

Note

Gas-liquid chromatographic analyses

XXXIX*. ω -Chloroethanols 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)

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Previously, the gas chromatographic (GC) retention behaviour of saturated and unsaturated aliphatic alcohols, together with their halogenated esters, has been investigated on low-polarity (SE-30) and polar (OV-351) capillary columns under various isothermal and temperature-programmed operating conditions¹⁻¹². Programmed studies have been used mainly to optimize the GC separations of complex mixtures, whereas retention index and increment studies of the compounds, allowing the examination of various structural parameters, have been investigated most frequently based on isothermal data, obtained at several temperatures.

The GC of the halogenated alcohols has received little attention, although the haloalkyl esters of aliphatic carboxylic acids have been investigated on both low-polarity and polar stationary phases¹³. Trace amounts of carboxylic acids occurring in environmental or biological samples are preferably analysed as more volatile derivatives, chlorinated ethyl esters being the most suitable, particularly with electron-capture detection (ECD)¹⁴⁻¹⁶.

In this work temperature-programmed and isothermal capillary GC on SE-30 and OV-351 stationary phases at a variety of temperatures of ethanol and its 2-chloro, 2,2-dichloro and 2,2,2-trichloro isomers is studied. Retention data and Kováts retention indices were determined and the retention index increments were used to examine the effects of the various chlorine substituents. The results are compared with those of the *n*-alkanols⁹ and the ω -chlorinated esters^{17,18} reported earlier.

EXPERIMENTAL

Materials

Ethanol was a commercial product (Oy ALKO, Finland), as also was 2-chloroethanol (Fluka, Buchs, Switzerland), which was used after redistillation. 2,2-Dichloroethanol and 2,2,2-trichloroethanol were prepared with LiAlH₄ from commer-

* For Part XXXVIII, see I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 324 (1985) 113.

cial dichloroacetic acid (Fluka) and trichloroacetyl chloride (Merck-Schuchardt, Darmstadt, F.R.G.), respectively, as described earlier¹⁹.

Commercial mixtures of *n*-alkanes used as the reference components 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, 230°C; nitrogen carrier gas velocities for methane at 120°C, 15.0 (SE-30) and 15.5 cm sec⁻¹ (OV-351); splitting ratio, 1:35; and chart speed, 10 mm min⁻¹. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 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°C at 2, 6 and 10°C min⁻¹ until elution of peaks had ceased, the isothermal data being recorded at 60, 80, 100, 120, 140, 160 and 180°C.

The chromatographic data were obtained with a Hewlett-Packard Model 3390A reporting integrator using standard programs. All retention times were measured from the time of sample injection and the dead volumes were determined by the injection of methane. The Kováts retention indices were calculated off-line by using two appropriate *n*-alkanes as described earlier²⁰.

RESULTS AND DISCUSSION

The relative retention data of the alcohols studied are presented in Table I, obtained on SE-30 and OV-351 under the operating conditions specified in Fig. 1. The retention indices of the components are presented in Table II, obtained on both

TABLE I

RETENTION DATA FOR ETHANOL AND ω -CHLOROETHANOLS, OBTAINED ON SE-30 AND OV-351 WITH TEMPERATURE PROGRAMMING

Conditions as shown in Fig. 1.

Compound	B.p.* (°C)	Column						
		SE-30			OV-351			
		ART**	RRT***	RRT [§]	ART**	RRT***	RRT [§]	RRT ^{§§}
Ethanol	78.5	2.72	0.21	1.00	3.01	0.48	1.00	1.11
2-Chloroethanol	128 (760)	3.06	0.24	1.13	6.14	0.97	2.04	2.01
2,2-Dichloroethanol	146 (760)	3.48	0.27	1.28	9.46	1.50	3.14	2.72
2,2,2-Trichloroethanol	151 (737)	4.08	0.32	1.50	11.11	1.76	3.69	2.72
<i>n</i> -Tetradecane	253.7 (760)	12.72	1.00	—	6.30	1.00	—	0.50

* From ref. 21. Pressure in mmHg in parentheses.

** Absolute retention times (min) were measured from sample injection (Fig. 1).

*** Relative retention time for *n*-tetradecane taken as 1.00.

§ Relative retention time for ethanol taken as 1.00.

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

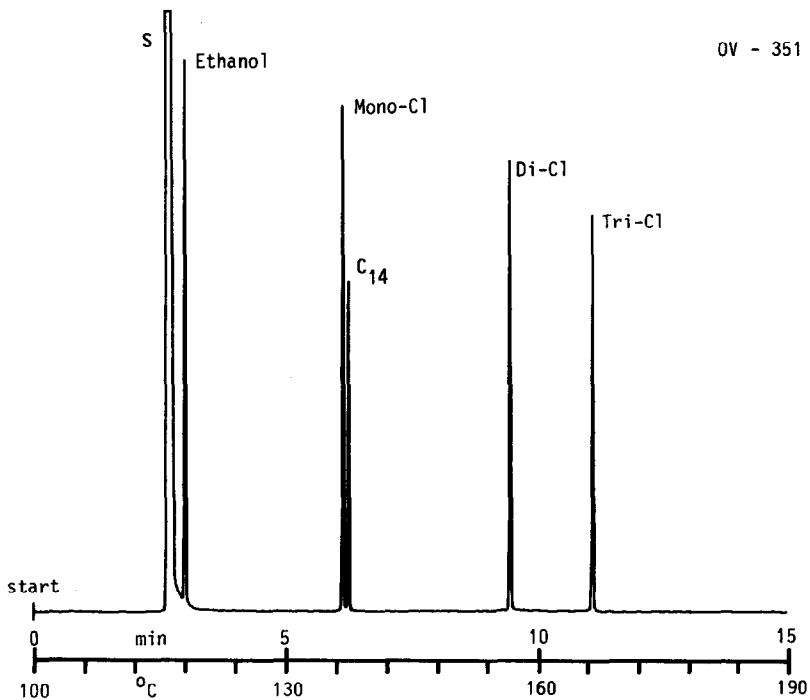
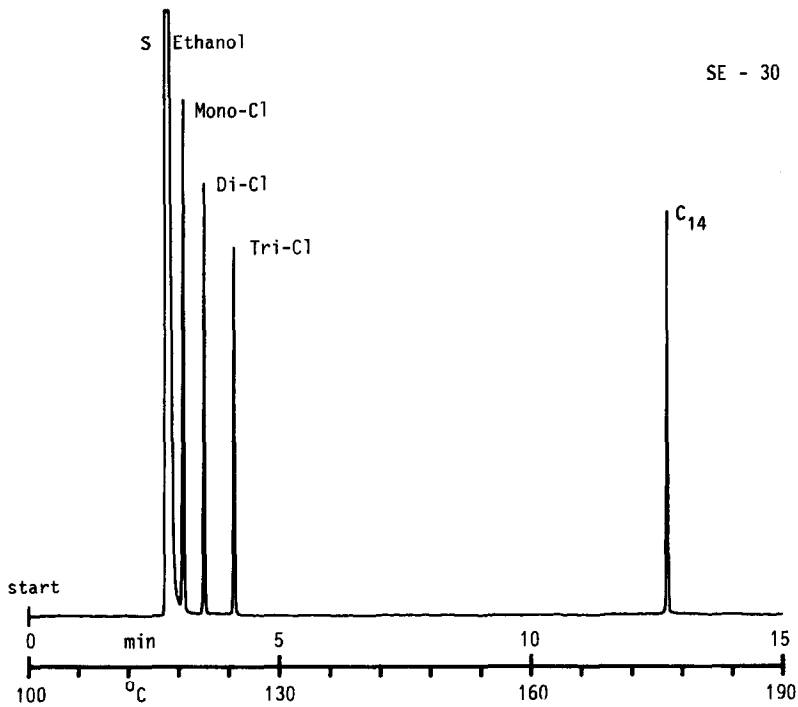


Fig. 1. Chromatograms of a mixture of ethanol and its ω -chlorinated mono-, di- and trichloro derivatives, separated on SE-30 and OV-351 quartz capillary columns with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane.

TABLE II

RETENTION INDICES FOR ETHANOL AND ITS ω -CHLORINATED DERIVATIVES ON SE-30 AND OV-351

Temperature	Column							
	SE-30				OV-351			
	Ethanol	ω -Chloroethanol			Ethanol	ω -Chloroethanol		
		Mono-Cl	Di-Cl	Tri-Cl		Mono-Cl	Di-Cl	Tri-Cl
Programmed from 100°C at:								
2°C min ⁻¹	450	633	752	854	920	1400	1633	1721
6°C min ⁻¹	432	623	738	843	918	1386	1610	1708
10°C min ⁻¹	416	614	733	838	893	1369	1604	1701
Isothermal at:								
80°C	443	629	690	741	—	—	—	—
100°C	427	638	694	750	927	1372	1594	1693
120°C	411	606	678	734	910	1378	1601	1698
140°C	415	600	665	721	890	1385	1609	1704
160°C	411	602	672	736	867	1394	1616	1707
180°C	406	607	683	775	860	1396	1623	1713
160°C	Ratio: OV-351/SE-30				2.11	2.32	2.40	2.32
160°C	Difference: OV-351 - SE-30				456	792	944	971

stationary phases at a variety of temperatures. Fig. 2 shows the retention enhancement at 160°C with increasing chlorine substitution, together with the increased retention that occurred on a polar column.

The alcohols are eluted on both the low-polarity and polar capillary columns in order of increasing degree of chlorination and boiling point (Table I and Fig. 2). The expected reversed elution order between the di- and trichloro isomers was not observed on OV-351, as always occurred with the esters of the chlorinated acetic acids^{5,7,8,17,22-24} and further with the esters of 2,2-di- and 2,2,2-trichloroethanols¹³. The retentions relative to ethanol varied in the ranges 1.13–1.50 on SE-30 and 2.04–3.69 on OV-351, the retention on OV-351 being 1.11–2.72 times higher than that on SE-30 (Table I).

The retention indices of the components, presented in Table II, are relatively constant at different temperatures, the programmed runs generally showing the highest values. The retention indices for the mono-, di- and trichloro isomers vary on SE-30 in the following ranges with the values on OV-351 given in parentheses: 600–638 (1369–1400), 665–752 (1594–1633) and 721–854 (1693–1721) retention index units (i.u.), respectively. The retention index ratios presented in Table II and Fig. 2 show that the retention enhancement is more than double (2.11–2.40) on the polar column, *i.e.*, at 160°C 456 i.u. for ethanol, 792 i.u. for mono-, 944 i.u. for di- and 971 i.u. for trichloroethanol.

The retention behaviour of *n*-alkanols on SE-30 and OV-351 has been reported previously⁹ and it is evident that on SE-30 2-chloroethanol is eluted between propanol and butanol, 2,2-dichloroethanol between butanol and pentanol and 2,2,2-

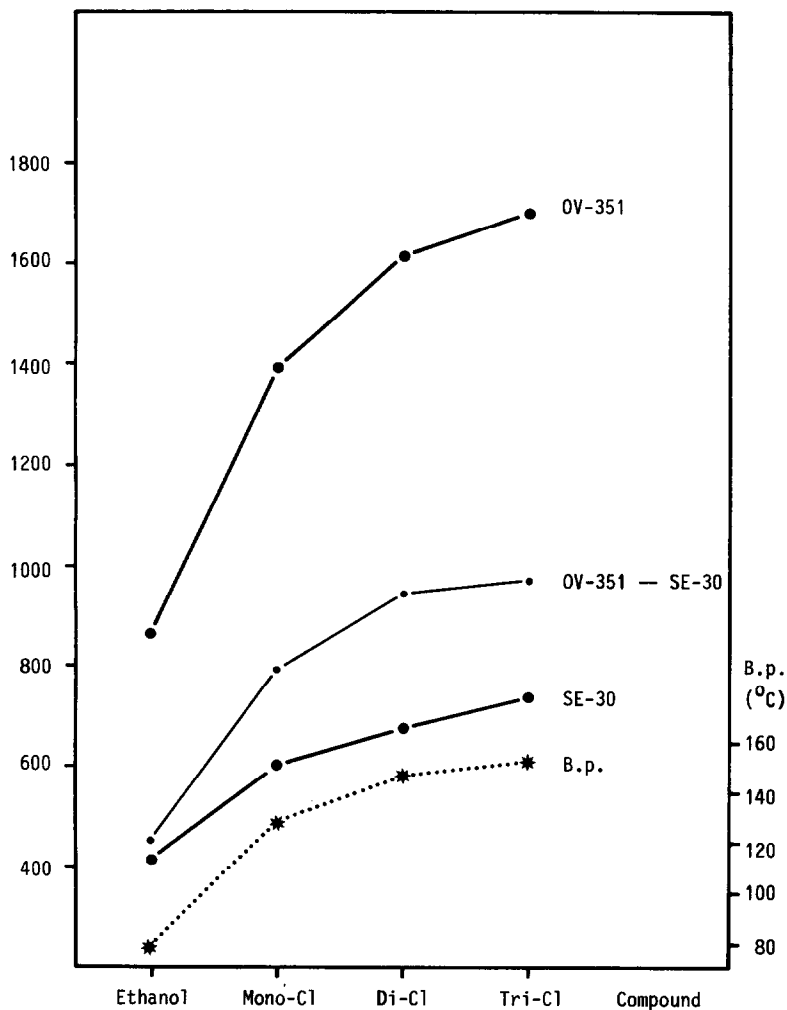


Fig. 2. Boiling points and retention indices (I) of ethanol and ω -chloroethanols on SE-30 and OV-351 at 160°C and the retention enhancements that occurred on a polar column, *i.e.*, $I_{OV-351} - I_{SE-30}$ (Table II).

trichloroethanol between pentanol and hexanol. This means that one ω -chlorine substituent corresponds to nearly two methylene groups introduced into ethanol, and two and three chlorine atoms to nearly three and four methylene groups, respectively. On OV-351 the effects of the ω -chlorine substitution is greater, *viz.*, one chlorine atom is equivalent to 4-5 methylene groups and two and three chlorine atoms correspond to 6-7 and 7-8 methylene groups, respectively.

The incremental effects of the chlorine substituents in ω -chlorinated ethanols are shown in Tables III (SE-30) and IV (OV-351), where it is apparent that the increments generally increase with increasing temperature. The data obtained at 160°C, presented in Fig. 3, show increments for the first, second and third chlorine atoms of 191, 70 and 64 i.u., respectively, on SE-30. As shown, the effect decreases with increasing degree of chlorination, *i.e.*, the amount of the substituents expected

TABLE IV
INCREMENTAL EFFECTS OF CHLORINE SUBSTITUENTS IN ω -CHLOROETHANOLS ON OV-351

Temperature	ω -Chloroethanol									
	2-Chloroethanol			2,2-Dichloroethanol			2,2,2-Trichloroethanol			
	$\Sigma\Delta I_{Cl}^*$	ΔI_{Cl}^{**}	$\Sigma\Delta I_{Cl}^*$	ΔI_{Cl}^{**}	ΔI_{Cl}^{***}	$\Sigma\Delta I_{Cl}^*$	ΔI_{Cl}^{**}	ΔI_{Cl}^{***}	ΔI_{2Cl}^{***}	ΔI_{3Cl}^{\S}
Programmed from 100°C at:										
2°C min ⁻¹	480	480	713	480	233	801	480	233	233	88
6°C min ⁻¹	468	468	692	468	224	790	468	224	224	98
10°C min ⁻¹	476	476	711	476	235	808	476	235	235	97
Isothermal at:										
100°C	445	445	667	445	222	766	445	222	222	99
120°C	468	468	691	468	223	788	468	223	223	97
140°C	495	495	719	495	224	814	495	224	224	95
160°C	527	527	749	527	222	840	527	222	222	91
180°C	536	536	763	536	227	853	536	227	227	90
Ratio: OV-351/SE-30 ^{§§} (160°C)	2.76	2.76	2.87	2.76	3.17	2.58	2.76	3.17	3.17	1.42
Difference: OV-351 - SE-30 ^{§§} (160°C)	336	336	488	336	152	515	336	152	152	27

* ** *** § As in Table III.

§§ For the retention increments on SE-30, see Table III.

TABLE V

COMPARISON BETWEEN RETENTION INDICES AND INCREMENTAL EFFECTS OF CHLORINE SUBSTITUENTS IN ω -CHLOROETHANOLS AND -ESTERS, OBTAINED ON LOW-POLARITY AND POLAR CAPILLARY COLUMNS AT 100°C

Compound	Stationary phase									
	Low-polarity (SE-30, OV-101)			Polar (OV-351)						
	<i>I</i>	$\Sigma \Delta I_{Cl}^*$	ΔI_{Cl}^{**}	ΔI_{2Cl}^{***}	ΔI_{3Cl}^{\S}	<i>I</i>	$\Sigma \Delta I_{Cl}^*$	ΔI_{Cl}^{**}	ΔI_{2Cl}^{***}	ΔI_{3Cl}^{\S}
Ethanol	427	—	—	—	—	927	—	—	—	—
2-Chloroethanol	638	211	211	—	—	1372	445	445	—	—
2,2-Dichloroethanol	694	267	211	56	—	1594	667	445	222	—
2,2,2-Trichloroethanol	750	323	211	56	56	1693	766	445	222	99
Propyl acetate	729 ^{§§}	—	—	—	—	1061 ^{§§}	—	—	—	—
Propyl chloroacetate	920 ^{§§}	191	191	—	—	1355 ^{§§}	294	294	—	—
Propyl dichloroacetate	991 ^{§§}	262	191	71	—	1425 ^{§§}	364	294	70	—
Propyl trichloroacetate	1064 ^{§§}	335	191	71	73	1396 ^{§§}	335	294	70	-29
Methyl propanoate	627 ^{§§§}	—	—	—	—	937 [†]	—	—	—	—
Methyl 3-chloropropanoate	831 ^{§§§}	204	204	—	—	1353 [†]	416	416	—	—
Methyl 3,3-dichloropropanoate	914 ^{§§§}	287	204	83	—	—	—	—	—	—
Methyl 3,3,3-trichloropropanoate	1018 ^{§§§}	391	204	83	104	—	—	—	—	—
Methyl butanoate	710 ^{§§§}	—	—	—	—	989 ^{††}	—	—	—	—
Methyl 4-chlorobutanoate	933 ^{§§§}	223	223	—	—	1445 ^{††}	456	456	—	—
Methyl 4,4-dichlorobutanoate	1045 ^{§§§}	335	223	112	—	—	—	—	—	—

*,**,***,§ As in Table III.

§ From ref. 17 on SE-30 and OV-351 (propyl acetate is the lowest isomer, examined on OV-351).

§§ From ref. 18 on OV-101.

† From ref. 9 on OV-351.

†† From ref. 10 on OV-351.

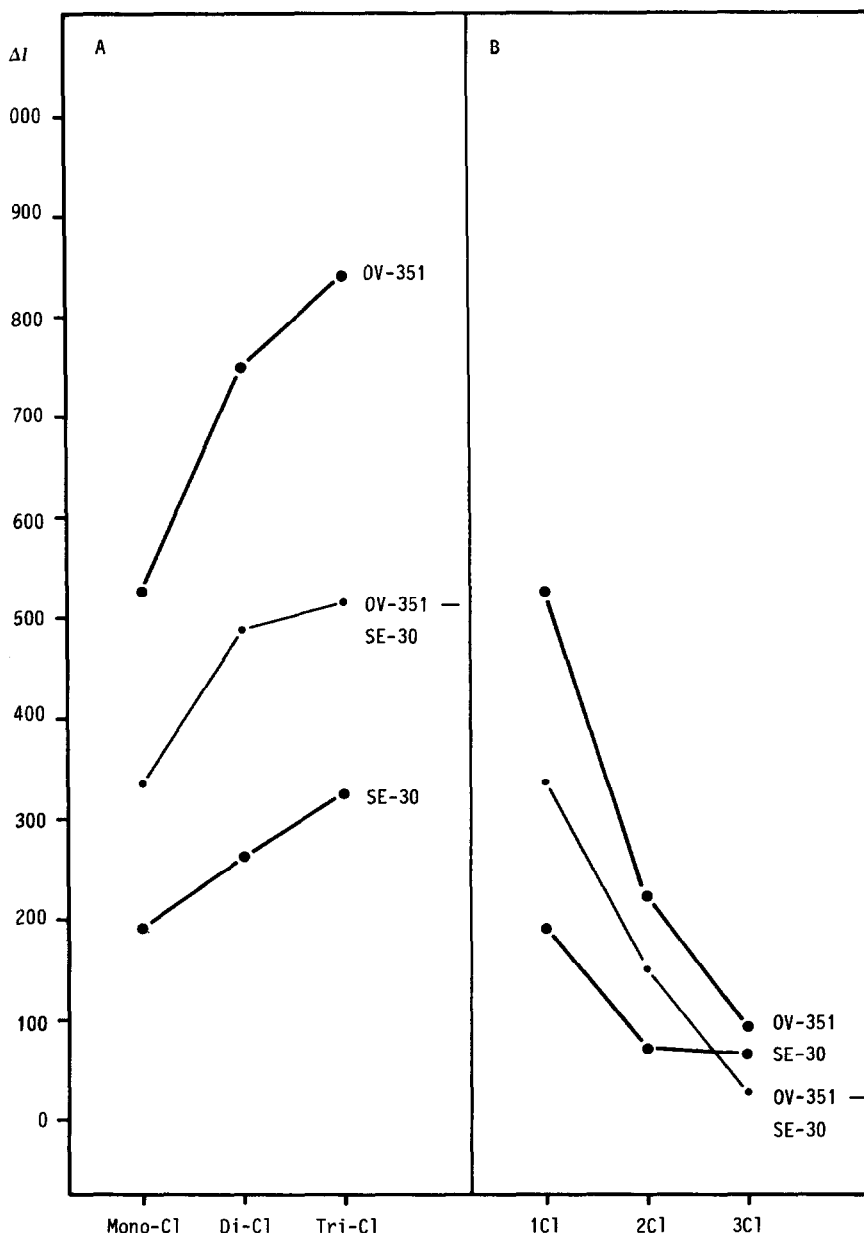


Fig. 3. Incremental effects (ΔI) of chlorine substituents in ω -chloroethanols on SE-30 and OV-351 at 160°C and the enhancements of the retention increments on OV-351, i.e., $\Delta I_{OV-351} - \Delta I_{SE-30}$. (A) Total retention index increments; (B) retention index increments for the first, second and third chlorine atoms.

based on the results for the simple branched-chain esters²⁵. Previous studies^{7,8,17} with the esters of chlorinated acetic acids on SE-30 showed that the addition of the third chlorine atom produces a greater increase in retention than the second chlorine atom, however.

On a polar column the increments for the first, second and third chlorine atoms are increased to 527, 222 and 91 i.u., respectively (Fig. 3), dichloroethanol showing the highest retention increment ratio (3.17) between OV-351 and SE-30, the ratio being reduced to 2.76 with mono- and to 1.42 with trichloroethanol (Table IV). Unlike the esters of trichloroacetic acid^{7,8,17}, the third chlorine atom in ethanol also shows an increase in retention. Obviously, the steric effects with more polar trichloroethanol are not as significant as those with the esters of trichloroacetic acid, and a reduction in the retention is not shown on OV-351.

Table V compares the retention indices and increments of the chlorine substituents in ω -chlorinated ethanols and some lower ω -chloro esters^{9,10,17,18}. On the low-polarity column the effects of the chlorine atoms increase with increasing acid chain length and the effect of the first chlorine atom with ethanol is higher than that with the acetate and propanoate esters. With further chlorine substituents the effects with ethanol are the lowest, however.

The data on OV-351, presented in Table V, are inconsistent, but it is apparent that with all series the effect of the first chlorine atom is markedly increased on a polar column, this trend being greatest with ethanol and lowest with the acetate ester. The effect of a second chlorine atom in ethanol is half that of the first chlorine atom, but nearly four times greater than that on SE-30. With the acetate ester, however, the effect is only a quarter of that of the first chlorine atom and equal to that on SE-30. The effect of the third chlorine atom with ethanol is further half of that of the second chlorine atom and less than double that on SE-30. With the acetate ester a reduction in retention is evident, however.

The phenomena discussed above are due to the fact that the smaller hydroxy group has little influence on the low-polarity column compared with that of the much larger acyl group, the polar effects being more significant on the polar OV-351 stationary phase. On the other hand, the steric effects with ethanols are not as significant as those with more bulky esters, causing an increase in the polarity of ethanol relative to that of the esters when the degree of chlorination increases.

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