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DETERMINATION OF TRACE PHENOLS IN WATER BY GAS CHROMATOGRAPHIC ANALYSIS OF HEPTAFLUOROBUTYRYL DERIVATIVES

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SUMMARY

An analytical procedure is described that permits the determination of phenol and substituted phenols, which do not possess inherent electron-capture sensitivity, at concentrations $\geqslant$10 ng/ml in aqueous media by gas chromatographic analysis of the heptafluorobutyryl derivatives. Sample pre-concentration is not required, and a single benzene extraction removes phenolics from the water matrix prior to derivatization. The gas chromatographic analysis is performed on a column packing which exhibits high efficiency and low column bleed. These characteristics allow the determination of a large number of components in a single temperature-programmed electron-capture gas chromatographic analysis in less than 15 min. Recoveries of ten phenolics at the 20–200 ppb level are *ca.* 75% or greater.

INTRODUCTION

The monitoring of industrial effluents and natural waters for trace concentrations of phenols is necessary because these compounds can adversely affect the palatability of water at low concentrations[1]. They can be determined in water by a variety of methods. 4-Aminoantipyrene is a commonly used reagent for the colorimetric determination of phenols[2]. This method, however, is non-specific and does not respond to compounds which are substituted in the *para* position. Recently, an electrochemical detector has been developed which, when coupled to a liquid chromatograph, can be used to detect concentrations of phenols in aqueous samples below the microgram per milliliter level[3].

The gas chromatographic determination of phenols in aqueous samples has been accomplished by direct aqueous injection[4] with flame-ionization detection (FID). Sensitivity is limited by this technique. Chlorinated phenols have been determined at nanogram per milliliter levels by derivatization with diazomethane[5], diazoethane[6] or silanizing reagents[7] followed by electron-capture (EC) detection. For compounds which do not possess an EC response, pre-concentration and/or derivatization is necessary in order to obtain these low detection limits by gas chromatography. Kawahara[8] found that pre-concentration followed by gas chromatographic analysis with a relatively non-specific detector (*i.e.*, FID) does little to enhance the response of

the phenols with respect to other compounds which co-elute. Derivatization can be used to improve the sensitivity and gas chromatographic characteristics of many phenolics[8–10].

Fenimore *et al.*[11] reported relative EC responses and retention times for derivatives of Δ^9-tetrahydrocannabinol. Of the compounds listed, the heptafluorobutyrate (HFB) and pentafluoroproprionate derivatives appeared to possess the best combination of detector response and volatility. The HFB derivatives of several phenols are relatively stable to hydrolysis and to gas chromatographic analysis on non-polar stationary phases[12].

Ehrsson *et al.*[12] have demonstrated reasonable stability for a variety of phenolic HFB derivatives when analysed on low-polarity column packings, generally silicones. They observed optimal stability for these derivatives using OV-1 (methylsilicone) and/or OV-17 (methylphenylsilicone) as the stationary phase. We have also observed high stability for phenolic HFB derivatives when separated on silicone stationary phases. However, when attempting to analyse samples containing a wide variety of closely related phenolics, separation of the HFB derivatives on these relatively non-polar phases was inadequate to permit differentiation of the various phenols.

In response to this problem, we developed a procedure which uses a "tailor-made" gas chromatographic column packing which has the following characteristics: high polarity stationary phase; HFB derivatives are highly stable; high chromatographic column efficiency; and low column "bleed", permitting temperature-programmed separations using an EC detector.

This report describes the application of high-efficiency, packed column, gas chromatography for the examination of a variety of aqueous samples for trace levels of many phenolics.

EXPERIMENTAL

Reagents

Heptafluorobutyrylimidazole (HFBI) and dimethyldichlorosilane (DMCS) were obtained from Pierce (Rockford, Ill., U.S.A.). Sodium sulfate and hydrochloric acid were of analytical-reagent grade quality purchased from J. T. Baker (Phillipsburg, N.J., U.S.A.). Phenolic standards were obtained from Aldrich (Milwaukee, Wisc., U.S.A.). Benzene was "distilled-in-glass" quality from Burdick & Jackson Labs. (Muskegon, Mich., U.S.A.).

Instrumental conditions

A Hewlett-Packard Model 5713 gas chromatograph, equipped with a ^{63}Ni linear electron-capture detector, was used. The electrometer was connected to a Sargent-Welch Model SRG (1 mV full scale) recorder. The septum was isolated from the chromatographic system with a Perkin-Elmer "septum swinger". The gas chromatographic conditions were as follows: column temperature, 80° (2-min initial hold), then programmed to 170° at 8°/min; injection port temperature, 200°; detector temperature, 350°; carrier gas (nitrogen) flow-rate, 33 ml/min; sample size, 2 μl; attenuation, 64–256×.

Trace amounts of oxygen and water were removed from the carrier gas with a Go-Getter (General Electric) gas purifier.

Columns

Prior to packing, glass columns (270 cm × 2 mm I.D.) were washed with distilled water, methanol, acetone, benzene and chloroform, silanized with a 20% (v/v) solution of DMCS in toluene for 15 min, washed with methanol and dried at 110°.

The silanized column was packed using a vibrator and gentle suction. The packed column was installed in the gas chromatograph, flushed with carrier gas at room temperature for 15 min, then programmed to 200° at 1°/min and maintained at this temperature for 16 h prior to use.

Preparation of bonded GC packing

The preparation of this gas chromatographic packing is a recent development of Dow Chem. (Midland, Mich., U.S.A.) and a more thorough discussion of their characteristics is being prepared for future publication.

Extraction and derivatization

The procedure is summarized in Fig. 1.

A 25-ml water sample was acidified to pH 1 with concentrated hydrochloric acid and 25 ml of benzene were added. The mixture was mechanically shaken for 15 min and allowed to stand until the layers separated. A 2-ml portion of the benzene extract was dried by passing through a 5 cm × 5 mm glass column packed with anhydrous sodium sulfate, which had been heated to 600° for 16 h. One milliliter of column effluent was collected in a 4-ml glass vial and 5 μl of HFBI reagent were added. The vial was capped and heated at 65° for 15 min. After cooling, excess of

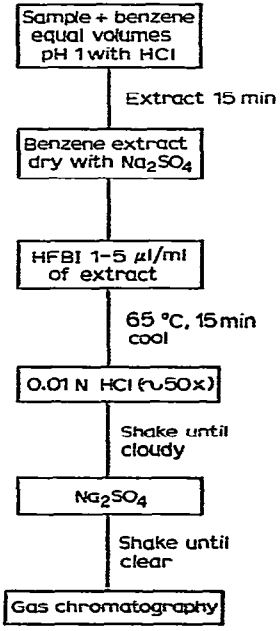

Fig. 1. General HFBI derivatization procedure.

reagent was hydrolyzed by adding 20 μl of 0.01 *N* hydrochloric acid and shaking vigorously for 1 min. Prior to gas chromatographic analysis, *ca.* 250 mg of anhydrous sodium sulfate were added to remove excess of water.

RESULTS AND DISCUSSION

Extraction and reaction efficiencies

In initial studies diethyl ether was employed as the extraction solvent for removal of phenols from water. Although extraction efficiencies of 70–85% were observed for a variety of phenols present in water at the 50 ng/ml level, analysis of reaction mixtures in diethyl ether indicated that the HFBI was reacting with the solvent (or impurities present in the solvent) to give large gas chromatographic peaks eluting throughout the temperature program. Use of benzene as the extraction solvent yielded efficiencies similar to those obtained with diethyl ether, but reaction mixtures contained fewer interferences.

Phenolic standards were added to water as methanolic solutions for determination of recoveries. A single benzene extraction was made, followed by the derivatization. The recoveries obtained are shown in Table I. The table is divided into two sections: section 1 shows compounds for which this procedure is most applicable and section 2 lists compounds which cannot be determined by this procedure. Polyhydric phenols are not extracted from water with benzene, but they do react with HFBI to form chromatographically stable diesters. Trichlorophenols show poor recoveries for a different reason. They are extracted from water efficiently, but do not react well with HFBI because of their increased acidity. Although recoveries for the phenols shown in section 1 in Table I vary from *ca.* 60 to 100%, the lower limit of concentrations for which these recoveries were determined was in the range of 20–40 ng/ml. At lower concentration levels (10–20 ng/ml), recoveries were generally

TABLE I

RECOVERY OF PHENOLICS FROM WATER

Section	*Component*	*Concentration range (PPB)*	*Recovery (%)*
1	Phenol	27–136	76–109
	4-Chlorophenol	19–93	74–95
	2-Chlorophenol	30–75	96–97
	2-Bromophenol	25–63	97–100
	2,4-Dichlorophenol	58	88
	2,6-Dichlorophenol	44	64
	2,4-Dibromophenol	23–65	88–91
	p-tert.-Butylphenol	38–188	92–113
	o-Phenylphenol	33–50	97–106
	o-sec.-Butylphenol	63	81
	o-Cresol	86	100
2	Resorcinol	45	2
	Catechol	48	2
	tert.-Butylcatechol	46	9
	2,4,5-Trichlorophenol	45	76
	2,4,6-Trichlorophenol	46	50

poorer. For most applications at these levels, corrections for average recoveries to give an approximate accuracy of ±20% relative is adequate.

Effect of reaction time and temperature

Standard solutions were reacted at room temperature and at 65° for periods of 5 min to 1 h. The room temperature samples contained many early eluting peaks, which interfered with the determination of phenyl heptafluorobutyrate (see Fig. 2). The samples reacted at 65° generally exhibited better response and contained fewer extraneous peaks. No differences were observed for reaction times longer than 10 min.

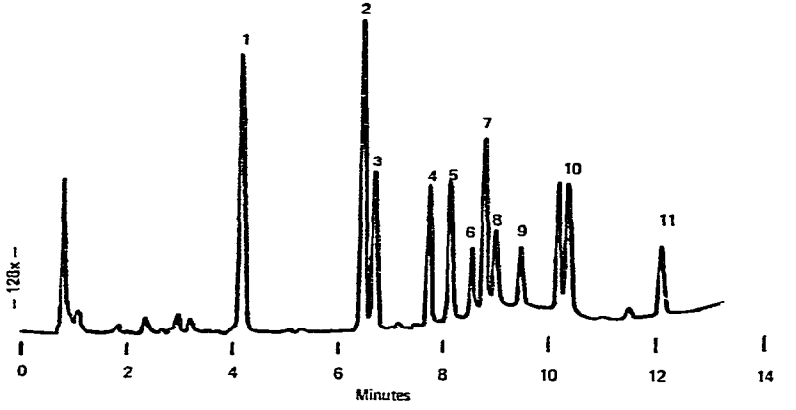

Fig. 2. ECD chromatogram of mixed phenylheptafluorobutyrates on nitro-DEGS column. GC conditions as described under Experimental. Peaks: 1 = phenol-HFB (136 ppb); 2 = 4-chlorophenol-HFB (93 ppb); 3 = 2-chlorophenol-HFB (75 ppb); 4 = 2-bromophenol-HFB (63 ppb); 5 = 2,4-dichlorophenol-HFB (58 ppb); 6 = 2,6-dichlorophenol-HFB (44 ppb); 7 = *p-tert.*-butylphenol-HFB (188 ppb); 8 = 2,4,6-trichlorophenol-HFB (46 ppb); 9 = 2,4,5-trichlorophenol-HFB (45 ppb); 10 = 2,4-dibromophenol-HFB (65 ppb); 11 = *o*-phenylphenol-HFB (83 ppb).

Effect of HFBI concentration

The amount of HFBI added to a mixed standard containing phenolics at a total concentration of *ca.* 1 μg/ml was varied from 0.25 to 15 mg per milliliter of sample solution. The lowest concentration of HFBI showed a decreased response, and the highest concentration contained a larger number of extraneous peaks. In most instances these peaks will not interfere with the determination of any of the compounds, but if a large excess of HFBI is used and small amounts of phenol or 2,4-dibromophenol are present, then peaks eluting slightly before these compounds could cause interference. The optimal HFBI ratio was 0.5–2 μl of HFBI per microgram of phenolic. This amount will, of course, vary with the reactivity of the phenols present, but large excesses of HFBI should be avoided.

Stability of derivatives

The derivatives of phenol, monochlorophenols and alkylphenols were relatively stable. No evidence of decomposition was observed after storage at *ca.* 4° for

72 h. The heptafluorobutyrates of the more highly halogenated phenols and the hydroxyphenols were less stable and new standards were derivatized daily. The derivatives of hydroxyphenols were much less stable, and significant decomposition was noted in less than 30 min at room temperature. Storage of these derivatives at *ca.* 4° greatly increased the stability, so that analysis over a 8-h period showed less than a 10% decrease in response.

The EC responses for catechol and resorcinol derivatives were approximately twice that of phenylheptafluorobutyrate, suggesting that both hydroxyl groups were derivatized. Apparently the instabilities were due to hydrolysis of at least one of the ester linkages so that the product would not elute from the gas chromatographic column under the conditions employed. After decomposition, no new peaks were noted in the chromatogram, and the peak height of phenylheptafluorobutyrate did not increase.

Gas chromatographic column stability

The nitro-DEGS column employed in this analysis was used for many samples over a 4-month period with no evidence of degradation. Because of the very small

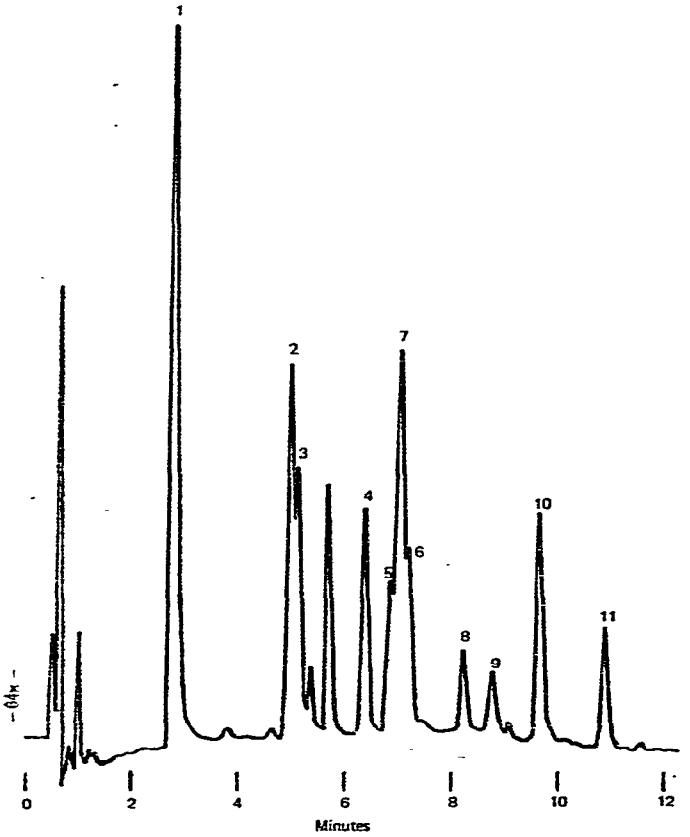

Fig. 3. ECD chromatogram of mixed phenylheptafluorobutyrates on OV-17 + OV-210 column. GC conditions as described under Experimental. Peaks as in Fig. 1.

amount of liquid phase present on the support (<0.5%, w/w), it is essential that precautions be taken to insure that oxygen or water do not enter the column.

Comparison of gas chromatographic column packings

Chromatograms of a mixed phenolic standard are shown in Figs. 2 and 3. Both were separated according to the same chromatographic conditions as previously described. Fig. 3 shows the separation obtained on a column packed with a mixed silicone liquid phase (1.95% OV-210 + 1.5% OV-17). The good peak shape indicates that the column is suitable for these types of compounds. However, the separation is poor with many of the esters being only partially resolved. The same standard solution chromatographed on the nitro-DEGS column (Fig. 2) exhibits a good peak shape, improved column efficiency and greatly enhanced separation. Fig. 4 shows

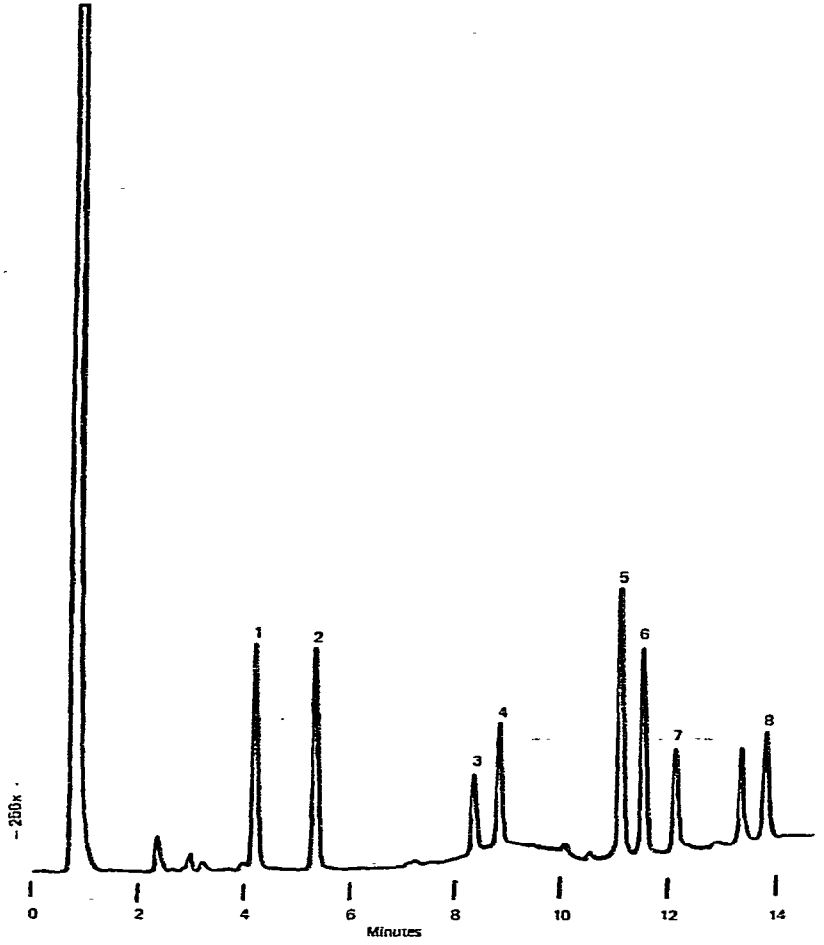

Fig. 4. ECD chromatogram of alkylphenylheptafluorobutyrates on nitro-DEGS column. GC conditions as described under Experimental. Peaks: 1 = phenol-HFB (108 ppb); 2 = *o*-cresol-HFB (214 ppb); 3 = *o-sec.*-butylphenol-HFB (157 ppb); 4 = *p-tert.*-butylphenol-HFB (115 ppb); 5 = resorcinol-HFB (112 ppb); 6 = catechol-HFB (120 ppb); 7 = *o*-phenylphenol-HFB (124 ppb); 8 = *tert.*-butylcatechol-HFB (116 ppb).

another mixture of phenolic compounds chromatographed on the nitro-DEGS column.

We have been using this technique for several months to determine many phenolics at the nanograms per milliliter concentration level in a variety of industrial and natural water samples. The formation of HFB esters of phenols and separation on high-efficiency gas chromatographic columns are applicable to a variety of trace phenol determinations. Derivatizations of phenolic natural products[13] and drug residues[11] have been reported but improved chromatographic separations may make these types of analyses more useful. With minor modifications, this procedure would apparently be applicable to the determination of a variety of phenolic pesticides and metabolites in biological matrices and phenolic monomers in resins. In addition to the HFB derivatives of phenols, numerous other halogenated species can be determined using the described chromatographic conditions. Table II lists several of these compounds, along with their respective retention times, which we have identified.

TABLE II

GAS CHROMATOGRAPHIC RETENTION TIMES ON NITRO-DEGS

Compound	*Retention time (min)*	*Compound*	*Retention time (min)*
1,4-Dichlorobenzene	1.7	2,6-Dichlorophenol-HFB	8.5
1,2-Dichlorobenzene	2.0	2,4,5-Trichloroanisole	8.6
1,2,4-Trichlorobenzene	3.1	*p-tert.*-Butylphenol-HFB	8.8
1,2,3-Trichlorobenzene	3.8	2,4,6-Trichlorophenol-HFB	9.0
Phenol-HFB	4.2	Hexachlorobenzene	9.4
1,2,4,5-Tetrachlorobenzene	4.9	2,4,5-Trichlorophenol-HFB	9.5
o-Cresol-HFB	5.2	2,4-Dibromophenol-HFB	10.4
2,4,6-Trichloroanisole	5.7	Pentachloroanisole	10.6
1,2,3,4-Tetrachlorobenzene	6.0	Resorcinol-HFB	11.1
4-Chlorophenol-HFB	6.4	2,3,4,5-Tetrachloroanisole	11.2
2-Chlorophenol-HFB	6.7	Catechol-HFB	11.5
Pentachlorobenzene	7.3	*p*-Nitrophenol-HFB	11.6
2-Bromophenol-HFB	7.75	*o*-Phenylphenol-HFB	12.1
4-Bromophenol-HFB	7.75	2,6-Dichlorophenoxyacetic acid, methyl ester	12.5
2,4-Dichlorophenol-HFB	8.1	2,4-Dichlorophenoxyacetic acid, methyl ester	13.6
2,3,4,6-Tetrachloroanisole	8.3	*tert.*-Butylcatechol-HFB	13.8
o-sec.-Butylphenol-HFB	8.35	2,4,5-Trichlorophenoxypropionic acid, methyl ester	14.0
		2,4,5-Trichlorophenoxyacetic acid, methyl ester	15.2

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