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

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### SUMMARY

Polar and non-polar liquid phases (Apiezon L, tricresyl phosphate and Carbowax 20M) were used for the analysis of linear and branched-chain alkyl bromides having four to eight carbon atoms. Specific retention volumes, retention index and relative molar heats of solution of alkyl bromides 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.

Mixed columns that ensure the best resolution of closely eluting isomeric alkyl bromides were tested.

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### INTRODUCTION

The gas chromatographic analysis of alkyl bromides has various applications, *e.g.*, when analysing the halocarbons formed by disinfection of drinking water (containing Br<sup>-</sup>) with chlorine, in the determination of the products of bromination reactions, and in the study of radiolysis mechanisms when halogen atoms are used as radical scavengers.

While quantitative analysis is achieved with satisfactory sensitivity by using electron-capture detectors, after the determination of proper calibration coefficients, both the complete separation of all of the possible linear and branched isomers and the identification of all peaks in a very complex mixture are still subject to uncertainty.

Previous papers have been published on the gas chromatography of halogenated alkanes. Adjusted retention times, retention relative to 1-iodopropane and Kováts' retention indices have been measured at 60, 100 and 120°C on a tricresyl phosphate (TCP) column, for linear and some branched-chain alkyl iodides<sup>1,2</sup>.

The retention-index values relative to *n*-iodides ( $I_{ni}$ ) were introduced as a means of identification of branched-chain compounds when very small amounts had to be determined by using electron-capture detectors which are insensitive to alkanes<sup>3,4</sup>.

Further studies on the correlation between the physical properties of halogenated alkanes (chloro-, bromo- and iodo-) and their gas chromatographic behaviour

on polar and non-polar stationary phases were carried out by using the  $I_{ni}$  values experimentally measured at 100°C<sup>5,6</sup>.

Regular dependence of  $I_{ni}$  values on the position of the halogen atom in the molecule and their correlations with boiling-points and molecular volumes were found.

In this paper, results are shown of experiments performed with different stationary phases in order to effect the complete separation of many isomeric alkyl-bromides (C<sub>5</sub>-C<sub>7</sub>) and to achieve positive identification on the basis of gas chromatographic data.

The use of mixed columns, the composition of which was previously theoretically calculated, was also tested in order to obtain satisfactory resolution of some compounds that were difficult to separate.

## EXPERIMENTAL

The analyses were carried out on a Varian 3760 gas chromatograph, with a micro thermal-conductivity detector and a CDS-111C integrating system. 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), TCP or Carbowax 20M on Chromosorb W AW DMCS (80-100 mesh).

Pure helium was used as the carrier gas, and the inlet pressure was adjusted to provide 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 refer the retention values to the nominal flow-rate of 30 ml/min.

Volumes of samples of *ca.* 0.2 μl, pure or dissolved in *n*-hexane, were injected directly into the column inlet. No appreciable difference in the retention time values was observed between glass and stainless-steel columns. The areas of some alkyl bromides peaks were smaller with stainless-steel columns, probably owing to sample decomposition, but this fact did not affect the results, as quantitative analysis was not carried out.

The accuracy of the retention time measurement was ± 0.01 min and the adjusted retention times,  $t'_R$ , were calculated with respect to the retention time of air. Specific retention volumes,  $V_g$ , were calculated<sup>7</sup> by using the formula:

$$V_g = \frac{F(P_o - P_w)}{P_o} \cdot \frac{1.5 (P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \cdot \frac{273}{TW} \cdot t'_R = F_o \cdot j \frac{273}{TW} t'_R \quad (1)$$

where  $F$  denotes the observed flow-rate (ml/min),  $F_o$  the corrected flow-rate,  $P_o$  the column-outlet and soap-bubble flowmeter pressure (torr),  $P_w$  the vapour pressure of water (torr) at temperature  $T$ ,  $P_i$  the column-inlet pressure (torr),  $T$  the temperature (°K) at which the gas flow-rate was measured,  $W$  the weight (g) of liquid phase in the column, and  $j$  the pressure gradient correction factor according to James and Martin<sup>8</sup>.

The  $\Delta H_s^\circ$  (relative molar heat of solution, *i.e.*, the difference between the molar heats of solution for the halogenated compound and the homomorphous alkane) was calculated from the following equation:

$$\Delta H_s^\circ = \frac{1.98 (\ln r_1 - \ln r_2)}{1/T_1 - 1/T_2} \quad (2)$$

where  $r$  denotes 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>9</sup>. The average values of the  $\Delta H_s^\circ$  calculated between 75 and 100°C and between 100 and 125°C were used.

## RESULTS AND DISCUSSION

The logarithms of the adjusted retention times,  $t'_R$ , of linear compounds (alkanes and 1-, 2- and 3-bromoalkanes) followed a linear relationship (correlation coefficient  $r > 0.999$ ) as a function of the number of carbon atoms,  $n$ , at all temperatures on all of the stationary phases tested. The Arrhenius plots ( $\ln t'_R = m + n/T$ , where  $T$  is the absolute temperature of analysis) were also linear ( $r > 0.99$ ) in the investigated temperature range for both straight- and branched-chain compounds.

Tables I and II show the values of the specific retention volumes,  $V_g$ , and of

TABLE I

VALUES OF THE SPECIFIC RETENTION VOLUMES,  $V_g$ , OF ALKYL BROMIDES ON DIFFERENT COLUMNS AT VARIOUS TEMPERATURES

Carrier gas flow-rate, 30 cm<sup>3</sup>/min. Amount of liquid 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-Bromobutane	7.12	3.15	1.66	7.29	3.57	1.82	4.94	2.60	1.25
2-Bromobutane	5.13	2.35	1.27	4.36	2.86	1.40	3.34	1.68	0.98
1-Bromopentane	15.03	6.34	3.12	16.09	7.05	3.40	9.40	4.48	2.08
2-Bromopentane	10.84	4.48	2.33	9.09	4.72	2.45	5.94	2.78	1.53
3-Bromopentane	11.44	4.71	2.27	10.44	5.16	2.62	6.48	2.96	1.61
1-Bromohexane	33.69	12.74	5.42	34.48	13.98	6.22	18.72	7.95	3.51
2-Bromohexane	22.55	8.89	4.22	22.78	9.42	4.38	11.10	4.71	2.40
3-Bromohexane	22.80	9.04	4.18	21.83	9.19	4.60	11.11	4.63	2.47
1-Bromoheptane	77.67	25.85	10.72	75.38	27.81	11.40	37.85	14.29	5.96
2-Bromoheptane	48.03	17.50	7.59	48.32	18.28	7.82	21.01	8.33	4.00
3-Bromoheptane	46.46	17.38	7.64	45.99	17.69	7.77	19.99	7.76	3.91
4-Bromoheptane	47.72	17.55	7.26	41.28	17.59	7.08	17.66	6.89	3.59
1-Bromooctane	160.37	52.85	18.64	16.39	55.03	21.07	73.68	24.98	10.01
1-Bromo-2-methylbutane	11.36	5.38	2.65	11.06	5.48	2.81	7.14	3.25	1.78
1-Bromo-3-methylbutane	11.53	4.87	2.49	11.15	5.10	2.57	6.54	3.05	1.61
2-Bromo-2-methylbutane	9.10	4.34	2.27	7.35	3.63	1.91	5.21	2.74	1.12
2-Bromo-3-methylbutane	7.99	4.15	2.25	7.39	3.58	1.96	4.35	2.10	1.20
1-Bromo-2-methylpentane	24.93	9.93	4.12	24.48	10.15	4.77	14.09	5.35	2.76
1-Bromo-4-methylpentane	24.82	9.83	4.63	25.59	10.58	4.97	12.73	5.83	2.93
2-Bromo-2-methylpentane	14.39	6.25	3.04	14.41	6.41	3.18	6.84	3.34	1.78
2-Bromo-4-methylpentane	19.58	8.55	4.15	14.16	6.26	4.74	7.13	3.25	1.86
3-Bromo-3-methylpentane	19.28	8.16	4.01	18.63	8.20	4.01	9.61	4.26	2.25
2-Bromo-2,3-dimethylbutane	16.37	6.82	3.48	15.32	6.97	2.89	8.42	3.70	2.03

TABLE II

VALUES OF THE RETENTION INDICES,  $I$ , OF ALKYL BROMIDES ON DIFFERENT COLUMNS AT VARIOUS TEMPERATURESCarrier gas flow-rate, 30 cm<sup>3</sup>/min. Amount of liquid 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-Bromobutane	793	794	803	859	873	870	948	975	960
2-Bromobutane	753	754	761	791	840	826	890	900	913
1-Bromopentane	885	893	904	963	974	976	1044	1068	1058
2-Bromopentane	845	844	857	888	915	921	976	986	999
3-Bromopentane	852	851	853	906	928	931	989	997	1009
1-Bromohexane	982	992	992	1060	1077	1078	1147	1167	1159
2-Bromohexane	934	941	952	1008	1018	1019	1069	1077	1091
3-Bromohexane	953	943	951	1003	1014	1027	1069	1073	1059
1-Bromoheptane	1088	1090	1102	1167	1180	1179	1252	1268	1262
2-Bromoheptane	1026	1037	1047	1105	1117	1117	1164	1175	1185
3-Bromoheptane	1022	1036	1048	1099	1112	1115	1156	1163	1181
4-Bromoheptane	1025	1037	1039	1085	1111	1099	1138	1142	1164
1-Bromooctane	1179	1195	1192	1268	1272	1267	1351	1365	1364
1-Bromo-2-methylbutane	851	870	878	913	937	943	1003	1013	1028
1-Bromo-3-methylbutane	853	856	867	915	926	929	991	1002	1009
2-Bromo-2-methylbutane	824	839	853	860	876	878	925	937	939
2-Bromo-3-methylbutane	808	833	851	861	874	883	929	938	951
1-Bromo-2-methylpentane	946	956	948	1017	1029	1033	1104	1099	1112
1-Bromo-4-methylpentane	945	954	967	1023	1035	1040	1089	1113	1124
2-Bromo-2-methylpentane	884	890	897	948	960	965	997	1018	1028
2-Bromo-4-methylpentane	917	935	950	946	957	1032	1003	1113	1037
3-Bromo-3-methylpentane	916	929	944	982	997	1004	1047	1059	1037
2-Bromo-2,3-dimethylbutane	896	903	921	956	973	948	1028	1035	1053

the retention indices,  $I$ , of the alkyl bromides on APL, TCP and Carbowax 20M columns, respectively.

The different columns required different correction factors for the calculation of  $V_g$  from  $t'_R$  values, notwithstanding that the support was the same and that the preparation was by a similar technique. This was probably due to the different viscosities of the liquid phases used that influenced both the packing density and the gas flow resistance.

The effect of the column temperature on the retention times was regular in the considered range; the Arrhenius plots ( $\ln t'_R$  or  $\ln V_g$  as a function of  $1/T$ ) were linear with correlation coefficients greater than 0.99, thus permitting the retention times at different temperatures to be calculated.

Table III shows the coefficients of equation  $\ln V_g = b_0 + b_1 n$  for straight-chain alkanes and alkyl bromides.

The slope values of both series of compounds were similar at any temperature, with correlation coefficients even greater than 0.999. 2-Bromoalkanes and 3-bromoalkanes also showed linear behaviour (correlation coefficients greater than 0.99) with smaller slope values than the 1-bromo homologues. The difference between the intercept values of alkanes and bromoalkanes, corresponding to the  $y$ -axis distance

TABLE III

COEFFICIENTS OF THE EQUATION  $\ln V_g = b_0 + b_1 n$  FOR STRAIGHT-CHAIN COMPOUNDS ANALYSED ON DIFFERENT STATIONARY PHASES

Homologous series	Temperature ( $^{\circ}\text{C}$ )	Apiezon L		Tricresyl phosphate		Carbowax 20M	
		$b_0$	$b_1$	$b_0$	$b_1$	$b_0$	$b_1$
<i>n</i> -Alkanes	75	-4.55	0.82	-4.65	0.77	-4.84	0.68
	100	-4.54	0.71	-4.68	0.68	-4.82	0.59
	125	-4.57	0.63	-4.68	0.60	-4.85	0.53
1-Bromoalkanes	75	-1.20	0.79	-1.12	0.78	-1.14	0.68
	100	-1.67	0.70	-1.47	0.68	-1.33	0.57
	125	-1.92	0.61	-1.84	0.61	-1.87	0.52
2-Bromoalkanes	75	-0.86	0.67	-1.80	0.81	-1.27	0.61
	100	-1.84	0.67	-1.50	0.62	-1.63	0.53
	125	-2.14	0.60	-1.97	0.57	-1.90	0.47
3-Bromoalkanes	75	-1.07	0.70	-1.36	0.74	-0.96	0.56
	100	-1.71	0.65	-1.45	0.62	-1.34	0.48
	125	-2.21	0.61	-1.75	0.54	-1.75	0.44

in a  $\ln V_g$  vs.  $n$  plot, was greater for more polar liquid phases (APL, TCP, Carbowax 20M, in this order), leading to greater values of the retention index,  $I$ . Fig. 1 shows that in the case of APL and TCP, the difference in retention-index values of 1-bromo compounds was due to the change in retention of alkanes rather than that of alkyl

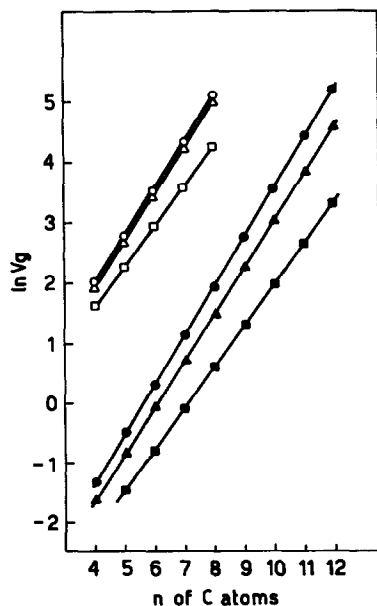


Fig. 1. Linearity of  $\ln V_g$  as a function of the chain length of 1-bromoalkanes (white symbols) and of linear alkanes (black symbols) on Apiezon L ( $\circ$ ), tricresyl phosphate ( $\triangle$ ) and Carbowax 20M ( $\square$ ) columns. Temperature,  $75^{\circ}\text{C}$ . Carrier gas flow-rate;  $30\text{ cm}^3/\text{min}$ .

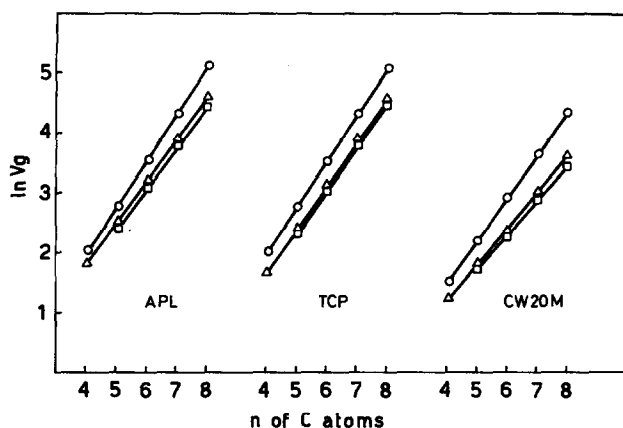


Fig. 2. Effect of the position of bromine atom in the straight alkane chain on the retention volume, as a function of the chain length.  $\circ$  = 1-bromoalkanes;  $\triangle$  = 2-bromoalkanes;  $\square$  = 3-bromoalkanes. Other conditions as in Fig. 1.

bromides, as the  $V_g$  values of the latter compounds on these two columns were very similar.

Fig. 2 shows the effect of the position of the halogen atom in the chain on the retention behaviour. By increasing the polarity of the stationary phase, the difference between the 1-bromo and the 2- and 3-bromo compounds increased.

By replacing an H atom with a Br atom in different sites of the linear alkyl chain, an increase in  $V_g$  and  $I$  values was observed, which can be expressed in terms of "equivalent methylenes" (EM) that should be added to the homomorphous alkane to obtain a straight-chain alkane with the same retention of the brominated compound (see Table IV). These approximate values were calculated by averaging the  $\Delta I$  values ( $I$  of bromoalkanes minus  $I$  of the homomorphous paraffin) obtained at 75, 100, 125°C and are therefore roughly independent of the column temperature. The EM value of 1-bromoalkanes did not depend on the chain length, while the corresponding 2-bromo and 3-bromo compounds showed a decrease in the EM values with increase in the number of carbon atoms. The increase in the column polarity also increased the EM values. The comparison between the  $V_g$  and the boiling-point ( $T_b$ ) of linear and branched-chain bromoalkanes (Fig. 3) showed no simple correla-

TABLE IV

VALUES OF THE "EQUIVALENT METHYLENES", EM, THAT SHOULD BE ADDED TO A STRAIGHT-CHAIN ALKANE TO OBTAIN A COMPOUND WITH THE SAME RETENTION TIME AS THE VARIOUS BROMOALKANES ON DIFFERENT STATIONARY PHASES

Position of substituent Br in the chain	Chain length	Stationary phase		
		Apiezon L	Tricresyl phosphate	Carbowax 20M
1	4-8	4	4.7	5.6
2	4-7	3.6-3.4	4.2-4.1	5.0-4.7
3	4-7	3.5-3.4	4.2-4.1	5.0-4.7

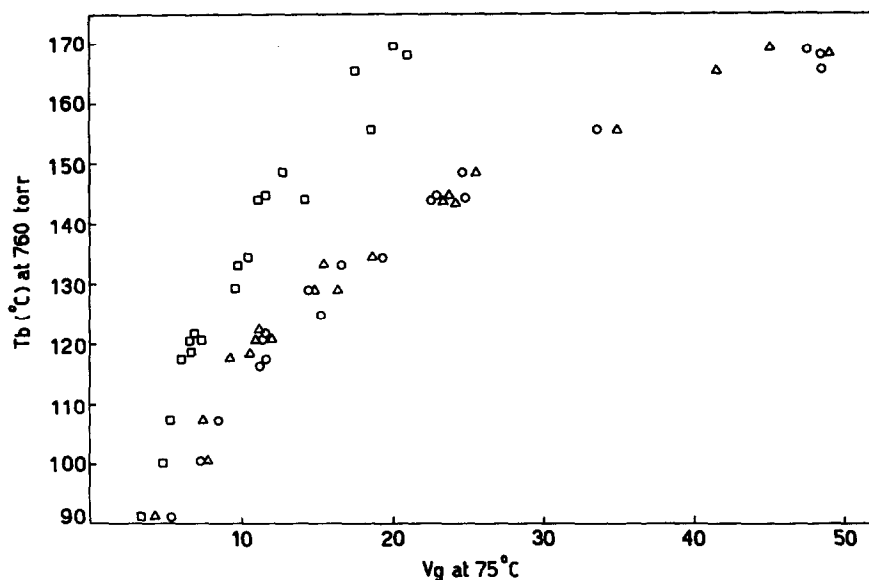


Fig. 3. Correlation between boiling-point at 760 Torr and specific retention volumes of straight- and branched-chain bromoalkanes.  $\circ$  = Apiezon L;  $\triangle$  = tricresyl phosphate;  $\square$  = Carbowax 20 M. Other conditions as in Fig. 1.

TABLE V

VALUES OF  $\Delta H_s^\circ$  OF BROMOALKANES WITH RESPECT TO THE HOMOMORPHOUS ALKANES ( $\text{kcal/mol}^{-1}$ )

Compound	Apiezon L	Tricresyl phosphate	Carbowax 20 M
1-Bromopentane	3.31	3.77	4.10
2-Bromopentane	3.10	2.45	3.22
3-Bromopentane	3.56	2.84	3.42
1-Bromohexane	3.65	3.71	4.10
2-Bromohexane	3.02	3.19	3.27
3-Bromohexane	3.05	2.83	3.11
1-Bromoheptane	3.52	3.85	4.31
2-Bromoheptane	2.79	3.47	3.28
3-Bromoheptane	2.58	3.24	3.10
4-Bromoheptane	2.42	3.20	2.86
1-Bromo-2-methylbutane	3.05	3.20	3.74
1-Bromo-3-methylbutane	3.43	3.72	3.82
2-Bromo-2-methylbutane	2.66	3.07	3.31
2-Bromo-3-methylbutane	2.01	2.94	3.18
1-Bromo-2-methylpentane	4.55	4.40	4.29
1-Bromo-4-methylpentane	3.85	3.73	3.45
2-Bromo-2-methylpentane	3.33	3.04	2.78
2-Bromo-4-methylpentane	3.16	3.03	2.70
3-Bromo-3-methylpentane	2.62	2.84	3.38

tion, owing to the influence of the molecular structure, and confirmed the higher selectivity of the polyglycol phase (Carbowax 20M), while no difference was shown by TCP and APL, whose points practically lie on the same line.

The values of  $\Delta H_s^0$  (relative molar heat of solution of bromoalkanes with respect to the homomorphous alkanes calculated with eqn. 2) are shown in Table V. These data refer to the difference in intermolecular forces for the halogen-substituted and non-substituted alkane molecules. Independent of the polarity of the liquid phase in straight-chain bromoheptanes and bromohexanes, the  $\Delta H_s^0$  values increases when the halogen atom is bonded near to the extremity of the chain and show the minimum values when it is connected to the central carbon atoms. The values on TCP columns are less spread than on other phases. Linear bromopentanes behave differently on the three liquid phases, probably owing to the increased influence of the heteroatom connected to a shorter alkyl chain.

The  $\Delta H_s^0$  values for branched compounds also increase on all the liquid phases when the halogen atom moves from the inner part of the carbon structures (3-bromo-3-methylpentane, 2-bromo-3-methylbutane) to their extremities (1-bromo-2-methyl- and 1-bromo-4-methylalkanes). Generally speaking, molecules with the bromine atom closely surrounded by several methyl groups and therefore with a

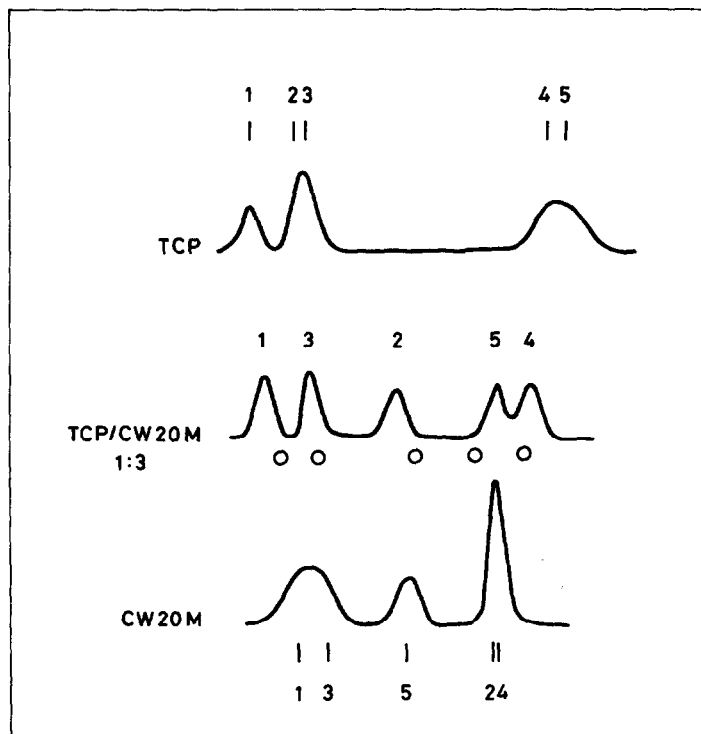


Fig. 4. Separation of isomeric bromo-pentanes and -hexanes on heterogeneously mixed TCP-Carbowax 20M (1:3) column. Peaks: 1 = 3-bromopentane; 2 = 1-bromo-2-methylbutane; 3 = 1-bromo-3-methylbutane; 4 = 2-bromo-4-methylpentane; 5 = 2-bromo-2-methylpentane. Column temperature, 75°C. White circles in the central chromatogram show the retention times calculated by interpolation.



compact and rounded shape show the lowest values of  $\Delta H_{\ddagger}^0$ . All the experimental results ( $V_R$ ,  $I$  and  $\Delta H_{\ddagger}^0$ ) confirm the lower interaction of highly branched compounds mainly when the halogen atom is bonded in the 2- or 3-position.

The results show that complete resolution of all the analysed isomers cannot be achieved with the columns used. Some attempts were therefore made to prepare mixed columns suitable for better separation. Different techniques can be used in order to obtain columns:

(1) Homogeneously mixed: when the two liquid phases are adsorbed on the same solid support by evaporation of a mixed solution in the proper solvent.

(2) Heterogeneously mixed (or mixed packing): when the support is coated with pure liquid phases and the two coated supports are mechanically mixed together in the correct proportion prior to filling the column.

(3) Multilayer packed: when the two coated packings are alternatively poured into the column to obtain the correct ratio (this technique has to be used when the two phases may react together).

(4) Coupled or series columns: when the two coated supports are separately packed in different lengths of the same tubing, or two simple columns are connected together.

The approximate calculation of the correct phases ratio can be made by linear interpolation of the retention index values obtained with pure liquid phases<sup>10,11</sup>. Fig. 4 shows the results of a heterogeneously mixed column prepared with a 1:3 ratio of TCP-Carbowax 20M stationary phases. A resolution of the tested isomeric mixture better than that obtained with pure liquid phases was obtained. The theoretical values of retention times, calculated by simple linear interpolation, slightly differ from experimental results, owing to the non-linearity of the change in retention index with the change in column composition. Temperature effects have also to be taken into account in order to correctly foresee the final behaviour and to calculate the composition of the "best column" for a given separation.

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