

CHROM. 18 263

## GAS CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION OF LINEAR AND BRANCHED-CHAIN ALKYL CHLORIDES

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### SUMMARY

Polar and non-polar liquid stationary phases (Apiezon L, tricresyl phosphate and Carbowax 20M) were used for the analysis of C<sub>5</sub>–C<sub>8</sub> linear and branched-chain alkyl chlorides. Specific retention volumes, retention index and relative molar heats of solution of alkyl chlorides with respect to the homomorphous alkanes were measured and correlated with molecular structure, in order to permit the identification of isomeric compounds in a mixture.

The behaviour of alkyl chlorides was compared with that of the corresponding bromo- and iodoalkanes, on the basis of previously published data.

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### INTRODUCTION

Increasing attention has been devoted in recent years to the analysis of halogenated compounds in the environment, owing to their possible carcinogenic effects. Trihalomethanes (THM) formed in the disinfection of water with chlorine, other volatile halocarbons resulting from water pollution by industrial and domestic solvents, pesticides and fumigation agents have all been detected and measured in various amounts<sup>1–10</sup>. Analyses of different environmental samples showed the presence of some halogenated compounds, not identified as commonly used solvents, that can be formed by thermal cracking or by biological degradation of polymeric substances, paints, complex halogenated molecules of different kinds, etc.

The identification of these unknown compound should be possible by gas chromatography–mass spectrometry (GC–MS), but this expensive technique is not available in many laboratories that routinely perform environmental analyses on restricted areas, river basins, water supplies, etc. Some attempts were therefore made to achieve such identification on the basis of GC only, by investigating the behaviour of many halogenated compounds on stationary phases of different polarities. In a first series of studies dealing with haloalkanes results were published on the analysis of alkyl bromides<sup>11</sup>, and other experiments are now in progress in order to establish the GC behaviour and the electron-capture detection (ECD) sensitivity of compounds containing different halogen atoms in the same molecule.

This paper describes experiments performed with various stationary phases in

order to obtain the complete separation of C<sub>5</sub>-C<sub>8</sub> isomeric chloroalkanes and to identify them on the basis of GC results.

## EXPERIMENTAL

The analyses were carried out on a Varian 3760 gas chromatograph with a thermal conductivity detector. The columns (3 m × 1/8 in. I.D.) were made of stainless steel or glass and filled with known amounts of 15% Apiezon L (APL), tricresyl phosphate (TCP) or Carbowax 20M (CW 20M) on Chromosorb W AW DMCS (80-100 mesh).

Pure helium was used as the carrier gas, and the inlet pressure was adjusted to give a constant flow-rate of 30 ± 0.5 ml/min at any temperature (75, 100 and 125°C). The flow-rate was measured after each analysis and a correction factor was applied in order to convert the retention values to the nominal flow-rate of 30 cm<sup>3</sup>/min.

Samples of about 0.2 μl, pure or dissolved in *n*-hexane, were injected directly into the column inlet. No appreciable difference in the retention times was observed between glass and stainless-steel columns. A Varian Vista 402 data system was used to measure the retention times, with an accuracy of ±0.01 min. The adjusted retention times, *t*'<sub>R</sub>, were calculated with respect to the retention time of air.

Specific retention volumes, *V*'<sub>s</sub>, were calculated<sup>12</sup> by using the equation

$$V'_s = \frac{F(P_0 - P_w)}{P_0} \cdot \frac{1.5 (P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \cdot \frac{273}{T W} \cdot t'_R \quad (1)$$

where

- F* = flow-rate (ml/min) measured by a soap-bubble flow meter;
- P*<sub>0</sub> = pressure at the column outlet (Torr);
- P*<sub>w</sub> = vapour pressure of water (Torr) at temperature *T*;
- P*<sub>i</sub> = column inlet pressure (Torr);
- T* = temperature (K) at which the gas flow was measured;
- W* = weight (g) of liquid stationary phase in the column.

Relative molar heats of solution, Δ*H*'<sub>s</sub><sup>0</sup>, *i.e.*, the difference between molar heats of solution for the chlorinated compound and the homomorphous alkane, were calculated from the equation

$$\Delta H'_s{}^0 = \frac{1.98 (\ln r_1 - \ln r_2)}{1/T_1 - 1/T_2}, \quad (2)$$

where *r* is the relative retention with respect to the homomorphous alkane, *T* is the absolute temperature of the column and subscripts 1 and 2 refer to the different temperatures<sup>13</sup>. The average values of Δ*H*'<sub>s</sub><sup>0</sup> calculated between 75 and 100°C and between 100 and 125°C were used.

## RESULTS AND DISCUSSION

Tables I and II give the specific retention volumes,  $V_g$ , and retention indices,  $I$ , of the alkyl chlorides on APL, TCP and CW 20M columns.

The logarithms of the  $V_g$  values of straight-chain 1-, 2- and 3-chloroalkanes followed a linear relationship (correlation coefficient  $r > 0.99$ ) with the number of carbon atoms,  $n$ , at all temperatures on all of the stationary phases tested. Table III shows the coefficients of the equation  $\ln V_g = b_0 + b_1 n$  for straight-chain alkyl chlorides. The Arrhenius plots ( $\ln V'_R = m + n/T$ , where  $T$  is the absolute temperature of analysis) were also linear ( $r > 0.97$ ) in the investigated temperature range for both straight- and branched-chain compounds.

The behaviour of the  $V_g$  values of 1-chloroalkanes is compared with those of linear alkanes and of other 1-haloalkanes<sup>11,14</sup> in Fig. 1. From Fig. 1 and the data in Tables I and II, one can see that the increase in the retention indices of halogenated compounds with increasing polarity of the column is due to the greater decrease in the retention of alkanes with respect of that of the alkyl halides. This can be expressed in terms of "equivalent methylenes" (EM), which should be added to the homomorphous alkane in order to obtain a straight-chain alkane with the same retention as the halogenated compounds.

The values in Table IV were calculated by averaging the  $\Delta I$  values ( $I$  of a haloalkane minus  $I$  of the alkane with the same number of carbon atoms) obtained at 75, 100 and 125°C and therefore do not take into account the effect of the column temperature. A fine structure of the EM values as a function of temperature was observed, mainly for 1-halo compounds and when the EM values are high enough to largely overcome the experimental fluctuations.

As an example, on the upper graph in Fig. 2 (average EM values for 1-iodoalkanes) are superimposed the EM values for the same compounds measured at 75, 100 and 125°C, showing that the average values are very close to the EM measured at the intermediate temperature of 100°C. The same behaviour was observed for other homologous series of 1-, 2- and 3-haloalkanes but, when the EM values decreased, the effect of temperature was of the same order of magnitude as the standard deviation of the EM averaged over compounds with a different number of carbon atoms. Fig. 2 also shows that the polarity of the TCP column is nearly intermediate between those of the APL and CW 20M columns for the separation of haloalkanes. Table IV shows that the replacement of a single hydrogen atom with a halogen drastically increases the retention time of the compounds, mainly when the polarity of the column is greater and when the substitution takes place at the end of the straight alkane chain. In contrast, small differences were observed between 2-, 3- and (where available) 4-halo compounds. The difference in the EM values between haloalkanes with the substituent atom at the end of the chain or in an internal position was about 0.4–0.5 on the APL, 0.6 on the TCP and 0.7–0.8 on the CW 20M column (see Table IV).

Branched-chain compounds showed similar behaviour (see Tables I and II): the increase in retention was greater when the halogen atom was in the 1-position, mainly when the side methyl group was in the 2-position. In contrast, when the halogen atom was on the same carbon atom of the side methyl group, the increase in the retention had the smallest value.

TABLE I  
 SPECIFIC RETENTION VOLUMES,  $V_s$ , OF ALKYL CHLORIDES ON DIFFERENT COLUMNS AT VARIOUS TEMPERATURES  
 Carrier flow-rate: 30 cm<sup>3</sup>/min. Amount of stationary phase: 15% (w/w).

Compound	Apiezon L			Tricresyl phosphate			Carbowax 20M		
	75°C	100°C	125°C	75°C	100°C	125°C	75°C	100°C	125°C
1-Chloropentane	8.17	3.28	1.72	7.27	3.66	1.92	4.76	2.10	1.16
2-Chloropentane	5.55	2.51	1.33	4.88	2.46	1.33	2.99	1.40	0.83
3-Chloropentane	5.88	2.51	1.33	5.28	2.51	1.46	3.07	1.50	0.92
1-Chlorohexane	16.46	6.61	3.20	16.73	7.27	3.51	9.18	3.68	1.91
2-Chlorohexane	11.68	4.92	2.44	10.65	4.79	2.44	5.58	2.38	1.31
3-Chlorohexane	11.38	4.95	2.45	10.92	4.84	2.50	5.54	2.49	1.40
1-Chloroheptane	36.32	13.40	5.98	37.51	14.54	6.39	18.20	6.59	3.35
2-Chloroheptane	30.70	9.70	4.40	22.68	9.45	4.41	10.76	4.18	2.16
3-Chloroheptane	24.76	9.02	4.44	22.88	9.39	4.40	10.29	4.21	2.26
4-Chloroheptane	23.95	9.41	4.40	20.29	9.19	4.30	10.18	3.90	2.08
1-Chlorooctane	75.54	26.88	11.13	87.97	29.61	11.83	35.56	12.60	5.09
1-Chloro-2-methylbutane	7.26	2.81	1.49	5.84	2.95	1.51	3.38	1.66	0.92
1-Chloro-3-methylbutane	6.34	2.61	1.40	6.72	2.67	1.46	3.25	1.50	0.92
2-Chloro-2-methylbutane	4.27	1.84	1.06	3.28	1.74	1.11	2.34	1.08	0.70
1-Chloro-2-methylpentane	12.93	5.45	2.70	12.29	5.36	2.75	6.06	2.81	1.54
2-Chloro-2-methylpentane	8.19	3.45	1.85	7.93	4.05	1.69	3.56	1.66	1.00
3-Chloro-2-methylpentane	10.79	4.67	2.41	10.82	4.43	2.23	4.96	2.28	1.22
3-Chloro-3-methylpentane	10.35	4.36	2.11	8.78	4.33	2.17	4.65	2.17	1.22
1-Chloro-3,3-dimethylbutane	9.65	4.12	2.11	8.56	4.00	2.07	4.55	2.07	1.16
2-Chloro-2,3-dimethylbutane	9.61	4.07	2.08	7.39	3.66	1.85	4.07	1.96	1.00

TABLE II  
RETENTION INDICES, *I*, OF ALKYL CHLORIDES ON DIFFERENT COLUMNS AT VARIOUS TEMPERATURES  
Carrier flow rate: 30 cm<sup>3</sup>/min. Amount of stationary phase: 15% (w/w).

Compound	Apiezon L			Tricresyl phosphate			Carbowax 20M		
	75°C	100°C	125°C	75°C	100°C	125°C	75°C	100°C	125°C
1-Chloropentane	810	800	808	858	877	879	943	938	945
2-Chloropentane	763	762	768	806	818	818	874	869	880
3-Chloropentane	770	762	768	816	821	834	878	880	900
1-Chlorohexane	897	897	908	968	979	981	1041	1034	1041
2-Chlorohexane	854	857	865	908	917	920	967	959	969
3-Chlorohexane	856	858	865	913	918	923	965	967	982
1-Chloroheptane	991	999	1008	1073	1083	1083	1142	1135	1150
2-Chloroheptane	971	953	959	1008	1018	1020	1064	1055	1065
3-Chloroheptane	945	943	960	1009	1017	1019	1057	1057	1074
4-Chloroheptane	941	949	959	993	1014	1016	1052	1044	1058
1-Chlorooctane	1085	1098	1109	1185	1090	1186	1242	1247	1232
1-Chloro-2-methylbutane	796	778	786	829	845	840	891	898	900
1-Chloro-3-methylbutane	779	768	776	848	830	834	886	880	900
2-Chloro-2-methylbutane	731	719	732	755	768	789	826	826	849
1-Chloro-2-methylpentane	867	871	880	927	934	940	979	988	1000
2-Chloro-2-methylpentane	811	807	820	870	892	858	899	898	916
3-Chloro-2-methylpentane	845	850	862	911	905	905	944	952	956
3-Chloro-3-methylpentane	839	840	841	883	902	900	939	944	956
1-Chloro-3,3-dimethylbutane	831	832	841	880	890	892	936	936	945
2-Chloro-2,3-dimethylbutane	830	831	836	860	877	873	919	927	916

TABLE III

COEFFICIENTS OF THE EQUATION  $\ln V_R + b_0 + b_1 n$  FOR STRAIGHT-CHAIN CHLOROALKANES ON DIFFERENT STATIONARY PHASES

Homologous series	Temperature (°C)	Apiezon L		Tricresyl phosphate		Carbowax 20M	
		$b_0$	$b_1$	$b_0$	$b_1$	$b_0$	$b_1$
1-Chloroalkanes	75	-1.65	0.75	-2.16	0.83	-1.80	0.67
	100	-2.37	0.71	-2.20	0.70	-2.11	0.57
	125	-2.57	0.66	-2.38	0.60	-2.34	0.50
2-Chloroalkanes	75	-2.60	0.85	-2.25	0.77	-2.11	0.64
	100	-2.46	0.68	-2.47	0.67	-1.91	0.45
	125	-2.70	0.60	-2.71	0.60	-2.70	0.50
3-Chloroalkanes	75	-1.83	0.72	-2.00	0.73	-1.91	0.60
	100	-2.26	0.64	-2.38	0.66	-2.18	0.52
	125	-2.73	0.60	-2.38	0.55	-2.34	0.45

The increase in the retention when hydrogen atom is replaced with a halogen is not linearly correlated with the increase in the boiling point, as shown previously for bromoalkanes<sup>11</sup>, or with the increase in molecular weight. The EM values of chloroalkanes on the non-polar stationary phase APL are similar to the ration between the weight of chlorine and that of a methylene group (2.54), but this is not true for bromo (Br/CH<sub>2</sub> ratio  $\approx$  5.7) and iodo compounds (I/CH<sub>2</sub> ratio  $\approx$  9.06) on

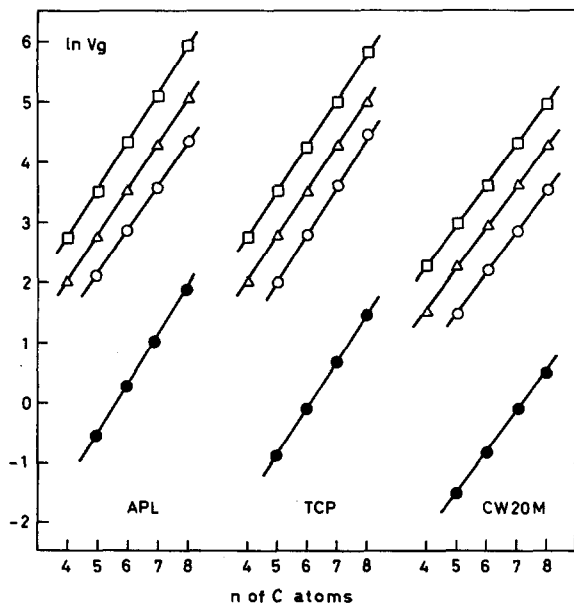


Fig. 1. Effect of the substituent halogen atom in the 1-position on the retention volume as a function of the chain length. ●, Alkanes; ○, 1-chloroalkanes; △, 1-bromoalkanes; □, 1-iodoalkanes. Temperature, 75°C. Carrier gas flow-rate, 30 cm<sup>3</sup>/min.

TABLE IV

AVERAGE VALUES OF THE "EQUIVALENT METHYLENES", EM, THAT SHOULD BE ADDED TO STRAIGHT-CHAIN ALKANES TO OBTAIN COMPOUNDS WITH THE SAME RETENTION TIMES AS THE VARIOUS HALOALKANES ON DIFFERENT STATIONARY PHASES

Halogen	Position in the chain	Carbon chain length	Stationary phase		
			APL	TCP	CW 20M
Cl	1	5-8	2.96	3.78	4.41
	2	5-7	2.61	3.15	3.67
	3	5-7	2.59	3.19	3.73
Br	1	4-8	3.92	4.70	5.59
	2	4-7	3.46	4.14	4.85
	3	4-7	3.45	4.15	4.77
I	1	4-8	4.97	5.75	6.63
	2	4-7	4.49	5.23	5.94
	3	4-7	4.43	5.18	5.88

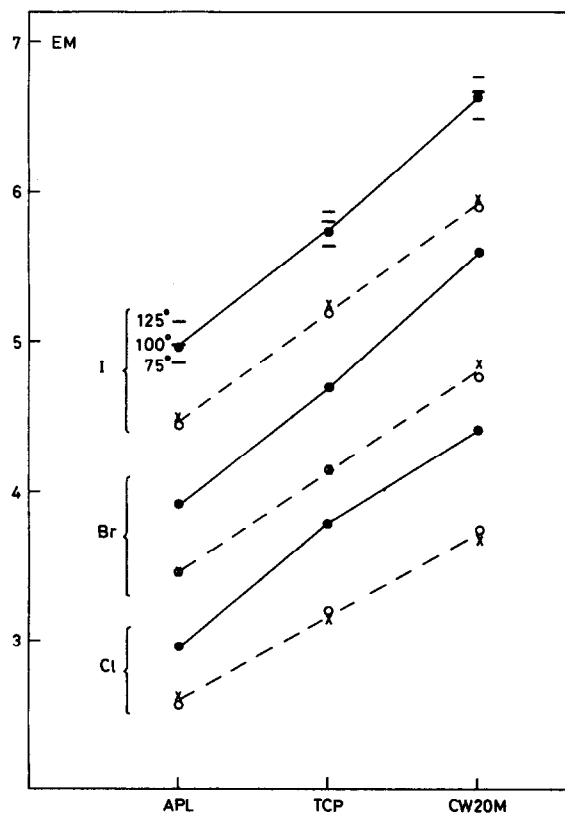


Fig. 2. Average values of equivalent methylenes (EM) for straight-chain chloro-, bromo- and iodoalkanes on different stationary phases. ●, 1-Halo; ×, 2-halo; ○, 3-halo. For 1-iodoalkanes the effect of column temperature is also shown (see text).

TABLE V

VALUES OF  $\Delta H_s^0$  OF CHLOROALKANES WITH RESPECT TO THE HOMOMORPHOUS ALKANES ON DIFFERENT STATIONARY PHASES

Compound	$\Delta H_s^0$ (kcal/mol)		
	APL	TCP	CW 20M
1-Chloropentane	3.18	2.56	3.56
2-Chloropentane	2.49	2.39	2.85
3-Chloropentane	2.80	2.28	2.43
1-Chlorohexane	2.60	2.89	3.45
2-Chlorohexane	2.21	2.40	2.79
3-Chlorohexane	2.26	2.40	2.40
1-Chloroheptane	2.54	3.21	3.42
2-Chloroheptane	2.27	2.49	2.98
3-Chloroheptane	2.05	2.54	2.46
4-Chloroheptane	1.94	2.03	1.85
1-Chlorooctane	2.10	3.54	4.15
1-Chloro-2-methylbutane	3.70	3.10	3.28
1-Chloro-3-methylbutane	3.30	2.98	3.03
2-Chloro-2-methylbutane	2.66	2.29	2.80
1-Chloro-2-methylpentane	3.24	3.95	2.89
2-Chloro-2-methylpentane	2.79	3.29	2.32
3-Chloro-2-methylpentane	2.87	3.39	3.08
3-Chloro-3-methylpentane	2.73	2.46	2.76

either non-polar, medium-polar or polar stationary phases. The increase on changing from Cl to Br to I is close to one EM on all of the stationary phases tested.

The values of  $\Delta H_s^0$  calculated using eqn. 2 are shown in Table V. These data refer to the difference in intermolecular forces for the halogen-substituted and unsubstituted alkane molecules. The values show appreciable fluctuations owing to the small temperature range available for calculation on the data. Notwithstanding this, as previously seen for bromoalkanes<sup>11</sup>, independent of the polarity of the stationary phase for straight-chain chlorohexanes and chloroheptanes, the  $\Delta H_s^0$  values increase when the halogen atom is bonded near to the extremity of the chain and show minimum values when it is connected to the central carbon atoms.

The  $\Delta H_s^0$  values for branched compounds also increase on all the stationary phases when the halogen atom moves from the inner part of the carbon structures to their extremities. Molecules with the chlorine atom closely surrounded by several methyl groups and therefore with a compact and rounded shape shown the lowest  $\Delta H_s^0$  values, as previously observed for bromoalkanes. This effect increases with increasing weight and shape of the substituent halogen atom; as an example, the ratios between the  $\Delta H_s^0$  values of 1-halo-2-methylpentanes and those of 3-halo-3-methylpentanes are (for Cl, Br and I, respectively) 1.19, 1.74, 2.07 on APL and 1.04, 1.27, 2.63 on CW 20M columns.

The resolution of the columns used (about 1000 theoretical plates per metre for APL and 1500 for TCP and CW 20M) did not permit the complete separation of all the isomers.

The chromatograms obtained with mixed samples showed that CW 20M elutes all the compounds having a retention time smaller than that of 4-chloroheptane as



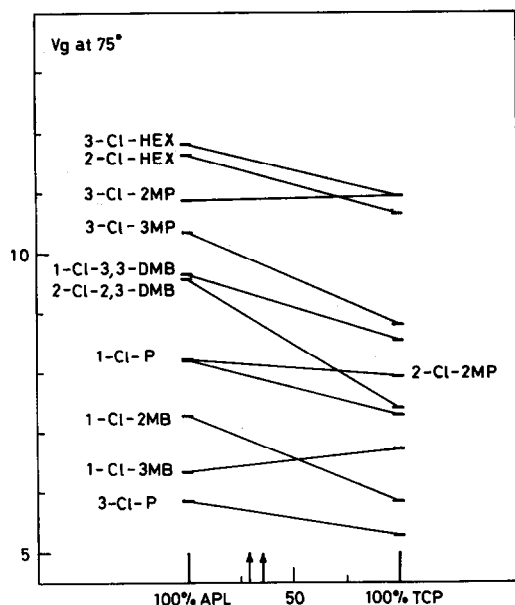


Fig. 3. Separation of closely eluting chloroalkane isomers on similar columns of different polarity and graphical choice of a suitable mixed column. Arrows show the phase composition range for the best separation.

four groups of closely grouped peaks. A longer packed or a capillary Carbowax column is therefore necessary for complete resolution. In contrast, the length of both the APL and TCP columns used permits a satisfactory resolution of most of the compounds. Interference of 1-chloropentane with 2-chloro-2-methylpentane and of 2-chloro-2,3-dimethylbutane with 1-chloro-3,3-dimethylbutane was observed at 75°C on the APL column, whereas on the TCP column coincident or closely eluting peaks were given, at the same temperature, by 1-chloropentane and 2-chloro-2,3-dimethylbutane, by 1-chloro-3,3-dimethylhexane and 3-chloro-3-methylpentane and by 3-chloro-2-methylpentane and 3-chlorohexane. Fig. 3 shows that a mixed column containing about 30% of TCP and 70% of APL, or an equivalent series arrangement of the two columns, should permit the best possible resolution of the grouped peaks. Further enhancement of the separation was obtained by temperature programming, but the observed changes in relative retention were too complex to be predicted on the basis of the available data measured on single columns at constant temperatures.

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