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GLASS CAPILLARY GAS CHROMATOGRAPHIC EVALUATION OF THE LIQUID EXTRACTION OF MONOHYDRIC ALKYLPHENOLS FROM WATER

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SUMMARY

Glass capillary gas chromatography was used for the examination of solvents (*n*-pentane, tetrachloromethane, trichloromethane, dichloromethane, benzene and diethyl ether) for the extraction of monohydric alkylphenols (25 compounds) from water at micrograms per litre concentrations. The recoveries were evaluated relative to *n*-octadecane. The highest recoveries were obtained for diethyl ether and the lowest for phenol and its lower alkyl derivatives.

INTRODUCTION

The presence of phenolics in the aquatic environment is of interest as several phenols have been found to be toxic against aquatic organisms at concentrations often below the milligrams per litre level. Certain phenols also have the ability to impart taste and odour to potable water supplies at the micrograms per litre level. A comprehensive survey of toxicity data and evaluations for different phenols have been published¹.

Capillary gas chromatography has become a widely used and sensitive tool for trace level determinations of phenolics in water. Although methods using direct injection of water samples have been described^{2,3}, such procedures have not been extensively used. In addition to the obvious risk of contamination of the chromatographic system by injection of samples containing different types of dissolved and suspended matter, the detection levels can be considerably lowered if an enrichment step is used. Many methods have been used successfully for the isolation and concentration of phenolic compounds from water samples. The most commonly used method is liquid-liquid extraction, *i.e.*, after acidification of the water sample to a pH less than the pK_a values of the components to be analysed, the sample is shaken one or several times with a suitable organic solvent, or mixtures thereof⁴⁻⁶.

This paper describes the application of glass capillary gas chromatography to the examination of solvents (*n*-pentane, tetrachloromethane, trichloromethane, dichloromethane, benzene and diethyl ether) for the extraction of monohydric alkylphenols (25 compounds) from water at micrograms per litre concentrations. The recoveries of the studied compounds were evaluated relative to *n*-octadecane. The extracts were analysed directly (without derivatization) by glass capillary gas chromatography.

EXPERIMENTAL

Chemicals

The monohydric alkylphenols examined were 2-methyl-(2-M), 3-methyl-(3-M), 4-methyl-(4-M), 2-ethyl-(2-E), 3-ethyl-(3-E), 2-isopropyl-(2-iP), 4-isopropyl-(4-iP), 2-*n*-propyl-(2-P), 3-*n*-propyl-(3-P), 4-*n*-propyl-(4-P), 2-*sec.*-butyl-(2-sB), 2-*tert.*-butyl-(2-tB), 4-*tert.*-butyl-(4-tB), 2-*n*-butyl-(2-B), 3-*n*-butyl-(3-B), 4-*n*-butyl-(4-B), 2,6-dimethyl-(2,6-DM), 2,3-dimethyl-(2,3-DM), 3,4-dimethyl-(3,4-DM), 3,4-diethyl-(3,4-DE), 2,6-di-*tert.*-butyl-(2,6-DtB), 2,3,5-trimethyl-(2,3,5-TM), 3,4,5-trimethyl-(3,4,5-TM) and 2,3,5,6-tetramethylphenol (2,3,5,6-TTM) and phenol (P). They were obtained from different manufacturers and were generally of 99% purity or better.

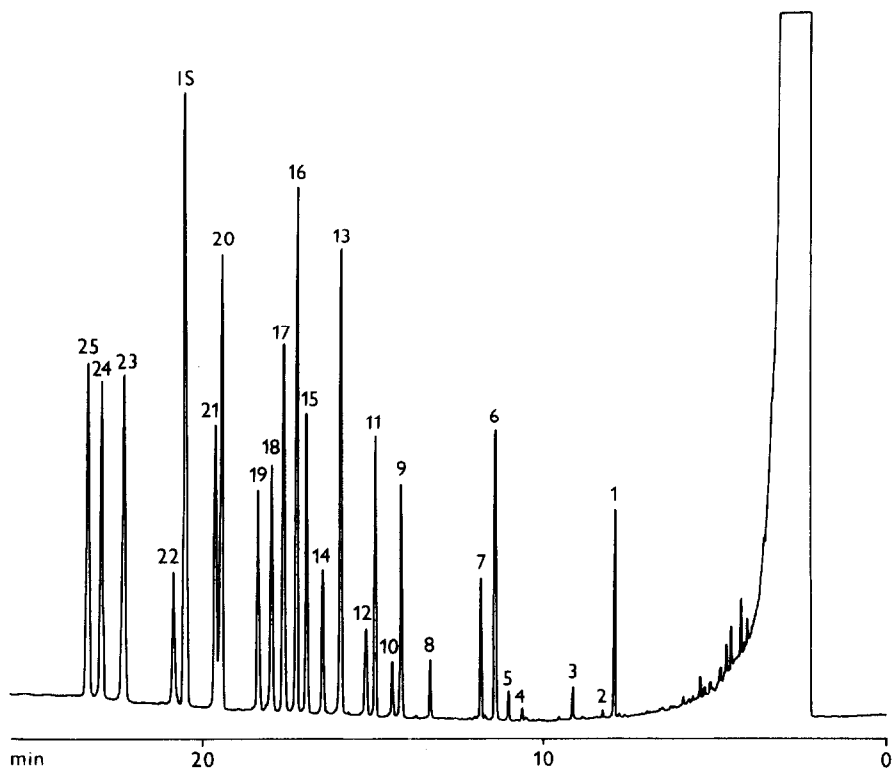


Fig. 1. Chromatogram of chloroform extract of a model sample of water. For identification of peaks, see Table I. IS = *n*-octadecane.

The extractants (*n*-pentane, tetrachloromethane, trichloromethane, dichloromethane, benzene and diethyl ether) were of analytical-reagent grade and redistilled prior use. The purity of each extractant was checked by gas chromatography.

Instrumental conditions

A Fractovap Model 2350 (Carlo Erba) gas chromatograph with a flame-ionization detector and an Autolab System I (Spectra-Physics) integrator were used. The column was a 50 m × 0.25 mm I.D. glass capillary coated with tri-2,4-xylenyl phosphate liquid stationary phase. The gas chromatographic conditions were as follows: column temperature, initially 110°C, then programmed to 150°C at 1.5°C/min; injection port and detector temperature, 175°C; carrier gas, hydrogen; injection technique, split/splitless; sample size, 1.5 µl; attenuation, 4–16 × .

RESULTS AND DISCUSSION

Model water samples of 1 l with known contents of the studied alkylphenols were acidified to pH 1 with concentrated hydrochloric acid, cooled to 5°C, extracted in the presence of *n*-octadecane by vigorous mechanical shaking for 3–5 min and allowed to stand until the layers separated. The volumes of the organic phase added (depending on solubility) were 1.0 ml for *n*-pentane and tetrachloromethane, 3 ml for benzene, 12 ml for trichloromethane, 25 ml for dichloromethane and 100 ml for diethyl ether. When extracting with trichloromethane, dichloromethane and diethyl ether, prior to chromatography the organic phases were concentrated (in a rotary vacuum evaporator) to a volume of 2–3 ml. After being dried (with anhydrous sodium sulphate) the extracts were chromatographed. Fig. 1 shows a chromatogram of a chloroform extract of a model water sample. The concentrations of the individual alkylphenols in the model samples ranged from 2 to 10 µg/l (10–50 µg/l for tetrachloromethane). The extraction recoveries relative to *n*-octadecane (recovery = 100%) are shown in Table I (the values represent arithmetic means of three measurements).

Table I shows that with increasing solvent polarity the extraction recoveries of alkylphenols increase, particularly with phenol and its lower alkyl derivatives. The recoveries of alkylphenols are influenced by the structure of the phenol, the length of the alkyl chain and the number of alkyl groups on the ring.

The highest recoveries were obtained for di-*ortho*-substituted lower for mono-*ortho*-substituted and the lowest for non-*ortho*-substituted phenols. The extraction recoveries are also slightly influenced by the length of the alkyl substituent chain and by steric effects due to the size of the substituent, which is particularly evident with 2,6-di-*tert*-butylphenol, the polarity of which is the lowest of the phenols studied. Its recovery even with non-polar solvents is about 100%. The lowest recovery was given by phenol itself, as it shows the highest solvation of the phenols studied.

The highest recovery was given by diethyl ether, which is thus the most suitable extractant, especially when the determination of phenol and its lower alkyl derivatives is required. It is readily available, volatile, but often requires additional purification. Its disadvantage is its water solubility, and it is therefore not recommended for micro-extraction.

Table I may be useful for selecting extractants for the isolation of microgram

TABLE I

EXTRACTION RECOVERIES OF ALKYLPHENOLS FROM WATER RELATIVE TO *n*-OCTADECANE (RECOVERY = 100%)

Peak	Compound	Recovery (%)					
		<i>n</i> -C ₅ H ₁₂	CCl ₄	CHCl ₃	CH ₂ Cl ₂	C ₆ H ₆	(C ₂ H ₅) ₂ O
1	2,6-DM	0.04	3.2	40.7	46.1	6.2	78.9
2	P	0.02	0.2	1.4	0.7	1.4	48.3
3	2-M	0.04	2.6	7.2	5.9	1.7	72.2
4	4-M	0.09	1.4	6.7	3.3	2.8	68.8
5	3-M	0.04	1.5	5.7	5.2	1.9	70.1
6	2,6-DtB	104	102	98.2	101	104	98.1
7	2-E	0.04	3.1	21.7	21.3	12.5	85.1
8	2,3-DM	0.07	3.0	20.8	22.2	9.5	83.1
9	2-iP	0.07	9.5	48.8	52.2	36.3	92.1
10	3-E	0.09	2.0	15.2	13.4	7.2	88.4
11	2-P	0.07	12.2	55.5	58.1	41.5	94.1
12	3,4-DM	0.04	2.6	14.5	14.3	5.4	81.6
13	2,3,5,6-TTM	6.7	56.0	88.3	94.2	73.1	89.7
14	4-iP	0.07	4.6	38.1	39.0	23.0	93.1
15	2,3,5-TM	0.05	8.5	47.6	57.4	28.7	90.8
16	2-sB	2.6	36.5	78.8	81.2	69.5	96.8
17	2-tB	6.9	49.8	87.2	87.2	79.5	96.9
18	4-P	0.05	6.4	46.7	46.5	29.9	92.8
19	3-P	0.06	5.8	44.9	46.6	29.5	93.2
20	2-B	4.5	46.8	86.1	88.1	77.0	95.3
21	4-tB	0.06	12.1	63.2	65.3	45.2	94.5
22	3,4,5-TM	0.09	2.1	35.4	23.8	15.1	87.8
23	3,4-DE	0.8	16.2	68.9	73.8	48.7	93.2
24	4-B	1.7	29.4	82.5	85.1	65.9	93.9
25	3-B	1.5	28.6	81.6	82.8	66.4	94.5

amounts of organic substances from water when the determination of alkylphenols is required. For instance, for the extraction of higher monohydric alkylphenols from water it is possible to use a less polar solvent (dichloromethane, benzene, chloroform). The non-polar solvents (*n*-pentane, tetrachloromethane) are suitable only for the extraction of highly shielded di-*ortho*-substituted alkylphenols.

REFERENCES

- 1 A. L. Buikema, M. J. McGinnis and J. Cairns, Jr., *Mar. Environ. Res.*, 2 (1979) 87.
- 2 R. B. Baird, C. L. Kuo, J. S. Shapiro and W. A. Yanko, *Arch. Environ. Contam.*, 2 (1974) 165.
- 3 L. E. Harris, W. L. Budde and J. W. Eichelberger, *Anal. Chem.*, 46 (1974) 1912.
- 4 L. L. Lamparski and T. J. Nestruck, *J. Chromatogr.*, 156 (1978) 143.
- 5 Q. V. Thomas, J. R. Stork and S. L. Lammert, *J. Chromatogr. Sci.*, 18 (1980) 583.
- 6 L. Renberg, in A. Bjorseth and G. Angeletti (Editors), *Analysis of Organic Micropollutants in Water*, Riedel, Dordrecht, 1982, p. 286.