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## OPTIMIZATION OF THE COMPOSITION OF MIXED-PHASE COLUMNS FOR GAS CHROMATOGRAPHIC SEPARATION OF C<sub>1</sub>–C<sub>2</sub> HALOCARBONS

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### SUMMARY

Mixed-phase polar and non-polar columns were used for the separation of many chloro-, bromo- and iodomethanes, ethanes and ethenes, having one or more of the same or different halogen atoms in the molecule. The optimum phase composition was determined by using the window-diagram method. A column comprising 60% of OV-1 and 40% of SP-1000 [both 10% (w/w) on Chromosorb W DMCS (80–100 mesh)] was found useful for the separation of 33 different halogenated compounds. The effect of the analysis temperature on the resolution of closely eluted groups of peaks was investigated.

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### INTRODUCTION

In previously published papers<sup>1–3</sup>, different stationary phases were used for the gas chromatographic (GC) separation of trihalomethanes (THMs) and other volatile halocarbons, in order to achieve their identification in samples of polluted water on the basis only of GC techniques, thus avoiding the use of mass spectrometry for routine environmental analysis.

Satisfactory results were obtained in the GC identification and quantitation of THMs and some industrial and domestic solvents, by using a series arrangement of polar and non-polar liquid stationary phases (30 cm of 10% SP-1000 followed by 350 cm of 10% OV-1, both supported on 80–100 mesh Chromosorb W DMCS) which permitted the complete resolution of CHCl<sub>3</sub>, CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl, CHBr<sub>3</sub>, CCl<sub>2</sub>=CH<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>2</sub>CH<sub>3</sub>, CCl<sub>3</sub>CH<sub>3</sub>, CCl<sub>4</sub>, CHCl=CCl<sub>2</sub>, CCl<sub>2</sub>=CCl<sub>2</sub><sup>1</sup>.

The sensitivity and linearity of electron-capture detection (ECD) applied to the analysis of these compounds have been measured, and the efficiency of two commonly used extraction methods, static headspace and liquid–liquid techniques, evaluated<sup>4</sup>.

Analyses carried out in different environmental samples<sup>5</sup> showed the presence of some halogenated compounds, not identified as commonly used solvents, which can be formed by thermal cracking or by biological degradation of polymeric substances, paints, complex halogenated molecules of different kinds, etc. Some attempts have therefore been made to obtain an identification on the basis of GC analysis, by

TABLE I

BOILING POINTS (b.p.), MOLECULAR WEIGHTS (MW), ADJUSTED RETENTION TIMES,  $t'_R$  (min) AND RETENTION RELATIVE TO TRI-CHLOROETHYLENE,  $r$ , OF HALOGENATED COMPOUNDS ON PURE STATIONARY PHASES AND HOMOGENEOUSLY MIXED PHASES OF DIFFERENT COMPOSITIONS

Temperature: 63°C. Carrier gas flow-rate: 20 cm<sup>3</sup>/min. Numbers refer to peaks on the chromatograms.

No.	Compound	B.p. (°C)	MW	OV-1		SP-1000		50% OV-1-50% SP-1000		60% OV-1-40% SP-1000	
				$t'_R$	$r$	$t'_R$	$r$	$t'_R$	$r$	$t'_R$	$r$
1	CH <sub>3</sub> CHCl <sub>2</sub>	57.28	98.96	2.10	0.34	4.44	0.47	3.50	0.399	4.02	0.415
2	CH <sub>2</sub> =CCl <sub>2</sub>	37	96.94	1.37	0.22	1.48	0.157	1.71	0.195	1.89	0.195
3	ClCH=CCl <sub>2</sub>	87	131.39	6.11	1	9.44	1	8.76	1	9.68	1
4	Cl <sub>2</sub> C=CCl <sub>2</sub>	121	165.83	14.93	2.44	12.16	1.288	15.17	1.73	18.05	1.86
5	CCl <sub>4</sub>	76.54	153.82	4.68	0.766	4.36	0.462	5.06	0.577	6.06	0.626
6	ClCH <sub>2</sub> CH <sub>2</sub> Cl	83.74	98.96	3.66	0.599	16.26	1.722	11.04	1.26	11.10	1.147
7	CHCl <sub>3</sub>	61.70	119.38	3.02	0.494	11.49	1.217	8.00	0.913	8.16	0.843
8	CHBr <sub>2</sub> Cl	119	208.29	12.15	1.988	77.54	8.21	48.88	5.58	48.44	5.00
9	CHBrCl <sub>2</sub>	90	163.83	6.11	1	30.54	3.235	19.86	2.267	19.98	2.06
10	CHBr <sub>3</sub>	149.5	252.75	23.97	3.92	196.74	20.84	120.62	13.77	117.84	12.17
11	CH <sub>3</sub> CCl <sub>3</sub>	74	133.41	3.93	0.64	4.41	0.467	4.59	0.524	5.51	0.57
12	CH <sub>2</sub> Cl <sub>2</sub>	40	84.93	1.44	0.235	5.68	0.60	3.97	0.453	4.19	0.43
13	CH <sub>3</sub> CH <sub>2</sub> I	72.3	155.97	2.99	0.489	4.34	0.459	3.98	0.454	4.67	0.48

14	BrCH=CHBr <i>cis</i>	112.5	185.76	10.58	1.73	53.78	5.697	35.27	4.026	35.28	3.64
	BrCH=CHBr <i>trans</i>	108	185.76	8.37	1.369	24.39	2.58	18.05	2.11	18.78	1.94
15	BrCH <sub>2</sub> CH <sub>2</sub> Br	131.36	187.87	13.23	2.165	58.05	6.15	39.17	4.47	39.96	4.13
16	Cl <sub>3</sub> CCHCl <sub>2</sub>	162	202.3	47.66	7.80	182.57	19.66	127.61	14.56	—	—
17	CH <sub>3</sub> I	42.4	141.94	1.38	0.226	2.69	0.285	2.31	0.263	2.46	0.254
18	Cl <sub>3</sub> CCH <sub>2</sub> Cl	130.5	167.85	18.24	2.98	59.62	6.32	43.54	4.970	45.67	4.72
19	ClCH=CHCl <i>trans</i>	47.5	96.94	1.96	0.320	3.65	0.386	3.09	0.352	3.27	0.337
20	ClCH=CHCl <i>cis</i>	60.3	96.94	2.99	0.489	9.34	0.989	6.71	0.766	6.92	0.71
21	BrCH <sub>2</sub> CH <sub>2</sub> Cl	107	143.42	7.02	1.149	30.97	3.28	20.88	2.383	21.12	2.18
22	CH <sub>2</sub> I <sub>2</sub>	182	267.84	28.51	4.666	254.41	26.95	154.90	17.68	149.72	15.46
23	BrCCl <sub>3</sub>	104.7	198.28	9.78	1.60	15.96	1.69	14.33	1.636	15.93	1.64
24	C <sub>2</sub> H <sub>5</sub> Br	38.40	108.97	1.36	0.22	1.67	0.200	1.88	0.214	2.10	0.22
25	Cl <sub>2</sub> CHCHCl <sub>2</sub>	146.2	167.85	27.87	4.56	344.34	36.47	200.29	22.86	193.88	20.03
26	Br <sub>2</sub> CHCHBr <sub>2</sub>	243.5	345.67	54.99	9.00	216.67	27.95	140.24	16.01	143.26	14.80
27	BrCH <sub>2</sub> Cl	68.11	129.39	2.90	0.474	14.16	1.50	9.39	1.072	9.45	0.976
28	ClCH <sub>2</sub> I	109	176.38	6.90	1.129	40.38	4.277	26.06	2.97	26.02	2.69
29	CH <sub>3</sub> Br <sub>2</sub>	97	173.85	5.73	0.938	32.28	3.42	20.88	2.38	20.88	2.16
30	Cl <sub>3</sub> CCCl <sub>3</sub>	186	236.74	102.83	16.83	172.32	18.25	151.89	17.34	172.92	17.86
34	ICH <sub>2</sub> CH <sub>2</sub> I	200	281.86	63.83	10.45	—	—	214.96	24.54	214.57	22.17
35	ClCH <sub>2</sub> CH <sub>3</sub>	12.27	64.52	0.586	0.096	0.783	0.083	0.822	0.094	0.948	0.098

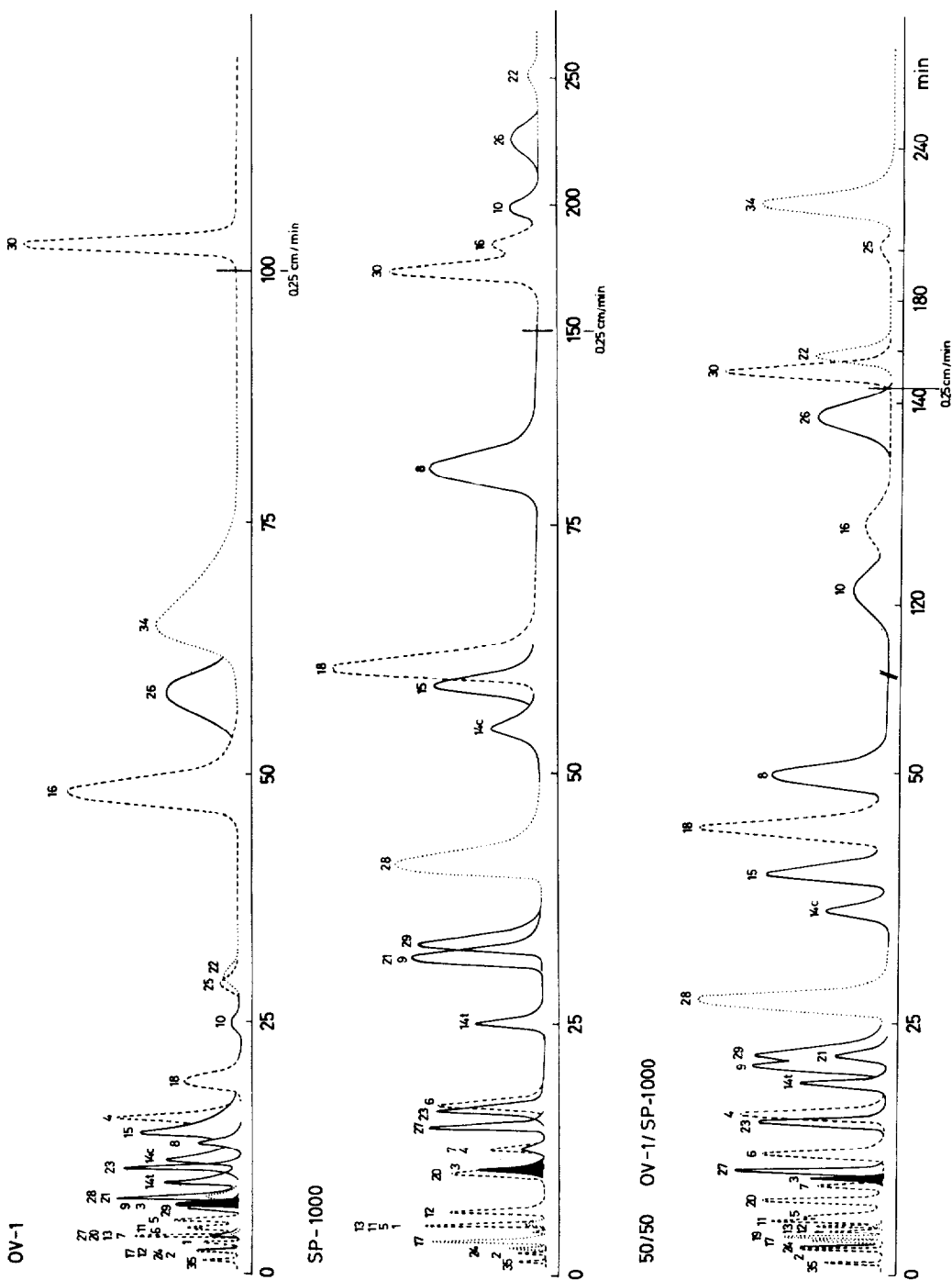


Fig. 1. Chromatograms of halogenated compounds on pure OV-1, pure SP-1000 and 50% OV-1-50% SP-1000. Column: 3 m  $\times$  1/8 in. O.D. Carrier gas flow-rate: 20 cm<sup>3</sup>/min. Temperature: 63°C. Peak numbers as in Table I. Full line: brominated compounds. Dotted line: chlorinated compounds. Dashed line: iodine-containing compounds.

investigating the behaviour of many halogenated compounds on stationary phases having different polarities. The aim of the first series of experiments was to find GC columns that can separate all the possible compounds with one and two carbon atoms and having different numbers of chlorine, bromine and iodine atoms.

## EXPERIMENTAL

The same stationary phases used previously<sup>1,4,5</sup>, *i.e.*, non-polar OV-1 and polar SP-1000 [both 10% (w/w) on Chromosorb W DMCS (80–100 mesh)], were tested, in stainless-steel columns (3 m × 1/8 in. O.D.). The columns were packed with a single phase or with homogeneously mixed phases<sup>6</sup>. A Varian 3760 gas chromatograph equipped with a <sup>63</sup>Ni(8 mCi) electron-capture detector and linear temperature programming was used.

Owing to the different ECD responses to compounds having different halogen atoms in the molecules, standard solutions of different concentrations in *n*-hexane or methanol were prepared, in order to obtain comparable peak sizes on the chromatograms. The analyses were carried out with pure standards after the addition of trichloroethylene, in order to determine the relative retention on the different columns at various temperatures, or with mixed samples, to test experimentally the effective resolving powers of the columns.

In order to optimize the performance of the mixed-phase columns, the optimum carrier gas velocity was chosen by finding the minimum value of the height equivalent to a theoretical plate (HETP) on the Van Deemter plot as a function of the carrier gas flow-rate.

## RESULTS AND DISCUSSION

Table I lists the compounds analysed, their molecular weights and boiling points and the retention, *r*, relative to trichloroethylene, on OV-1 and SP-1000 columns (length 3 m) used isothermally with a nitrogen flow-rate of 20 cm<sup>3</sup>/min. The *r* values on a 50:50 mechanically mixed packing are also shown. In all three instances, the chromatograms obtained showed some poorly resolved groups of peaks (Fig. 1).

For optimization purposes, the window-diagram method was used<sup>1,7-9</sup>, by plotting as a function of the column composition the  $\alpha$  values for those of the  $|n!/2(n-2)!|$  pairs of solutes that show interference;  $\alpha$  was calculated as  $\alpha_{ji} = r_j/r_i$  and was maintained greater than or equal to unity by inversion where necessary of the *i/j* assignment of each pair of solutes. Several windows formed by intersection of lines of  $\alpha$  show the phase composition range where the best separation can be achieved. Taking into account both the resolution and the analysis speed, this method showed that a column containing 40–43% of SP-1000 and 57–60% of OV-1 should be the most suitable for obtaining the complete separation. The last column of Table I shows the values of *r* obtained with this composition of the mixed phase.

Figs. 2 and 3 show the *r* values as a function of the column composition. The experimental determination of the retention times on the 50:50 mixed column is very useful due to the non-linear variation of *r* for many compounds when the stationary phase composition changes from pure non-polar to pure polar. Linear interpolation between the *r* values on pure OV-1 and on the 50:50 mixed-phase column permits

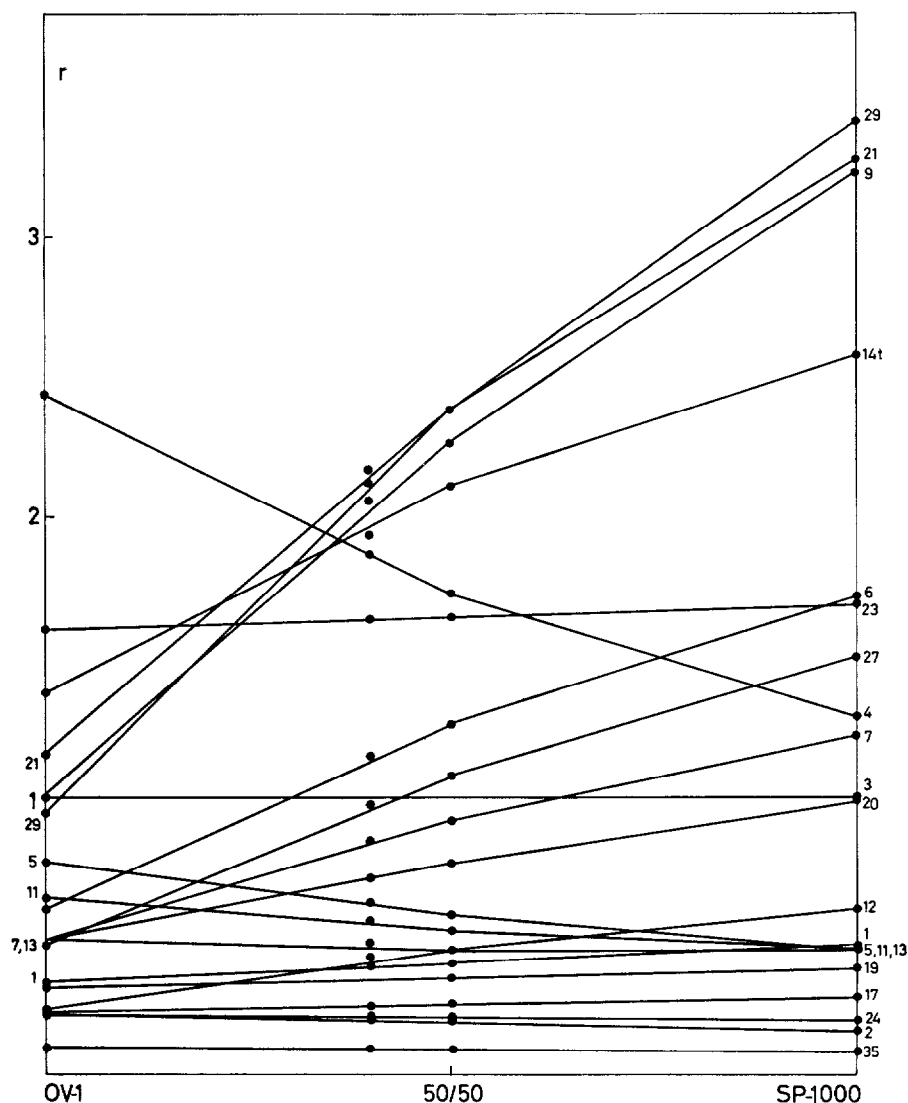


Fig. 2. Plots of the retention relative to trichloroethylene,  $r$ , against column composition for halogenated compounds. The numbers refer to the compounds listed in Table I.

the retention on the 60:40 column to be predicted with satisfactory accuracy. The experimental values are generally little greater than the linearly interpolated values, depending on the convexity of the curves.

Normalization methods have been suggested<sup>10-12</sup>, but in this instance the accuracy obtained by using the  $\alpha$  values was good enough to indicate the most suitable range of column composition, by taking into account the slightly different compositions of commercially available stationary phases.

Fig. 4 shows the values of the  $\log r$  as a function of the reciprocal of the

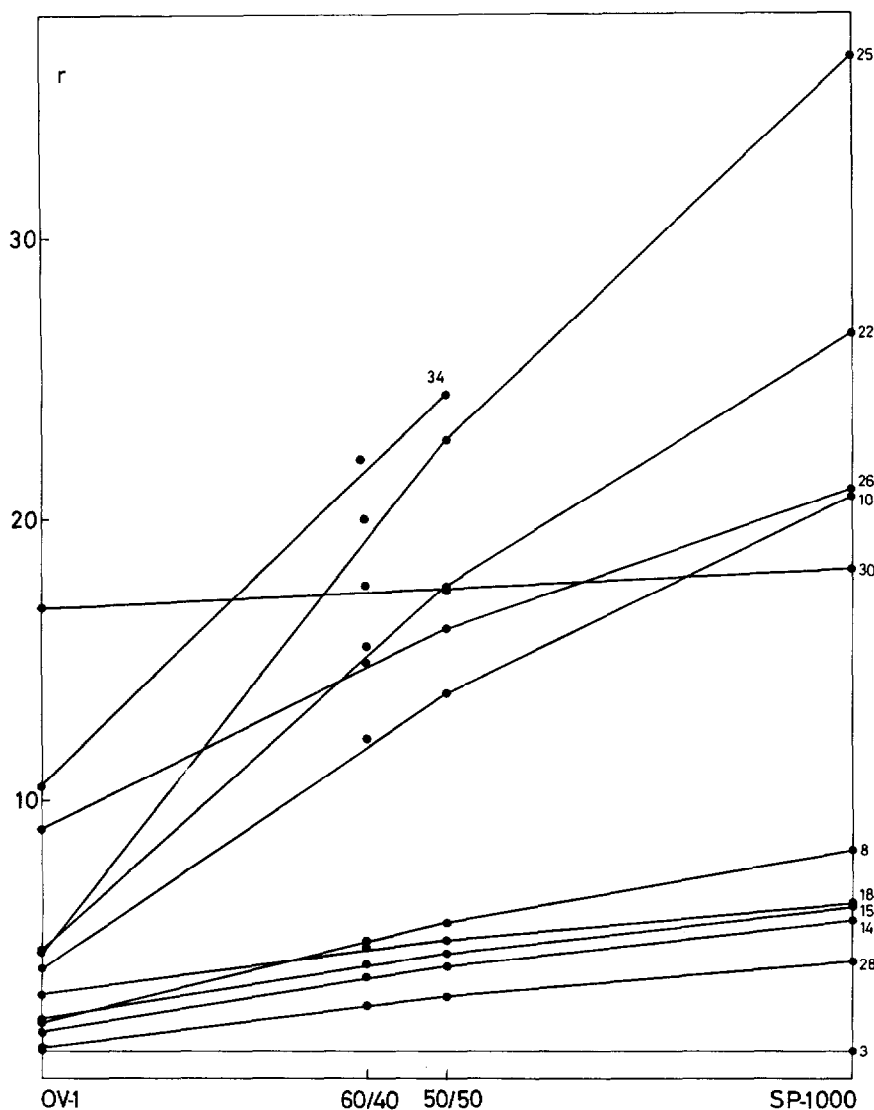


Fig. 3. Expanded  $y$ -axis plot of the retention relative to trichloroethylene,  $r$ , against column composition for halogenated compounds having short elution times. Other details as in Fig. 2.

absolute temperature. The graphs for the analysed compounds are linear, except for a few substances eluted with very short retention times (bromoethane, methyl iodide, chloroethane, 1,1-dichloroethylene) and whose behaviour at low column temperatures may be influenced by the rapid expansion of the solvent in the heated injector. The different slopes of the lines in Fig. 4 for closely eluting compounds results in some peak interference at different temperatures. On the basis of those graphs, the best resolution is predicted to occur between 65 and 70°C. In this temperature range all the analysed compounds show different retention times, but, of course, the pos-

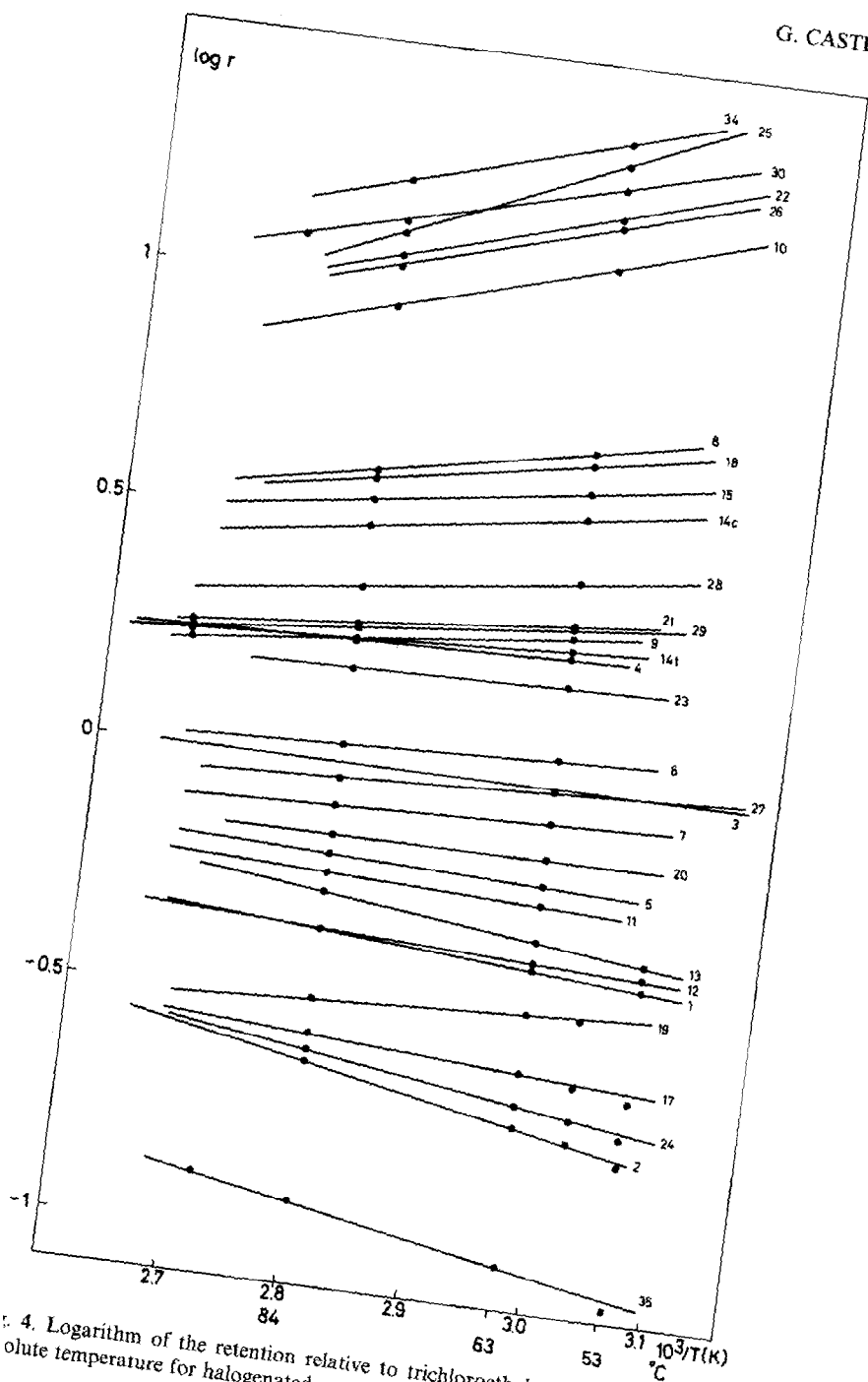


Fig. 4. Logarithm of the retention relative to trichloroethylene as a function of the reciprocal of the absolute temperature for halogenated compounds listed in Table I.



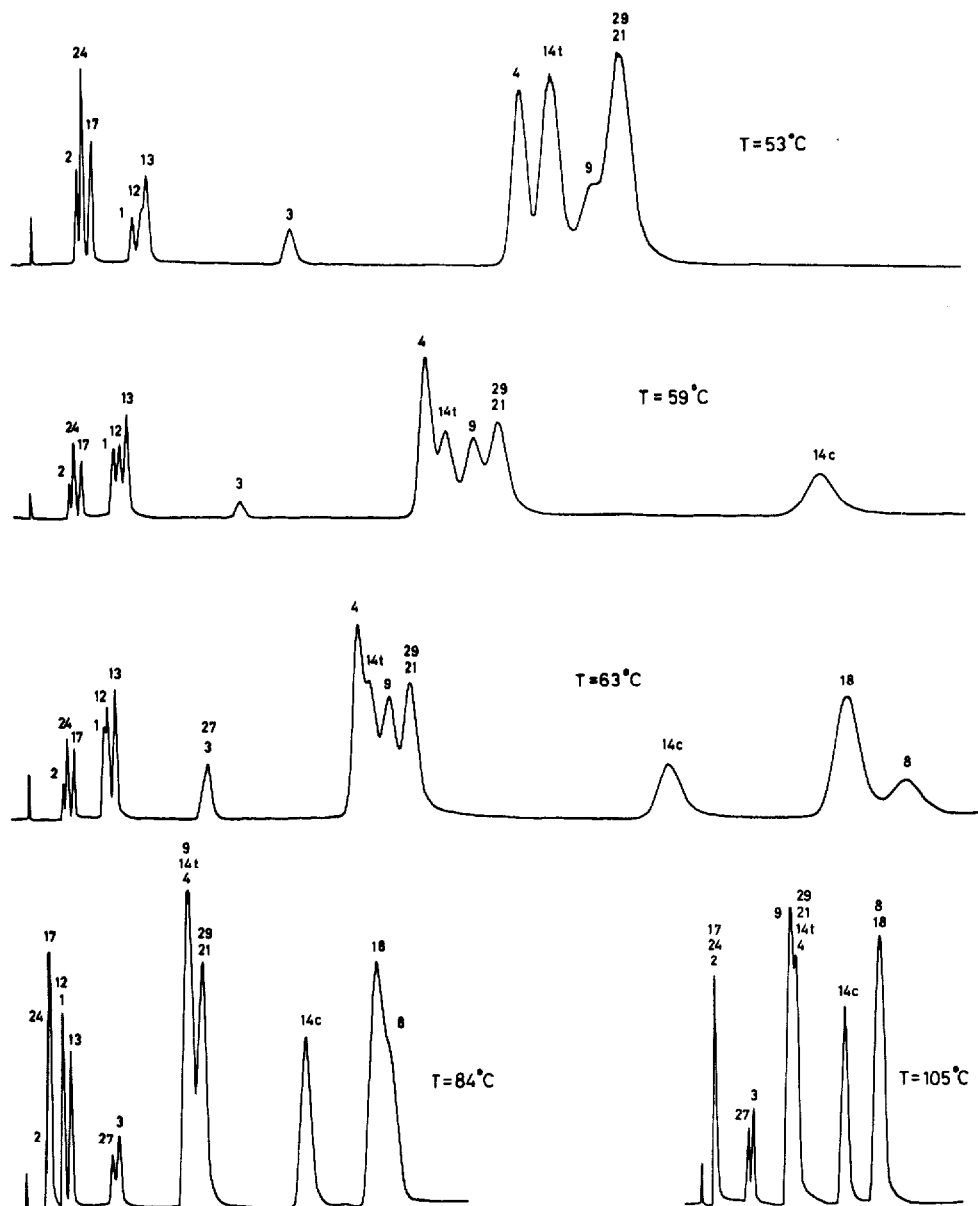


Fig. 5. Chromatograms of not completely resolved halogenated compounds on the mixed-phase column 60% OV-1-40% SP-1000 at various temperatures. Peak numbers as in Table I. Carrier gas flow-rate: 30 cm<sup>3</sup>/min.

sibility of true separation depends on the peak width, *i.e.*, on the number of theoretical plates, *n*, of the column used. In this instance, the 60:40 mixed-phase column gives a value of *n* of about 2600 for trichloroethylene, and therefore some groups of closely eluting peaks are not completely resolved, notwithstanding that the column

was used near to the optimum carrier gas flow-rate (about 30 cm<sup>3</sup>/min), as determined by interpolation of the Van Deemter plot of HETP as a function of the gas velocity.

Fig. 5 shows the change in resolution of these groups of peaks with changing temperature. In the region of rapidly eluted peaks, the most difficult separation is between 1,1-dichloroethane (peak 1), iodoethane (peak 13) and dichloromethane (peak 12). The latter compound shows a retention time close to that of peak 13 at low temperature and moves toward the retention time of peak 1 upon increasing temperature (see Fig. 4). The best resolution is obtained at 59°C (see Fig. 5).

A similar problem arises in the region between the elution time of tetrachloroethylene (peak 4) and those of dibromomethane (peak 29) and 1-chloro-2-bromoethane (peak 21). The last two compounds cannot be resolved on mixed-phase columns or on SP-1000, while a sufficient separation is achieved on the OV-1 column (see Fig. 1). The other peaks eluted in this retention time range, *i.e.*, *trans*-1,2-dibromoethylene (peak 14 t) and dichlorobromomethane (peak 9), are best resolved on the mixed phase at 59°C (see Fig. 5) and can easily be separated on SP-1000 (see Fig. 1).

In environmental samples, the simultaneous presence of all of the compounds listed in Table I is unlikely, and therefore many of the possible peak interferences are avoided. Furthermore, the sensitivity of ECD to compounds having different halogen atoms in the molecule can differ by two orders of magnitude<sup>4</sup> or more, and therefore a proper choice of the sample amount can reduce the reciprocal interference of the peaks of some closely eluted compounds.

Under isothermal conditions, the resolution of all the compounds tested requires more than 3 h. As the peaks with greater retention times are generally well resolved, temperature programming can shorten the analysis time, within the limits due to the ECD baseline change with changing temperature.

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