Journal of Chromatography, 454 (1988) 129–143
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 805

GAS CHROMATOGRAPHIC SEPARATION OF HALOGENATED COMPOUNDS ON NON-POLAR AND POLAR WIDE BORE CAPILLARY COLUMNS

G. CASTELLO*, A. TIMOSSI and T. C. GERBINO
Istituto di Chimica Industriale, Università, Corso Europa 30, I-16132 Genova (Italy)
(First received February 24th, 1988; revised manuscript received June 7th, 1988)

SUMMARY

Thirty five halogenated compounds (chloro-, bromo- and iodomethanes, ethanes and ethenes, with one or more different halogen atoms in the molecule) which can be found as contaminants in surface or waste water were analysed on non-polar (SPB-1) and polar (Supelcowax-10) wide bore capillary columns (60 m × 0.75 mm I.D.). Adjusted retention times and retention index values with respect to homologous series of *n*-alkanes and 1-iodoalkanes were measured for identification purposes. The use of capillary columns permits a more efficient separation than by using packed columns, mainly when non-polar stationary phases are used. Only 9 compounds were not resolved on SPB-1 (compared with 14 on packed OV-1), while compounds (different from those not separated on SPB-1) remained poorly resolved on Supelcowax-10 and on packed SP-1000, owing to coincidence of the partition coefficients. The simultaneous use of polar and non-polar capillary columns permits analysis of all of the components of the mixture.

INTRODUCTION

Gas chromatographic (GC) analysis of chlorinated contaminants in drinking water was previously carried out by using headspace and liquid–liquid extraction[1–3]. Packed columns of different polarities were used[4–8] that did not permit the complete separation of very complex mixtures of compounds. The connection of two columns of different polarities or the use of mixed polar–non-polar liquid phases[9,10] allowed a more efficient resolution of trihalogenomethanes and other halogenated compounds.

When these methods are applied to environmental samples, such as waste waters, surface water, contaminated soil and underground water supplies, many peaks, not identified as commonly used solvents, but probably formed by cracking or biological degradation of halogenated polymers, paints, pesticides, etc., are detected by specific electron-capture detection (ECD) and packed columns do not ensure their complete separation. Packed columns, having a maximum of about 4000 theoretical plates when a practically suitable length is used (the mixed polar–non-polar columns previously described[10] had about 2600 theoretical plates for trichloroethylene), do not

0021-9673/88/$03.50

permit the complete separation of all of the possible compounds. By changing the column polarity by use of different amounts of polar and non-polar liquid phases and by using the window diagram method[11,12] to select the best temperature for a given separation[13], a suitable resolution can be achieved between many compounds, but some groups of peaks are still partially overlapped. The retention indices of many halogenated aliphatic and alicyclic compounds were measured by using a fused-silica narrow bore (0.2 mm I.D.) capillary column coated with a non-polar liquid phase (methylsilicone)[14], and a linear relationship was found between the retention index values and the boiling points. Narrow bore capillary columns (0.20–0.25 mm I.D.) show a great resolving power (up to 150 000 plates) but are easily saturated (maximum load capacity 50–100 ng per component). Organic halogenated pollutants are often found in a very wide range of concentrations. The injection of sample volumes large enough to permit the detection of the less concentrated compounds can overload the column with too large amounts of the most common contaminants, yielding non-symmetrical and tailing peaks. Furthermore, the use of the splitting systems necessary in order to inject into the capillary column very small amounts of sample may result in a non-constant splitting ratio as a function of the molecular weight and vapour pressure of the halocarbons, which contributes to the differences in partition ratio during the liquid–liquid or headspace extraction, and to the lack of linearity of some specific detectors. For this reason, many EPA methods[3] still suggest the use of packed columns. Wide-bore glass capillary columns[15–19] permit direct sample injection without better inlet splitting and have higher efficiency compared with packed columns and a good inertness. They were used for the analysis of volatile priority pollutants in water by purge-and-trap extraction and gas chromatography–mass spectrometry (GC–MS)[20] and the factors influencing the behaviour of wide bore columns and their interfacing with the purge-and-trap device were investigated[21].

The search for analysis conditions that permit the best resolution of very complex mixtures, and the possibility of obtaining a positive identification of many compounds on the basis of different polarities, require an exhaustive investigation of many analytical parameters, as the carrier gas flow-rate and the column temperature. This paper describes the results of experiments carried out with polar and non-polar wide-bore capillary columns, for the separation of complex mixtures of halogenated methanes, ethanes and ethenes.

EXPERIMENTAL

The analyses were carried out by using a Varian 3700 gas chromatograph (Varian Associates, Palo Alto, CA, U.S.A.) equipped with nickel-63 electron-capture detection (ECD), linear temperature programming and a Varian Vista 402 integration and data acquisition computer. Flame ionization detection (FID) was also used in order to analyze non-electron-absorbing compounds (alkanes, alcohols) whose GC behaviour was compared with those of halogenated compounds.

Two wide-bore capillary columns (0.75 mm I.D.) were used: non-polar SPB-1 (dimethylpolysiloxane polymer, maximum allowable temperature 320°C) and polar Supelcowax-10 (polyethylene glycol, maximum allowable temperature 280°C with FID, 200°C with ECD) (Supelco, Bellefonte, PA, U.S.A.) both 60 m long. In both columns the stationary phase was chemically bonded to the column wall. The analyses

TABLE I

RETENTION TIMES, t_R, AND NUMBER OF THEORETICAL PLATES, n, ON NON-POLAR (SPB-1) AND POLAR (SUPELCOWAX-10) COLUMNS

Nitrogen flow-rate 4 ml/min.

Compound	*SPB-1*		*Supelcowax-10*	
	t_R *(min)*	$n \cdot 10^{-3}$	t_R *(min)*	$n \cdot 10^{-3}$
Tribromomethane	15.7	76		
Pentachloroethane	25.7	59		
Hexachloroethane	47.3	51		
Bromodichloromethane			22.3	50
Chloroiodomethane			27.9	53
1,1,1,2-Tetrachloroethane			37.5	41
Dibromochloromethane			46.3	45

were carried out on the two columns installed in the GC oven by using the Supelco conversion kit for direct injection and a make-up gas detector adapter in order to supply the proper amount of carrier gas for ECD without influencing the flow-rate into the capillary column. Nitrogen was used as the carrier gas, at a flow-rate of 4 ml/min, selected after a series of experiments carried out to determine the resolving power of the columns as a function of the carrier gas velocity. Flow-rates below 3 ml/min should give an higher number of theoretical plates, n, but the detector response becomes irregular, probably due to imperfect mixing between the gas coming from the column and the make-up gas (30 ml/min). The flow-rate selected represents a good compromise between speed and efficiency. Table I shows the values of t_R and n for some compounds on polar and non-polar columns.

The true temperature of the column was monitored by inserting between its coils a thermocouple connected to a digital thermometer with 0.1°C precision. The gas pressure at the column inlet was monitored by connecting a mercury micromanometer to a capillary T-piece at the injection port. The increase in dead volume was negligible (no appreciable effect on the values of n was found) and the pressure was measured within $\pm$ 1 Torr (133 Pa). The injector and detector temperatures were set at 210 and 260°C, respectively.

Standard solutions of the compounds listed in Table II were prepared at concentrations ranging between 10^{-3} and 1 g/l, taking into account the different sensitivity of ECD to various compounds, in order to have peaks with similar areas. The sample volume injected was 0.5 μl; therefore, the most concentrated samples contained about 0.5 μg of halocarbons, too low to saturate the columns, having a capacity of about 15 μg per peak.

RESULTS AND DISCUSSION

Table II shows the analysed compounds, their boiling points, molecular weights, t'_R and retention relative to 1,1,2-trichloroethylene, r, on SPB-1 and Supelcowax-10 columns at 75°C. Figs. 1 and 3 show the chromatograms of the mixture on the

TABLE II

ADJUSTED RETENTION TIMES, t'_R, AND RETENTION RELATIVE TO 1,1,2-TRICHLOROETHYLENE, r, OF HALOGENATED HYDROCARBONS ANALYZED ON NON-POLAR AND POLAR WIDE BORE CAPILLARY COLUMNS AT 75°C

Boiling points and molecular weights are also reported.

No.	*Compound*	*B.p.* (°C)	*Mol.wt.*	*SPB-1*		*Supelcowax-10*	
				t'_R	r	t'_R	r
1	1,1,1,2-Tetrabromoethane	112	345.67	2.72	0.96	6.24	1.17
2	1,1,1,2-Tetrachloroethane	130.5	167.85	8.14	2.88	29.55	5.53
3	1,1,2,2-Tetrabromoethane	243.5	345.67	19.19	6.80	–	–
4	1,1,2,2-Tetrachloroethane	146.2	167.85	11.66	4.13	145.78	27.27
5	1,1,2-Trichloroethane	113.8	133.41	4.32	1.53	30.30	5.67
6	1,1,2-Trichloroethylene	87	131.39	2.82	1.00	5.35	1.00
7	1,1-Dichloroethane	57.28	98.96	1.06	0.38	2.57	0.48
8	1,1-Dichloroethylene	37	96.94	0.74	0.26	0.96	0.18
9	1,2-Dibromoethane	131.36	187.87	5.73	2.03	29.55	5.53
10	1,2-Dichloroethane	83.74	98.96	1.76	0.63	8.65	1.62
11	1,2-Diiodoethane	200	281.86	24.72	8.77	–	–
12	1-Bromo-2-chloroethane	107	143.20	3.19	1.13	15.84	2.96
13	Bromochloromethane	68.11	129.39	1.24	0.44	7.62	1.43
14	Bromoethane	38.4	108.97	0.74	0.26	1.23	0.23
15	Tribromomethane	149.5	252.75	9.99	3.54	91.05	17.03
16	Tetrabromomethane	189	331.65	33.93	12.03	91.42	17.09
17	Tetrachloromethane	76.54	153.82	2.26	0.80	2.57	0.48
18	*cis*-1,2-Dichloroethylene	60.3	96.94	1.23	0.44	5.20	0.97
19	Trichloromethane	61.7	119.38	1.23	0.44	6.24	1.17
20	Chloroiodomethane	109	176.38	3.10	1.10	20.62	3.86
21	Dibromochloromethane	119	208.29	5.31	1.89	37.62	7.04
22	Dibromomethane	97	173.85	2.72	0.96	16.62	3.11
23	Dichlorobromomethane	90	163.83	2.82	1.00	15.37	2.88
24	Dichloromethane	40	84.93	0.74	0.26	3.44	0.64
25	Diiodomethane	182	267.84	11.98	4.25	116.93	21.88
26	Hexachloroethane	186	236.74	41.80	14.82	80.53	15.07
27	Iodoethane	72.3	155.97	1.28	0.46	2.57	0.48
28	Triiodomethane	218	393.73	20.08	7.12	–	–
29	Iodomethane	42.4	141.94	0.74	0.26	1.67	0.31
30	1,1,1-Trichloroethane	74	133.41	1.91	0.68	2.57	0.48
31	Pentachloroethane	162	202.30	20.08	7.12	84.47	15.80
32	Tetrachloroethylene	121	165.83	6.61	2.34	6.63	1.24
33	*trans*-1,2-Dichloroethylene	47.5	96.94	1.00	0.36	2.18	0.41
34	Trichlorobromomethane	104.7	198.28	4.54	1.61	8.45	1.58
35	1-Iodopropane	102.4	169.99	–	–	4.76	0.89
36	1-Iodobutane	130.5	184.02	–	–	8.45	1.58
37	1-Iodopentane	157	198.05	–	–	15.84	2.96
38	1-Iodohexane	181.3	212.08	–	–	29.55	5.53
39	1-Iodoheptane	204	226.10	–	–	56.33	10.54

non-polar and polar columns respectively. Numbers refer to the compounds listed in Table II. Some compounds were not included in the complete sample, due to the presence of impurities that could interfere with other peaks. Fig. 2 shows an example of a chromatogram of these compounds on the non-polar column.

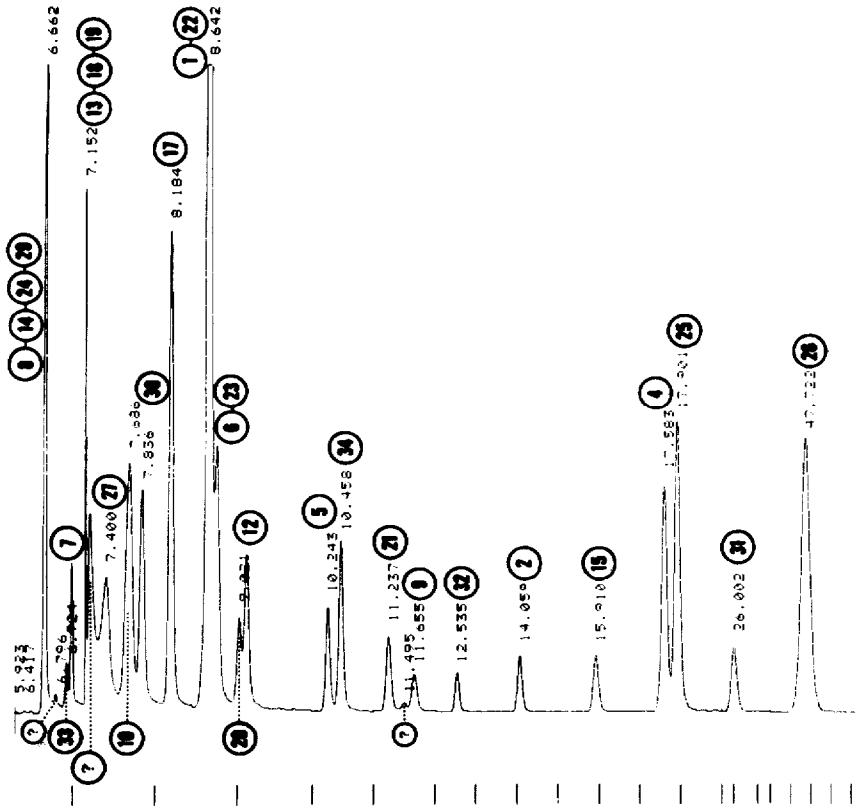

Fig. 1. Chromatogram of halogenated compounds on an SPB-1 wide bore capillary column, 60 m × 0.75 mm I.D., 1.0-μm film. Carrier gas (nitrogen) flow-rate: 4 cm^3/min. Temperature: 75°C. Peak numbers as in Table II.

Some experiments were carried out in order to investigate the effect of temperature on the resolution. On a non-polar column, five groups of peaks are not well resolved (see Fig. 1) at 75°C. (a) 1,1-dichloroethylene; bromoethane; dichloromethane; iodomethane (peaks 8, 14, 24, 29); (b) bromochloromethane; *cis*-1,2-dichloroethylene; chloroform (peaks 13, 18, 19); (c) 1,1,1,2-tetrabromoethane; dibromomethane (peaks 1, 22); (d) 1,1,2-trichlorocthylene; dichlorobromomethane (peaks 6, 23); (e) iodoform; pentachloroethane (peaks 28, 31) (see Fig. 2).

Group (a) consists of low boiling compounds, and therefore is suitable to investigate the influence of decreasing temperature. Fig. 4 shows the separation at 33 and 22°C and with temperature programming from 8 to 15°C at about 0.5°C/min obtained by a subambient temperature accessory. Groups (b)–(d) are resolved [except for peaks 1 and 22 (1,1,1,2-tetrabromoethane and dibromomethane)] at 45°C in about 15 min (see Fig. 5). The resolution of group (c) at low temperature on the non-polar column is also possible, but the retention times are too long for practical purposes.

It is known that sometimes the resolution of closely eluting compounds increases with increasing temperature, and that at different temperatures the elution order can

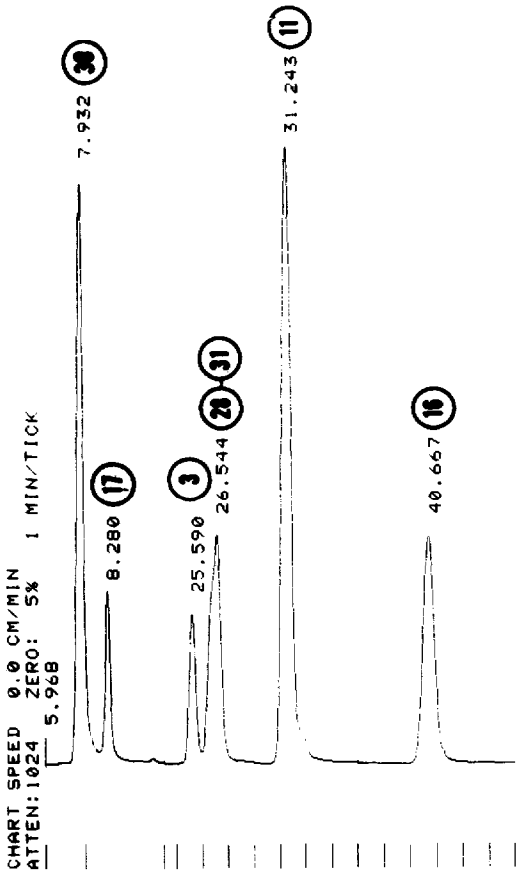

Fig. 2. Chromatogram of halogenated compounds (not included in the mixture of Fig. 1) on an SPB-1 wide bore capillary column. Other details as in Fig. 1.

change. Also in the analysis of these compounds this phenomenon has to be taken into account. As an example, Fig. 6 shows the effect of temperature on the separation of 1,1,1,2-tetrabromoethane, 1,1,2-trichloroethylene, chloroform, tetrachloroethylene (peaks 1,6,19,32), which exhibits an inversion of the elution times between peaks 1 and 19 and a perfect coincidence at 75.5°C. Fig. 7 shows the relative retention, r, of compounds 1, 19 and 32 as a function of the reciprocal of the absolute temperature (Arrhenius plot).

In general, temperature programming offers the best way for separation of complex mixtures, due to both the reduction in analysis time and to the enhanced resolution when intersection of the Arrhenius plots takes place, because peaks separated at low temperature are not combined again when the temperature increases. Therefore, some different programming rates were tested for the separation of the complete mixture. A good compromise between resolution and analysis time was obtained by an initial isotherm at 75°C followed by a linear increment of 20°C/min for

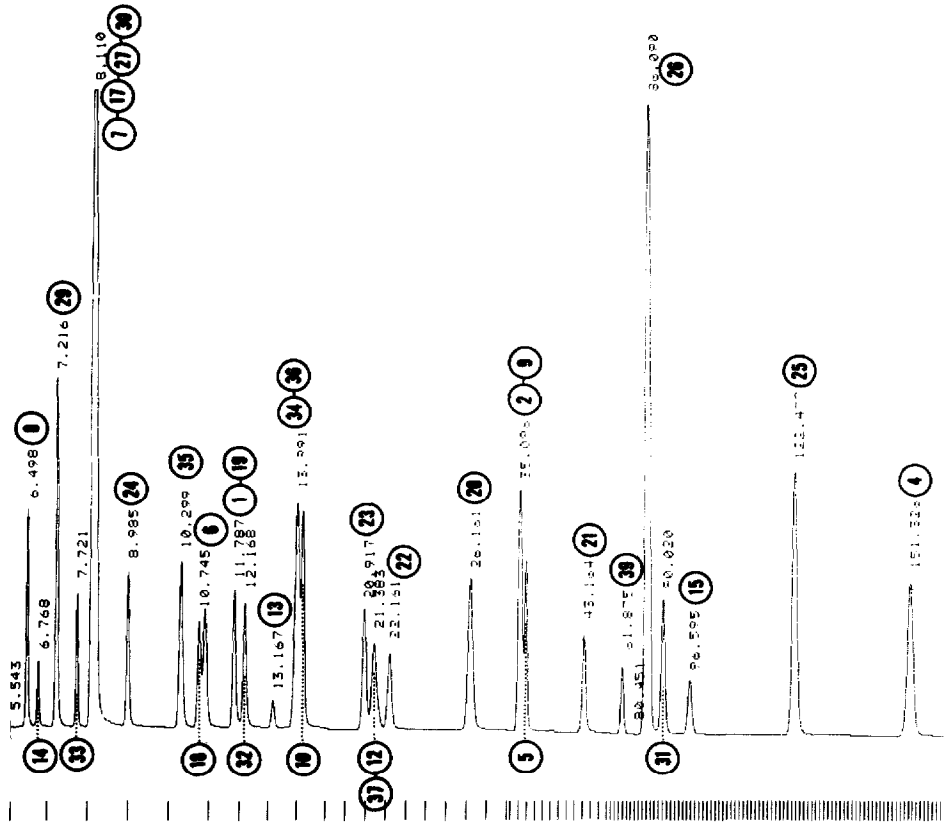

Fig. 3. Chromatograms of halogenated compounds and 1-iodoalkanes on Supelcowax-10 wide bore capillary column, 60 m × 0.75 mm I.D., 1.0-μm film. Carrier gas (nitrogen) flow-rate: 4 cm^3/min. Temperature: 75°C. Peak numbers as in Table II.

the non-polar and of 10°C/min for the polar column up to 120 and 110°C, respectively. Figs. 8 and 9 show the resulting chromatograms. A better resolution can be obtained by using a lower initial temperature, but the time needed for complete analysis strongly increases, as a programming rate greater than 25°C/min may damage the columns.

Polar and non-polar columns can be connected in parallel, by using two detectors and two injectors or a 50/50 capillary splitter on the same injector. Existing data processing systems, such as the dedicated Varian Vista 402 with the two-channel option or the all-purpose software Nelson Series 3000 Laboratory Data System (Nelson Analytical, Cupertino, CA, U.S.A.) with one standard two-channel Model 760 intelligent interface, can automatically integrate and correlate both chromatograms, which ensures a satisfactory resolution of the majority of the peaks of the mixture tested, because the results are complementary. As an example, simultaneous elution of the compounds belonging to group (a), discussed above, which on the non-polar column gives an unique peak at 6.66 min (see Fig. 1) and can be resolved only by decreasing the column temperature with sub-ambient temperature programming, were

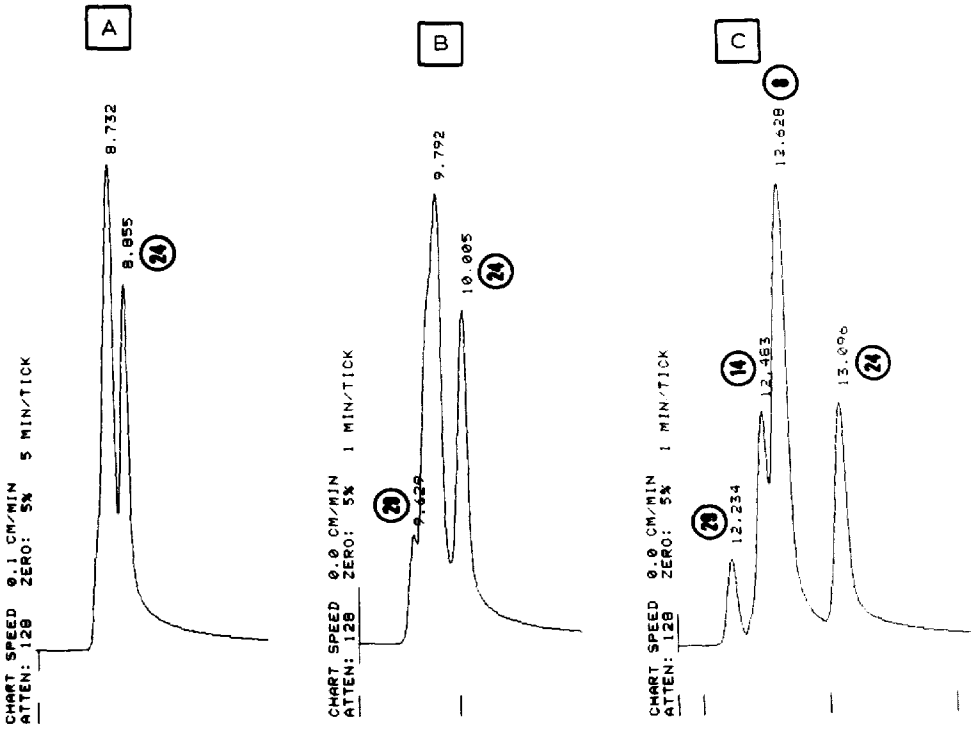

Fig. 4. Chromatogram of incompletely resolved halogenated compounds on an SPB-1 wide bore capillary column at various temperatures: (A) column temperature = 33°C; (B) column temperature = 22°C; (C) temperature programmed from 8 to 15°C at about 0.5°C/min.

completely resolved on the polar column (see Fig. 2). On the contrary, the compounds that coeluted in a peak at 8.11 min on the polar column (1,1-dichloroethane; carbon tetrachloride; iodoethane and methylchloroform, peaks 7, 17, 27 and 30) were easily separated on the non-polar phase.

Nine compounds only were not resolved on non-polar capillary SPB-1, compared with 14 compounds not resolved by using the non-polar packed column OV-1[3–5]. The performance of polar Supelcowax-10 and packed SP-1000 was about the same: 8 compounds (different from those not resolved on SPB-1) were coeluted on both the capillary and packed column; this is due to identical or very similar partition coefficients on the polyethylene glycol liquid phase of the two polar columns, because the efficiency was much greater for the capillary column (40 000–70 000 theoretical plates compared with 3000–4000 for packed columns).

The identification of the compounds on the basis of GC analysis requires a knowledge of the elution order and of the relative positions of the peaks more accurate than that permitted by the use of retention relative to 1,1,2-trichloroethylene, r mainly for substances with longer retention times. The use of the retention index, I, is more suitable, because this parameter refers to the elution of an homologous series. In the analysis of halogenated compounds, the use of linear alkanes as in the standard

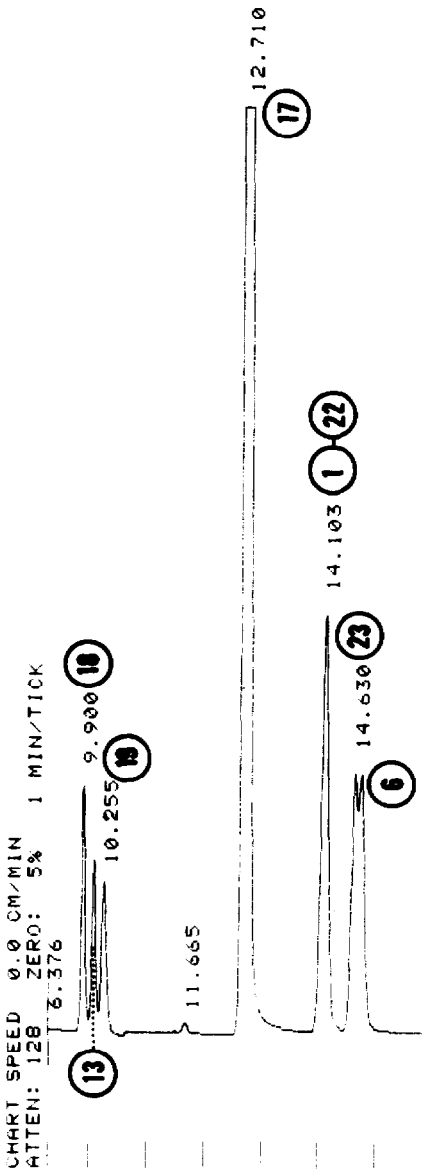

Fig. 5. Chromatogram of incompletely resolved halogenated compounds on an SPB-1 wide bore capillary column at 45°C. Other details as in Fig. 1.

Kováts method[22] is impractical when ECD is used, which is not sensitive to saturated compounds. The homologous series of 1-iodoalkanes was therefore used[23,24] and a correlation between the Kováts I and the I_{ni} with respect to normal iodides can be calculated by using FID and injecting similar amounts of *n*-alkanes and 1-iodoalkanes. Fig. 10 and Table III respectively show the linear behaviour of these homologous series

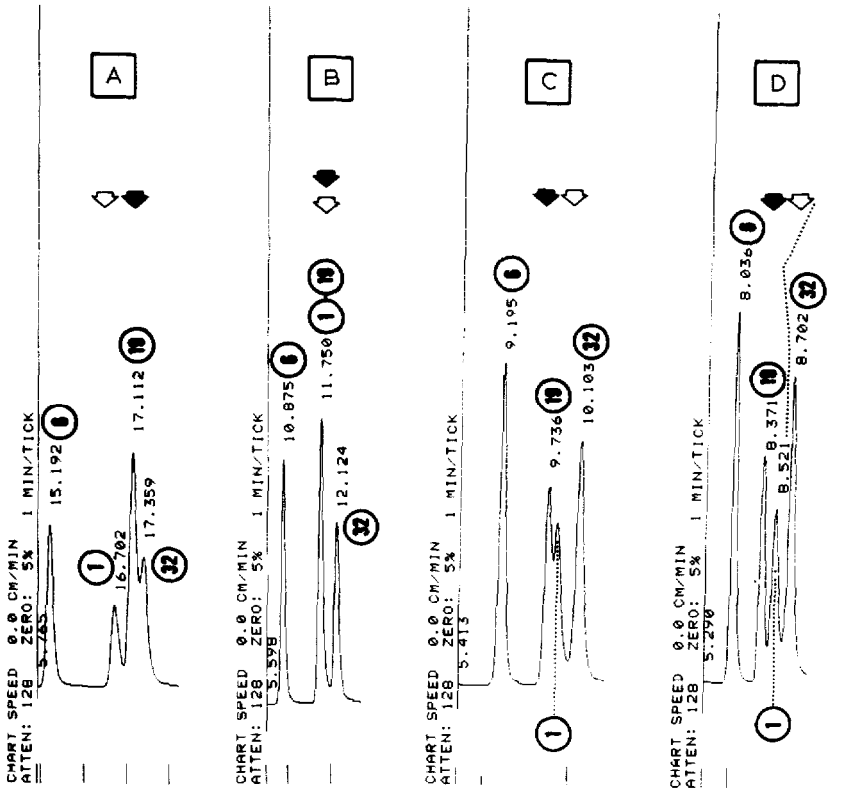

Fig. 6. Effect of temperature on the separation of incompletely resolved halogenated compounds on a Supelcowax-10 wide bore capillary column, showing inversion of the elution order. Column temperatures: (A) 59.8; (B) 75.5; (C) 85.6; (D) 96.3°C.

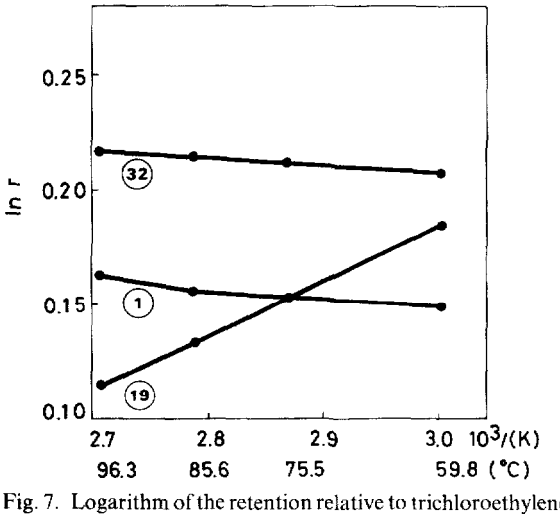

Fig. 7. Logarithm of the retention relative to trichloroethylene as a function of the reciprocal of the absolute temperature for some of the halogenated compounds listed in Table II.

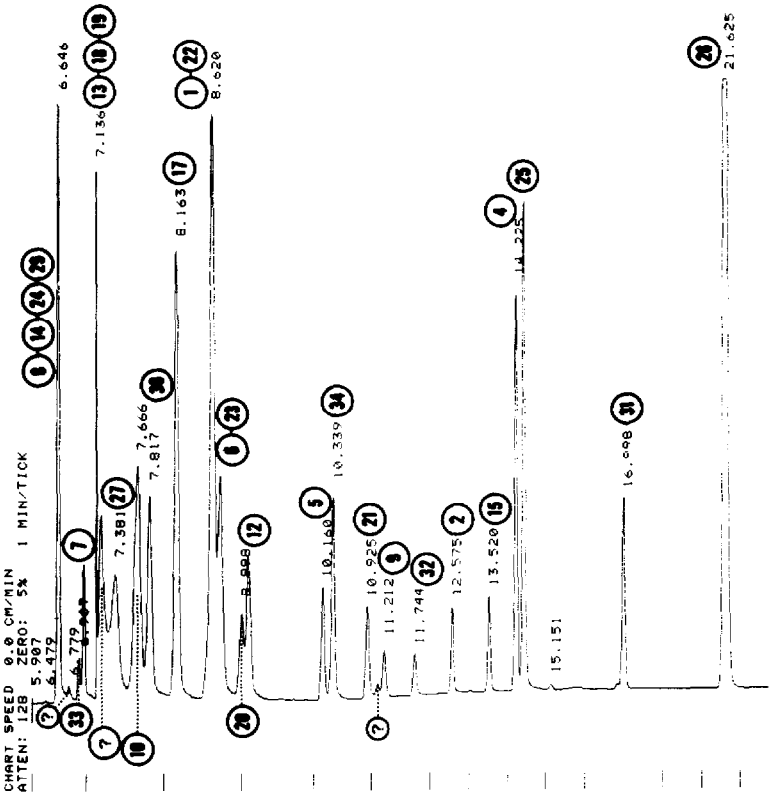

Fig. 8. Chromatograms of halogenated compounds on SPB-1. Temperature programming: isothermal at 75°C for 10 min, then increased at 20°C/min up to 120°C. Peak numbers as in Table II. Other details as in Fig. 1.

on non-polar and polar column, and the slope, m, and intercept, q, of the equations:

$$y_i = q_i + (m_i I_{ni}/100) \quad \text{for 1-iodoalkanes}$$

$$y_p = q_p + (m_p I/100) \quad \text{for } n\text{-alkanes}$$

The Kováts retention index with respect to n-alkanes, I, can therefore be calculated

$$I = \frac{(q_i - q_p) \cdot 100}{m_p} + \frac{m_i - I_{ni}}{m_p} = A_0 + A_1 I_{ni}$$

and the constants A_0 and A_1 permit a quick conversion of I_{ni} into I values. For the columns used, the values of these constants are: SPB-1, $A_0 = 418.35$, $A_1 = 0.973$; Supelcowax-10, $A_0 = 715.3$, $A_1 = 0.927$. The parallel behaviour of the lines in Fig. 10 also permits a graphical determination of the I values, with horizontal lines drawn from the position of the substance on the 1-iodoalkane line to cross the n-alkane line.

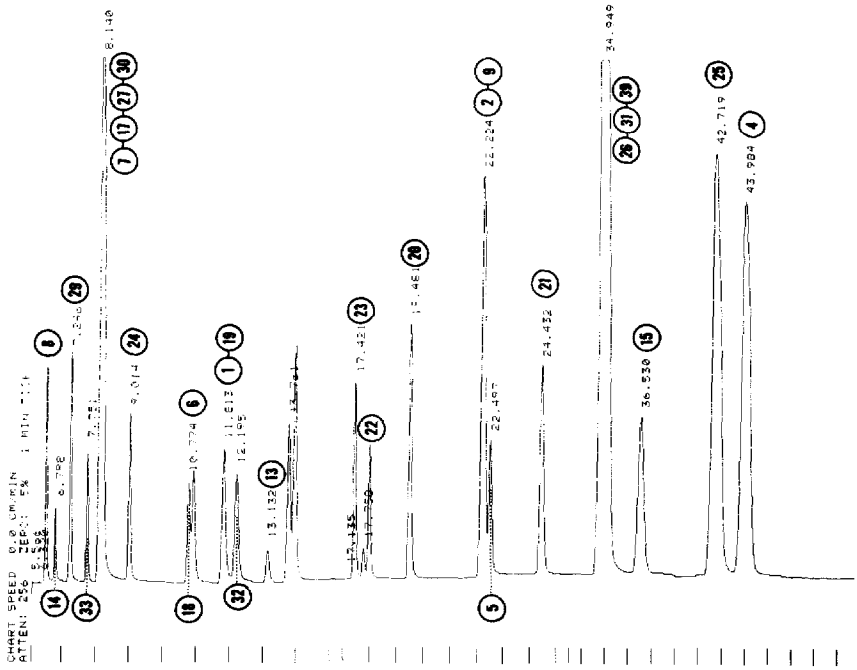

Fig. 9. Chromatograms of halogenated compounds on Supelcowax-10. Temperature programming: isothermal at 75°C for 10 min, then increased at 10°C/min up to 110°C. Peak numbers as in Table II. Other details as in Fig. 3.

Fig. 10 and Table III also show the linear behaviour of other homologous series (1-bromoalkanes and 1-alcohols), which were analyzed in order to test the validity of a quick method for the determination of the column polarity. The Rohrschneider's and McReynolds' constants[25,26] calculated from the I values are the most often used

TABLE III

SLOPE, m, INTERCEPT, p, CORRELATION COEFFICIENT, r, OF STRAIGHT LINES ln t'_R AS A FUNCTION OF THE NUMBER OF CARBON ATOMS IN VARIOUS HOMOLOGOUS SERIES, AND HORIZONTAL DISTANCE BETWEEN PARALLEL LINES IN FIG. 10, ΔC, USED AS A MEASUREMENT OF THE COLUMN POLARITY

	m	p	r	ΔC
Non-polar				
n-Alkanes	0.774	−4.182	1.000	–
1-Iodoalkanes	0.753	−0.944	1.000	4.11
1-Bromoalkanes	0.757	−1.521	1.000	3.36
1-Alcohols	0.781	−2.231	0.998	2.55
Polar				
n-Alkanes	0.673	−4.977	1.000	–
1-Iodoalkanes	0.623	−0.163	0.999	7.01
1-Bromoalkanes	0.655	−1.027	1.000	5.79
1-Alcohols	0.618	0.303	0.991	7.75

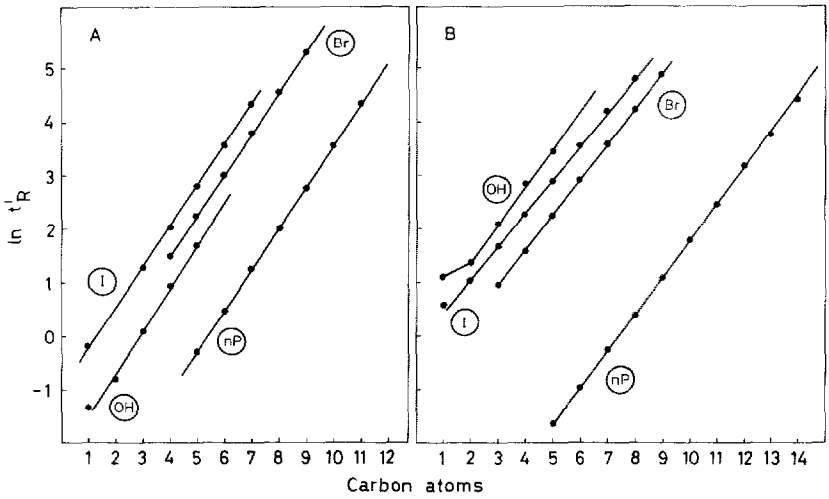

Fig. 10. ln t'_R for different homologous series as a function of number of carbon atoms in the linear chain: (A) non-polar column; (B) polar column; nP = linear alkanes; OH = alcohols; Br = 1-bromoalkanes; I = 1-iodoalkanes.

method for polarity classification. Table IV shows the values of t'_R, I and of the ΔI (difference between the I values on polar and non-polar liquid phases) on SPB-1 and Supelcowax capillary columns for the Rohrschneider's and some of the McReynolds' probes. The latter values cannot correctly be identified with the McReynolds

TABLE IV

VALUES OF t'_R AND I OF ROHRSCHNEIDER'S AND McREYNOLDS' PROBES ON A NON-POLAR AND POLAR CAPILLARY COLUMN, AND DIFFERENCES CORRELATED TO POLARITY (SEE TEXT)

t_M = Column dead time (min).

Compound	*SPB-1* $t_M = 6.701$		*Supelcowax-10* $t_M = 6.516$		$I^{(P)} - I^{(NP)}$
	t'_R	I	t'_R	I	
1 Benzene	2.59	661.6	4.69	967.7	306.1
2 Ethanol	0.38	414.4	3.89	940.7	526.3
3 1-Butanol	2.53	658.7	16.44	1145.9	487.2
4 Methyl ethyl ketone	1.40	582.7	3.44	923.3	340.6
5 Methyl propyl ketone	2.66	664.8	5.78	997.6	332.8
6 Nitromethane	1.03	543.6	18.11	1160.9	617.3
7 Nitropropane	3.77	709.8	26.16	1219.3	509.5
8 Pyridine	4.45	731.5	21.86	1190.1	458.6
9 1-Iodobutane	7.88	806.2	9.61	1067.0	260.8
Sum ΔI Rohrschneider (1+2+4+6+8)					2248.6
Sum ΔI McReynolds (1+3+5+7+8)					2094.2

constants, because the polarity of the SPB-1 liquid phase (dimethylpolysiloxane polymer) is probably higher than that of the standard squalane liquid phase, taken as the non-polar reference term in both polarity classification methods. The relative distances of the parallel lines in Fig. 10, expressed by the values of the corresponding intercepts or by the horizontal distance ΔC along the x axis (Table III), are correlated to the column polarity. The distance, ΔC, between n-alkanes and 1-alcohols is probably the best and most rapid way to identify the difference in polarities of two liquid phases. It can be obtained by injecting only four compounds (two n-alkanes and two alcohols) with carbon atom numbers different enough to permit a precise calculation of the parameters of the straight lines in Fig. 10. This procedure is much easier than the determination of the Rohrschneider's and McReynolds' constants, requiring the analysis of the polarity probes on squalane and on the column under evaluation, and can be useful mainly when different columns are connected in series.

CONCLUSIONS

The use of wide bore capillary columns for the analysis of volatile chlorinated compounds in water supplies offers some advantages from the point of view of resolution of complex mixtures when compared with classical packed columns. At the same time, the introduction of the whole sample without inlet splitting, owing to the relatively high capacity of these columns compared to narrow bore capillaries, permits the use of different extraction and concentration procedures without introducing further uncertainty due to the splitting system. Simultaneous analysis on polar and non-polar stationary phases permits resolution of the 39 compounds tested. Suitable identification procedures on the basis of tabulated retention index values can be carried out. The analysis of homologous series of polar and non-polar compounds also permits the relative polarity of the columns to be measured more easily than by using Rohrschneider's or McReynolds' methods.

REFERENCES

1 *The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method*, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1979, Method 501.1.
2 *The Analysis of Trihalomethanes in Drinking Water by Liquid/liquid Extraction*, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1979, Method 501.2.
3 G. Castello, T. C. Gerbino and S. Kanitz, *J. Chromatogr.*, 351 (1986) 165.
4 L. D. Hinshaw, *J. Gas Chromatogr.*, 8 (1966) 300.
5 D. A. Solomons and J. S. Ratcliffe, *J. Chromatogr.*, 76 (1973) 101.
6 L. Žilka and M. Matucha, *J. Chromatogr.*, 148 (1978) 229.
7 E. A. Dietz, Jr. and K. F. Singley, *Anal. Chem.*, 51 (1979) 1809.
8 G. Agazzotti and G. Predieri, *Water Res.*, 8 (1986) 959.
9 G. Castello, T. C. Gerbino and S. Kanitz, *J. Chromatogr.*, 247 (1982) 263.
10 G. Castello and T. C. Gerbino, *J. Chromatogr.*, 366 (1986) 59.
11 R. J. Laub and J. H. Purnell, *J. Chromatogr.*, 112 (1975) 71.
12 J. H. Purnell, in F. Bruner (Editor), *The Science of Chromatography* (*Journal of Chromatography Library*, Vol. 32), Elsevier, Amsterdam, 1985, p. 362.
13 G. Castello and T. C. Gerbino, *J. Chromatogr.*, 437 (1988) 33.
14 A. Yasuhara, M. Morita and K. Fuwa, *J. Chromatogr.*, 328 (1985) 35.
15 L. S. Ettre, *Chromatographia*, 17 (1983) 553.

16 L. S. Ettre, *Chromatographia*, 18 (1984) 477.
17 M. L. Duffy, *Int. Lab.*, April (1986) 78.
18 R. T. Wiedermer, S. L. McKinley and T. W. Rendl, *Int. Lab*, May (1986) 68.
19 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. Chromatogr.*, 279 (1983) 9.
20 V. Lopez-Avila, R. Wood, M. Flanagan and R. Scott, *J. Chromatogr. Sci.*, 25 (1987) 286.
21 N. H. Mosesman, L. M. Sidinsky and S. D. Corman, *J. Chromatogr. Sci.*, 25 (1987) 351.
22 E. Kovats, *Helv. Chim. Acta*, 41 (1958) 1915.
23 G. Castello and G. D'Amato, *J. Chromatogr.*, 76 (1973) 293.
24 G. Castello and G. D'Amato, *J. Chromatogr.*, 79 (1973) 33.
25 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
26 W. A. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.