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APPLICATION OF HEADSPACE GAS CHROMATOGRAPHY TO THE DETERMINATION OF CHLORINATED HYDROCARBONS IN WASTE WATERS*

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SUMMARY

A method is described for the determination of C_2 chlorinated hydrocarbons in waste waters. The headspace method was used for the quantitative analysis. The method was tested for individual components in the concentration range of 0.5–200 ppm. The efficiency of the purification of waste waters from industrial plants was determined by the method described. For quantitative analysis the external standard method was applied.

INTRODUCTION

Headspace gas chromatography (GC) is useful for the determination of trace amounts of substances in samples that are not suitable for direct injection into the chromatographic column. The theory and applications of headspace GC have been presented previously[1–9]. An example of an application is the analysis of a mixture of cyclohexane, dichloromethane and trichloromethane in water and also trace amounts of vinyl chloride in water[10].

In this paper, an external standard method is presented for the determination of chlorinated hydrocarbons in waste waters at individual concentrations of 0.5–200 ppm and total contents of 2–600 ppm.

EXPERIMENTAL

A Perkin-Elmer Sigma 3 gas chromatograph with an HS-6 semi-automatic headspace sampler, equipped with a Spectra Physics, SP 4000 Chromatography Data System or a Hewlett-Packard HP 3380A Reporting Integrator, was used. The column was a 2.4 m × 2.1 mm I.D. stainless-steel tube packed with 10% 2-ethylhexyl sebacate +2% sebacic acid on Chromaton N AW (0.16–0.20 mm). This system allowed the injection of the vapour phase without changing of its composition.

The column temperature was 80°C, the detector temperature 100°C, the

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TABLE I

COMPOSITION OF THE CALIBRATION MIXTURE AND RELATIVE RETENTION TIMES OF INDIVIDUAL COMPOUNDS AND DETERMINATION OF CHOSEN CHLORINATED COMPOUNDS IN MODEL MIXTURES

Compound	*Concentration (ppm)*	*Retention time (sec)*	*Relative retention time*	*Concentration in model mixture (ppm)**											
				1	2	3	*4*	*1*	2	3	*4*	*1*	2	3	*4*
1,1-Dichloroethylene	6.2	81	0.1059	6.2	7.3	6.0	6.6	18.6	18.3	17.2	17.75	62	63.1	59.6	61.35
1,1-Dichloroethane	5.8	135	0.1997	5.8	6.1	5.6	5.85	17.4	17.4	17.1	17.25	17.4	16.7	16.7	16.7
1,2-Dichloroethane	6.2	253	0.4045	6.2	6.3	6.0	6.15	18.6	19.1	18.9	19.0	18.6	17.8	18.4	18.1
Trichloroethylene	7.2	310	0.5035	7.2	7.7	7.0	7.35	21.6	21.0	19.2	20.1	21.6	22.4	22.5	22.45
Tetrachloroethylene	12.2	596	1.0	12.2	11.7	10.6	11.15	36.6	37.1	33.2	35.15	36.6	39.8	42.6	41.2
1,1,2-Trichloroethane	10.2	780	1.3194	10.2	9.9	9.8	9.85	30.5	29.8	29.1	29.45	30.5	38.9	30.1	29.5
1,1,1,2-Tetrachloroethane	11.6	1157	1.9740	11.6	11.7	11.2	11.45	34.8	40.6	38.8	39.7	34.8	34.8	36.5	35.65

* 1 = Weighed amount; 2 = determined amount; 3 = duplicate determined amount; 4 = mean of 2 and 3.

injection temperature 100°C and the carrier gas (nitrogen) flow-rate 30 ml/min. A flame-ionization detector with a sensitivity of 10 × 1 was used. For the HS-6 headspace sampler, the temperature was 80°C, the temperature controlled time 30 min, the compression time 30 sec and the injection time 5 sec.

RESULTS AND DISCUSSION

For quantitative analysis we used the external standard method. The calibration mixture included seven characteristic chlorinated compounds in waste waters with boiling points in the range 31–140°C. This mixture was used also as a model mixture for optimization of the operating conditions of the chromatographic column. Its composition and the relative retention times of the individual compounds are given in Table I.

Calibration was carried out as follows. Into the 7-ml glass container of the HS-6 was weighed 2 cm^3 of calibration mixture (CM). The glass was closed with a rubber stopper with help of an aluminium ring and placed into the head injection part of the HS-6. A constant amount of sample was injected from the vapour phase by the semi-automatic injection system every 30 min at a constant inlet pressure and constant injection time. Results for various calibration mixtures are given in Table I.

For calculation of the concentrations of individual compounds in samples, we used the mean peak areas from two measurements. For the calculation of the concentrations of unknown compounds absent from the calibration mixture but present in samples at concentrations below 5 ppm, comparison with the components of the calibration mixture was used, as shown in Table II.

TABLE II

DETERMINATION OF UNKNOWN COMPOUNDS IN WASTE WATERS USING THE CALIBRATION MIXTURE

$$\text{Concentration of compound (ppm)} = \frac{\text{peak area of compound} \times \text{ppm of standard in CM}}{\text{peak area of standard in CM}}$$

Standard compound in CM	*Retention time (sec)*	*Retention time of standard compound (sec)*
1,1-Dichloroethylene	0– 76	76
1,1-Dichloroethane	86– 136	136
1,2-Dichloroethane	148– 253	253
Trichloroethylene	260– 338	338
Tetrachloroethylene	350– 592	592
1,1,2-Trichloroethane	600– 811	753
1,1,1,2-Tetrachloroethane	857–1200	1130

The efficiency of separation of single components of model mixture under optimized conditions is shown in Fig. 1.

A wide range of substances are present in waste waters from plants and a typical chromatogram of a waste water before and after purification is illustrated in Fig. 2. The determination is sufficiently accurate for practical use and for evaluating

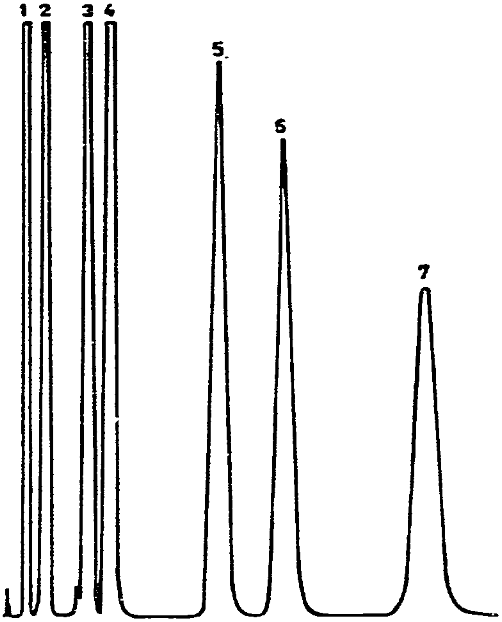

Fig. 1. Chromatogram of a model mixture of the chlorinated hydrocarbons. Peaks: 1 = 1,1-dichloroethylene; 2 = 1,1-dichloroethane; 3 = 1,2-dichloroethane; 4 = trichloroethylene; 5 = tetrachloroethylene; 6 = 1,1,2-trichloroethane; 7 = 1,1,1,2-tetrachloroethane.

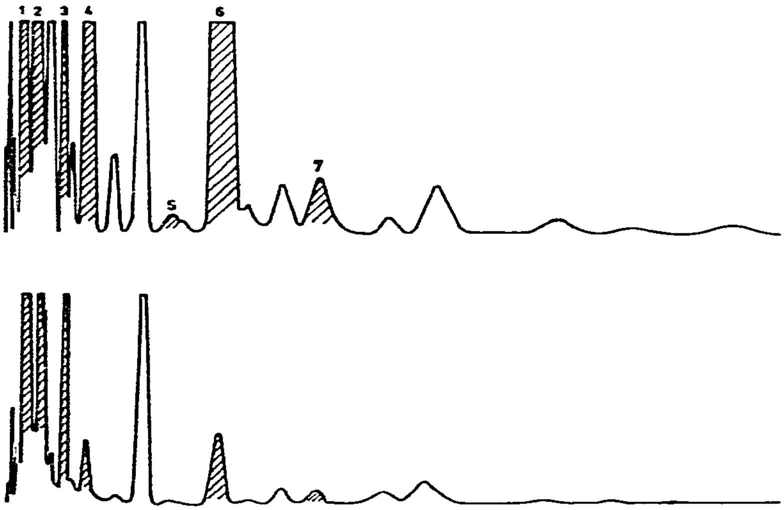

Fig. 2. Characteristic chromatograms of waste waters before and after purification. Hatched peaks are the calibration compounds.

purification processes. The choice of standards with a sufficiently wide range of boiling points covers most of the C_1–C_2 chlorinated hydrocarbons.

The application of the method to the evaluation of the efficiency of a purification process is shown in Table III.

TABLE III

CONCENTRATIONS OF CHLORINATED HYDROCARBONS IN WASTE WATERS BEFORE AND AFTER PURIFICATION

Compound	*Concentration (ppm)*					
	Sample 1		*Sample 2*		*Sample 3*	
	Before	*After*	*Before*	*After*	*Before*	*After*
1,1-Dichloroethylene	348	12.6	293	13.3	72 •	3.7
1,2-Dichloroethane	51	2.5	45	2.1	1.6	0.6
1,2-Dichloroethane	0.3	0.07	0.2	0.04	254	6.5
Trichloroethylene	81	1.2	44	1.0	13	0.4
1,1,2-Trichloroethylene	153	6.4	130	4.2	40	2.0
Tetrachloroethylene	—	—	—	—	58	0.1
Others	15	9	14	9.5	140	12.3
Total	648.3	31.8	526.2	30.1	578.6	25.6

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