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Analysis of haloalkanes on wide-bore capillary columns of different polarity connected in series

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ABSTRACT

Thirty chloro-, bromo- and iodo-methanes, -ethanes and -ethenes, with one or more identical or different halogen atoms in the molecule, that can be present as contaminants in polluted surface or underground water were separated by using non-polar (SPB-1) and polar (Supelcowax-10) wide-bore capillary columns connected in series. Retention times and indices were measured at different temperatures and carrier gas flow-rates. The most efficient combination was obtained by connecting the two columns in the order non-polar + polar, which permitted the complete resolution of 26 compounds, while two were partially separated and two were co-eluted. The non-polar column alone co-eluted nine, the polar column eight and the polar + non-polar arrangement four compounds. The polarity of the coupled columns system was evaluated by using Rohrschneider and McReynolds constants with respect to various polarity probes, and by comparison of the slopes and intercept values of the straight lines obtained by plotting the retention values of various homologous series of compounds as a function of the number of carbon atoms in the molecule.

INTRODUCTION

The use of wide-bore capillary columns for the gas chromatographic analysis of halogenated contaminants in environmental samples such as waste water, surface and underground water and contaminated soil, was discussed previously [1] as an improvement of the classical methods that use polar and non-polar packed columns [2–8] after extraction with headspace, purge-and-trap or liquid–liquid partition methods [9,10]. The use of non-polar (SPB-1) and polar (Supelcowax-10) wide-bore columns permitted the separation and identification of 35 different halo-methanes, -ethanes and -ethenes, containing one or more chlorine, bromine or iodine atoms in the molecule. Only nine compounds were not completely resolved on the non-polar and eight on the polar column, compared with 14 and 8, respectively, that gave coincident peaks on packed columns. The simultaneous (parallel) use of two capillary columns of different polarity requires a dual-channel capillary gas chromatograph with two simultaneous injections of the same sample, which can be difficult when the headspace

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method is used for the sample extraction and concentration. In this instance, a unique injection followed by 50:50 splitting of the sample in the two columns installed in the same oven and connected to two identical detectors may be a better choice, but this technique often requires complex changes of the standard pneumatic connections of the instrument (pressure and flow controllers, detector make-up lines) and a precise inter-calibration of the response of the two electron-capture detectors.

Satisfactory results were obtained previously by using mixed polar and non-polar packed columns, obtained by homogeneous mixing of two stationary phases in the same tubing [3] or by a series arrangement of different lengths of polar and non-polar columns [2]. Therefore, the series connection of two wide-bore capillary columns was tested in order to establish whether this technique could permit the complete separation of a very complex mixture of many haloalkanes, similar to the samples that can be found in the polluted environment.

In spite of the better efficiencies and shorter analysis times obtainable with narrow-bore capillary columns, the use of wide-bore columns, whose application is becoming more popular [11], seems to be convenient for the analysis of volatile halocarbons in polluted waters, owing to the possible effect on the quantitative results of the complex procedure of sample extraction and concentration. Some causes of errors were investigated previously: different partition coefficients when liquid–liquid extraction procedures are followed [12]; different polarities, vapour pressures, extraction temperatures, salt concentrations and air/water volume ratios in the headspace methods [2,12]; and different sensitivities and linear dynamic ranges of the electron-capture detector for various compounds whose concentrations in authentic samples may cover a range of several order of magnitude [12].

This means that, when precise quantitative analyses are required, *e.g.*, for official or forensic purposes, a series of calibrations and linearity checks have to be carried out previously: linearity and reproducibility of liquid–liquid or headspace extraction method and linearity and relative response of the electron-capture detector to the various compounds. The use of narrow-bore capillary columns, which requires splitting injectors owing to their reduced sample capacity, may add further uncertainty to the precision of quantitative analysis. The split injection technique is notorious for showing severe discrimination and poor quantitation [13]. First, the linearity of the available splitting systems, which is good enough when mixtures of compounds having similar vapour pressures are injected (methyl and butyl esters, silyl ethers, heptofluorobutyrate derivatives), may be questionable when samples containing compounds whose boiling points range between 30 and 250°C are injected, and would require a further calibration procedure for the determination of correction factors to be applied when different extraction techniques are used.

Experimental tests carried out by using different arrangements of split–splitless systems with narrow-bore columns showed that an relative standard deviation of 5% of the quantitative results is obtained in multiple consecutive samples by skilled operators by using simple splitting systems (manually adjusted at a fixed splitting ratio). This deviation increases to $\pm 10\%$ when manual systems are used by different operators or when they are re-tuned to the same nominal splitting ratio after any change of the column or of the operating conditions, and may be as high as 12% when more complex automatic systems operated by electronic devices (which control system back-pressures following keyboard input of the desired splitting ratio, column parameters, etc.) are used.

These deviations are much greater than other fluctuations due to the sampling procedure (effects on the headspace technique of temperature, partition coefficients, etc.) and are likely to be the main reason for unacceptable quantitative results. Therefore, the direct injection of the whole sample without any splitting or partition, possible with wide-bore columns, will ensure that all of the injected compounds are delivered to the detector.

Moreover, a high sample capacity is sometimes needed in trace analysis, when the compounds of interest are present in very low concentrations in the organic solvent or in the gas sample coming from liquid–liquid or headspace extraction: injections of microlitres of liquid or hundreds of microlitres of gas are common when the detection of compounds in the sub-ppb range is required.

A further advantage of wide-bore over narrow-bore capillary columns is their greater resistance to contamination from unexpected compounds that can be present in environmental samples, in industrial effluents or in landfill sites. Thousands of samples coming from heavily polluted environments or hazardous waste sites were analysed, as received or after simple clean-up, by means of wide-bore columns with a negligible decrease in efficiency, while narrow-bore columns had to be replaced or frequently decontaminated if a complicated clean-up procedure was not carefully followed.

EXPERIMENTAL

The analyses were carried out by using a Varian (Palo Alto, CA, U.S.A.) Model 3700 gas chromatograph equipped with a nickel-63 electron-capture detector, a flame ionization detector, linear temperature programming and a Varian Vista 402 integration and data acquisition system.

Two wide-bore glass capillary columns (60 m × 0.75 mm I.D.) were used: a non-polar dimethylpolysiloxane (SPB-1) and a polar polyethylene glycol (Supelcowax-10) (Supelco, Bellefonte, PA, U.S.A.). The two columns were installed in the instrument oven by using the Supelco conversion kit for direct injection (without initial sample splitting) and a make-up gas detector adapter that supplied the correct amount of carrier gas (nitrogen) to the electron-capture detector. The two columns were connected in series with flexible fused-silica capillary tubing and zero-volume connectors. The carrier gas flow-rate into the columns was set at 4 ml/min, a good compromise between maximum efficiency and suitable analysis speed. The column back-pressure was monitored at the injection port with an accuracy of ± 1 Torr (133 Pa) by using a mercury micromanometer.

Standard solutions of the analysed compounds were prepared at various concentrations (between 10^{-3} and 1 g/l) to take into account the different responses of the electron-capture detector to various halogenated components and obtain peaks of comparable area or height. The shape of the peaks could therefore change slightly when concentrated samples were injected, but the capacity of the columns (about 15 μg per peak) was greater than the maximum amount of a single compound injected (about 0.5 μg) and therefore column saturation phenomena were avoided.

RESULTS AND DISCUSSION

The compounds studied are listed in Table I, and their boiling points, molecular weights, adjusted retention times and retentions relative to 1,1,2-trichloroethylene are

TABLE I

ADJUSTED RETENTION TIMES, t'_R, AND RETENTION RELATIVE TO 1,1,2-TRICHLOROETHYLENE, r, OF HALOGENATED HYDROCARBONS ANALYZED ON SERIES ARRANGEMENTS OF POLAR (P) AND NON-POLAR (NP) WIDE BORE CAPILLARY COLUMNS AT 75°C (BOILING POINTS AND MOLECULAR WEIGHTS ARE ALSO REPORTED)

No.	Compound	B.p. (°C)	Mol.wt.	P + NP		NP + P	
				t'_R (min)	r	t'_R (min)	r
1	1,1,1,2-Tetrabromoethane	112	345.67	10.03	1.10	9.92	1.09
2	1,1,1,2-Tetrachloroethane	130.5	167.85	42.61	4.69	41.40	4.55
3	1,1,2,2-Tetrabromoethane	243.5	345.67	–	–	–	–
4	1,1,2,2-Tetrachloroethane	146.2	167.85	182.27	20.00	171.87	18.90
5	1,1,2-Trichloroethane	113.8	133.41	39.65	4.36	37.80	4.15
6	1,1,2-Trichloroethylene	87	131.39	9.09	1.00	9.10	1.00
7	1,1-Dichloroethane	57.28	98.96	4.12	0.45	4.06	0.45
8	1,1-Dichloroethylene	37	96.94	1.81	0.20	1.86	0.20
9	1,2-Dibromoethane	131.36	187.87	40.24	4.43	38.66	4.25
10	1,2-Dichloroethane	83.74	98.96	11.86	1.30	11.39	1.25
11	1,2-Diiodoethane	200	281.86	–	–	–	–
12	1-Bromo-2-chloroethane	107	143.20	22.01	2.42	21.04	2.31
13	Bromochloromethane	68.11	129.39	10.28	1.13	9.67	1.06
14	Bromoethane	38.4	108.97	2.13	0.23	2.14	0.23
15	Tribromomethane	149.5	252.75	116.37	12.80	110.23	12.10
16	Tetrabromomethane	189	331.65	–	–	–	–
17	Tetrachloromethane	76.54	153.82	5.27	0.58	5.42	0.60
18	*cis*-1,2-Dichloroethylene	60.3	96.94	7.39	0.81	7.05	0.77
19	Trichloromethane	61.7	119.38	8.75	0.96	8.19	0.90
20	Chloroiodomethane	109	176.38	27.14	2.98	25.88	2.84
21	Dibromochloromethane	119	208.29	49.20	5.41	46.87	2.84
22	Dibromomethane	97	173.85	22.01	2.42	21.04	2.31
23	Dichlorobromomethane	90	163.83	20.72	2.28	19.87	2.18
24	Dichloromethane	40	84.93	4.72	0.52	4.55	0.50
25	Diiodomethane	182	267.84	148.83	16.40	140.66	15.46
26	Hexachloroethane	186	236.74	137.30	15.10	136.70	15.02
27	Iodoethane	72.3	155.97	4.56	0.50	4.37	0.48
28	Triiodomethane	218	393.73	–	–	–	–
29	Iodomethane	42.4	141.94	2.66	0.29	2.63	0.29
30	1,1,1-Trichloroethane	74	133.41	5.00	0.55	5.01	0.56
31	Pentachloroethane	162	202.30	119.15	13.10	115.13	12.65
32	Tetrachloroethylene	121	165.83	14.45	1.59	14.98	1.65
33	*trans*-1,2-Dichloroethylene	47.5	96.94	3.53	0.39	3.49	0.38
34	Trichlorobromomethane	104.7	198.28	14.45	1.59	14.42	1.58
35	1-Iodopropane	102.4	169.99	8.75	0.96	8.87	0.97
36	1-Iodobutane	130.5	184.02	16.69	1.84	17.02	1.87
37	1-Iodopentane	157	198.05	32.84	3.61	33.64	3.70
38	1-Iodohexane	181.3	212.08	64.94	7.14	66.79	7.34
39	1-Iodoheptane	204	226.10	129.19	14.20	133.33	14.60

shown for the two series arrangements. Some compounds are listed that were not analysed on the coupled column system, owing to their too long retention times. They were included in Table I in order to maintain the same reference numbers used in a previously published paper on the behaviour of separate columns [1]. Figs. 1 and 2 show the chromatograms obtained by injecting the mixture of compounds.

The P + NP arrangement required about 200 min for the complete analysis, which is much longer than needed with the non-polar column alone (about 50 min) and about 25% greater than that with the polar column alone (150 min), but the resolution of the components increased greatly in comparison with the analyses carried out on separate columns. While nine compounds were not resolved on the non-polar and eight on the polar column [1], with the P + NP arrangement there were only three unresolved peaks, due to simultaneous elution of the compounds: 1-bromo-2-chloroethane and dibromomethane (peaks 12 and 22); tetrachloroethylene and trichlorobromomethane (peaks 32 and 34); and trichloromethane and 1-iodopropane (peaks 19 and 35). Lack of resolution of the last pair of peaks is not important from a practical point of view, because 1-iodopropane is not generally present in environmental samples and was added to the mixture only for the determination of the retention indices of other compounds with respect to the 1-iodoalkane homologous series, I_{ni} [1,14,15].

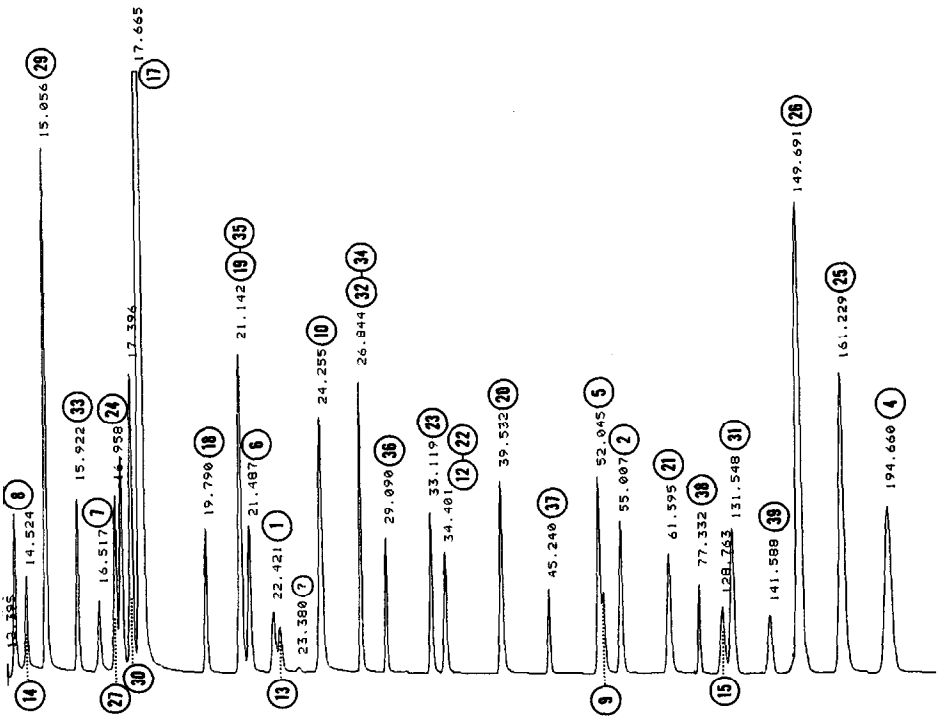

Fig. 1. Chromatogram of the mixture of compounds listed in Table I with a series arrangement of polar (Supelcowax 10) followed by non-polar (SPB-1) wide-bore columns (each 60 m × 0.75 mm I.D.). Temperature, 75°C. Carrier gas (nitrogen) flow-rate, 4 cm^3/min. Variable chart speed: time markers on abscissa represent 1-min intervals; retention times (min) are shown on peak apices.

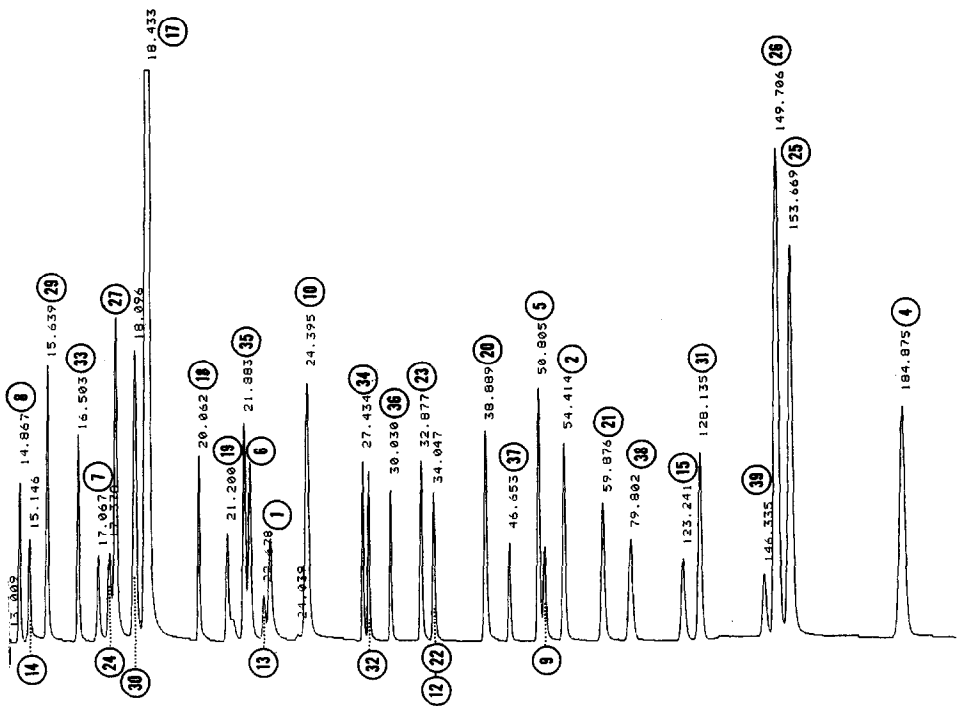

Fig. 2. Chromatogram of the mixture of compounds listed in Table I with a series arrangement of non-polar (SPB-1) followed by polar (Supelcowax 10) wide-bore columns (each 60 m × 0.75 mm I.D.). Temperature, 75°C. Carrier gas (nitrogen) flow-rate, 4 cm^3/min. Variable chart speed: time markers on abscissa represent 1-min intervals; retention times (min) are shown on peak apices.

The NP + P arrangement permitted the resolution of all the compounds, except the pair 1-bromo-2-chloroethane and dibromomethane (peaks 12 and 22), in a time slightly shorter than that needed for complete elution with the P + NP arrangement. This confirms that, for complete resolution of complex mixtures, the selectivity of the column due to slight changes in polarity may be more important than the simple increase in efficiency. In fact, it was observed that the number of theoretical plates, n, was slightly higher in the P + NP arrangement, whereas the separation was better and faster with the reversed column sequence. Moreover, peaks 12 and 22, which were easily resolved on both non-polar and polar individual columns [1], were not separated on coupled columns, showing that the different polarities of the two phases are nearly exactly compensated.

Effect of the polar/non-polar phase ratio

The optimization ("tuning") of the selectivity of coupled columns requires a proper choice of the lengths of the polar and non-polar sections. The optimization of the gas chromatographic separation by using the "window analysis" method was previously suggested for packed columns by Laub and Purnell [16] and further applied by the same group to capillary columns connected in series [17]. More recently, Purnell and Williams [18] published a general theory on the series connection of

chromatographic columns that permits the optimization of the speed of analysis in systems of two columns in series by using the window method and taking into account the pressure gradient.

In this method, the tuning is carried out by optimization of the weight ratio of homogeneously mixed liquid phases or by changing the relative lengths of columns connected in series.

Other selectivity tuning methods have also been suggested that modify the residence times of the carrier gas in the two columns or change the temperature of the column in a different way by using appropriate programming rates [19,20] or installing the column in separate ovens and operating them with different temperature programming [21].

These methods of selectivity tuning of multiple columns in series have also been denoted "multi-chromatography", which should not be confused with the similar term "multi-dimensional chromatography" (MDGC), which indicates a technique in which separate columns are operated in a parallel arrangement and some components that are not well resolved are selectively removed from one column and transferred to the other in order to permit a better resolution of some peak groups.

The aim of this work was to devise a procedure that, by using standard gas chromatographic equipment, without modification of the flow or pressure controls [20] or the need for two separately temperature programmed column ovens [21], would permit the selectivity of the mixed columns to be tuned in order to achieve a satisfactory separation of the compounds present in environmental samples.

This procedure seems rapid enough to be used routinely in control laboratories: the analysis of a standard mixture or of an authentic sample on separate non-polar and polar columns, the tracing of the graphs, the choice of the best arrangement and the connection of two different lengths of columns can permit a column tuned for the required separation to be rapidly obtained. Being a simple system, without a variable initial splitting or separate control of pressure, flow-rates and temperature in the two parts of the column, this series arrangement would behave in an unchanged manner for long periods and does not require frequent calibration and checking of the various parameters.

It should be taken into account, from the practical point of view, that simply by increasing the temperature this column can be used for the analysis of high-boiling samples such as chlorinated pesticides and polychlorinated biphenyls (PCBs), therefore requiring less frequent column changes and reconditioning of the column–electron-capture detector system.

Previous studies on mixed packed columns [2,3] showed that the best resolution of a mixture of compounds similar to that studied in this work can be obtained by using a column made with a 40:60 ratio of polar (SP-1000) and non-polar (OV-1) stationary phases. Further, a nearly linear variation of the resolution of the various compounds with the composition of the mixed phase was found.

The same behaviour was observed with wide-bore capillary columns. Figs. 3–5 show the retention values with respect to trichloroethylene, r, of the compounds listed in Table I, on polar (left) and non-polar (right) columns. The three graphs are shown with different expansions of the vertical axis (where r values are reported), in order to reduce the coincidence of lines for different compounds that eluted close together. On each line the experimental r values with the P + NP arrangement (triangles) and

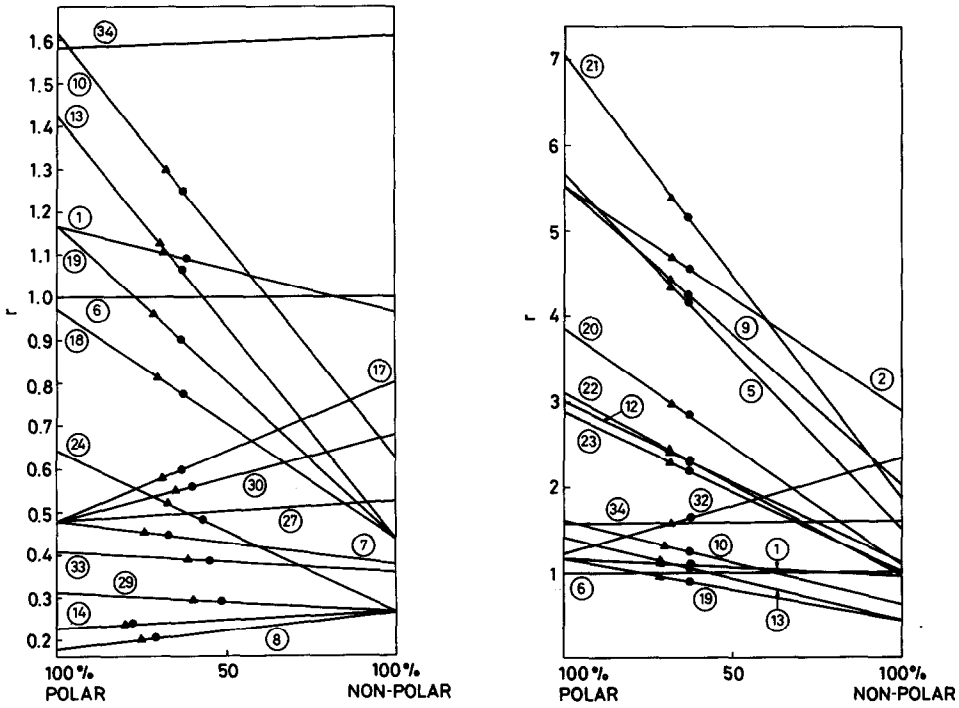

Fig. 3. Retention values with respect to trichloroethylene on polar (Supelcowax 10, left) and non-polar (SPB-1, right) wide-bore columns of compounds listed in Table II. On the connecting lines (theoretical r values on mixed-phase columns) the experimental r values obtained with polar column upstream (▲) and downstream (●) are shown.

Fig. 4. Same as Fig. 3 with a smaller vertical scale in order to show slowly eluted compounds.

NP + P arrangement (circles) are shown, indicating that the behaviour of the series connection of two wide-bore columns having the same length does not correspond to a 50:50 ratio of stationary phases, but is equivalent to a mixed-phase column having a nominal composition with 68–69% of polar phase when the polar column is upstream (directly connected to the injector), and with 63–64% of polar phase when the polar column is downstream (connected to the detector). Some deviations from these values were observed for the fast-eluted compounds, but this is probably due both to errors in the determination of short retention times and to the near-horizontal behaviour of the lines, which causes large variations of the abscissa value with small changes in the r values.

The constant values of the nominal phase composition show that the influence of the polar column is greater than that of the non-polar column, and that this influence increases when the column is connected upstream and thus operates at higher pressure and with a lower linear velocity of the carrier gas. This permits the r value of each compound on mixed columns to be calculated with a good approximation when the r values on each separate column are known and some reference compounds have previously been analysed in order to find their nominal phase ratio. Further, the choice of the abscissa value where the vertical distance between the lines of every pair of

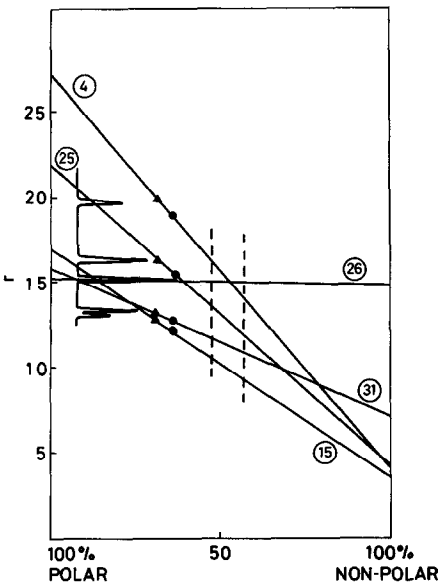

Fig. 5. Same as Figs. 3 and 4 with a smaller vertical scale in order to show the last-eluted compounds. The chromatogram of these compounds at 75°C with the polar column upstream is also shown. Dashed vertical lines show the nominal polar/non-polar ratios where the best resolution of these compounds is expected.

compounds is greatest obtained directly on the graphs in Figs. 3, 4 and 5, or by using the window diagram method [16], permits the preparation of coupled columns with different lengths of non-polar and polar wide-bore capillaries, in order to optimize both resolution and speed of analysis.

As an example, in Fig. 5 the chromatogram of five slow-eluting peaks (Nos. 4, 15, 25, 26 and 31 as listed in Table I) is superimposed on the graph with a scale that shows the correspondence of each peak with r at the nominal composition (68% of polar phase) with the polar column upstream (triangles). The circles on the same graph show that with the polar column downstream the resolution between peaks 25 and 26 decreases, as confirmed by the t'_R values given in Table I. The simple observation of Fig. 5 or the more reliable use of the window diagram method shows that the best separation of the five compounds would be obtained with two different columns having a nominal composition of about 53% or 43% of polar phase (dashed vertical lines in Fig. 5). The better choice (43%) shows an inversion of the elution order between peaks 4 and 26, and gives the shortest analysis time.

The experimental preparation of a P + NP column having the above nominal composition must take into account that a column made by combination of equal lengths of Supelcowax 10 and SPB-1 columns (with the polar column upstream) behaves as a mixed column with 68:32 polar/non-polar ratio. Simple proportion leads to the conclusion that a ratio between polar and non-polar column lengths of 39:61 and 32:68, respectively, would correspond to 53% and 43% nominal concentrations of the polar phase. In practice, the intact non-polar column used in this study (SPB-1, 60 m long) should be connected downstream to a shorter length of polar Supelcowax 10 column, (40 or 28 m, respectively) in order to obtain the separations indicated with

dashed lines in Fig. 5. These length values are valid as a first-degree approximation and for the compounds in Fig. 5 only, and should be recalculated by taking into account all the components of the mixture, which may give interfering peaks, but it is interesting to observe that the 39:61 ratio calculated above is identical with the 40:60 ratio found suitable for the best resolution in mixed-phase packed columns [3].

Effect of temperature

It is known that relative retention values of compounds having different polarities change with column temperature in different ways, mainly on polar columns. The values of r shown on the left-hand ordinate in Figs. 3–5 change slightly with temperature and therefore the intersection points of the lines for different compounds move toward more or less polar compositions of the stationary phase, but it has been found experimentally that temperature changes (in the range 60–115°C) of the two wide-bore columns connected in series (isothermal analysis) do not appreciably change the elution order of peaks. Only a few unresolved peaks show inversion of elution order: peaks 32 and 34 at 70°C and peaks 1 and 13 at 87°C with the P + NP arrangement; peaks 1 and 13 at 63°C on the NP + P column. Of course, higher temperatures often decrease the resolution of partially coincident peaks and lower temperatures lead to very long analysis times.

The greatest influence on the separation was observed when the temperature of the columns was programmed during analysis. Many combinations of the initial isothermal value and programming rate were tested, giving various relative changes of the retentions of many peaks. As commercially available capillary columns (even if from the same producer) may differ in performance, only experimental tests can lead to the correct choice of the best temperature programme for a given separation. A general rule is that temperature increase has a greater effect on the behaviour of slowly eluted compounds, and decreases the influence of the downstream column. In fact, less retained compounds elute when the column temperature is not appreciably changed, while slowly moving peaks are retained at low temperatures in the upstream column and increase their migration speed in the second column at higher temperatures. This effect is more evident with the P + NP arrangement. For example, with the P + NP column connection, an initial isothermal hold at 75°C for times ranging between 15 and 25 min, followed by programming rates of 5–10°C/min up to 120–150°C, produced a separation that, on the basis of the r values, would correspond to a nominal phase composition of about 80% of polar phase, compared with 68% observed with a 75°C isothermal run.

In contrast, with the NP + P arrangement, similar programming rates only gave a change of nominal phase composition from 63 to 60% of polar phase. Temperature programming can therefore be used as a method to change the overall polarity of the coupled columns system slightly, which is obviously more convenient than cutting the column. On the other hand, it was reported above that equal lengths of polar and non-polar columns correspond to a nominal P/NP ratio (P column upstream) of about 70:30. The best choice therefore seems to be to use a coupled column formed with a shorter length of polar column mounted upstream and to change the overall polarity by suitable temperature programming, which can also reduce the total analysis time to below 1 h.

Evaluation of the polarity of coupled columns

The methods of Rohrschneider [22] and McReynolds [23] for the classification of the polarity of stationary phases requires the determination of the retention indices values of various "polarity probes" on squalane and on the stationary phase under study, and the calculation of the ΔI values for each probe. An average polarity value is also obtained by sum of the ΔI values for five probes (benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine in the Rohrschneider method; benzene, 1-butanol, methyl propyl ketone, nitropropane and pyridine in the McReynolds method). These methods are therefore complicated, requiring the analysis of complex mixtures of the probes with *n*-alkanes. For capillary columns, moreover, columns filled with squalane are often unavailable or cannot be used at high temperatures.

By taking into account the low polarity of the non-polar SPB-1 wide-bore column used, filled with polymeric dimethylpolysiloxane, which shows low values of the McReynolds constants, similar to those for OV-1, SE-30, etc., *i.e.*, 16, 55, 44, 65 and 42 for the probes listed above [24], the calculation of the ΔI values with respect to SPB-1 is accurate enough for the comparison of the behaviour of the coupled column with respect of those of the individual non-polar and polar columns.

Table II shows the I, t'_R and ΔI values for P + NP and NP + P arrangements. The average polarity values, *i.e.*, the sum of ΔI values for the Rohrschneider and McReynolds probes, differ slightly and are equal to about half of the sums for the polar column alone. This does not agree with the experimental results discussed above, showing that the polarity of the coupled columns is more similar to that of the polar column (60–70%, depending on the carrier gas flow direction). The use of ΔI values therefore gives information on the physical composition of the column (the same lengths of P and NP sections) but does not permit the prediction of its behaviour in the analysis of halogenated compounds.

The use of CP-index values suggested by ChromPack International [25] for the polarity classification of capillary columns leads to the same results for the simple sum of ΔI values discussed above, because it is also derived from the McReynolds constants. Moreover, it requires a knowledge of the I values for the most polar stationary phase actually known (cyanosilicone OV-275), used as the upper reference term, while squalane is the lower polarity reference, and this further increases the complexity of its determination. The CP-index values calculated for the columns used in this work were 5 for non-polar SPB-1, 52 for polar Supelcowax 10, 27.4 for the P + NP and 27.9 for the NP + P arrangement. Again, the values for coupled columns represent the physical composition of the system but are not correlated with the effective separation behaviour.

Another and simpler method for the determination of relative polarity values of capillary columns was suggested previously [1] that compares the behaviour of polar columns with that of non-polar columns by measuring the difference between the intercept values of the straight lines obtained by plotting the ln t'_R values for compounds belonging to various homologous series as a function of the number of carbon atoms in the molecule, or by graphical determination of the horizontal distance between parallel lines for different homologous series, expressed as the difference in equivalent carbon atoms number (ΔC). Fig. 6 shows the linear behaviour of *n*-alkanes, 1-alkanols and 1-bromo- and 1-iodoalkanes on NP + P and P + NP coupled columns. Table III reports the values of the slope, m, intercept, p, correlation

TABLE II

I VALUES OF ROHRSCHNEIDER AND McREYNOLDS PROBES ON NON-POLAR SPB-1 (NP) AND POLAR SUPELCOWAX 10 (P) WIDE-BORE CAPILLARY COLUMNS; t'_R AND *I* VALUES ON P + NP AND NP + P COUPLED COLUMNS, AND DIFFERENCES (ΔI) CORRELATED WITH POLARITY (SEE TEXT)

t_M = Column dead time (min).

No.	Compound	$I^{(NP)}$	$I^{(P)}$	$I^{(P)} - I^{(NP)}$	P + NP (t_M = 13.93)			NP + P (t_M = 14.14)		
					t'_R	$I^{(P+PN)}$	$I^{(P+NP)} - I^{(NP)}$	t'_R	$I^{(NP+P)}$	$I^{(NP+P)} - I^{(NP)}$
1	Benzene	661.6	967.7	306.1	7.59	766.7	105.1	7.42	776.1	114.5
2	Ethanol	414.4	940.7	526.3	5.13	714.4	300.0	4.27	702.8	288.4
3	1-Butanol	658.7	1145.9	487.2	21.07	905.1	246.4	18.92	903.1	244.4
4	Methyl ethyl ketone	582.7	923.3	340.6	5.08	713.2	130.5	4.86	719.9	137.2
5	Methyl propyl ketone	664.6	997.6	332.8	8.94	788.6	124.0	8.72	797.6	133.0
6	Nitromethane	543.4	1160.9	617.3	20.89	904.0	360.6	18.87	902.8	359.4
7	Nitropropane	709.8	1219.3	509.5	32.12	960.7	250.9	29.90	963.1	253.3
8	Pyridine	731.5	1190.1	458.1	27.98	942.5	211.0	26.27	946.2	214.7
9	1-Iodobutane	806.2	1067.0	260.8	18.54	887.9	81.7	18.50	900.2	94.0
Sum ΔI (Rohrschneider) (1+2+4+6+8)				2248.6			1107.2			1114.2
Sum ΔI (McReynolds) (1+3+5+7+8)				2093.7			937.4			959.9

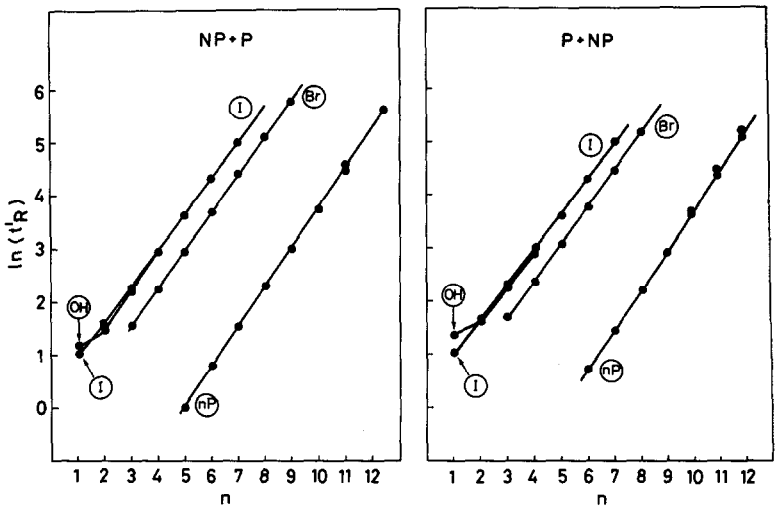

Fig. 6. Linear behaviour of the $\ln(t'_R)$ of terms of homologous series of linear alkanes (nP), 1-bromoalkanes (Br), 1-iodoalkanes (I) and n-alkanols (OH) as a function of the number of carbon atoms in the molecule (n) with series column arrangements.

coefficient, r, and ΔC measured from the horizontal distance between the line for n-alkanes and that for other homologous series.

As suggested previously [1], the ΔC value for 1-alkanols is probably the best way to identify rapidly the difference in polarity due to hydrogen-bond formation. These values for coupled columns are the average of the values for the non-polar and polar columns alone, and therefore agree with the values of average polarity listed in Table II and obtained by the sum of the ΔI values of Rohrschneider or McReynolds constants, and with the CP-index values reported above.

The determination of ΔC values for 1-alkanols is much easier than the calculation of ΔI or CP-index values, because it can be obtained by injecting

TABLE III

SLOPE, m, INTERCEPT, p, AND CORRELATION COEFFICIENT, r, OF STRAIGHT LINES OF $\ln t'_R$ AS A FUNCTION OF THE NUMBER OF CARBON ATOMS IN VARIOUS HOMOLOGOUS SERIES, AND HORIZONTAL DISTANCE BETWEEN PARALLEL LINES IN FIG. 6, Δc, USED AS A MEASURE OF THE COLUMN POLARITY

Column arrangement	Compounds	m	p	r	Δc
NP + P	n-Alkanes	0.755	−3.772	1.000	–
	1-Iodoalkanes	0.674	0.273	1.000	4.80
	1-Bromoalkanes	0.705	−0.559	1.000	3.90
	1-Alkanols	0.744	−0.036	1.000	4.40
P + NP	n-Alkanes	0.752	−3.832	1.000	–
	1-Iodoalkanes	0.660	0.315	0.999	5.10
	1-Bromoalkanes	0.699	−0.417	1.000	4.30
	1-Alkanols	0.707	0.218	1.000	5.00

only four compounds, *i.e.*, two *n*-alkanes and two 1-alkanols with a number of carbon atoms different enough to permit a precise calculation of the parameters of the straight lines in Fig. 6.

CONCLUSIONS

The use of a series arrangement of wide-bore capillary columns of different polarity permits the complete separation of many halogenated compounds that can occur in polluted environmental samples by application of the standard extraction and concentration procedures: headspace extraction, liquid–liquid partition, purge-and-trap method, etc. The high capacity of wide-bore columns compared with narrow-bore capillaries does not require injection splitting of the sample, which may be the source of uncertainty in quantitative analysis owing to different volatilities of the analyte compounds. The same columns, by increasing the temperature, can be used for the analysis of high-boiling samples such as chlorinated pesticides and PCBs, therefore requiring less frequent column changes and reconditioning of the column–detector system.

The overall polarity of the coupled column system changes when the order of connection is reversed, and this can be used to optimize the separation of closely eluting compounds, in conjunction with temperature programming. Twenty-six compounds were separated with this technique, compared with nineteen resolved on a non-polar wide-bore capillary, 20 on a polar wide-bore capillary and 24 with a series arrangement of non-polar and polar packed columns.

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