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GAS-LIQUID CHROMATOGRAPHIC ANALYSES

XXXVI*. SEPARATION OF 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 WITH TEMPERATURE PROGRAMMING

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SUMMARY

The gas chromatographic separation of a mixture of ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of C₂-C₂₀ *n*-alkanoic acids on low-polarity (SE-30) and polar (OV-351) quartz capillary columns with temperature programming was investigated. The retention data for all 76 individual components are given and their elution order on both columns is discussed, together with the effect of chlorine substitution.

INTRODUCTION

The gas chromatography (GC) of homologous series of halogenated esters with substitution in either the alcohol or the acid moiety of the ester on several low-polarity and polar packed and capillary columns has been studied mainly by Haken and Korhonen¹, Komárek *et al.*² and Korhonen and Lind³. The retention behaviour of the following haloalkyl esters has been reported: chloromethyl esters of C₂-C₂₀⁴ and C₃-C₁₂^{5,6} *n*-alkanoic acids and aliphatic C₅ carboxylic acids⁷, 2-chloroethyl^{2,8,9}, 2-bromoethyl^{8,9}, 2-iodoethyl⁸ and 2,2,2-trichloroethyl^{2,8} esters of lower carboxylic acids and 3-chloropropyl, 2,3-dichloropropyl and 1,3-dichloroisopropyl esters of *n*-C₂-C₁₀ and *iso*-C₄-C₆ alkanolic acids¹⁰.

In order to overcome difficulties in the GC determination of free carboxylic acids, they are generally determined as more volatile derivatives¹¹. To increase the sensitivity of the method several halogenated derivatives, *e.g.*, 2-chloroethyl¹² and 2,2,2-trichloroethyl^{13,14} esters, particularly with an electron-capture detection (ECD), have been used.

This paper describes the GC of ethyl, 2-chloroethyl, 2,2-dichloroethyl and 2,2,2-trichloroethyl esters of aliphatic C₂-C₂₀ *n*-alkanoic acids. A model mixture of

* For Part XXXV, see ref. 3.

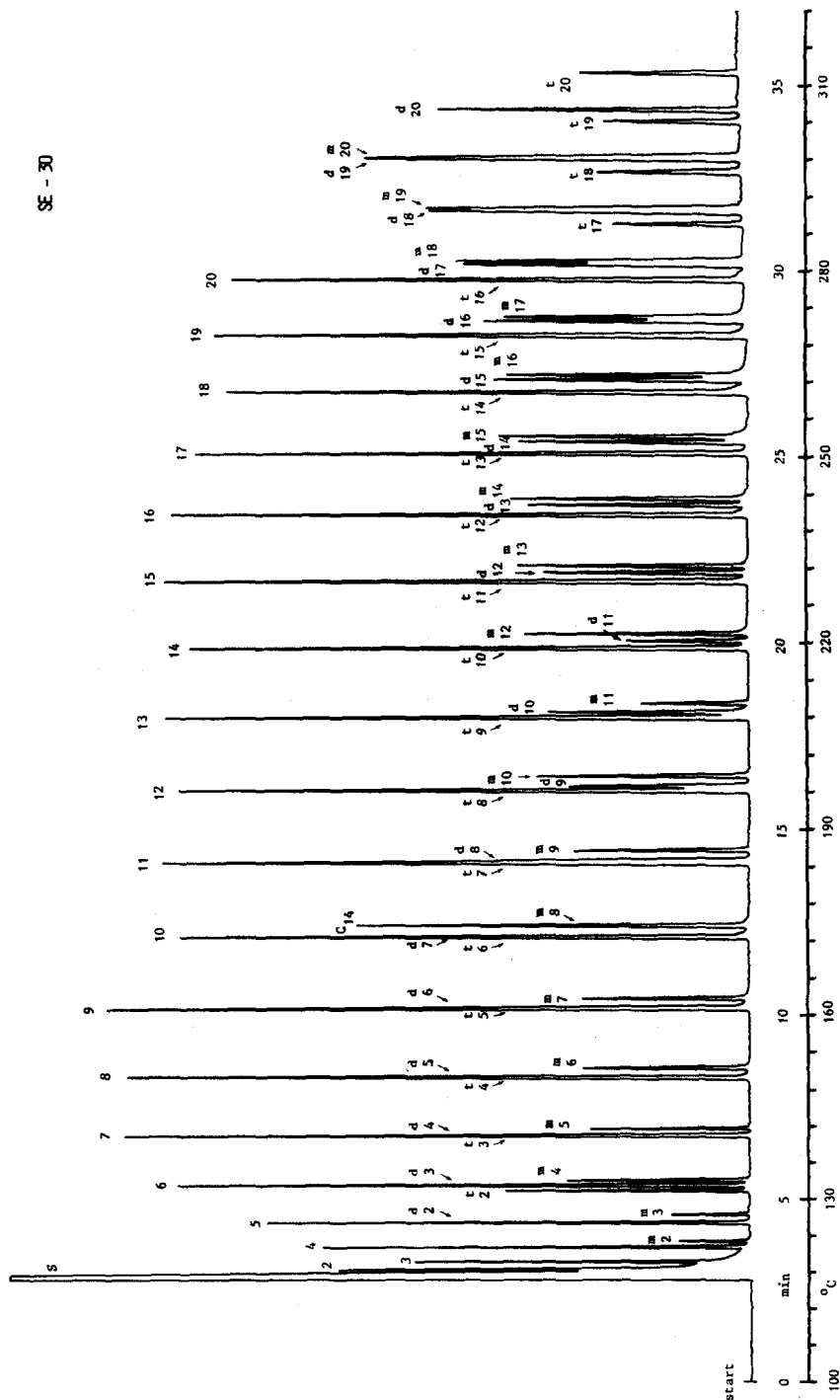


Fig. 1. Chromatogram of a mixture of ethyl (2-20), 2-chloroethyl (m/2-m/20), 2,2-dichloroethyl (d/2-d/20) and 2,2,2-trichloroethyl (t/2-t/20) esters of C_2 - C_{20} *n*-alkanoic acids, separated on an SE-30 quartz capillary column with temperature programming from 100 to 320°C at 6°C min⁻¹. S = Solvent; C_{14} = *n*-tetradecane; peaks are identified in Table I.

all 76 components was separated on low-polarity (SE-30) and polar (OV-351) quartz capillary columns with temperature programming. The retention data for all compounds are given and the retention behaviour on both columns is discussed, together with the effect of chlorine substitution.

EXPERIMENTAL

Materials

Ethyl (2-20), 2-monochloroethyl (m/2-m/20), 2,2-dichloroethyl (d/2-d/20) and 2,2,2-trichloroethyl (t/2-t/20) esters of C_2 - C_{20} *n*-alkanoic acids were prepared by the usual sulphuric acid-catalysed esterification of commercial acids (Fluka, Buchs, Switzerland) or from *n*-alkanols and acid chlorides, obtained by the reaction of redistilled thionyl chloride (Fluka) with acids. Ethanol (Oy Alko, Finland) and 2-chloroethanol (Fluka) were commercial products, the latter being used after redistillation; commercial dichloroacetic acid (Fluka) and trichloroacetyl chloride (Merck-Schuchardt, Darmstadt, F.R.G.) were converted with $LiAlH_4$ into 2,2-dichloroethanol and 2,2,2-trichloroethanol as described earlier¹⁵. *n*-Tetradecane used as a reference component was obtained from Fluka.

The model mixtures of the esters analysed contained suitable amounts of the individual components for the sensitivity of the flame-ionization detection used, *i.e.*, the amounts increase with increasing chain length and degree of chlorination.

Methods

GC separations 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, 15 and 50 cm sec⁻¹, respectively; splitting ratio, 1:25; 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 to 320°C (SE-30) and from 100 to 230°C (OV-351) at 6°C min⁻¹ and held on OV-351 at the final temperature until elution of peaks had ceased.

The retention times were measured from the time of sample injection; a Hewlett-Packard Model 3390A reporting integrator was used.

RESULTS AND DISCUSSION

Separations of a complex mixture of four series of esters on SE-30 and OV-351 are shown in Figs. 1 and 2, respectively. The corresponding retention data for the components are given in Table I, showing the absolute and relative retention times, relative (= 1.00) to *n*-tetradecane (C_{14}), relative to the decanoic acid esters 10, m/10, d/10 and t/10, relative to the parent esters 2-20 and relative to the corresponding compounds on SE-30. Fig. 3 shows the retention plots of the chloro esters on both columns, relative to the corresponding ethyl esters.

The alkanols and their esters are eluted from the low-polarity SE-30 column

OV - 351

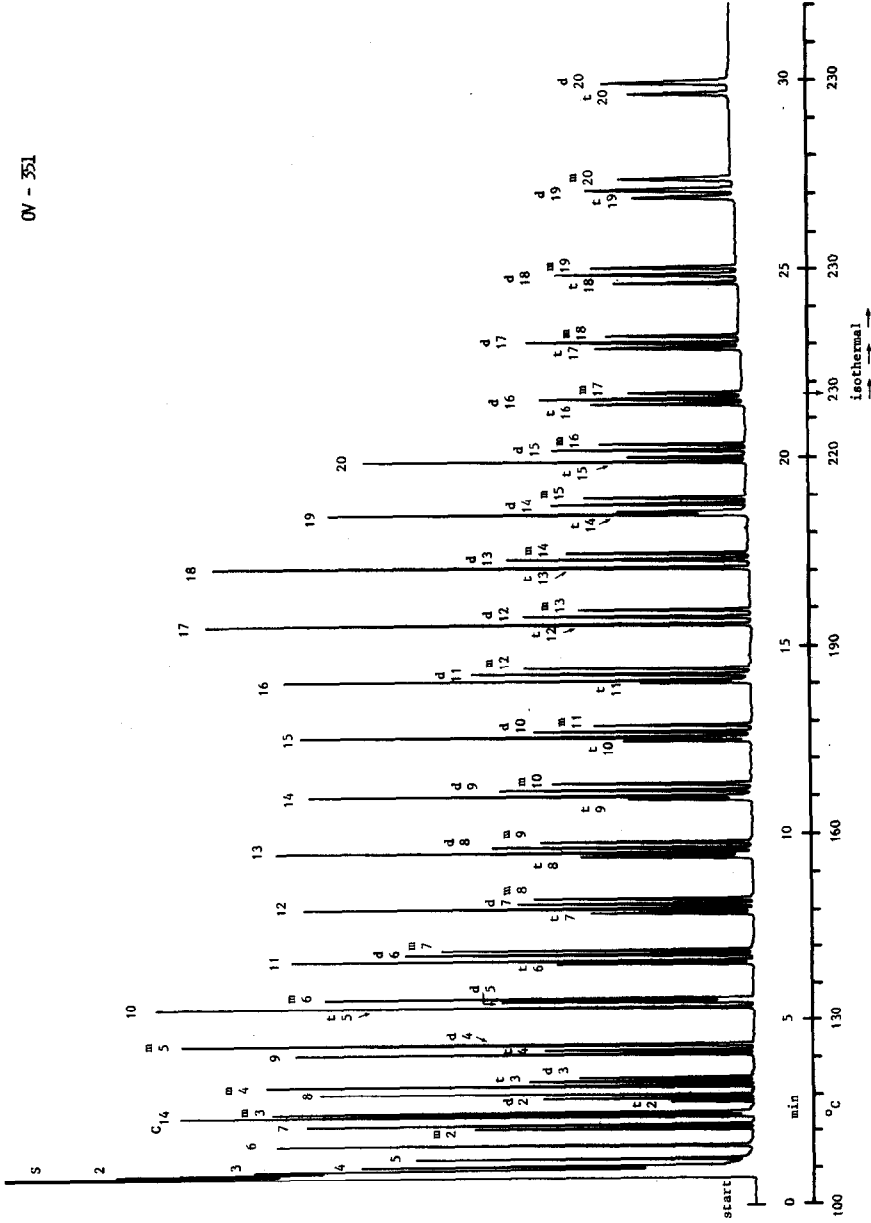


Fig. 2. Chromatogram of the same mixture as in Fig. 1, separated on an OV-351 quartz capillary column with temperature programming from 100 to 230°C at 6°C min⁻¹ and held at the final temperature until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane; peaks are identified in Table I.

TABLE I
RETENTION DATA FOR ETHYL, 2-CHLOROETHYL, 2,2-DICHLOROETHYL AND 2,2,2-TRICHLOROETHYL ESTERS OF C₂-C₂₀ n-ALKANOIC ACIDS, OBTAINED ON SE-30 AND OV-351 QUARTZ CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING
Conditions as in Figs. 1 and 2.

Peak No.	Chain length of ester of n-acid	SE-30 column				OV-351 column				
		ART*	RRT**	RRT***	RRT [§]	ART*	RRT**	RRT***	RRT [§]	
Ethyl ester:										
2	C ₂	3.08	0.25	0.25	1.00	0.90	0.36	0.17	1.00	0.29
3	C ₃	3.32	0.27	0.27	1.00	0.96	0.38	0.18	1.00	0.29
4	C ₄	3.69	0.30	0.30	1.00	1.09	0.44	0.20	1.00	0.30
5	C ₅	4.36	0.35	0.36	1.00	1.30	0.52	0.24	1.00	0.30
6	C ₆	5.39	0.43	0.44	1.00	1.65	0.66	0.31	1.00	0.31
7	C ₇	6.71	0.54	0.55	1.00	2.10	0.84	0.39	1.00	0.31
8	C ₈	8.40	0.68	0.69	1.00	3.02	1.21	0.56	1.00	0.36
9	C ₉	10.20	0.82	0.84	1.00	4.11	1.64	0.76	1.00	0.40
10	C ₁₀	12.14	0.98	1.00	1.00	5.39	2.16	1.00	1.00	0.44
11	C ₁₁	14.13	1.14	1.16	1.00	6.65	2.66	1.23	1.00	0.47
12	C ₁₂	16.09	1.30	1.33	1.00	8.07	3.23	1.50	1.00	0.50
13	C ₁₃	18.03	1.45	1.49	1.00	9.54	3.82	1.77	1.00	0.53
14	C ₁₄	19.89	1.60	1.64	1.00	11.07	4.43	2.05	1.00	0.56
15	C ₁₅	21.66	1.74	1.78	1.00	12.64	5.06	2.35	1.00	0.58
16	C ₁₆	23.44	1.89	1.93	1.00	14.12	5.65	2.62	1.00	0.60
17	C ₁₇	25.11	2.02	2.07	1.00	15.65	6.26	2.90	1.00	0.62
18	C ₁₈	26.72	2.15	2.20	1.00	17.13	6.85	3.18	1.00	0.64
19	C ₁₉	28.25	2.27	2.33	1.00	18.55	7.42	3.44	1.00	0.66
20	C ₂₀	29.74	2.39	2.45	1.00	19.97	7.99	3.71	1.00	0.67

(Continued on p. 102)

TABLE I (continued)

Peak No.	Chain length of ester of <i>n</i> -acid	SE-30 column				OV-351 column				
		ART*	RRT**	RRT***	RRT [†]	ART*	RRT**	RRT***	RRT [†]	
2-Chloroethyl ester:										
m/2	C ₂	3.89	0.31	0.24	1.26	2.09	0.84	0.18	2.32	0.54
m/3	C ₃	4.58	0.37	0.28	1.38	2.58	1.03	0.23	2.69	0.56
m/4	C ₄	5.51	0.44	0.33	1.49	3.29	1.32	0.29	3.02	0.60
m/5	C ₅	6.93	0.56	0.42	1.59	4.40	1.76	0.39	3.38	0.63
m/6	C ₆	8.61	0.69	0.52	1.60	5.62	2.25	0.49	3.41	0.65
m/7	C ₇	10.47	0.84	0.64	1.56	6.92	2.77	0.61	3.30	0.66
m/8	C ₈	12.45	1.00	0.76	1.48	8.35	3.34	0.73	2.76	0.67
m/9	C ₉	14.49	1.17	0.88	1.42	9.84	3.94	0.86	2.39	0.68
m/10	C ₁₀	16.46	1.33	1.00	1.36	11.39	4.56	1.00	2.11	0.69
m/11	C ₁₁	18.42	1.48	1.12	1.30	12.97	5.19	1.14	1.95	0.70
m/12	C ₁₂	20.29	1.63	1.23	1.26	14.50	5.80	1.27	1.80	0.71
m/13	C ₁₃	22.10	1.78	1.34	1.23	16.01	6.40	1.41	1.68	0.72
m/14	C ₁₄	23.91	1.93	1.45	1.20	17.51	7.00	1.54	1.58	0.73
m/15	C ₁₅	25.55	2.06	1.55	1.18	18.98	7.59	1.67	1.50	0.74
m/16	C ₁₆	27.19	2.19	1.65	1.16	20.40	8.16	1.79	1.44	0.75
m/17	C ₁₇	28.72	2.31	1.74	1.14	21.77	8.71	1.91	1.39	0.76
m/18	C ₁₈	30.21	2.43	1.84	1.13	23.30	9.32	2.05	1.36	0.77
m/19	C ₁₉	31.67	2.55	1.92	1.12	25.12	10.05	2.21	1.35	0.79
m/20	C ₂₀	33.04	2.66	2.01	1.11	27.49	11.00	2.41	1.38	0.83
2,2-Dichloroethyl ester:										
d/2	C ₂	4.40	0.35	0.24	1.43	2.90	1.16	0.23	3.22	0.66
d/3	C ₃	5.43	0.44	0.36	1.64	3.50	1.40	0.27	3.65	0.64
d/4	C ₄	6.74	0.54	0.37	1.83	4.40	1.76	0.34	4.04	0.65
d/5	C ₅	8.44	0.68	0.46	1.94	5.57	2.23	0.44	4.28	0.66
d/6	C ₆	10.22	0.82	0.56	1.90	6.81	2.72	0.53	4.13	0.67
d/7	C ₇	12.19	0.98	0.67	1.82	8.21	3.28	0.64	3.91	0.67
d/8	C ₈	14.19	1.14	0.78	1.69	9.69	3.88	0.76	3.21	0.68
d/9	C ₉	16.22	1.31	0.89	1.59	11.22	4.49	0.88	2.73	0.69
d/10	C ₁₀	18.19	1.46	1.00	1.50	12.79	5.12	1.00	2.37	0.70

d/11	C ₁₁	20.10	1.62	1.11	1.42	14.32	5.73	1.12	2.15	0.71
d/12	C ₁₂	21.91	1.76	1.20	1.36	15.86	6.34	1.24	1.97	0.72
d/13	C ₁₃	23.74	1.91	1.31	1.32	17.35	6.94	1.36	1.82	0.73
d/14	C ₁₄	25.41	2.05	1.40	1.28	18.82	7.53	1.47	1.70	0.74
d/15	C ₁₅	27.05	2.18	1.49	1.25	20.26	8.10	1.58	1.60	0.75
d/16	C ₁₆	28.62	2.30	1.57	1.22	21.62	8.65	1.69	1.53	0.76
d/17	C ₁₇	30.12	2.43	1.66	1.20	23.13	9.25	1.81	1.48	0.77
d/18	C ₁₈	31.59	2.54	1.74	1.18	24.92	9.97	1.95	1.45	0.79
d/19	C ₁₉	32.96	2.65	1.81	1.17	27.19	10.88	2.13	1.47	0.82
d/20	C ₂₀	34.29	2.76	1.89	1.15	30.03	12.01	2.35	1.50	0.88
2,2,2-Trichloro-										
roethyl ester:										
t/2	C ₂	5.20	0.42	0.26	1.69	2.82	1.13	0.22	3.13	0.54
t/3	C ₃	6.69	0.54	0.34	2.02	3.39	1.36	0.27	3.53	0.51
t/4	C ₄	8.31	0.67	0.42	2.25	4.23	1.69	0.34	3.88	0.51
t/5	C ₅	10.16	0.82	0.51	2.33	5.39	2.16	0.43	4.15	0.53
t/6	C ₆	12.10	0.97	0.61	2.24	6.58	2.63	0.52	3.99	0.54
t/7	C ₇	14.11	1.14	0.71	2.10	7.96	3.18	0.63	3.79	0.56
t/8	C ₈	16.05	1.29	0.81	1.91	9.44	3.78	0.75	3.13	0.59
t/9	C ₉	17.99	1.45	0.91	1.76	10.97	4.39	0.87	2.67	0.61
t/10	C ₁₀	19.83	1.60	1.00	1.63	12.54	5.02	1.00	2.33	0.63
t/11	C ₁₁	21.62	1.74	1.09	1.53	14.09	5.64	1.12	2.12	0.65
t/12	C ₁₂	23.41	1.88	1.18	1.45	15.64	6.26	1.25	1.94	0.67
t/13	C ₁₃	25.06	2.02	1.26	1.39	17.14	6.86	1.37	1.80	0.68
t/14	C ₁₄	26.70	2.15	1.35	1.34	18.62	7.45	1.48	1.68	0.70
t/15	C ₁₅	28.21	2.27	1.42	1.30	20.09	8.04	1.60	1.59	0.71
t/16	C ₁₆	29.70	2.39	1.50	1.27	21.45	8.58	1.71	1.52	0.72
t/17	C ₁₇	31.21	2.51	1.57	1.24	22.92	9.17	1.83	1.46	0.73
t/18	C ₁₈	32.61	2.63	1.64	1.22	24.71	9.88	1.97	1.44	0.76
t/19	C ₁₉	34.00	2.74	1.71	1.20	26.92	10.77	2.15	1.45	0.79
t/20	C ₂₀	35.30	2.84	1.78	1.19	29.80	11.92	2.38	1.49	0.84
C ₁₄	<i>n</i> -Tetradecane	12.42	1.00	—	—	2.50	1.00	—	—	0.20

* Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).

** Relative retention time for *n*-tetradecane (C₁₄) taken as 1.00.

*** Relative retention time for the decanoic acid ester (10, m/10, d/10 and t/10) taken as 1.00.

§ Relative retention time for the corresponding ethyl ester (2-20) taken as 1.00.

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

in order of increasing degree of chlorination, as is evident from Fig. 1. The individual components in the mixture appeared in the order 2,2,2-trichloroethyl C_n -ester < ethyl C_{n+4} -ester < 2,2-dichloroethyl C_{n+1} -ester < 2-chloroethyl C_{n+2} -ester. This retention order is the same as previously reported for lower ethyl, 2-chloroethyl and 2,2,2-trichloroethyl esters on glass capillary columns coated with low-polarity SP-400² and OV-101⁸ stationary phases.

Fig. 1 shows that on SE-30 a complete resolution occurred between all ethyl esters (2-20) and monochloroethyl esters (m/2-m/20) and also between all monochloroethyl esters (m/2-m/20) and trichloroethyl esters (t/2-t/20). The ethyl (7-20)

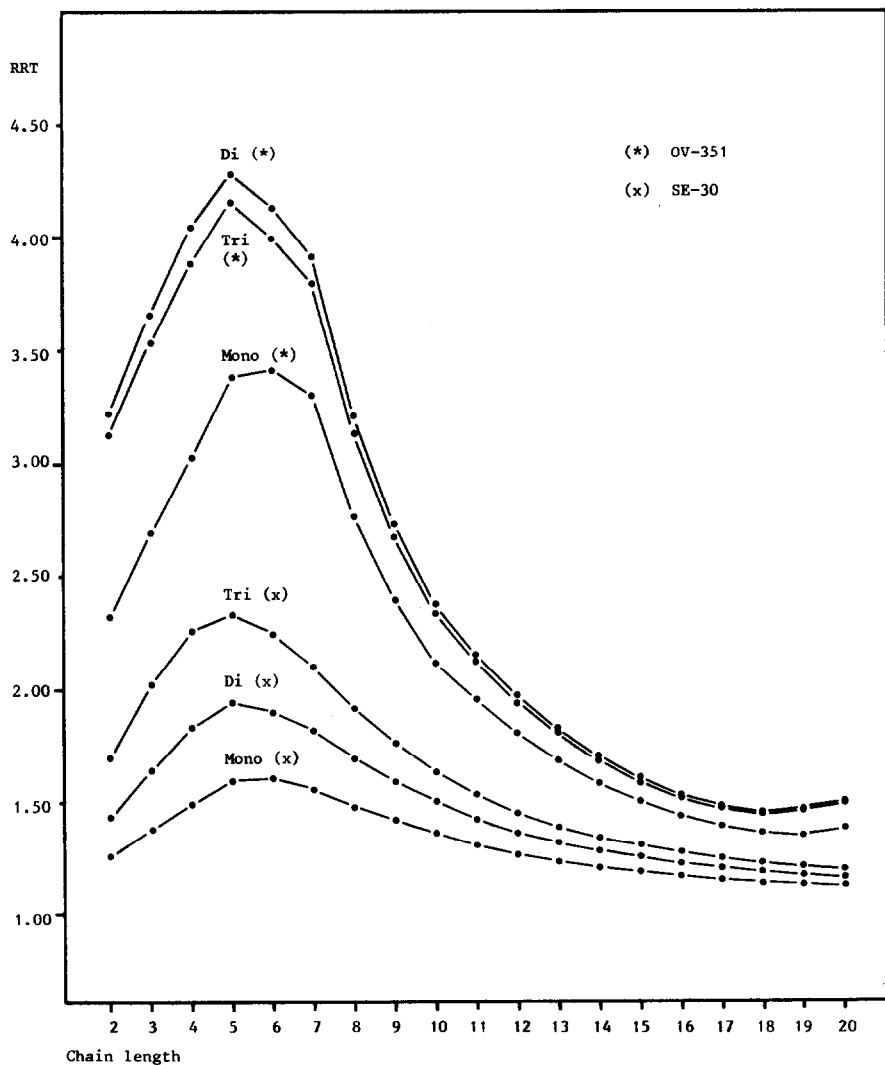


Fig. 3. Plot showing relative retentions of mono-, di- and trichloroethyl esters, analysed on SE-30 and OV-351 capillary columns. Relative retention time (RRT) for the corresponding ethyl ester taken as 1.00 (Table I).

and trichloroethyl (t/3-t/16) esters are coincident, however. The same trend is shown by the ethyl (5-10) and dichloroethyl (d/2-d/7) esters, but with increasing chain length the components gradually separated, the resolution being complete with the compounds 14-20 and d/11-d/17. The di- and trichloroethyl esters are most frequently separated, except for the d/4-d/8 and t/3-t/7 esters. The peaks of the mono- and dichloroethyl esters are completely separated up to the compound pair d/13 and m/14 inclusive, but with increasing chain length the isomers gradually overlap, the overlapping being almost complete with the compound pair d/19 and m/20 (Fig. 1).

On the highly polar OV-351 capillary column the elution order of chlorinated ethanols remains unchanged, whereas the elution order between the isomeric esters is altered, viz., the 2,2,2-trichloroethyl esters eluted earlier than the 2,2-dichloroethyl esters. This trend is the same as previously found with all esters of tri- and dichloroacetic acids on the polar columns, the effect being accentuated with increasing stationary phase polarity and with complete substitution of all ω -hydrogen atoms¹⁶; the steric effects are of such significance that the trichloroethyl esters, in spite of their higher boiling points, eluted earlier than the corresponding dichloroethyl esters (Fig. 3).

Most frequently, the individual components are eluted from OV-351 in the order 2,2,2-trichloroethyl C_n -ester < ethyl C_{n+5} -ester < 2,2-dichloroethyl C_n -ester < 2-chloroethyl C_{n+1} -ester ($5 \leq n \leq 11$). With the chain lengths $n \geq 12$ the retention order of the trichloroethyl and ethyl esters is changed (Fig. 2). OV-351 separated a mixture much better than SE-30, although some overlappings occurred, viz., m/5 with d/4, t/5 with 10, 17 with t/12, and 18 with t/13. Owing to the high carrier gas flow-rate and initial temperature used, the volatile isomers 2-4 are not completely resolved from the solvent peak.

The relative retention times of the compounds generally increase with increasing column polarity, as is evident from Table I and Fig. 3. The retention ratio due to chloro substitution on SE-30 varied in the following ranges with the values on OV-351 given in parentheses: 1.11-1.60 (1.35-3.41) for mono-, 1.15-1.94 (1.45-4.28) for di- and 1.19-2.33 (1.44-4.15) for trichloroethyl esters. On both columns the retention is maximal with 2-chloroethyl hexanoate (m/6), 2,2-dichloroethyl pentanoate (d/5) and 2,2,2-trichloroethyl pentanoate (t/5), as is evident from Table I and Fig. 3.

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