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Note

Determination of chlorophenols in water by direct acetylation and solid-phase extraction

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Phenols can be converted into their acetates directly in a dilute aqueous solution by a simple reaction with acetic anhydride[1–3]. The method used for the isolation and concentration of phenol acetates from water is usually repeated liquid–liquid extraction with subsequent concentration of the derivatives by solvent evaporation. Another enrichment method uses solid-phase extraction of phenols from acidified water samples, elution with an organic solvent, derivatization of phenols in the eluate and gas chromatographic (GC) analysis[4,5]. Retention data and mass spectra of chlorophenol acetates have been published[6].

The method described in this paper combines both of the above procedures. It consists of direct acetylation of chlorophenols in water, solid-phase extraction of chlorophenol acetates and GC analysis of the eluate. The advantages of this method are as follows: (1) non-ionogenic acetates may be isolated from water more easily than highly polar free chlorophenols; (2) derivatization in the aqueous solution is very fast and results in the formation of products suitable for direct GC analysis; and (3) in comparison with repeated liquid–liquid extraction, manipulations with large volumes of solvents are avoided.

EXPERIMENTAL

For solid-phase extraction, polypropylene cartridges packed with C_{18} reversed phase were used (Tessek) and/or Sep-Pak (Waters Assoc.). The volume of packing material in both cartridges used was about 0.5 ml.

A Varian 3700 gas chromatograph was used with flame ionization (FID) and/or electron-capture detection (ECD). Data were processed on an HP 3388 integrator (Hewlett-Packard). A wide-bore fused-silica capillary column (30 m × 0.5 mm I.D.) coated with RSL-150 (Alltech) was used for the separation of the chlorophenol acetates. No inlet splitter was used.

The GC parameters were as follows: carrier gas flow-rate [helium for FID and argon–methane (95:5) for ECD], 6 ml/min; temperature of injection block, 200°C; FID

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temperature, 260°C; ECD temperature, 315°C. The flow-rate of the make-up gas for ECD was 15 ml/min; no make-up gas was used for FID as the capillary column was led directly into the jet of the detector. The oven temperature was programmed from 140 to 225°C at 8°C/min for GC with ECD and from 60 to 220°C at 8°C/min for GC with FID.

Two different schemes were used for recovery measurements, the first being a simulated water sample and the other a 100% recovery standard:

Simulated water sample:

acetylation of chlorophenols in water
↓
solid-phase extraction
↓
removal of residual water from cartridge
↓
elution with organic solvent
↓
drying of eluate
↓
addition of internal standard
↓
gas chromatography

100% recovery standard:

acetylation of chlorophenols in organic solvent
↓
separation of organic layer
↓
drying of organic solvent
↓
addition of I.S.
↓
gas chromatography

Procedure

Tap water was spiked with different chlorophenols. Acetylation of chlorophenols was performed using a procedure similar to that described by Coutts *et al.*[1]. Sodium hydrogencarbonate (10 g) and acetic anhydride (1 ml) were added to the water sample (250 ml) and the mixture was shaken until evolution of carbon dioxide ceased. An aliquot of 100 ml of acetylated water sample was then pushed through the cartridge by means of a syringe. This enrichment step took 2 min, which corresponds to a flow-rate of 50 ml/min. Volumes of water up to 250 ml were tested and no breakthrough of the chlorophenol acetates tested was observed. The cartridge was then connected to a water evacuator in order to remove residual water, which took 2 min. Chlorophenol acetates trapped in the cartridge were desorbed with 1 ml of benzene. Desorption was performed stepwise three times using about 0.3 ml of solvent each time, so each portion corresponds to the cartridge dead volume. Each portion of desorption solvent was allowed to equilibrate in the cartridge for about 1 min. Benzene

was pushed through the cartridge by means of an all-glass syringe. The combined eluates were dried with a small amount of anhydrous sodium sulphate and, after addition of internal standard (*p*-bromophenol acetate), GC analysis was performed.

Solutions representing 100% recovery of chlorophenols from water were prepared by a method described by Renberg and Lindström[4]. An amount of chlorophenols corresponding to 100 ml of water sample was added in a methanolic solution to a reaction–extraction mixture containing 3 ml of 0.1 mol/l potassium carbonate, 1 ml of benzene and 50 μl of acetic anhydride. A test-tube containing the reaction mixture was shaken for 5 min. The aqeous phase was drained and the organic layer was dried with anhydrous sodium sulphate. The same amount of internal standard as was added to the cartridge eluate of water samples was also added to the organic phase of the reaction mixture. Then the solution was analysed by GC.

The recovery of the procedure was calculated from the ratio of the peak areas of chlorophenol acetates obtained from spiked water samples and from 100% recovery standards after correcting for the peak areas of the internal standard (I.S.) in the different GC runs.

RESULTS AND DISCUSSION

Recoveries were measured for various concentrations of chlorophenols in water and the results are summarized in Table I for FID and in Table II for ECD measurements. The recoveries were always higher than 90%.

Examples of chromatograms are shown in Figs. 1 and 2. Fig. 1 refers to the determination of chlorophenols in a spiked water sample for the concentrations given in the first column of Table I. Fig. 2 applies to a reference mixture corresponding to the concentrations given in the second column of Table II.

TABLE I

RECOVERY OF CHLOROPHENOLS FROM WATER BY GC WITH FID

Concentrations are given in parentheses.

Compound	*Recovery (%) (concentration in mg/l)*		
o-Chlorophenol	103.0 (5.51),	105.1 (0.330),	96.3 (0.165)
p-Chlorophenol	100.0 (2.72),	100.7 (0.163),	95.6 (0.082)
3,4-Dichlorophenol	98.2 (2.57),	99.1 (0.154),	93.9 (0.077)
2,4,5-Trichlorophenol	96.5 (2.44),	102.1 (0.146),	97.8 (0.073)
Pentachlorophenol	97.1 (4.80),	95.1 (0.288),	95.6 (0.144)

TABLE II

RECOVERY OF CHLOROPHENOLS FROM WATER BY GC WITH ECD

Concentrations are given in parentheses.

Compound	*Recovery (%) (concentration in μg/l)*	
o-Chlorophenol	92.0 (218),	96.2 (21.8)
3,4-Dichlorophenol	94.1 (218),	98.3 (21.8)
2,4,5-Trichlorophenol	101.2 (28.4),	105.2 (4.36)
Pentachlorophenol	93.0 (2.9),	92.1 (0.72)

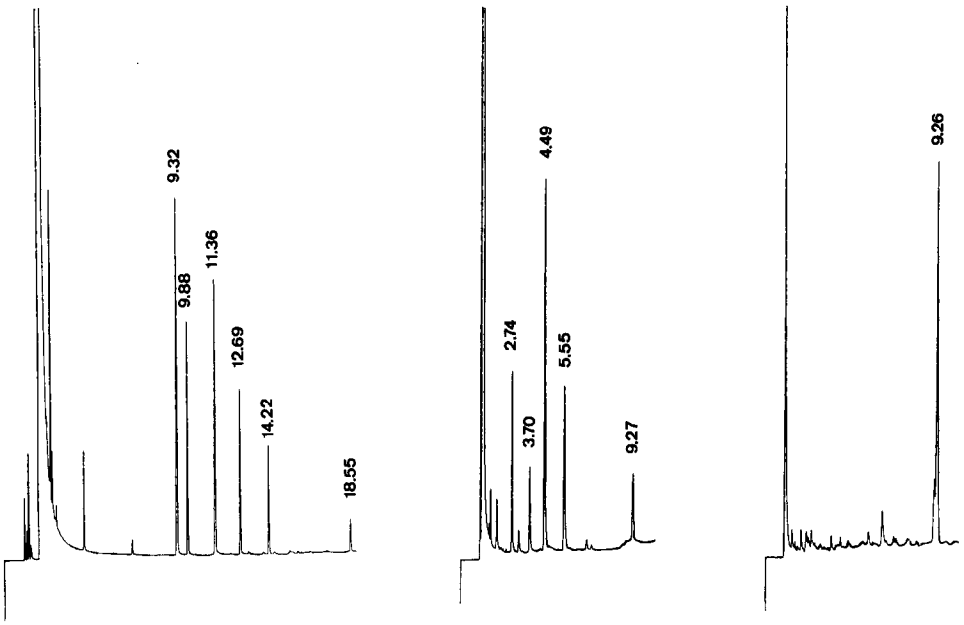

Fig. 1. Determination of chlorophenols in spiked water samples by GC with FID. Chromatographic conditions are given in the text. Concentrations of chlorophenols are given in the first column of Table I. Injection volume, 0.2 μl. Retention times (min): *o*-chlorophenol, 9.32; *p*-chlorophenol, 9.88; 3,4-dichlorophenol, 12.69; 2,4,5-trichlorophenol, 14.42; pentachlorophenol, 18.55; *p*-bromophenol (I.S.), 11.36 (all compounds as acetates).

Fig. 2. Determination of chlorophenol acetates in a 100% recovery standard by GC with ECD. Chromatographic conditions are given in the text. Concentrations of chlorophenols are given in the second column of Table II. Injection volume, 0.5 μl. Retention times (min): *o*-chlorophenol, 2.74; 3,4-dichlorophenol, 4.49; 2,4,5-trichlorophenol, 5.55; pentachlorophenol, 9.27; *p*-bromophenol (I.S.), 3.7 (all compounds as acetates).

Fig. 3. Analysis of a tap water sample spiked with 1.5 μg/l of pentachlorophenol by GC with ECD. Retention time of pentachlorophenol acetate: 9.26 min.

The applicability of the method is demonstrated in Fig. 3; tap water spiked with 1.5 μg/l of pentachlorophenol was analysed by the described procedure. The time necessary for one analysis is less than 25 min.

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REFERENCES

1 R. T. Coutts, E. E. Hargesheimer and F. M. Pasutto, *J. Chromatogr.*, 179 (1979) 291.
2 R. T. Coutts, E. E. Hargesheimer and F. M. Pasutto, *J. Chromatogr.*, 195 (1980) 105.
3 A. Cassista and V. N. Mallet, *Chromatographia*, 18 (1984) 305.
4 L. Renberg and K. Lindström, *J. Chromatogr.*, 214 (1981) 327.
5 K. Norén and J. Sjövall, *J. Chromatogr.*, 414 (1987) 55.
6 I. O. O. Korhonen and J. Knuutinen, *J. Chromatogr.*, 256 (1983) 135.