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GAS CHROMATOGRAPHIC ANALYSIS OF HALOCARBONS IN DRINKING WATER BY HEADSPACE EXTRACTION AND MIXED COLUMN SEPARATION

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SUMMARY

Series arrangement of polar and non-polar liquid stationary phases (30 cm of 10% SP-1000 on 80–100-mesh Chromosorb W DMCS, followed by 350 cm of 10% OV-1 on the same support) were used for the complete resolution of the trihalomethanes $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$, formed in drinking water facilities by the action of the chlorine used as a disinfectant. Other halocarbons ($CCl_2=CH_2$, CH_2Cl_2, $CHCl_2CH_3$, CCl_3CH_3, CCl_4, $CHCl=CCl_2$, $CCl_2=CCl_2$) not formed during chlorination but coming from polluted water sources, which interfere in the analysis of trihalomethanes due to peak overlap, can be separated with the same column arrangement, and are eluted in the order listed. Homogeneously mixed columns with similar polar–non-polar liquid phase ratios were also tested but showed lower resolving powers and required a more complex preparation method.

A headspace extraction technique and a ^{63}Ni electron-capture detector were used for quantitation. With proper temperature programming of the column, gas chromatographic analysis could be completed within 30 min, making this technique suitable for the rapid screening of large numbers of samples coming different water supplies in order to monitor the quality of community drinking water. Lack of interferences between the halocarbon peaks and those of commonly used liquid–liquid extraction solvents (*n*-pentane, *n*-hexane, isooctane) makes the proposed column also suitable for liquid exchange based trihalomethane extraction techniques.

INTRODUCTION

Chlorine has been used as a disinfectant for drinking water supplies for several decades, and until fairly recently its use has never been questioned. In 1974 it was reported[1,2] that chlorine reacts with organic precursors occurring in raw water to produce a potential carcinogen, chloroform ($CHCl_3$), together with other trihalomethanes (THMs): $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$[3–6]. In addition, the increasing use of

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chlorinated hydrocarbons in industrial solvents increased the possibility of pollution of rivers, lakes and well waters with halogenated compounds that cannot be easily removed during standard purification treatments.

Many analytical methods have been suggested for the determination of THMs in drinking water, and EPA official methods are also available. Method 501.1[7] is a procedure for the analysis of THMs by the purge and trap technique while method 501.2[8] is based on liquid–liquid extraction. Headspace techniques[9–16] with manual or automatic sampling was found to be a useful method for the rapid screening of large numbers of water samples from different supplies, in order to monitor the quality of community drinking water utilities. The simplicity of the manual headspace extraction technique and its easy application by different laboratories was the reason for the choice of this method for the wide monitoring of the concentration of THMs in the water systems of various Italian towns, sponsored by the Italian Public Health Ministry and the Istituto Superiore di Sanità, Rome. All of the laboratories involved used the technique fully described in refs. 14 and 17 and the results will be published officially in the near future.

Owing to the possibility of halocarbons other than THMs from chlorination that could be present in raw waters, and which have identical retention times on a particular column, two liquid stationary phases were chosen for use in combination: OV-101 (non-polar methylsilicone) and SP-1000 (polar polyethylene glycol Carbowax 20M plus terephthalic acid). Table I shows the McReynolds constants[18] of these two phases and of similar columns previously used for the separation of chlorinated hydrocarbons[5,14,17,19–29], which lie near to the opposite extremes of the McReynolds polarity scale.

TABLE I

McREYNOLDS CONSTANTS OF NON-POLAR AND POLAR LIQUID STATIONARY PHASES USED FOR GC SEPARATION OF THMs

Stationary phase	*McReynolds constants*					*Ref.*
	ΔI benzene (x')	*ΔI butanol (y')*	*ΔI 2-pentanone (z')*	*ΔI nitropropane (v')*	*ΔI pyridine (s')*	
Squalane	0	0	0	0	0	28
SE-30	15	53	44	64	41	25
OV-1	16	55	44	65	42	17,23,24
OV-101	17	57	45	67	43	21,26
SP-2100	17	57	45	67	43	14,28
Apiezon L	32	22	15	32	42	19
Di(2-ethylhexyl) sebacate	72	168	108	180	123	15
OV-11	102	142	145	219	178	28
OV-17	119	158	162	243	202	26
Tricresyl phosphate	176	321	250	374	299	22
OV-210	146	238	358	468	310	25
Carbowax 20M	322	536	368	572	510	25,27,22
Carbowax 1500	347	605	418	626	589	14
SP-1000	332	355	393	583	546	17,28,29
FFAP	340	580	397	602	627	17,25,27
TCEPE	526	782	677	920	837	20

Injection of the sample on both columns was necessary because the non-polar phase could not separate 1,2-dichloroethane from carbon tetrachloride or trichloroethylene from dichlorobromomethane, and the polar phase showed identical retentiontion times for carbon tetrachloride and 1,1,1-trichloroethane. As a consequence, the advantage, in terms of analysis time, due to the rapid injection technique of the headspace method was lost owing to the need to repeat the analysis on two columns. When a dual-column instrument with two electron-capture detectors (ECDs) is available, simultaneous analyses could be accomplished on the two columns mounted in parallel, but this solution is expensive, as two complete analytical lines are necessary (ECD, amplifier, recorder and data system), and some correction factors have to be taken into account because two samples are extracted from two different vials, and the standing currents of the ECDs may be different on the two sides of the instrument. When a parallel arrangement of the two columns is not available, a complete set of analyses has to be repeated on the polar column, installed in the oven to replace the non-polar column, and additional time is lost waiting for ECD stabilization.

Therefore, a method was developed which, by using a polar and a non-polar column mounted in series and connected to a ^{63}Ni ECD, permitted the separation, by temperature programming, of all of the halocarbons that could be present in the samples.

Pre-columns were previously used in the purge and trap method[28] but they were filled with a higher concentration of the same phase used in the main column, and did not change the order of elution of the compounds. A small amount (0.1 %) of Carbowax 1500 was also mixed with the 20 % of the main liquid phase SP-2100[14], and probably had the function of a tail reducer. A mixed phase typically tailored for pesticide analysis (6 % OV-210 + 4 % SE-30) has also been used[25].

EXPERIMENTAL

The headspace technique described in refs. 14 and 17 was used with some modifications. Screw-capped vials of volume 40 ml with PTFE-faced septa, washed with distilled water and methanol and dried overnight at 200°C, were used; the caps and septa were washed with light petroleum and dried overnight at 80°C; laboratory glassware was washed with distilled water and methanol and dried at 300°C.

The addition of sodium chloride to the standards and to the samples that had to be analysed immediately was effected by adding 4 ml of 40 % sodium chloride solution in doubly distilled water to each vial before the final drying at 200°C. This procedure removed all traces of organic substances and avoided contamination due to salt addition during the sample pick-up. This procedure was not followed during the preparation of samples that had to be analysed 24 and 72 h after sampling in order to study the formation of THMs due to long contact of precursors with free chlorine[30], because of the influence of sodium chloride and its impurities on the formation of bromine derivatives. Sodium thiosulphate solution (*ca.* 150 mg/l) was added to remove residual chlorine immediately after sample pick-up (for samples that had to be analysed at time zero) and before analysis (for samples analysed after 24 and 72 h). The vials were completely filled with the sample, tightly sealed and stored in the dark at 15°C.

Before analysis, 5 ml of water were removed from each vial in order to create

the headspace volume, and the samples were thermostated at 30°C for 1 h in a water-bath. The injections (200 μl) were made by using 250-μl Hamilton gas-tight syringes.

Stainless-steel columns (3 m × $\frac{1}{8}$ in. O.D.) were used at 60°C for the isothermal analysis on polar and non-polar stationary phases (10% of SP-1000 and 10% of OV-1 on Chromosorb W DMCS, 80–100 mesh). Mixed columns were prepared by homogeneously mixing suitable amounts of the packings. Series arrangements of the two phases were accomplished by filling a single column with different lengths of the two coated supports or by using separate columns connected by means of standard Swagelock unions (1/8 in. to 1/8 in., stainless steel). The resulting small dead volume between the two columns could be reduced by drilling a hole with the same diameter as the tubing through the union, and facing the two columns closely end-to-end. The effect of this volume reduction on the plate height was negligible for total column lengths greater than 1.5 m.

A Varian 3700 gas chromatograph, equipped with a ^{63}Ni (8 mCi) ECD was used for experiments with mixed columns and linear temperature programming. Isothermal analysis with a parallel column arrangement was also carried out with a Varian 660 dual-column, dual-ECD (250 mCi tritium each) gas chromatograph. Quantitative analysis was accomplished by manual integration or by using Varian CDS-111C and Vista 401 data systems. The external standard technique, by injection of the headspace volumes from vials with known contents of each halocarbon, was used for calibration.

RESULTS AND DISCUSSION

The choice of the optimum ratio between polar and non-polar stationary phases in the column was made on the basis of the retention times obtained on columns filled with the two phases (10% each). Table II shows adjusted retention times, t'_R, on pure OV-1, pure SP-1000 and 1:1 mechanically blended packings. The widely accepted hypothesis that this type of mixed-bed packing yields retentions that are linear as a function of column composition[31] was confirmed to a reasonable

TABLE II

ADJUSTED RETENTION TIMES, t'_R (min), OF HALOGENATED COMPOUNDS ON PURE OV-1, PURE SP-1000 AND 1:1 MIXED PHASES

Temperature, 60°C; carrier gas flow-rate, 25 cm^3/min.

Compound	*OV-1*	*SP-1000*	*OV-1–SP-1000 (1:1)*
Methylene chloride	2.32	5.85	4.10
Chloroform	4.1	11	7.6
1,1,1-Trichloroethane	5.4	4.1	4.6
Carbon tetrachloride	6.4	4.1	5.0
Trichloroethylene	8.3	9.0	8.3
Dichlorobromomethane	8.3	28.4	18.8
Dibromochloromethane	16.6	81.1	47.2
Tetrachloroethylene	20.1	11.1	14.7
Bromoform	29	184	100

extent, because the t'_R values obtained on the mixed column are near to the straight lines connecting the t'_R values given by the pure packings in separate columns. Mechanically mixed columns having different polar–non-polar ratios permitted a more accurate dependence of the retention on column composition to be calculated, which is reported as retention relative to trichloroethylene (r) in Fig. 1. The relative retention values are independent of small changes in carrier gas flow-rate and temperature, and therefore permit an easier comparison of results obtained with different columns, showing that complete separation of the considered compounds is impossible with either pure stationary phase, because of overlapping of some peaks, whereas complete resolution may be obtained by using a suitable mixture of the two packings.

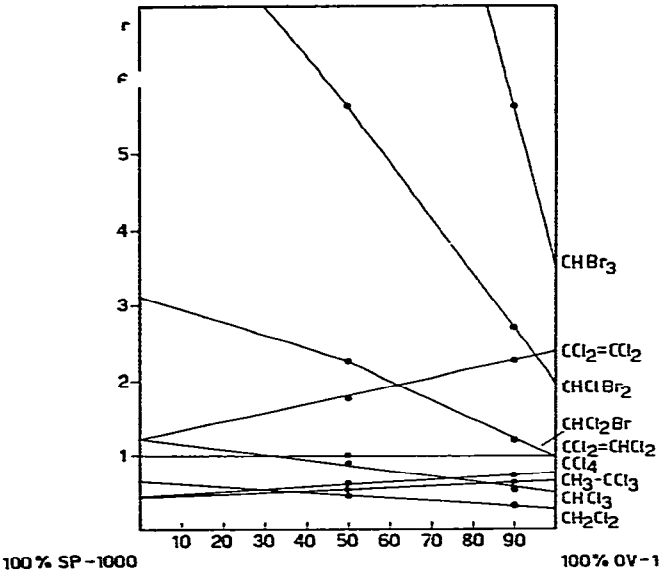

Fig. 1. Relative retention (r) with respect of trichloroethylene as a function of column composition. Data for pure SP-1000, pure OV-1, a 1:1 mixture and a 1:10 mixture were obtained experimentally. Lines are interpolated.

In order to obtain both complete resolution and short analysis times, mixed stationary phases with a large excess of non-polar OV-1 were preferred. In this situation, mechanical mixing would ensure a homogeneous distribution of the two phases along the column only after prolonged, vigorous shaking. As this could crush the packing particles with adverse effects on its mesh size distribution, surface deactivation and impregnation, the series arrangement of two separate columns may be used.

When series-connected columns are used instead of homogeneously mixed packings, the effect of the upstream column is increased, because it operates between the inlet pressure, P_i, of the system and the pressure at the connection point, P_c, which differs from the oulet pressure owing to the flow resistance of the downstream column. It was shown[32] that the contribution of the upstream column to the total retention time is equivalent to the values measured when the same column is operated alone between P_i and P_c. The results therefore differ, depending on the order of installation of the two columns, as shown in Table III, where the values of r obtained

with direct and reversed connection of 30 cm of polar and 300 cm of non-polar column are given. Resolution values, calculated as $R = 2d/(w_1 + w_2)$, where d is the distance between the tops of two consecutive peaks and w_1 and w_2 are their base widths, are also reported and show that the best result is obtained when the polar section of the column is upstream.

TABLE III

RETENTIONS RELATIVE TO TRICHLOROETHYLENE (r) OF HALOGENATED COMPOUNDS ON PURE STATIONARY PHASES AND HOMOGENEOUSLY MIXED (1:1) AND SERIES (10:1) COLUMNS

Resolutions, R, are also reported (for series arrangement with non-polar and polar columns, respectively, upstream) between each peak and the following peak. Temperature, 60°C.

Compound	*OV-1*	*SP-1000*	*OV-1–SP-1000 (1:1)*	*OV-1–SP-1000 (10:1)*			
				OV-1 upstream		*SP-1000 upstream*	
	r	r	r	r	R	r	R
Methylene chloride	0.28	0.65	0.50	0.33	5.0	0.33	3.25
Chloroform	0.49	1.23	0.91	0.54	1.6	0.54	0.38
1,1,1-Trichloroethane	0.65	0.45	0.55	0.63	1.1	0.63	1.30
Carbon tetrachloride	0.77	0.45	0.60	0.74	2.15	0.74	2.27
Trichloroethylene	1.0	1.0	1.0	1.0	0.72	1.0	1.66
Dichlorobromomethane	1.0	3.15	2.26	1.15	5.49	1.23	5.43
Dibromochloromethane	2.0	9.01	5.68	2.27	0.076	2.72	7.4
Tetrachloroethylene	2.42	1.23	1.77	2.42	6.4	2.29	1.44
Bromoform	3.49	20.5	12.04	5.16	–	5.48	–

By taking into account the different effects of the same column working at the higher pressure of the upstream section, a small correction to the two lengths of the polar and non-polar stationary phases should be applied, by increasing the non-polar section. In order to avoid a time-consuming trial-and-error method, a window diagram[33] was drawn by plotting as a function of the column composition the α values for these of the $[n!/2(n-2)!]$ pairs of solutes that show peak interference. α was calculated as

$$\alpha_{j/i} = \frac{t'_{R_j}}{t_{R_i}} \text{ or } \alpha_{j/i} = \frac{r_j}{r_i}$$

In Fig. 2, α is everywhere maintained greater than or equal to unity by inversion where necessary of the i/j assignment of each pair of solutes. Several windows (shaded regions) formed by intersection of lines of α indicate the phase composition range where the separation of a given pair can be achieved. On the basis of these results, a column containing 0.7% of SP-1000 and 9.3% of OV-1 should be the best choice in order to obtain complete separation. This polar–non-polar ratio was achieved by connecting 30 cm of 10% SP-1000 with 350 cm of 10% OV-1 or by filling a single column with a mechanical mixture of 7 parts of the polar and 93 parts of the non-polar phase. For both columns, the minimum of the HETP values of the Van

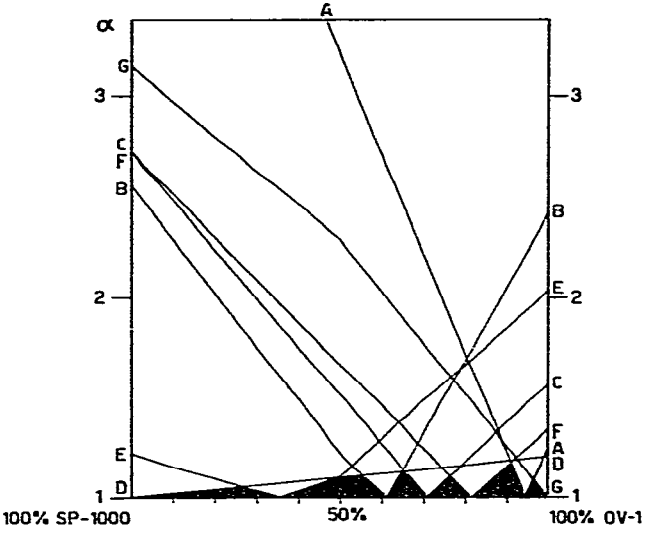

Fig. 2. α values of solvent pairs that show interference as a function of mixed column composition. A, Dibromochloromethane–tetrachloroethylene; B, tetrachloroethylene–dichlorobromomethane; C, chloroform–carbon tetrachloride; D, carbon tetrachloride–1,1,1-trichloroethane; E, chloroform–trichloroethylene; F, chloroform–1,1,1-trichloroethane; G, trichloroethylene–dichlorobromomethane.

Deemter equation[34,35] was found to lie in the nitrogen flow-rate range 16–20 cm^3/min, which agrees with those required for a satisfactory sensitivity of the ^{63}Ni ECD.

At 60°C, the resolution was practically the same on both series and mixed phases having the same polar–non-polar ratio (Table IV). By increasing the temperature in order to decrease the time of analysis, the best resolution was obtained for the series arrangement at 78°C, while the $CHCl_2{=}CHCl_2$ and $CHBr_2Cl$ peaks overlapped on the homogeneously mixed phase.

In order to compensate for the prevailing influence of the upstream polar section in the series system, small variations of the composition of the mixed phase were tested (Table IV). Mixed columns containing 9% of OV-1 and 1% of SP-1000 increased the resolution between $CHCl_2{=}CHCl_2$ and $CHBr_2Cl$, but yielded very close retention times for $CHCl_3$ and CCl_3CH_3, which could not be separated when one of the two compounds was in excess with respect to the other.

Therefore, the series arrangement gives better results than the theoretically equivalent homogeneously mixed columns, as it permits, at any temperature, the separation of THMs and other halocarbons (Fig. 3). Also 1,1-dichloroethane and 1,1-dichloroethylene can easily be resolved (r = 0.38 and 0.24, respectively).

As the aim of this work was mainly the reduction of the analysis time, further attempts in this direction were made by temperature programming. Fig. 3 shows the chromatogram obtained with the best combination of the initial and final isothermal temperature and programming rate, and Table IV shows the t'_R and r values. Temperature programming could only be used with ^{63}Ni ECD, because the baseline drift of this detector with temperature was negligible with respect to the ^3H ECD. The rise of the baseline during programming was small enough to permit easy quantitation

TABLE IV

ADJUSTED RETENTION TIMES (t'_R) AND RETENTION RELATIVE TO TRICHLOROETHYLENE (r) ON SERIES COLUMNS (30 cm OF 10% SP-1000 UPSTREAM AND 350 cm OF 10% OV-1 DOWNSTREAM) AND HOMOGENEOUSLY MIXED COLUMNS OF DIFFERENT COMPOSITIONS

Carrier gas flow-rate, 18 cm^3/min. Temperature programme: 9 min at 78°C, increased at 5°C/min to 110°C.

n*	Compound	Series columns (60°C)		Mixed column (9.3%) OV-1–0.7% SP-1000 (60°C)		Series columns (78°C)		Mixed column (9.3%) OV-1–0.7% SP-1000) (78°C)		Mixed column (9% OV-1–1% SP-1000) 60°C		Mixed column (9% OV-1–1% SP-1000) 78°C		Mixed column (9.15% OV-1–0.85% SP-1000) 60°C		Mixed column (9.15% OV-1–0.85% SP-1000) 78°C		Series column temperature programming)	
		t'_R	r	t'_R	r	t'_R	r	t'_R	r	t'_R	r	t'_R	r	t'_R	r	t'_R	r	t'_R	r
–	1,1-Dichloroethylene	–	–	–	–	2.20	0.24	–	–	–	–	–	–	–	–	–	–	2.20	0.24
0	Methylene chloride	5.5	0.3	3.4	0.30	2.58	0.28	2.1	0.32	2.76	0.25	2.10	0.34	2.50	0.25	1.7	0.27	2.58	0.28
–	1,1-Dichloroethane	–	–	–	–	3.52	0.38	–	–	–	–	–	–	–	–	–	–	3.52	0.38
1	Chloroform	9.25	0.56	6.3	0.55	5.36	0.58	3.6	0.56	6.30	0.58	3.55	0.58	5.3	0.53	3.4	0.55	5.36	0.59
2	1,1,1-Trichloroethane	10.2	0.61	7.2	0.63	5.98	0.64	4.3	0.67	6.70	0.61	3.65	0.60	6.3	0.63	4.1	0.66	5.98	0.66
3	Carbon tetrachloride	11.8	0.72	8.4	0.73	6.92	0.75	5.0	0.78	7.88	0.72	4.60	0.75	7.4	0.75	4.7	0.76	6.92	0.76
4	Trichloroethylene	16.5	1.00	11.4	1.00	9.23	1.00	6.4	1.00	10.87	1.00	6.11	1.00	9.9	1.00	6.2	1.00	9.10	1.00
5	Dichlorobromomethane	20.4	1.23	13.5	1.36	10.94	1.18	7.4	1.15	13.85	1.27	7.30	1.20	11.2	1.31	6.9	1.1	10.48	1.15
6	Tetrachloroethylene	38.6	2.30	26.9	2.42	20.34	2.20	14.34	2.20	25.72	2.36	13.40	2.19	23.5	2.37	13.8	2.22	15.28	1.68
7	Dibromochloromethane	45.9	2.80	28.9	2.53	22.37	2.42			30.04	2.76	14.82	2.42					16.30	1.79
8	Bromoform	100	6.05	67.2	5.90	46.24	5.01	32.0	5.0	–	–	30.1	4.92	–	–	–	–	24.41	2.68

* Refers to peaks in Fig. 3.

with both manual and electronic (Varian CDS-111 C) integration. As the baseline deviation is quite reproducible owing to the thermal stability of the liquid phase used, it can easily be stored and substracted by suitable computer programs or by using GC-dedicated data systems (Varian Vista 401 equipped with at least one floppy disk drive unit); ten samplings per minute of the baseline level permitted nearly complete suppression of the baseline deviations in the plotted chromatogram.

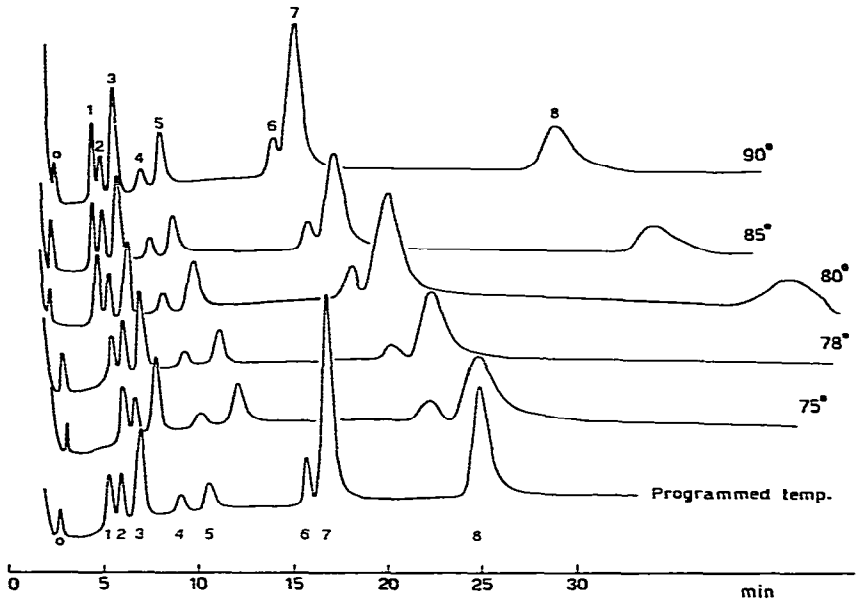

Fig. 3. Chromatograms of THMs and other halogenated compounds on series columns (30 cm of 10% SP-1000 and 350 cm of 10% OV-1) at various temperatures. Carrier gas flow-rate, 18 cm^3/min. Temperature programme: isothermal at 78°C for 9 min, then increased at 5°C/min to 110°C and held at this temperature for 16 min. Peak numbers refer to Table IV.

Some tests were also carried out to check if the suggested column system could also be used for the analysis of THMs and other halocarbons with the liquid–liquid extraction technique. The solvents generally used in this technique, *n*-pentane, *n*-hexane[25,29] and isooctane[25], were injected together with a complete standard mixture of the halocarbons listed in Table II. *n*-Pentane was eluted before all of the chlorinated compounds, *n*-hexane between methylene chloride and chloroform and isooctane between carbon tetrachloride and trichloroethylene.

Owing to the specific response of the ECD, peaks corresponding to the injection of 4 μl of hydrocarbons had the same shape and area as those due to the amounts of halogenated compounds found in drinking waters, and little interference was therefore found. Of course, liquid–liquid extraction requires "ECD pure" solvents, and some problems can be caused by the extraction of non-volatile ECD-sensitive compounds present in the sample that are not detected with the headspace technique.

CONCLUSIONS

The suggested arrangement of polar and non-polar stationary phases, in connection with a proper temperature programming, permitted the time needed for com-

plete analysis of each headspace sample to be reduced to less than 30 min. This increases the usefulness of the headspace technique for the rapid and wide screening of water supplies in order to monitor the amount of THMs and other volatile halocarbons. The columns and conditions described also permit the analysis of samples with the liquid–liquid extraction technique.

The series configuration is more efficient than a homogeneously mixed column with a similar polar–non-polar ratio, as the upstream position of the polar phase assures that its effect predominates during the initial isothermal stage of temperature programming, thus enhancing the resolution of low-boiling compounds. Small adjustments of the retention times of some peaks in complex mixtures can be obtained by slightly changing the length of the polar section, whereas a cumbersome trial-and-error method must be used for satisfactory modification of the homogeneously mixed columns.

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