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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

IX*. GLASS CAPILLARY GAS CHROMATOGRAPHY OF ALIPHATIC C_1–C_8 *n*-ALKYL MONOCHLORO ESTERS OF ACETIC, CHLOROACETIC, DICHLOROACETIC AND TRICHLOROACETIC ACIDS

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SUMMARY

The gas chromatography (GC) of *n*-alkyl acetates (CH_3–COOR), chloroacetates (CH_2Cl–COOR), dichloroacetates ($CHCl_2$–COOR) and trichloroacetates (CCl_3–COOR), where the alcohol chain length (R) varied between 1 and 8, and certain of their monochlorinated derivatives, 176 compounds altogether, has been studied on SE-30 and OV-351 glass capillary columns under the same operating conditions. The isomeric monochlorinated esters are eluted in direct order from the 1-chloro to the ω-chloro isomer, the separation of the isomers being complete on OV-351. On SE-30, however, the peaks of the 6- and 7-chlorooctyl esters are partly overlapped. The separation of the mixtures of odd- and even-carbon-number esters was better on a non-polar column.

The GC analysis of the combined mixtures of all isomers resulted in several overlapping peaks, particularly with the chloroacetates. The isomeric chloro esters are eluted on SE-30 in the order mono-, di- and trichloro isomers, whereas on OV-351 the di- and trichloro esters are eluted in the reverse order while the 1-chloroalkyl C_2–C_8 trichloroacetates are eluted before the corresponding monochloro isomers. A different elution order of the compounds is observed on a polar column, 1-chloro and ω-chloro isomers giving rise to the greatest difference in elution order. The gas chromatograms of the mixtures and the relative retention times of the compounds are given.

INTRODUCTION

Recently, the gas chromatographic (GC) separation of mixtures with a wide range of chain lengths of aliphatic *n*-alkyl acetates and their monochlorinated derivatives on SE-30 and Carbowax 20M glass capillary columns has been reported[1]. Also, the GC of a series of *n*-alkyl esters of acetic acid and its chlorinated derivatives has

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been studied on polar and non-polar columns[2], as have halogenated esters[3].

This paper describes a GC study of homologous series of aliphatic *n*-alkyl acetates, chloroacetates and certain of their monochlorinated derivatives. The parent esters are CH_3COOR, $CH_2ClCOOR$, $CHCl_2COOR$ and CCl_3COOR, where the carbon number of the alcohol chain (R) varied between 1 and 8. The separations of mixtures of the parent esters and their isomeric chloroalkyl derivatives were carried out on a non-polar SE-30 and a highly polar OV-351 glass capillary column under the same operating conditions. The relative retention times for all 176 compounds are given and the retention order on both columns is discussed.

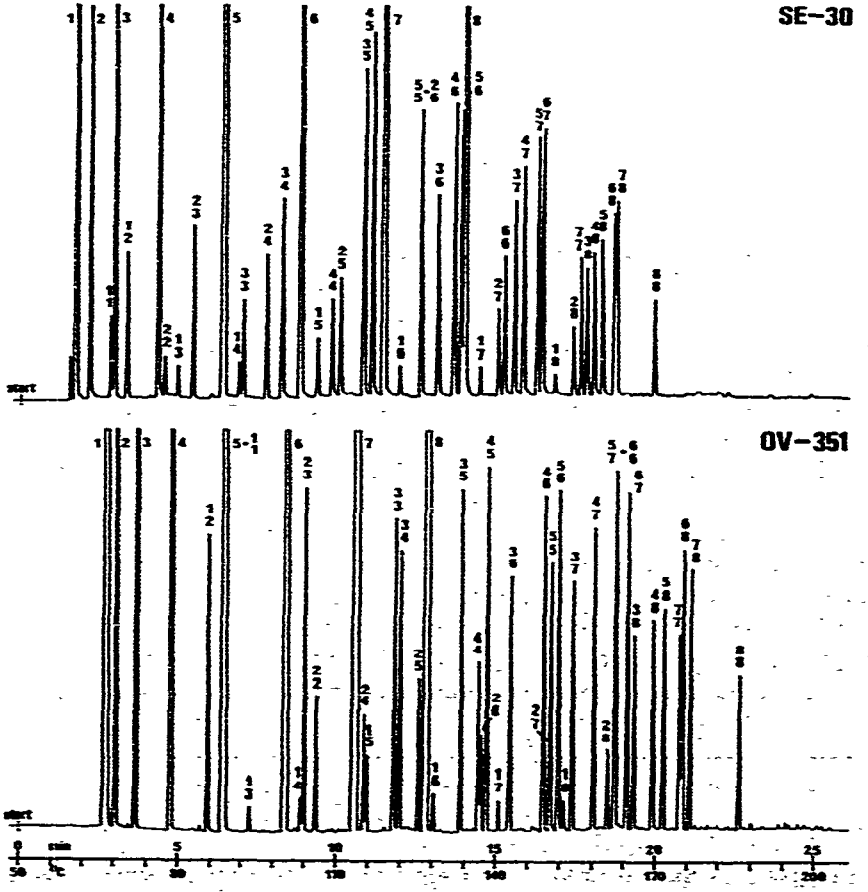

Fig. 1. Chromatograms of the mixture of aliphatic C_1–C_8 *n*-alkyl acetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. Methyl acetate (1) = solvent. Notation of compounds: 1–8 are the parent esters from methyl acetate (1) to *n*-octyl acetate (8); the upper number indicates the position of the Cl-substituent, the lower number the alcohol chain length (*e.g.*, $^{3}_{6}$ denotes 3-chlorohexyl acetate). The additional peaks are unidentified polychloro isomers.

TABLE I

RELATIVE RETENTION TIMES (RRT) OF ALIPHATIC C_1–C_8 *n*-ALKYL ACETATES AND THEIR MONOCHLORINATED DERIVATIVES ANALYSED ON SE-30 AND OV-351 GLASS CAPILLARY COLUMNS

Conditions as shown in Fig. 1.

n-Alkyl acetate, CH_3–COOR, R=	*Column*						
	SE-30			*OV-351*			
	*Time (min)**	*RRT***	*RRT****	*Time (min)**	*RRT***	*RRT****	*RRT§*
Methyl	1.65	1.00	0.19	2.65	1.00	0.32	1.61
Chloromethyl	2.80	1.70	0.32	6.34	2.39	0.76	2.26
Ethyl	2.10	1.00	0.24	3.01	1.00	0.36	1.43
1-Chloroethyl	3.30	1.57	0.38	5.94	1.97	0.72	1.80
2-Chloroethyl	4.48	2.13	0.52	9.36	3.11	1.13	2.09
Propyl	2.86	1.00	0.33	3.61	1.00	0.44	1.26
1-Chloropropyl	4.87	1.70	0.56	7.27	2.01	0.88	1.49
2-Chloropropyl	5.39	1.88	0.62	8.99	2.49	1.08	1.67
3-Chloropropyl	6.95	2.43	0.80	11.83	3.28	1.43	1.70
Butyl	4.21	1.00	0.49	4.71	1.00	0.57	1.12
1-Chlorobutyl	6.81	1.62	0.79	8.88	1.89	1.07	1.30
2-Chlorobutyl	7.69	1.83	0.89	10.86	2.31	1.31	1.41
3-Chlorobutyl	8.15	1.94	0.94	11.99	2.55	1.45	1.47
4-Chlorobutyl	9.74	2.31	1.12	14.46	3.07	1.74	1.48
Pentyl	6.21	1.00	0.72	6.34	1.00	0.76	1.02
1-Chloropentyl	9.30	1.50	1.07	10.95	1.73	1.32	1.18
2-Chloropentyl	10.00	1.61	1.15	12.58	1.98	1.52	1.26
3-Chloropentyl	10.75	1.73	1.24	13.92	2.20	1.68	1.30
4-Chloropentyl	11.02	1.77	1.27	14.73	2.32	1.78	1.34
5-Chloropentyl	12.51	2.01	1.44	16.70	2.63	2.01	1.33
Hexyl	8.67	1.00	1.00	8.29	1.00	1.00	0.96
1-Chlorohexyl	11.87	1.37	1.37	13.05	1.57	1.57	1.10
2-Chlorohexyl	12.51	1.44	1.44	14.53	1.75	1.75	1.16
3-Chlorohexyl	13.05	1.51	1.51	15.46	1.86	1.86	1.18
4-Chlorohexyl	13.57	1.57	1.57	16.50	1.99	1.99	1.22
5-Chlorohexyl	13.79	1.59	1.59	16.97	2.05	2.05	1.23
6-Chlorohexyl	15.13	1.75	1.75	18.76	2.26	2.26	1.24
Heptyl	11.26	1.00	1.30	10.45	1.00	1.26	0.93
1-Chloroheptyl	14.39	1.28	1.66	15.11	1.45	1.82	1.05
2-Chloroheptyl	14.98	1.33	1.73	16.70	1.60	2.01	1.11
3-Chloroheptyl	15.45	1.37	1.78	17.42	1.67	2.10	1.13
4-Chloroheptyl	15.72	1.40	1.81	18.08	1.73	2.18	1.15
5-Chloroheptyl	16.18	1.44	1.87	18.76	1.80	2.26	1.16
6-Chloroheptyl	16.33	1.45	1.88	19.11	1.83	2.31	1.17
7-Chloroheptyl	17.55	1.56	2.02	20.78	1.99	2.51	1.18

(Continued on p. 72)

TABLE I *(continued)*

n-Alkyl acetate, CH_3–COOR, R=	*Column*						
	SE-30			*OV-351*			
	*Time (min)**	*RRT***	*RRT****	*Time (min)**	*RRT***	*RRT****	*RRT§*
Octyl	13.80	1.00	1.59	12.70	1.00	1.53	0.92
1-Chlorooctyl	16.75	1.21	1.93	17.14	1.35	2.07	1.02
2-Chlorooctyl	17.31	1.25	2.00	18.51	1.46	2.23	1.07
3-Chlorooctyl	17.74	1.29	2.05	19.32	1.52	2.33	1.09
4-Chlorooctyl	17.97	1.30	2.07	19.92	1.57	2.40	1.11
5-Chlorooctyl	18.20	1.32	2.10	20.27	1.60	2.45	1.11
6-Chlorooctyl	18.60	1.34	2.15	20.85	1.64	2.52	1.12
7-Chlorooctyl	18.66	1.35	2.15	21.10	1.66	2.55	1.13
8-Chlorooctyl	19.85	1.44	2.29	22.64	1.78	2.73	1.14

* Absolute retention times (min) measured from Fig. 1.
** Relative retention times for the parent esters taken as 1.00.
*** Relative retention time for *n*-hexyl acetate taken as 1.00.
§ Relative retention times for compounds on SE-30 taken as 1.00.

EXPERIMENTAL

Gas chromatography

GC analyses were carried out on a Perkin-Elmer Model Sigma 3 gas chromatograph with the following operating conditions: injector temperature, 250°C; flame-ionization detector temperature, 270°C; nitrogen carrier gas flow-rate, 0.9 ml/min; splitting ratio, 1:20; chart speed, 10 mm/min. The two columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.22 mm I.D.), supplied by Scientific Glass (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 50°C at 6°C/min until elution of peaks had ceased.

Samples

Aliphatic C_1–C_8 *n*-alkyl acetates, chloroacetates, dichloroacetates and trichloroacetates were prepared in our laboratory as described earlier[1,2]. The corresponding chloroalkyl esters were obtained by chlorination of the parent esters with chlorine in the liquid phase[4]. The products were identified by gas chromatography–mass spectrometry (GC–MS). The crude chlorination mixtures were used for GC analyses. The additional peaks illustrated in Figs. 1, 3, 4 and 5 are unidentified higher chlorinated isomers formed in the chlorinations.

RESULTS AND DISCUSSION

Recently, the GC separation of mixtures of aliphatic C_1–C_8 *n*-alkyl acetates and their monochlorinated derivatives on SE-30 and Carbowax 20M glass capillary

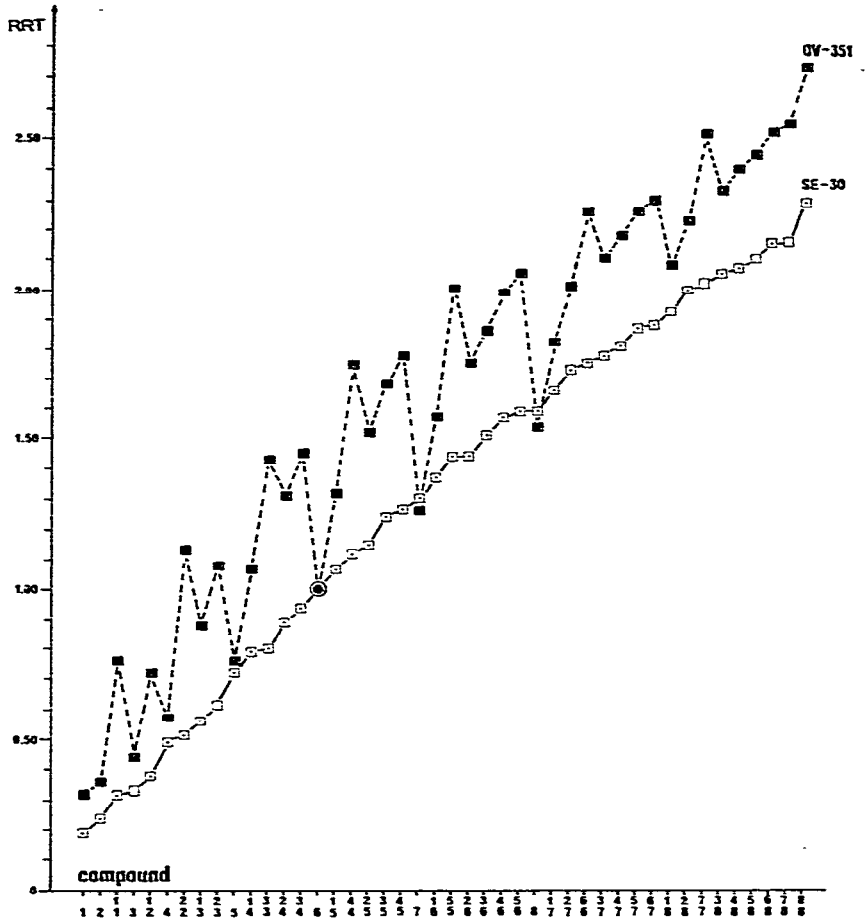

Fig. 2. Relative retention times (RRT) of aliphatic C_1–C_8 *n*-alkyl acetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. Relative retention time for *n*-hexyl acetate (6) taken as 1.00 (see Table I). Notation of compounds as in Fig. 1.

columns has been reported[1]. To compare the GC behaviour, the separation of these acetates has now been studied under the same experimental conditions with their chlorinated derivatives.

The gas chromatograms of the mixture of all C_1–C_8 *n*-alkyl acetates are illustrated in Fig. 1 for both SE-30 and OV-351 columns. Table I gives the absolute and relative retention times of the compounds. All retention times were measured from sample injection and are tabulated relative to the parent esters and relative to *n*-hexyl acetate = 1.00 (Fig. 2). The retentions are also expressed as the ratios of the retention times of the compounds on OV-351 divided by those on SE-30.

The results show that the separations of the esters are similar on a highly polar OV-351 column and, as previously reported, on Carbowax 20M[1]. Methyl and ethyl acetates are completely separated, but 2-chloroheptyl and 5-chloropentyl isomers

overlap. *n*-Pentyl and chloromethyl acetates and 5-chloroheptyl and 6-chlorohexyl isomers completely overlap, as on Carbowax 20M.

Figs. 3–5 illustrate the GC separations of the mixtures of odd- and even-carbon-number C_1–C_8 *n*-alkyl chloro-, dichloro- and trichloroacetates and their monochlorinated derivatives, respectively. However, the GC analysis of the combined mixtures of all isomeric esters resulted in several overlapping peaks, making the chromatograms complicated. Tables II–IV give the retention data for the compounds, the retention also being expressed relative to the corresponding *n*-alkyl acetates = 1.00, given in Table I. The retention times relative to *n*-hexyl esters = 1.00 are illustrated in Figs. 6–8.

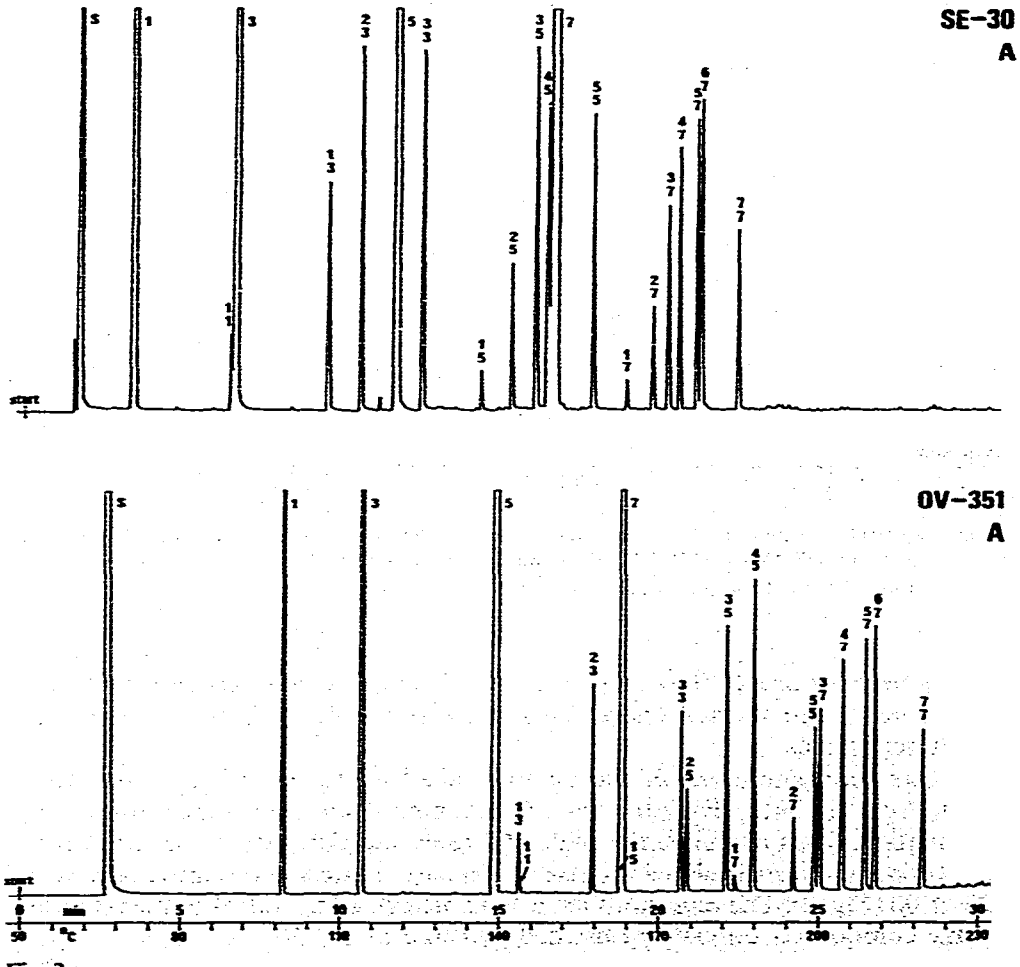

Fig. 3.

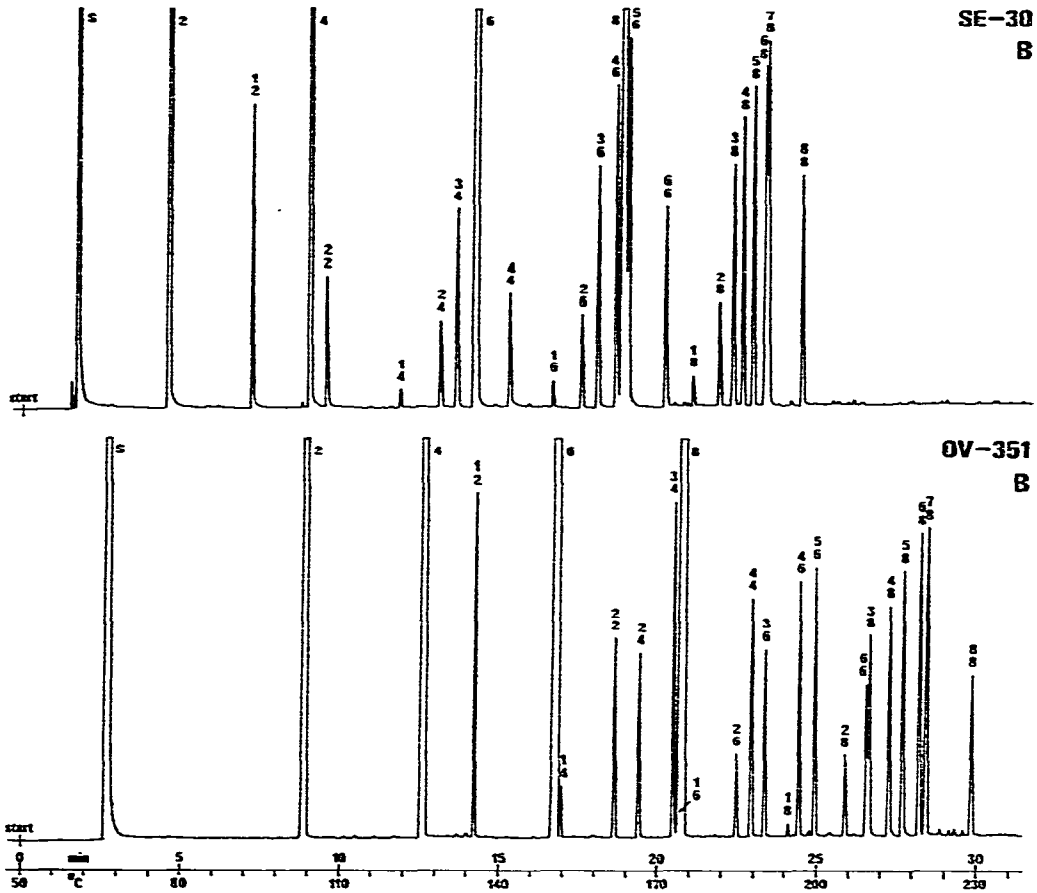

Fig. 3. Chromatograms of the mixtures of aliphatic odd- (A) and even-carbon-number (B) C_1–C_8 *n*-alkyl chloroacetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. S = solvent. Notation of compounds: 1–8 are the parent esters from methyl chloroacetate (1) to *n*-octyl chloroacetate (8); the upper number indicates the position of the Cl-substituent, the lower number the alcohol chain length (*e.g.*, $\frac{3}{6}$ denotes 3-chlorohexyl chloroacetate). The additional peaks are unidentified polychloro isomers.

Figs. 3–5 show that the separations of the mixtures are better on SE-30 than on OV-351. The isomeric monochlorinated esters are eluted in direct order from the 1-chloro to the ω-chloro compound, their separation being complete on a polar column[1]. On SE-30, however, the peaks of 6- and 7-chlorooctyl esters partly overlap. As can be seen from Fig. 3, the following chloroacetates are poorly separated on SE-30: chloromethyl and *n*-propyl, 4-chloropentyl and *n*-heptyl and *n*-octyl and 5-chlorohexyl esters. Figs. 4 and 5 show that the corresponding di- and trichloroacetates are separated from each other.

TABLE II

RELATIVE RETENTION TIMES (RRT) OF ALIPHATIC C_1-C_8 *n*-ALKYL CHLOROACETATES AND THEIR MONOCHLORINATED DERIVATIVES ANALYSED ON SE-30 AND OV-351 GLASS CAPILLARY COLUMNS

Conditions as shown in Fig. 3.

n-Alkyl chloroacetate, CH_2Cl-COOR, R =	*Column*								
	SE-30				*OV-351*				
	*Time (min)**	*RRT***	*RRT****	*RRT†*	*Time (min)**	*RRT***	*RRT****	*RRT†*	*RRT††*
Methyl	3.26	1.00	0.23	1.98	8.19	1.00	0.49	3.09	2.51
Chloromethyl	6.41	1.97	0.46	2.29	15.65	1.91	0.94	2.47	2.44
Ethyl	4.49	1.00	0.32	2.14	8.77	1.00	0.53	2.91	1.95
1-Chloroethyl	7.17	1.60	0.51	2.17	14.27	1.63	0.86	2.40	1.99
2-Chloroethyl	9.50	2.12	0.68	2.12	18.62	2.12	1.12	1.99	1.96
Propyl	6.43	1.00	0.46	2.25	10.63	1.00	0.64	2.94	1.65
1-Chloropropyl	9.46	1.47	0.67	1.94	15.65	1.47	0.94	2.15	1.65
2-Chloropropyl	10.52	1.64	0.75	1.95	17.96	1.69	1.08	2.00	1.71
3-Chloropropyl	12.40	1.93	0.88	1.78	20.73	1.95	1.25	1.75	1.67
Butyl	8.90	1.00	0.63	2.11	12.49	1.00	0.75	2.65	1.40
1-Chlorobutyl	11.84	1.33	0.84	1.74	16.94	1.36	1.02	1.91	1.43
2-Chlorobutyl	13.08	1.47	0.93	1.70	19.39	1.55	1.17	1.79	1.48
3-Chlorobutyl	13.58	1.53	0.97	1.67	20.47	1.64	1.23	1.71	1.51
4-Chlorobutyl	15.23	1.71	1.08	1.56	22.93	1.84	1.38	1.59	1.51
Pentyl	11.49	1.00	0.82	1.85	14.74	1.00	0.89	2.32	1.28
1-Chloropentyl	14.25	1.24	1.01	1.53	18.86	1.28	1.14	1.72	1.32
2-Chloropentyl	15.20	1.32	1.08	1.52	20.90	1.42	1.26	1.66	1.38
3-Chloropentyl	15.95	1.39	1.14	1.48	22.16	1.50	1.34	1.59	1.39
4-Chloropentyl	16.35	1.42	1.16	1.48	23.03	1.56	1.39	1.56	1.41
5-Chloropentyl	17.75	1.54	1.26	1.42	24.93	1.69	1.50	1.49	1.40

Hexyl	14.05	1.00	1.00	1.62	16.59	1.00	1.00	2.00	1.18
1-Chlorohexyl	16.61	1.18	1.18	1.40	20.50	1.24	1.24	1.57	1.23
2-Chlorohexyl	17.50	1.25	1.25	1.40	22.45	1.35	1.35	1.55	1.28
3-Chlorohexyl	18.01	1.28	1.28	1.38	23.34	1.41	1.41	1.51	1.30
4-Chlorohexyl	18.57	1.32	1.32	1.37	24.40	1.47	1.47	1.48	1.31
5-Chlorohexyl	18.91	1.35	1.35	1.37	24.91	1.50	1.50	1.47	1.32
6-Chlorohexyl	20.12	1.43	1.43	1.33	26.54	1.60	1.60	1.41	1.32
Heptyl	16.37	1.00	1.17	1.45	18.75	1.00	1.13	1.79	1.15
1-Chloroheptyl	18.82	1.15	1.34	1.31	22.43	1.20	1.35	1.48	1.19
2-Chloroheptyl	19.66	1.20	1.40	1.31	24.25	1.29	1.46	1.45	1.23
3-Chloroheptyl	20.12	1.23	1.43	1.30	25.08	1.34	1.51	1.44	1.25
4-Chloroheptyl	20.49	1.25	1.46	1.30	25.79	1.38	1.55	1.43	1.26
5-Chloroheptyl	21.01	1.28	1.50	1.30	26.51	1.41	1.60	1.41	1.26
6-Chloroheptyl	21.16	1.29	1.51	1.30	26.79	1.43	1.61	1.40	1.27
7-Chloroheptyl	22.31	1.36	1.59	1.27	28.30	1.51	1.71	1.36	1.27
Octyl	18.70	1.00	1.33	1.36	20.55	1.00	1.24	1.62	1.10
1-Chlorooctyl	21.00	1.12	1.49	1.25	24.09	1.17	1.45	1.41	1.15
2-Chlorooctyl	21.81	1.17	1.55	1.26	25.88	1.26	1.56	1.40	1.19
3-Chlorooctyl	22.25	1.19	1.58	1.25	26.61	1.29	1.60	1.38	1.20
4-Chlorooctyl	22.56	1.21	1.61	1.26	27.26	1.33	1.64	1.37	1.21
5-Chlorooctyl	22.89	1.22	1.63	1.26	27.70	1.35	1.67	1.37	1.21
6-Chlorooctyl	23.25	1.24	1.65	1.25	28.20	1.37	1.70	1.35	1.21
7-Chlorooctyl	23.32	1.25	1.66	1.25	28.40	1.38	1.71	1.35	1.22
8-Chlorooctyl	24.41	1.31	1.74	1.23	29.82	1.45	1.80	1.32	1.22

* Absolute retention times (min) measured from Fig. 3.

** Relative retention times for the parent esters taken as 1.00.

*** Relative retention time for *n*-hexyl chloroacetate taken as 1.00.

§ Relative retention times for the corresponding *n*-alkyl acetates (Table I) taken as 1.00.

§§ Relative retention times for compounds on SE-30 taken as 1.00.

TABLE III

RELATIVE RETENTION TIMES (RRT) OF ALIPHATIC C_1-C_8 *n*-ALKYL DICHLOROACETATES AND THEIR MONOCHLORINATED DERIVATIVES ANALYSED ON SE-30 AND OV-351 GLASS CAPILLARY COLUMNS

Conditions as shown in Fig. 4.

n-Alkyl dichloroacetate, $CHCl_2$-COOR, R=	*Column*								
	SE-30				*OV-351*				
	*Time (min)**	*RRT***	*RRT****	*RRT‡*	*Time (min)**	*RRT***	*RRT****	*RRT‡*	*RRT‡‡*
Methyl	4.49	1.00	0.29	2.72	10.22	1.00	0.57	3.86	2.28
Chloromethyl	8.06	1.80	0.51	2.88	17.29	1.69	0.96	2.73	2.15
Ethyl	5.97	1.00	0.38	2.84	10.62	1.00	0.59	3.53	1.78
1-Chloroethyl	8.65	1.45	0.55	2.62	15.42	1.45	0.85	2.60	1.78
2-Chloroethyl	11.32	1.90	0.72	2.53	20.45	1.93	1.13	2.18	1.81
Propyl	8.18	1.00	0.52	2.86	12.19	1.00	0.68	3.38	1.49
1-Chloropropyl	11.02	1.35	0.70	2.26	16.45	1.35	0.91	2.26	1.49
2-Chloropropyl	12.21	1.49	0.78	2.27	19.25	1.58	1.07	2.14	1.58
3-Chloropropyl	14.12	1.73	0.90	2.03	22.01	1.81	1.22	1.86	1.56
Butyl	10.65	1.00	0.68	2.53	14.14	1.00	0.78	3.00	1.33
1-Chlorobutyl	13.28	1.25	0.85	1.95	17.78	1.26	0.99	2.00	1.34
2-Chlorobutyl	14.67	1.38	0.94	1.91	20.70	1.46	1.15	1.91	1.41
3-Chlorobutyl	15.16	1.42	0.97	1.86	21.69	1.53	1.20	1.81	1.43
4-Chlorobutyl	16.91	1.59	1.08	1.74	24.30	1.72	1.35	1.68	1.44
Pentyl	13.21	1.00	0.84	2.13	16.01	1.00	0.89	2.53	1.21
1-Chloropentyl	15.60	1.18	1.00	1.68	19.32	1.21	1.07	1.76	1.24
2-Chloropentyl	16.72	1.27	1.07	1.67	21.93	1.37	1.22	1.74	1.31
3-Chloropentyl	17.45	1.32	1.12	1.62	23.12	1.44	1.28	1.66	1.32
4-Chloropentyl	17.89	1.35	1.14	1.62	24.15	1.51	1.34	1.64	1.35
5-Chloropentyl	19.43	1.47	1.24	1.55	26.20	1.64	1.45	1.57	1.35

Hexyl	15.65	1.00	1.00	1.81	18.04	1.00	1.00	2.18	1.15
1-Chlorohexyl	17.92	1.15	1.15	1.51	21.11	1.17	1.17	1.62	1.18
2-Chlorohexyl	18.95	1.21	1.21	1.51	23.52	1.30	1.30	1.62	1.24
3-Chlorohexyl	19.48	1.24	1.24	1.49	24.38	1.35	1.35	1.58	1.25
4-Chlorohexyl	20.12	1.29	1.29	1.48	25.59	1.42	1.42	1.55	1.27
5-Chlorohexyl	20.54	1.31	1.31	1.49	26.24	1.45	1.45	1.55	1.28
6-Chlorohexyl	21.78	1.39	1.39	1.44	27.85	1.54	1.54	1.48	1.28
Heptyl	18.00	1.00	1.15	1.60	19.88	1.00	1.10	1.90	1.10
1-Chloroheptyl	20.14	1.12	1.29	1.40	22.85	1.15	1.27	1.51	1.13
2-Chloroheptyl	21.11	1.17	1.35	1.41	25.17	1.27	1.40	1.51	1.19
3-Chloroheptyl	21.60	1.20	1.38	1.40	25.97	1.31	1.44	1.49	1.20
4-Chloroheptyl	22.04	1.22	1.41	1.40	26.79	1.35	1.49	1.48	1.22
5-Chloroheptyl	22.65	1.26	1.45	1.40	27.64	1.39	1.53	1.47	1.22
6-Chloroheptyl	22.78	1.27	1.46	1.39	27.93	1.40	1.55	1.46	1.23
7-Chloroheptyl	23.95	1.33	1.53	1.36	29.43	1.48	1.63	1.42	1.23
Octyl	20.25	1.00	1.29	1.47	21.79	1.00	1.21	1.72	1.08
1-Chlorooctyl	22.31	1.10	1.43	1.33	24.62	1.13	1.36	1.44	1.10
2-Chlorooctyl	23.21	1.15	1.48	1.34	26.81	1.23	1.49	1.45	1.15
3-Chlorooctyl	23.67	1.17	1.51	1.33	27.57	1.27	1.53	1.43	1.16
4-Chlorooctyl	24.05	1.19	1.54	1.33	28.31	1.30	1.57	1.42	1.18
5-Chlorooctyl	24.44	1.21	1.56	1.34	28.81	1.32	1.60	1.42	1.18
6-Chlorooctyl	24.79	1.22	1.58	1.33	29.35	1.35	1.63	1.41	1.18
7-Chlorooctyl	24.88	1.23	1.59	1.33	29.56	1.36	1.64	1.40	1.19
8-Chlorooctyl	25.96	1.28	1.66	1.31	30.94	1.42	1.72	1.37	1.19

* Absolute retention times (min) measured from Fig. 4.

** Relative retention times for the parent esters taken as 1.00.

*** Relative retention time for *n*-hexyl dichloroacetate taken as 1.00.

† Relative retention times for the corresponding *n*-alkyl acetates (Table I) taken as 1.00.

†† Relative retention times for compounds on SE-30 taken as 1.00.

TABLE IV

RELATIVE RETENTION TIMES (RRT) FOR ALIPHATIC C_1–C_8 *n*-ALKYL TRICHLOROACETATES AND THEIR MONOCHLORINATED DERIVATIVES ANALYSED ON SE-30 AND OV-351 GLASS CAPILLARY COLUMNS

Conditions as shown in Fig. 5.

n-Alkyl trichloroacetate, CCl_3–$COOR$, R=	*Column*								
	SE-30				*OV-351*				
	*Time**	*RRT***	*RRT****	*RRT†*	*Time**	*RRT***	*RRT****	*RRT†*	*RRT††*
Methyl	6.29	1.00	0.36	3.81	9.86	1.00	0.57	3.72	1.57
Chloromethyl	9.98	1.59	0.57	3.56	16.19	1.64	0.93	2.55	1.62
Ethyl	7.83	1.00	0.45	3.73	10.09	1.00	0.58	3.35	1.29
1-Chloroethyl	10.38	1.33	0.59	3.15	13.73	1.36	0.79	2.31	1.32
2-Chloroethyl	13.36	1.71	0.76	2.98	20.10	1.99	1.16	2.15	1.50
Propyl	10.18	1.00	0.58	3.56	11.59	1.00	0.67	3.21	1.14
1-Chloropropyl	12.70	1.25	0.73	2.61	14.79	1.28	0.85	2.03	1.16
2-Chloropropyl	14.08	1.38	0.81	2.61	18.62	1.61	1.07	2.07	1.32
3-Chloropropyl	15.98	1.57	0.91	2.30	21.40	1.85	1.23	1.81	1.34
Butyl	12.71	1.00	0.73	3.02	13.42	1.00	0.77	2.85	1.06
1-Chlorobutyl	14.94	1.18	0.85	2.19	16.03	1.19	0.92	1.81	1.07
2-Chlorobutyl	16.40	1.29	0.94	2.13	19.93	1.49	1.15	1.84	1.22
3-Chlorobutyl	16.97	1.34	0.97	2.08	21.00	1.56	1.21	1.75	1.24
4-Chlorobutyl	18.76	1.48	1.07	1.93	23.92	1.78	1.37	1.65	1.28
Pentyl	15.10	1.00	0.86	2.43	15.40	1.00	0.89	2.43	1.02
1-Chloropentyl	17.15	1.14	0.98	1.84	17.71	1.15	1.02	1.62	1.03
2-Chloropentyl	18.35	1.22	1.05	1.84	21.12	1.37	1.21	1.68	1.15
3-Chloropentyl	19.15	1.27	1.10	1.78	22.32	1.45	1.28	1.60	1.17
4-Chloropentyl	19.61	1.30	1.12	1.78	23.60	1.53	1.36	1.60	1.20
5-Chloropentyl	21.24	1.41	1.22	1.70	25.90	1.68	1.49	1.55	1.22

Hexyl	17.48	1.00	1.00	2.02	17.40	1.00	1.00	2.10	1.00
1-Chlorohexyl	19.40	1.11	1.11	1.63	19.50	1.12	1.12	1.49	1.01
2-Chlorohexyl	20.54	1.18	1.18	1.64	22.72	1.31	1.31	1.56	1.11
3-Chlorohexyl	21.11	1.21	1.21	1.62	23.62	1.36	1.36	1.53	1.12
4-Chlorohexyl	21.80	1.25	1.25	1.61	25.06	1.44	1.44	1.52	1.15
5-Chlorohexyl	22.21	1.27	1.27	1.61	25.85	1.49	1.49	1.52	1.16
6-Chlorohexyl	23.47	1.34	1.34	1.55	27.59	1.59	1.59	1.47	1.18
Heptyl	19.70	1.00	1.13	1.75	19.35	1.00	1.11	1.85	0.98
1-Chloroheptyl	21.55	1.09	1.23	1.50	21.32	1.10	1.23	1.41	0.99
2-Chloroheptyl	22.60	1.15	1.29	1.51	24.38	1.26	1.40	1.46	1.08
3-Chloroheptyl	23.13	1.17	1.32	1.50	25.21	1.30	1.45	1.45	1.09
4-Chloroheptyl	23.60	1.20	1.35	1.50	26.29	1.36	1.51	1.45	1.11
5-Chloroheptyl	24.24	1.23	1.39	1.50	27.31	1.41	1.57	1.46	1.13
6-Chloroheptyl	24.39	1.24	1.40	1.49	27.61	1.43	1.59	1.44	1.13
7-Chloroheptyl	25.52	1.30	1.46	1.45	29.19	1.51	1.68	1.40	1.14
Octyl	21.91	1.00	1.25	1.59	21.27	1.00	1.22	1.67	0.97
1-Chlorooctyl	23.61	1.08	1.35	1.41	23.20	1.09	1.33	1.35	0.98
2-Chlorooctyl	24.62	1.12	1.41	1.42	26.06	1.23	1.50	1.41	1.06
3-Chlorooctyl	25.09	1.15	1.44	1.41	26.85	1.26	1.54	1.39	1.07
4-Chlorooctyl	25.50	1.16	1.46	1.42	27.83	1.31	1.60	1.40	1.09
5-Chlorooctyl	25.95	1.18	1.48	1.43	28.53	1.34	1.64	1.41	1.10
6-Chlorooctyl	26.30	1.20	1.50	1.41	29.08	1.37	1.67	1.39	1.11
7-Chlorooctyl	26.39	1.20	1.51	1.41	29.30	1.38	1.68	1.39	1.11
8-Chlorooctyl	27.49	1.25	1.57	1.38	30.80	1.45	1.77	1.36	1.12

* Absolute retention times (min) measured from Fig. 5.
** Relative retention times for the parent esters taken as 1.00.
*** Relative retention time for *n*-hexyl trichloroacetate taken as 1.00.
† Relative retention times for the corresponding *n*-alkyl acetates (Table I) taken as 1.00.
†† Relative retention times for compounds on SE-30 taken as 1.00.

The use of a highly polar OV-351 column resulted in more overlapping peaks, particularly with the chloroacetates (Fig. 3), chloromethyl and 1-chloropropyl, *n*-heptyl and 1-chloropentyl and 3-chlorobutyl and 1-chlorohexyl esters being completely overlapped. Also, a poor separation of 6-chlorohexyl and 3-chlorooctyl chloroacetates is observed. As can be seen from Figs. 4 and 5, however, 1-chloroalkyl di- and trichloroacetates are separated better owing to their relatively short retention times in comparison with the other isomers.

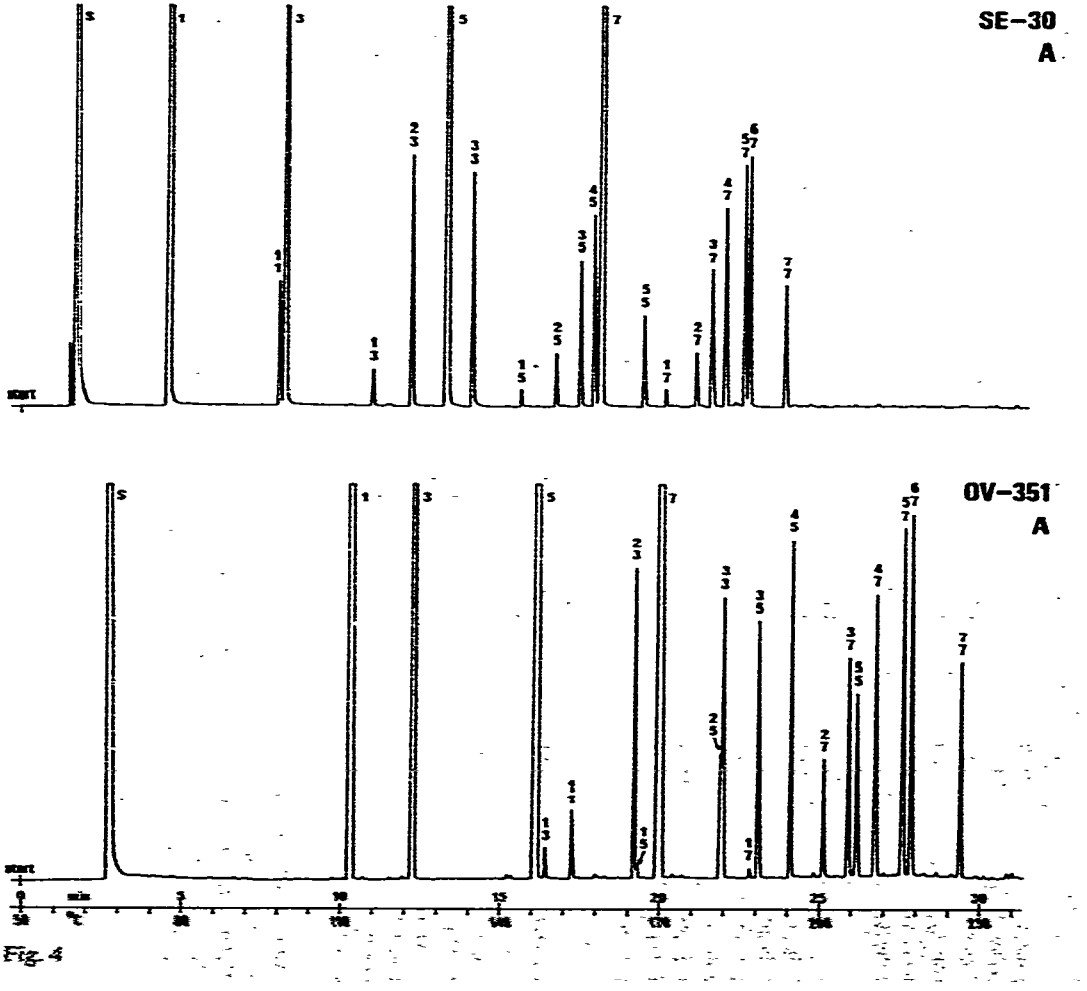

Fig. 4

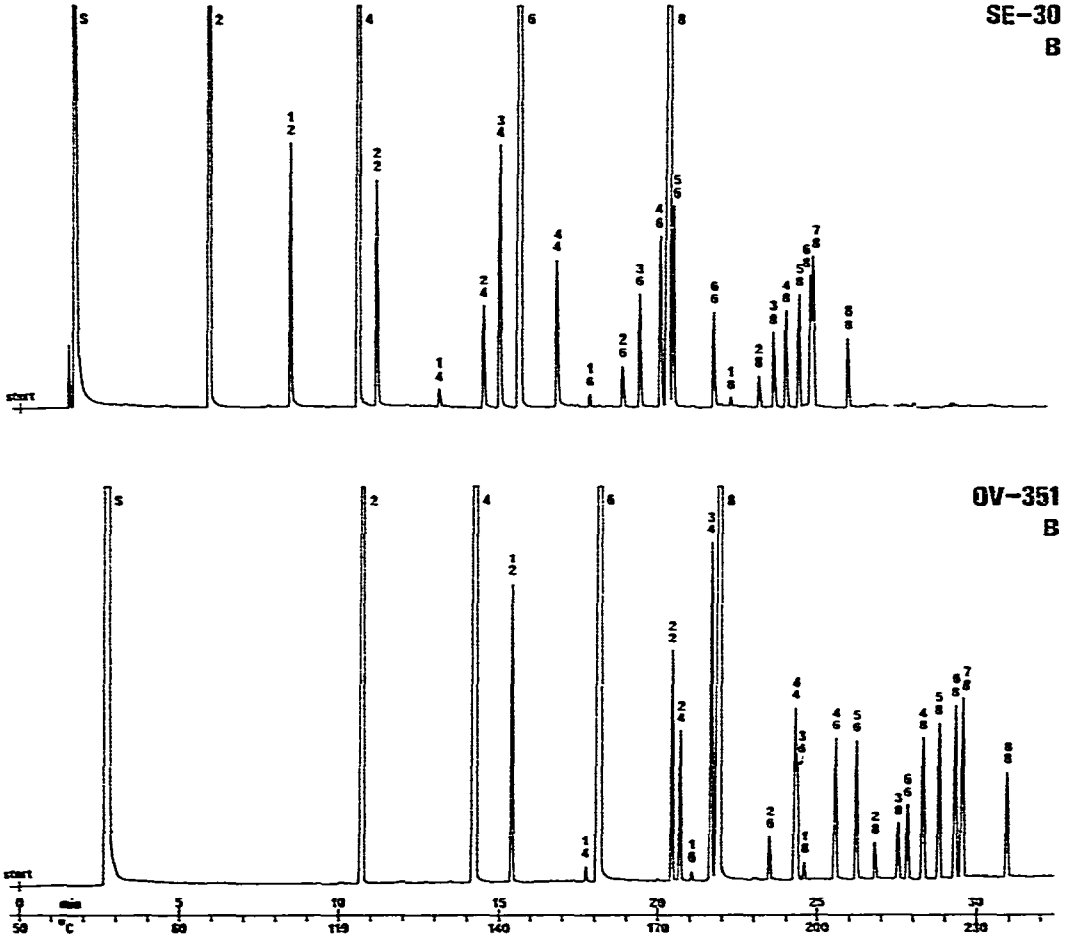

Fig. 4. Chromatograms of the mixtures of aliphatic odd- (A) and even-carbon-number (B) C_1–C_8 *n*-alkyl dichloroacetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. S = solvent. Notation of compounds: 1–8 are the parent esters from methyl dichloroacetate (1) to *n*-octyl dichloroacetate (8); the upper number indicates the position of the Cl-substituent, the lower number the alcohol chain length (*e.g.*, $\frac{3}{6}$ denotes 3-chlorohexyl dichloroacetate). The additional peaks are unidentified polychloro isomers.

Tables II–IV show that the chloroacetates are always eluted on SE-30 in the order mono-, di- and trichloro esters. On a polar OV-351 column the elution order is generally mono-, tri- and dichloro esters. With the 1-chloroalkyl esters, except for the chloromethyl isomers, however, trichloroacetates are eluted before monochloro isomers.

The last column of Tables I–IV shows that the retention times of the compounds are generally longer on OV-351 than on SE-30. As can be seen from Figs. 2, 6, 7 and 8, relatively short retention times for the parent esters on a polar column are observed, giving rise to lower values for *n*-hexyl, *n*-heptyl and *n*-octyl acetates (Table I). As with chlorinated chloromethyl esters[5,6], the chlorine substituent at a carbon

atom adjacent (*i.e.* at C-1) to the ether oxygen has a stronger effect on the polarity of the compound than a substituent further away. This leads to relatively short retention times of the 1-chloro isomers on a polar column, 1-chloroheptyl and 1-chlorooctyl trichloroacetates being eluted on OV-351 before than on SE-30 (Table IV).

The ω-chloroalkyl esters have longer retention times on a polar column than the other isomers, as have also the ω-chloromethyl[7] and chloromethyl esters[5]. The values for the ω-chloroalkyl acetates (relative to the parent esters = 1.00) varied on OV-351 between 3.28 and 1.78 and on SE-30 between 2.43 and 1.44 (Table I), *n*-propyl acetate giving the highest and *n*-octyl acetate the lowest value. Tables II–IV show that the lower relative retention times for the ω-chloro isomers of chlorinated acetic acids are observed. On OV-351 the values vary from 2.12 to 1.45 for mono-,

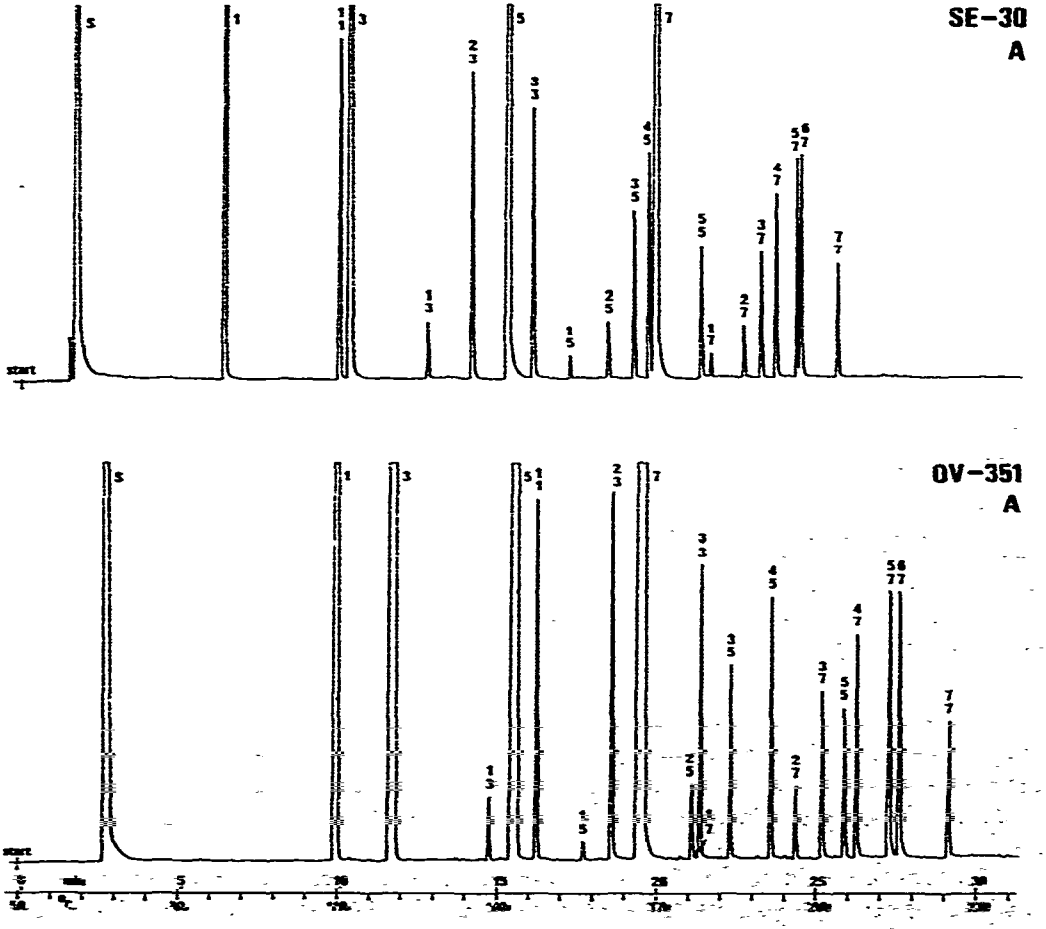

Fig. 5

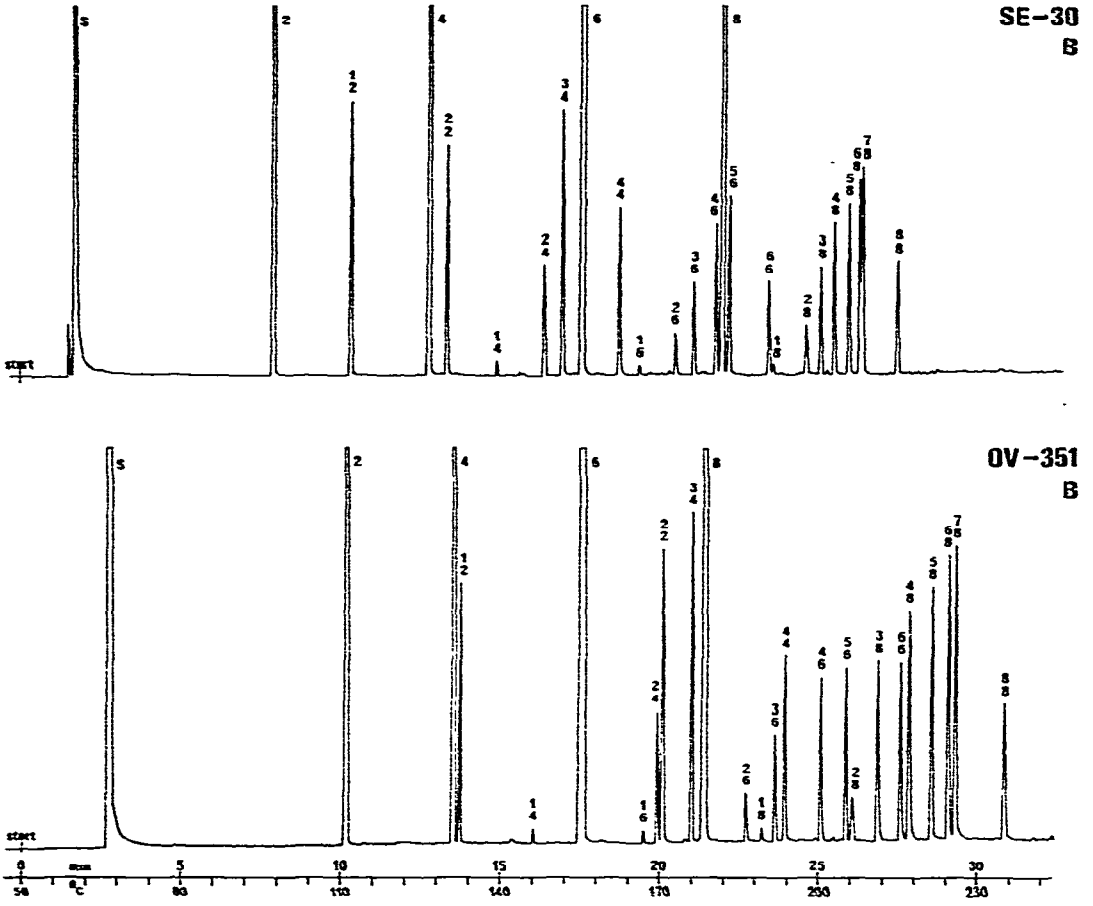

Fig. 5. Chromatograms of the mixtures of aliphatic odd- (A) and even-carbon-number (B) C_1–C_8 *n*-alkyl trichloroacetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. S = solvent. Notation of compounds: 1–8 are the parent esters from methyl trichloroacetate (1) to *n*-octyl trichloroacetate (8); the upper number indicates the position of the Cl-substituent, the lower number the alcohol chain length (*e.g.*, $\frac{3}{6}$ denotes 3-chlorohexyl trichloroacetate). The additional peaks are unidentified polychloro isomers.

from 1.93 to 1.42 for di- and from 1.99 to 1.45 for trichloroacetates. The corresponding values on SE-30 are 2.12–1.31, 1.90–1.28 and 1.71–1.25, respectively. The highest relative retention times for the ω-chloroethyl and the lowest values for the ω-chlorooctyl esters are observed under the operating conditions used.

As can be seen from Figs. 1–8, different elution orders of the esters are observed on OV-351 and on SE-30. By separating the mixtures of closely related compounds, the order of elution on a non-polar column is largely determined by the

TABLE V

ELUTION ORDER OF ALIPHATIC C_1–C_8 *n*-ALKYL ACETATES, CHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES AND THEIR MONOCHLORINATED DERIVATIVES ON SE-30 AND OV-351 GLASS CAPILLARY COLUMNS

Compound R = *n*-C_1–C_8 *and n*-C_1(Cl)–C_8(Cl)	*Column*	*Elution order of compounds**
CH_3–COOR	SE-30	1 2 1 3 2 4 1 1 2 3 3 4 1 2 2 4 3 5 1 3 2 3 4 5 4 6 1 4 2 3 4 5 5 6 1 5 + 2 3 4 5 6 6 6 6 8 1 2 6 7 7 6 3 4 5 6 7 7 7 7 8 1 2 7 3 4 5 6 7 8 8 8 7 8 8 8 8 8
CH_2Cl–COOR		1 2 1 3 2 4 1 1 3 2 3 4 1 2 2 3 4 5 1 3 2 3 4 4 6 1 2 4 3 4 5 5 4 5 5 7 6 6 1 2 5 3 4 5 6 6 8 7 1 5 2 6 + 6 7 6 3 4 1 5 7 7 8 7 6 2 3 7 4 5 6 7 8 7 8 8 7 8 8 8 8
$CHCl_2$–COOR		1 2 1 3 2 4 1 1 3 2 3 4 1 2 2 4 3 5 1 3 2 3 1 4 5 6 2 4 3 4 1 5 4 5 5 6 2 5 3 4 1 6 7 6 5 2 3 6 4 1 5 7 7 8 6 2 3 7 4 5 6 7 8 7 8 8 7 8 8 8 8
CCl_3–COOR		1 2 1 3 2 3 4 1 1 2 3 4 5 2 2 3 4 5 1 3 2 3 1 4 5 6 2 4 3 1 4 5 4 5 6 2 3 5 1 4 6 5 7 6 5 2 3 6 4 1 5 6 7 7 6 2 3 4 7 5 6 7 8 7 8 8 8 7 8 8 8 8
CH_3–COOR	OV-351	1 2 3 4 2 5 + 1 1 1 3 6 4 3 2 7 4 5 1 2 2 3 4 5 8 2 1 3 3 2 6 5 4 6 1 3 4 2 5 7 6 6 7 4 1 3 4 2 + 5 6 8 5 5 1 7 7 8 7 3 4 2 5 + 6 7 8 6 6 3 4 5 7 6 7 8 8 8 7 8 8 8
CH_2Cl–COOR		1 2 3 4 2 5 1 + 1 3 6 4 3 2 7 5 1 2 2 4 4 6 1 2 3 1 8 3 2 3 5 7 1 2 6 4 4 6 8 3 1 2 5 5 7 6 4 5 6 8 7 4 5 5 6 6 5 3 4 2 5 7 7 8 7 6 3 6 4 5 6 7 7 8 6 8 7 8 8 8 7 8 8
$CHCl_2$–COOR		1 2 3 4 2 5 1 1 3 1 4 6 1 1 3 5 2 7 1 2 2 4 6 1 3 2 4 6 8 3 2 3 5 7 1 3 2 5 6 4 4 6 8 7 4 3 5 6 7 5 5 4 2 3 6 7 8 8 5 6 6 4 5 6 7 7 8 7 6 7 8 8 8 7 8 8
CCl_3–COOR		1 2 3 4 2 3 5 1 1 4 1 6 1 1 5 3 7 2 1 2 2 4 6 4 2 3 2 4 5 8 1 3 3 2 7 3 5 6 1 4 3 4 2 8 5 6 4 7 4 3 5 6 7 6 5 2 4 3 5 8 7 6 7 8 8 8 7 8 8

* Notation of compounds: 1–8 are the parent esters from the methyl ester (1) to the *n*-octyl ester (8); the upper number indicates the position of the Cl-substituent, the lower number the alcohol chain length.

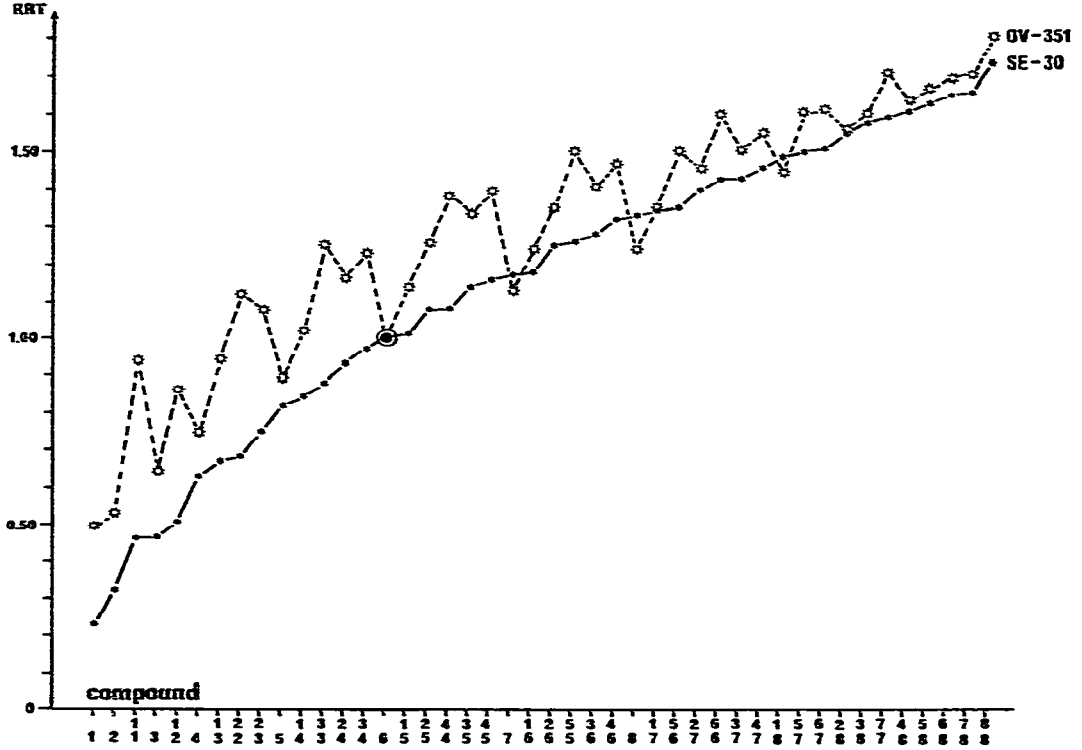

Fig. 6. Relative retention times (RRT) of aliphatic C_1–C_8 *n*-alkyl chloroacetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. Relative retention time for *n*-hexyl chloroacetate (6) taken as 1.00 (see Table II). Notation of compounds as in Fig. 3.

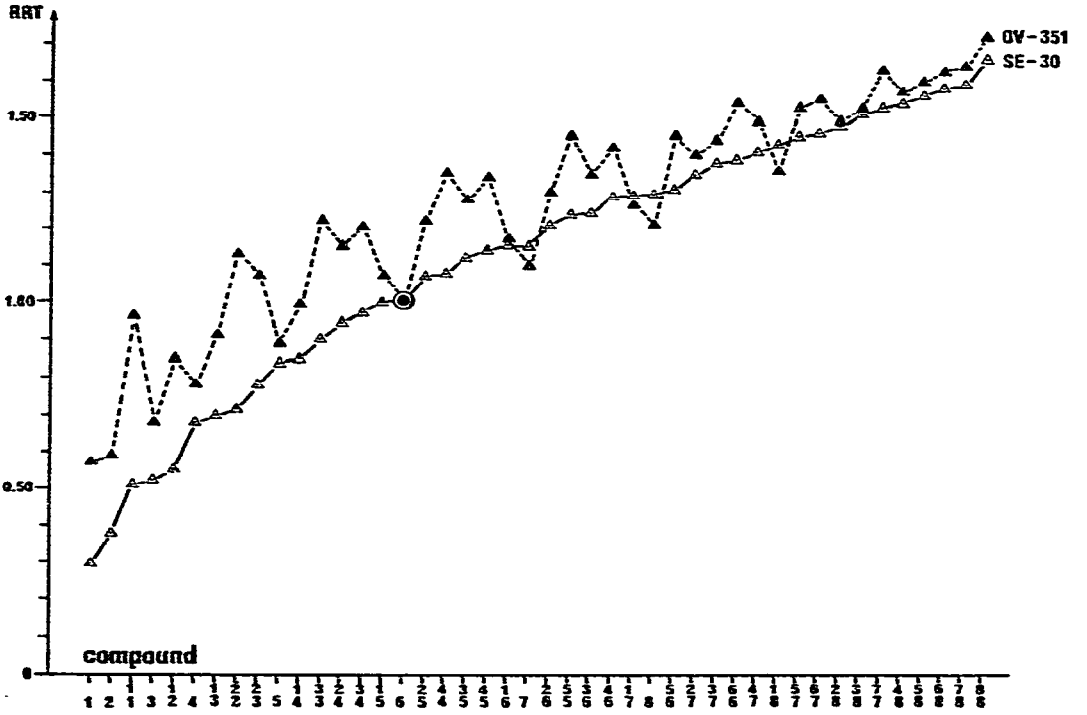

Fig. 7. Relative retention times (RRT) of aliphatic C_1–C_8 *n*-alkyl dichloroacetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. Relative retention time for *n*-hexyl dichloroacetate (6) taken as 1.00 (see Table III). Notation of compounds as in Fig. 4.

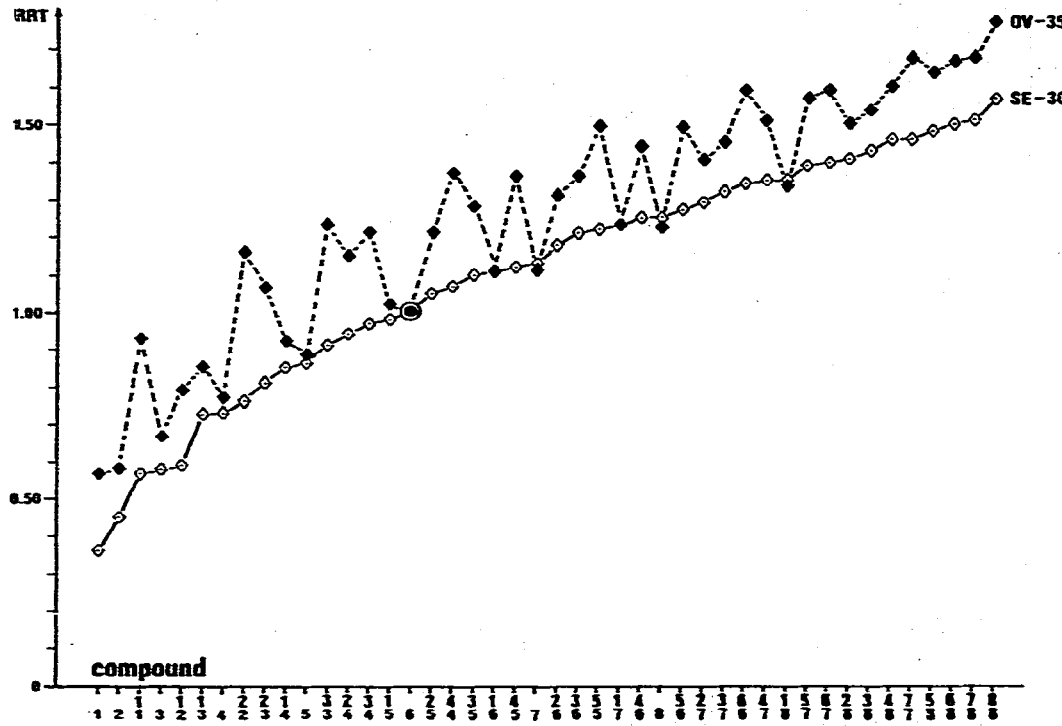

Fig. 8. Relative retention times (RRT) of aliphatic C_1–C_8 *n*-alkyl trichloroacetates and their monochlorinated derivatives, analysed on SE-30 and OV-351 glass capillary columns. Relative retention time for *n*-hexyl trichloroacetate (6) taken as 1.00 (see Table IV). Notation of compounds as in Fig. 5.

boiling point of the compounds. On a polar column, however, the order in which the compounds appear is greatly influenced by their structure[6]. Table V gives the retention order of the compounds. It can be seen that with increasing degree of chlorination 1-chloro and ω-chloro isomers give rise to the greatest difference in elution orders, the former being eluted before and the latter after the other isomers. As expected, this tendency is stronger on OV-351 than on SE-30, particularly with the less polar 1-chloroalkyl trichloroacetates. The decrease in the polarity of the 2- and 3-chloro isomers on increasing the degree of chlorination seems to be smaller.

ACKNOWLEDGEMENT

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REFERENCES

1 I. O. O. Korhonen, *J. Chromatogr.*, 246 (1982) 241.
2 I. O. O. Korhonen, *Chromatographia*, in press.
3 I. O. O. Korhonen, *Chromatographia*, 15 (1982) in press.
4 I. O. O. Korhonen and J. N. J. Korvola, *Acta Chem. Scand. Ser. B*, 35 (1981) 139.
5 I. O. O. Korhonen, *J. Chromatogr.*, 219 (1981) 306.
6 I. O. O. Korhonen, *J. Chromatogr.*, 240 (1982) 377.
7 I. O. O. Korhonen, *J. Chromatogr.*, 211 (1981) 267.