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Note

Determination of chlorophenols by capillary gas chromatography

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Phenolic compounds are introduced into the environment in several ways: directly as industrial effluents and indirectly as transformation products from natural and synthetic chemicals, including pesticides[1,2]. These compounds, and chlorophenols in particular, possess odour- and taste-spoiling properties [2,3], which makes it desirable to establish their concentration levels in the environment. Several methods have been employed to determine the concentrations of phenols in surface waters. Colorimetric determination based on condensation with 4-aminoantipyrine is well known[4], but this overall determination does not permit differentiation between the many possible phenols, however. Some components, such as *para*-substituted phenols, show little reactivity towards the colour reagent.

During the past decade, much attention has been paid to gas chromatographic procedures. However, phenols do not possess favourable properties for this technique: their polarities are high and their vapour pressures are low[5,6]. When no precautions are taken, asymmetric peaks are obtained and, as a consequence, the separation and quantitation of the phenols are difficult. Use of polar stationary phases may suppress the peak tailing effect.

Another means of overcoming tailing involves derivatization of the phenols to less polar compounds. Many derivatization methods have been published, *e.g.*, formation of ethers[1], esters[7], phosphorus esters[8] and silyl derivatives[9].

For the determination of chlorophenols in a single step, capillary gas chromatography can be useful. In this study, the chlorophenols were acetylated prior to injection on to a capillary column coated with SE-30. This stationary phase can easily be coated on to the column and kept in operation for a long period. The column was connected to an electron-capture detector, thus allowing determinations in the nanogram and sub-nanogram ranges.

Several aspects make the developed method attractive for the determination of chlorophenols in environmental samples: (1) selectivity of the extraction; (2) high separation power of the capillary column; and (3) specificity and sensitivity of the electron-capture detector.

EXPERIMENTAL

Materials

For extraction purposes, toluene (p.a., Merck, Darmstadt, G.F.R.) and *n*-hexane (zür Ruckstand, Merck) were used.

A 0.1 *M* solution of potassium carbonate was shaken with toluene (1 l of solution with two 100-ml volumes for 2 min) before use.

Acetic anhydride (AnalaR, BDH, Poole, Great Britain) was twice distilled at 139.5° before use as an acetylation reagent.

Extraction and derivatization procedure

Macro-scale syntheses of chlorophenol acetates were carried out according to the method of Chau and Coburn[10]. The structures of these products were checked by infrared spectroscopy.

For the determination of the recoveries, 200 ml of twice-distilled water spiked with chlorophenols in the parts per 10^9 range was extracted successively with 40, 40 and 20 ml of toluene, each time for 1 min. The combined toluene extracts were shaken with three 20-ml volumes of 0.1 *M* potassium carbonate solution for 2 min and 0.5 ml of acetic anhydride was added to the combined potassium carbonate phases and thoroughly mixed at room temperature. After a few minutes, the mixture was extracted with 5 ml of *n*-hexane for 2 min and 1 μl of the *n*-hexane phase was injected into the gas chromatograph.

Gas chromatographic apparatus

A Tracor Model 550 chromatograph, equipped with a nickel-63 electron-capture detector, was modified for capillary column operation[11]. Instead of a constant flow controller for the carrier gas, in this study a constant pressure regulator (Model 8286, Veriflo, Richmond, Calif., U.S.A.) was used. With this regulator, it was easy to switch from splitless to split injection. The splitting ratio was adjustable by means of a needle valve. Septum bleeding was minimized by the use of a septum sweeper (Type PH4, Scientific Glass, North Melbourne, Australia).

The glass capillary column was coated dynamically with SE-30 (GC grade)[12].

The gas flow diagram of the gas chromatographic system is shown in Fig. 1.

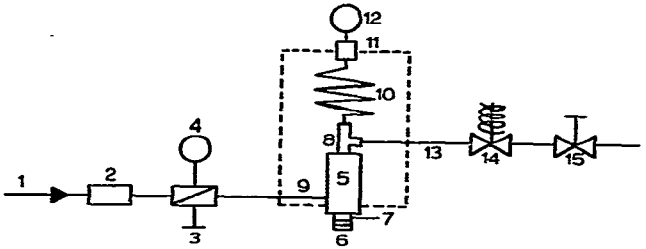

Fig. 1. Gas flow diagram of the gas chromatographic system. 1 = Carrier gas; 2 = Oxisorb cartridge (Messer Griesheim, Düsseldorf, G.F.R.); 3 = constant-pressure controller (Model 8286, Veriflo); 4 = pressure meter, 100 p.s.i.; 5 = injection block; 6 = septum; 7 = septum sweeper (Type PH4, Scientific Glass); 8 = union tee, 1/16 in., Swagelok; 9 = gas chromatograph oven; 10 = capillary column; 11 = union connector, 1/16 in., Swagelok; 12 = ^{63}Ni electron-capture detector; 13 = stainless-steel tubing, O.D. 1/16 in., length 30 cm; 14 = needle valve (Nupro, Cleveland, Ohio, U.S.A.); 15 = toggle valve (Whitey Co., Emeryville, Calif., U.S.A.).

Gas chromatographic procedure

The gas chromatographic conditions were as follows: separation column, Pyrex (25 m × 0.35 mm I.D.); stationary phase, SE-30 (GC grade); temperatures, oven 180° isothermal and 95–180° at 3°/min with a linear temperature programme, injection block 215°, detector 290°; carrier gas (helium) flow-rate 2–3 ml/min; splitting gas (helium) flow-rate, 0–60 ml/min; purge gas (nitrogen) flow-rate, 80–100 ml/min; detector pulse interval, 130 μsec; pulse width, 6.5 μsec; polarization voltage, 55 V.

RESULTS AND DISCUSSION

Table I gives the retention times of all possible chlorophenol acetates together with some bromo- and nitrophenol acetates relative to pentachlorophenol acetate

TABLE I

RELATIVE RETENTION TIMES OF CHLORO-, BROMO- AND NITROPHENOL ACETATES IN THE ISOTHERMAL MODE AND WITH TEMPERATURE PROGRAMMING

Retention times relative to pentachlorophenol acetate.

Compound	*Isothermal*		*Programmed, 95° to 180° at 3°/min*
	150°	*180°*	
Chlorophenol acetate			
2-	0.15	0.29	0.24
3-	0.16	0.30	0.27
4-	0.16	0.33	0.28
2,6-Di-	0.20	0.33	0.34
2,5-Di-	0.21	0.35	0.37
2,4-Di-	0.21		0.38
3,4-Di-	0.22	0.35	0.40
2,3-Di-	0.23	0.36	0.43
3,5-Di-	0.24	0.38	0.46
2,4,6-Tri-	0.27	0.41	0.49
2,3,6-Tri-	0.31		0.54
2,3,5-Tri-	0.33		0.56
2,4,5-Tri-	0.33	0.46	0.57
2,3,4-Tri-	0.38		0.64
3,4,5-Tri-	0.40		0.67
2,3,5,6-Tetra-	0.50	0.61	0.73
2,3,4,6-Tetra-	0.50	0.61	0.74
2,3,4,5-Tetra-	0.64	0.71	0.83
Penta-	1.00 (17.5 min)	1.00 (8.0 min)	1.00 (25.5 min)
Bromophenol acetate			
2-	0.18	0.32	0.32
3-	0.20	0.33	0.36
4-	0.20	0.33	0.37
2,6-Di-	0.32	0.45	0.55
2,4-Di-	0.35	0.48	0.61
Nitrophenol acetate			
2-	0.23	0.36	0.46
3-	0.29	0.41	0.58
4-	0.31	0.42	0.61

at different column temperatures. The retention times were reproducible (better than 1%) and did not change with time: during 1 month the retention times did not change

TABLE II

RELATIVE PEAK HEIGHTS OF CHLOROPHENOL ACETATES COMPARED WITH PENTACHLOROPHENOL ACETATE WITH LINEAR PROGRAMMING FROM 95° TO 180° AT 3°/MIN

Chlorophenol acetate	*Relative peak height (%)*
Mono-	0.5
Di-	15
Tri-	30
Tetra-	55
Penta-	100

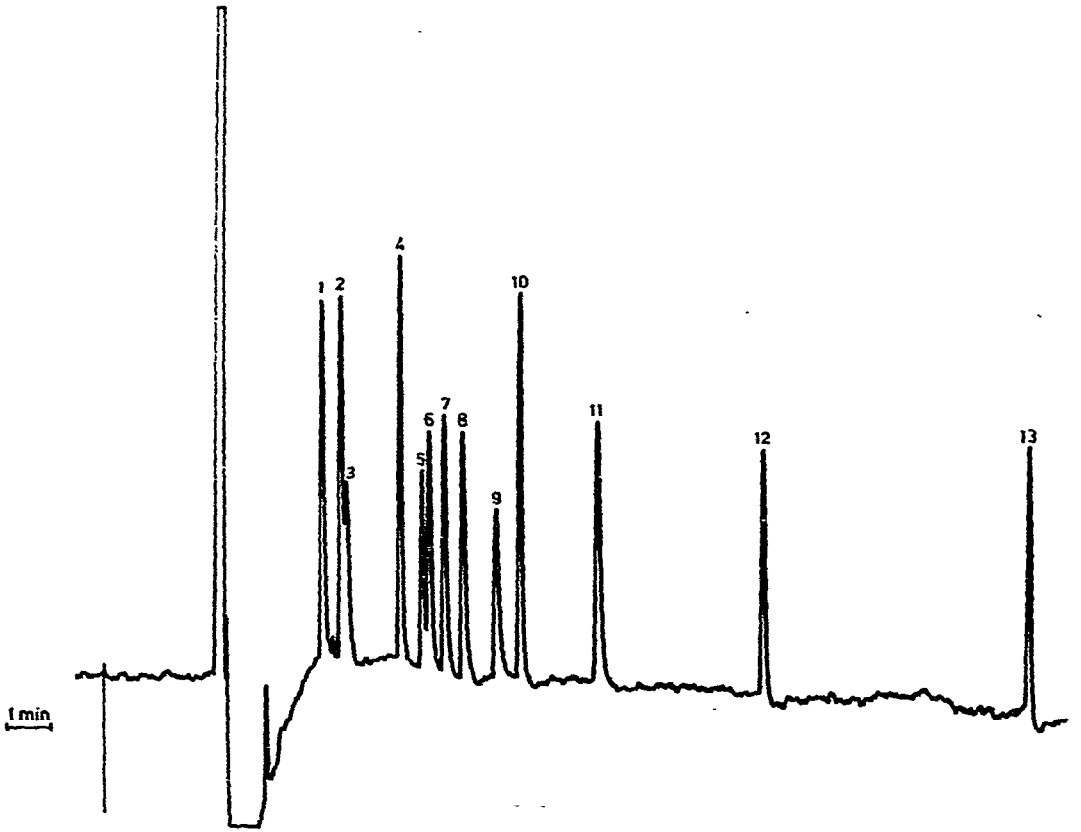

Fig. 2. Separation of chlorophenol acetates with linear programming from 95° to 180° at 3°/min. The concentration of the components (ng/μl) are given in parentheses. Peaks: 1 = 2-chlorophenol acetate (2.21); 2 = 3-chlorophenol acetate (2.22); 3 = 4-chlorophenol acetate (2.12); 4 = 2,6-dichlorophenol acetate (0.090); 5 = 2,5-dichlorophenol acetate (0.081); 6 = 2,4-dichlorophenol acetate (0.086); 7 = 3,4-dichlorophenol acetate (0.086); 8 = 2,3-dichlorophenol acetate (0.092); 9 = 3,5-dichlorophenol acetate (0.084); 10 = 2,4,6-trichlorophenol acetate (0.049); 11 = 2,4,5-trichlorophenol acetate (0.059); 12 = 2,3,4,6-tetrachlorophenol acetate (0.026); 13 = pentachlorophenol acetate (0.018).

significantly in spite of many intermediate injections. For most components the separation was satisfactory, thus allowing determination in a single step.

In Table II the relative peak heights of different chlorophenol acetates compared with pentachlorophenol acetate are given. The limit of detection of pentachlorophenol acetate is about 1 pg.

The recovery of the extraction–acetylation step of chlorophenols, determined by comparing the gas chromatographic signals of the micro- and macro-scale preparations, was 80–100%.

As an illustration of the possibilities of the proposed method, a gas chromatogram of a mixture of several chlorophenol acetates is shown in Fig. 2.

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