	ΔI^{**}	<i>I</i> *	ΔI^{**}	<i>I</i> *	ΔI^{**}
Ethyl heptanoate	C ₉ H ₁₈ O ₂	1088		1360		272	
Ethyl benzoate	C ₉ H ₁₀ O ₂	1143	55	1674	314	531	259
2-Chloroethyl heptanoate	C ₉ H ₁₇ ClO ₂	1302		1770		468	
2-Chloroethyl benzoate	C ₉ H ₉ ClO ₂	1368	66	2138	368	770	302
2,2-Dichloroethyl heptanoate	C ₉ H ₁₆ Cl ₂ O ₂	1388		1860		472	
2,2-Dichloroethyl benzoate	C ₉ H ₈ Cl ₂ O ₂	1459	71	2238	378	779	307
2,2,2-Trichloroethyl heptanoate	C ₉ H ₁₅ Cl ₃ O ₂	1482		1843		361	
2,2,2-Trichloroethyl benzoate	C ₉ H ₇ Cl ₃ O ₂	1531	49	2208	365	677	316

* Determined with temperature programming from 100°C at 6°C min⁻¹; the retention indices for the heptanoic acid esters are taken from Tables I and II, and those for the benzoic acid esters from ref. 13.

** $\Delta I = I_{\text{benzoic acid ester}} - I_{\text{heptanoic acid ester}}$.

TABLE V
 INCREMENTS OF RETENTION INDICES FOR METHYLENE GROUPS AND CHLORINE ATOMS, OBTAINED ON SE-30 WITH TEMPERATURE PROGRAMMING

Chain length of <i>n</i> -acid	2-Chloroethyl		2,2-Dichloroethyl				2,2,2-Trichloroethyl												
	Ethyl ΔI_{CH_2}	$\Sigma \Delta I_{Cl}^*$	ΔI_{Cl}^{**}	ΔI_{Cl}^*	$\Sigma \Delta I_{Cl}^*$	ΔI_{CH_2}	ΔI_{Cl}^{**}	ΔI_{Cl}^{***}	ΔI_{CH_2}	ΔI_{Cl}^*	$\Sigma \Delta I_{Cl}^*$	ΔI_{Cl}^{**}	ΔI_{Cl}^{***}	ΔI_{CH_2}	ΔI_{Cl}^*	$\Sigma \Delta I_{Cl}^*$	ΔI_{Cl}^{**}	ΔI_{Cl}^{***}	
C ₂	—	204	204	204	275	—	204	71	—	204	364	204	71	204	364	204	204	71	89
C ₃	88 ^{§§}	204	204	204	285	98	204	81	98	285	375	204	81	204	375	204	204	81	90
C ₄	88 ^{§§}	204	204	204	292	95	204	88	95	292	385	204	88	204	385	204	204	88	93
C ₅	93	210	210	210	298	99	210	88	99	298	393	210	88	210	393	210	210	88	95
C ₆	100	210	210	210	296	98	210	86	98	296	391	210	86	210	391	210	210	86	95
C ₇	95	214	214	214	300	99	214	86	99	300	394	214	86	214	394	214	214	86	94
C ₈	102	211	211	211	296	98	211	85	98	296	389	211	85	211	389	211	211	85	93
C ₉	99	212	212	212	300	102	212	88	99	300	390	212	88	212	390	212	212	88	90
C ₁₀	98	214	214	214	303	101	214	89	98	303	390	214	89	214	390	214	214	89	87
C ₁₁	97	218	218	218	307	101	218	89	99	307	392	218	89	218	392	218	218	89	85
C ₁₂	98	220	220	220	310	101	220	90	102	310	396	220	90	220	396	220	220	90	86
C ₁₃	100	221	221	221	312	102	221	91	97	312	393	221	91	221	393	221	221	91	81
C ₁₄	98	225	225	225	316	102	225	91	101	316	396	225	91	225	396	225	225	91	80
C ₁₅	99	227	227	227	319	102	227	92	99	319	396	227	92	227	396	227	227	92	77
C ₁₆	100	229	229	229	323	104	229	94	102	323	398	229	94	229	398	229	229	94	75
C ₁₇	99	231	231	231	328	104	231	97	105	328	404	231	97	231	404	231	231	97	76
C ₁₈	100	234	234	234	330	102	234	96	101	330	405	234	96	234	405	234	234	96	75
C ₁₉	100	236	236	236	331	101	236	95	103	331	408	236	95	236	408	236	236	95	77
C ₂₀	102	235	235	235	329	100	235	94	100	329	406	235	94	235	406	235	235	94	77
Average	99	219	219	219	308	101	219	89	100	308	393	219	89	219	393	219	219	89	85

* $\Sigma \Delta I_{Cl}$ = $I_{2\text{-chloroethyl ester}} - I_{\text{ethyl ester}}$; $I_{2,2\text{-dichloroethyl ester}} - I_{\text{ethyl ester}}$; $I_{2,2,2\text{-trichloroethyl ester}} - I_{\text{ethyl ester}}$.
 ** ΔI_{Cl} = $I_{2\text{-chloroethyl ester}} - I_{\text{ethyl ester}}$.
 *** ΔI_{2Cl} = $I_{2,2\text{-dichloroethyl ester}} - I_{2\text{-chloroethyl ester}}$.
 § ΔI_{3Cl} = $I_{2,2,2\text{-trichloroethyl ester}} - I_{2,2\text{-dichloroethyl ester}}$.
 §§ Not included in average values.

TABLE VI
 INCREMENTS OF RETENTION INDICES FOR METHYLENE GROUPS AND CHLORINE ATOMS, OBTAINED ON OV-351 WITH TEMPERATURE PROGRAMMING

Footnotes as in Table V.

Chain length of <i>n</i> -acid	2-Chloroethyl			2,2-Dichloroethyl			2,2,2-Trichloroethyl							
	ΔI_{CH_2}	ΔI_{Cl}^{**}	$\Sigma \Delta I_{Cl}^*$	ΔI_{CH_2}	ΔI_{Cl}^{**}	$\Sigma \Delta I_{Cl}^*$	ΔI_{CH_2}	ΔI_{Cl}^{**}	$\Sigma \Delta I_{Cl}^*$	ΔI_{CH_2}	ΔI_{Cl}^{**}	$\Sigma \Delta I_{Cl}^*$	ΔI_{Cl}^{***}	ΔI_{Cl}^{δ}
C ₂	—	449	449	—	449	555	—	449	546	—	449	546	106	—9
C ₃	78 ^{§§}	439	439	66 ^{§§}	439	543	66 ^{§§}	439	533	65 ^{§§}	439	533	104	—10
C ₄	87 ^{§§}	436	436	75 ^{§§}	436	531	75 ^{§§}	436	516	70 ^{§§}	436	516	95	—15
C ₅	103	426	426	90	426	518	90	426	501	88	426	501	92	—17
C ₆	101	417	417	87	417	504	87	417	489	89	417	489	87	—15
C ₇	99	410	410	95	410	500	95	410	483	93	410	483	90	—17
C ₈	101	408	408	96	408	495	96	408	479	97	408	479	87	—16
C ₉	102	402	402	100	402	493	100	402	476	99	402	476	91	—17
C ₁₀	102	403	403	102	403	493	102	403	477	103	403	477	90	—16
C ₁₁	89	415	415	102	415	506	102	415	490	102	415	490	91	—16
C ₁₂	96	422	422	103	422	513	103	422	499	105	422	499	91	—14
C ₁₃	96	427	427	104	427	521	104	427	506	103	427	506	94	—15
C ₁₄	100	432	432	106	432	527	106	432	512	106	432	512	95	—15
C ₁₅	102	436	436	106	436	531	106	436	518	108	436	518	95	—13
C ₁₆	98	444	444	101	444	534	101	444	521	101	444	521	90	—13
C ₁₇	103	442	442	108	442	539	108	442	524	106	442	524	97	—15
C ₁₈	102	449	449	104	449	541	104	449	529	107	449	529	92	—12
C ₁₉	102	450	450	104	450	543	104	450	531	104	450	531	93	—12
C ₂₀	104	451	451	103	451	542	103	451	534	107	451	534	91	—8
Average	100	429	429	101	429	523	101	429	509	101	429	509	93	—14

TABLE VII

SUMMARY AND COMPARISON OF THE RETENTION INCREMENTS PRESENTED IN TABLES V AND VI

Retention increment*	Ester			
	Ethyl	2-Chloroethyl	2,2-Dichloroethyl	2,2,2-Trichloroethyl
<i>SE-30</i>				
ΔI_{CH_2}	88-102 (99)	88-103 (101)	95-104 (101)	97-105 (100)
$\Sigma \Delta I_{Cl}$		204-236 (219)	275-331 (308)	364-408 (393)
ΔI_{1Cl}		204-236 (219)	204-236 (219)	204-236 (219)
ΔI_{2Cl}			71-97 (89)	71-97 (89)
ΔI_{3Cl}				75-95 (85)
<i>OV-351</i>				
ΔI_{CH_2}	78-104 (100)	68-109 (101)	66-108 (101)	65-108 (101)
$\Sigma \Delta I_{Cl}$		402-451 (429)	493-555 (523)	476-546 (509)
ΔI_{1Cl}		402-451 (429)	402-451 (429)	402-451 (429)
ΔI_{2Cl}			87-106 (93)	87-106 (93)
ΔI_{3Cl}				-8 to -17 (-14)
<i>OV-351/SE-30**</i>				
$\Sigma \Delta I_{Cl}$		1.96	1.70	1.30
ΔI_{1Cl}		1.96	1.96	1.96
ΔI_{2Cl}			1.04	1.04
ΔI_{3Cl}				-
<i>OV-351 - SE-30**</i>				
$\Sigma \Delta I_{Cl}$		210	215	116
ΔI_{1Cl}		210	210	210
ΔI_{2Cl}			4	4
ΔI_{3Cl}				-99

* As in Tables V and VI.

** Based on the average values, given in parentheses.

with increasing degree of chlorination, 2,2,2-trichloroethanol¹⁵, for example, being eluted between 2,2,2-trichloroethyl pentanoate and hexanoate.

It has previously been reported¹⁶ for the pair *n*-butyl hexanoate and *n*-propyl benzoate that the retention index increase effected by the polarity of the stationary phase is much larger (approximately double) for the aromatic than for the aliphatic ester, apparently due to the increased retention contribution of the benzene ring. The same effect is shown by the four series of esters of heptanoic and benzoic acids presented in Table IV. The retention enhancements for the latter, having the same total number of carbon atoms as the former, on SE-30 are in the range 49-71 i.u., increasing to 314-378 i.u. on OV-351. The largest differences are shown by the 2,2-dichloroethyl esters.

The retention index increments for the methylene groups and the various chlorine atoms are shown in Tables V and VI, determined on SE-30 and OV-351 respectively with temperature programming. A summary and a comparison of the increments on the columns are presented in Table VII.

As expected, the methylene increments on both columns are close to 100 i.u.,

TABLE VIII
COMPARISON BETWEEN THE RETENTION INCREMENTS OF THE ω -CHLORINATED ESTERS OF HEPTANOIC AND BENZOIC ACIDS

Compound	SE-30				OV-351				OV-351 - SE-30			
	$\Sigma \Delta I_{Cl}^*$	ΔI_{1Cl}^{**}	ΔI_{2Cl}^{***}	ΔI_{3Cl}^{\S}	$\Sigma \Delta I_{Cl}^*$	ΔI_{1Cl}^{**}	ΔI_{2Cl}^{***}	ΔI_{3Cl}^{\S}	$\Sigma \Delta I_{Cl}^*$	ΔI_{1Cl}^{**}	ΔI_{2Cl}^{***}	ΔI_{3Cl}^{\S}
2-Chloroethyl heptanoate	214	214	-	-	410	410	-	-	196	196	-	-
2-Chloroethyl benzoate	225	225	-	-	464	464	-	-	239	239	-	-
2,2-Dichloroethyl heptanoate	300	214	86	-	500	410	90	-	200	196	4	-
2,2-Dichloroethyl benzoate	316	225	91	-	564	464	100	-	248	239	9	-
2,2,2-Trichloroethyl heptanoate	394	214	86	94	483	410	90	-17	89	196	4	-111
2,2,2-Trichloroethyl benzoate	388	225	91	72	534	464	100	-30	146	239	9	-102

*,**,*** \S As in Table V; the increments for the heptanoic acid esters are taken from Tables V and VI and those for the benzoic acid esters from ref. 13, determined with temperature programming from 100°C at 6°C min⁻¹.

the chlorine substitution having a negligible effect, as shown previously for other series of esters¹⁷⁻¹⁹.

The increments for the first, second and third chlorine atoms on SE-30 are in the ranges 204-236 (219), 71-97 (89) and 75-95 (85) i.u., with the average increments given in parentheses. On OV-351 the increments for the first chlorine atom are doubled to 402-451 (429) i.u., those for the second chlorine atom generally being in the same range as on SE-30, viz., 87-106 (93) i.u. The third chlorine atom shows a reduction in retention from -8 to -17 (-14) i.u., as is evident from Tables VI and VII.

The results given above are in good accord with those for the chlorinated acetic acid esters²⁰⁻²² and 2-chloro- and 2,2,2-trichloroethyl esters of C₂-C₁₀ *n*-alkanoic acids^{8,9}, a comparison between the increments of the aliphatic and aromatic esters being given in Table VIII. On both columns the increments for the first and second chlorine atoms, unlike that for the third chlorine atom, are higher with the benzoic acid esters than those with the heptanoic acid esters. The differences between the highly and weakly polar stationary phases, as presented in Table VIII, are also higher for the aromatic esters also.

From a practical point of view, the mobility of the volatile halogenated alcohols on the low-polarity columns can be decreased by esterification, even by acetylation. If polar columns are used, halogenated alcohols can be analysed by GC as their acetate esters, the relative mobility of the compounds increasing with increasing degree of halogenation.

Trace amounts of carboxylic acids occurring in several environmental and biological samples can be analysed by GC as their haloalkyl esters using a highly sensitive electron-capture detector.

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REFERENCES

- 1 I. O. O. Korhonen, *J. Chromatogr.*, 209 (1981) 96.
- 2 I. O. O. Korhonen, *J. Chromatogr.*, 219 (1981) 306.
- 3 J. K. Haken, B. G. Madden and I. O. O. Korhonen, *J. Chromatogr.*, 298 (1984) 150.
- 4 I. O. O. Korhonen, *J. Chromatogr.*, 240 (1982) 377.
- 5 I. O. O. Korhonen, *J. Chromatogr.*, 246 (1982) 241.
- 6 I. O. O. Korhonen, *J. Chromatogr.*, 268 (1983) 19.
- 7 I. O. O. Korhonen, *J. Chromatogr.*, 248 (1982) 69.
- 8 K. Komárek, J. Kříž, J. Churáček and K. Tesařík, *J. Chromatogr.*, 292 (1984) 105.
- 9 K. Komárek, L. Hornová and J. Churáček, *J. Chromatogr.*, 252 (1982) 293.
- 10 A. Horna, K. Komárek, J. Churáček and O. Dufka, *J. Chromatogr.*, 290 (1984) 45.
- 11 K. Komárek, L. Hornová, A. Horna and J. Churáček, *J. Chromatogr.*, 281 (1983) 299.
- 12 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 322 (1985) 97.
- 13 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 325 (1985) 433.
- 14 G. Guiochon, *Anal. Chem.*, 36 (1964) 661.
- 15 I. O. O. Korhonen, *J. Chromatogr.*, 324 (1985) 181.

- 16 J. K. Haken, H. N. T. Hartley (nee Dinh) and D. Srisukh, *Chromatographia*, 17 (1983) 589.
- 17 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 319 (1985) 131.
- 18 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 320 (1985) 325.
- 19 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 322 (1985) 83.
- 20 J. K. Haken, B. G. Madden and I. O. O. Korhonen, *J. Chromatogr.*, 256 (1983) 221.
- 21 I. O. O. Korhonen, *J. Chromatogr.*, 288 (1984) 51.
- 22 I. O. O. Korhonen, *J. Chromatogr.*, 288 (1984) 329.