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RECOVERY OF PHENOLS FROM WATER BY CONTINUOUS STEAM DISTILLATION–EXTRACTION

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SUMMARY

Continuous steam distillation–continuous liquid–liquid extraction was used for the isolation of phenols from water and the extract was analysed by capillary gas chromatography. The recovery for a concentration range about 0.1–30 mg l^{-1} approaches 100% using acidification and strong salting of the water sample and a distillation–extraction time of 1.5 h. The detection limit of the method using splitless injection and glass capillary columns is approximately 10 μg l^{-1} of each phenol tested.

INTRODUCTION

In addition to direct injection[1], which provides detection limits only at the mg l^{-1} level, for the gas chromatographic (GC) analysis of phenols in water isolation of the compounds to be determined in a non-aqueous medium is used. For the isolation of phenols from water, liquid–liquid extraction[2–4] and sorbent[5,6] or anion-exchange[7] extraction are mostly used, and the sorbed phenols are eluted with an organic solvent[5,7] or desorbed thermally[6].

The derivatization of phenols into less polar products is also often used. The high polarity of phenols causes low extraction recoveries if low-polarity extraction solvents are used[4,8] and difficulties in the GC itself (peak tailing and sorption of phenols on non-deactivated columns). The techniques that can be used are direct acylation of phenols in the aqueous phase and extraction of the acylphenols with dichloromethane[9], extractive acylation[10] or extractive alkylation[11].

The phenols are also often converted into halogenated derivatives, which enables the full benefit of the high sensitivity of electron-capture detection (ECD) for their determination to be utilized. The phenols are converted into halogenated derivatives either directly in the aqueous phase, followed by extraction of the derivatives (*e.g.*, bromophenols[12]), or after extraction, mostly into pentafluorobenzoyl derivatives[2,3].

Pinkerton[13] analysed water for phenols with detection limits in the μg l^{-1} range using direct high-performance liquid chromatography. Reviews of methods for

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the determination of phenolics in water have been published by Štekláč[4] and Renberg[14].

In this study, the possibility of the isolation of phenols from water using continuous steam distillation–continuous liquid–liquid extraction before GC analysis was investigated.

EXPERIMENTAL

The microapparatus employed, similar to that utilized for the isolation of polychlorinated biphenyls and organochlorine pesticides[15], is shown in Fig. 1.

The organic compounds are distilled from the water sample, which is placed in flask 1, and simultaneously the extraction solvent is distilled from flask 3. The vapours are condensed by the cold finger. The aqueous and the organic phase, separated at the bottom of the central part of the apparatus 2, return through their return arms 4 and 5 to flasks 1 and 3. The organic compounds are thus extracted from the condensate on the condenser and in the bottom of the central part with an efficient extraction solvent, which is continuously supplied fresh. The extraction solvent used must have a very low boiling point, in order for the vapour pressure of the sample compounds to be as little above that of the extraction solvent as possible.

Diethyl ether was chosen as the extraction solvent because phenols have higher

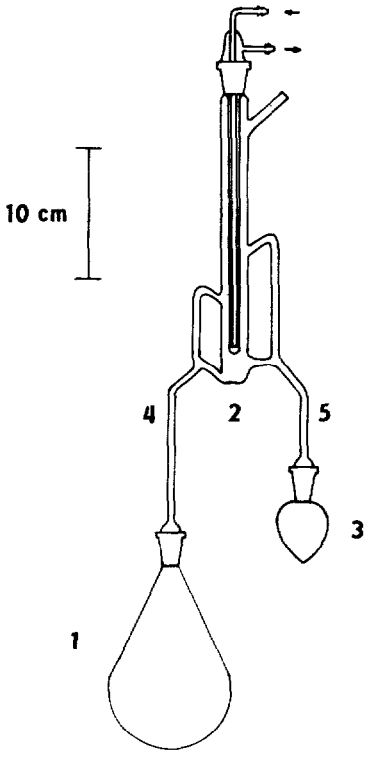

Fig. 1. Micro-apparatus for continuous steam distillation–extraction.

distribution constants between diethyl ether and water than between other solvents and water[4] (regarding low-boiling solvents which may be used in the described procedure).

After the steam distillation–extraction is finished, the extract is analysed by GC (Chrom 41 or Chrom 5 gas chromatograph; Laboratorní přístroje, Prague, Czechoslovakia). For the separation of phenols a home-made 18 m × 0.25 mm I.D. glass capillary column coated with OV-210 was used.

All phenols and solvents used were of analytical-reagent grade (Lachema, Brno, Czechoslovakia).

The measurements were carried out as follows: 200 μl or less of the phenols solution in acetone were added to 150 ml of tap water, which was placed in flask 1 (Fig. 1). For some experiments several millilitres of 1 mol l^{-1} sulphuric acid or sodium chloride solution (15 ml of saturated solution or 60 g of solid sodium chloride) were also added to the water sample. Then, small amounts of water and diethyl ether were introduced into the central part of the apparatus with a syringe. Diethyl ether was also introduced into flask 3. The total volume of diethyl ether was 3 ml. Then the cooling in the central part and the heating in baths 1 and 3 were started. The temperature of the silicone oil and the water-bath were 130 and 55°C, respectively.

After the required distillation–extraction time both baths were removed. The volume of the extract was approximately 2 ml; approximately 1 ml of diethyl ether remains in the central part. For drying of the extract a small amount of sodium sulphate was added, then the internal standard (α-naphthol) was added to the extract and the extract was analysed by GC.

Simultaneously, a reference mixture of phenols in diethyl ether was prepared by adding the solution of phenols in acetone (the same amount as was previously added to the water sample) to 2 ml of diethyl ether. The same amount of the internal standard as was added to the extract was also added. This reference mixture, which represents a standard of 100% recovery by steam distillation–extraction, was also analysed by GC.

RESULTS AND DISCUSSION

The recovery of the procedure was determined according to eqn. 1.

$$E = \frac{R_i R_{sr}}{R_{ir} R_s} \cdot 100 \qquad (1)$$

where E is recovery (%), R is flame-ionization detector response, the subscripts i and ir refer to the responses of a particular phenol in the extract and in the reference mixture, respectively, and the subscripts s and sr refer to the responses of the internal standard in the extract and in the reference mixture, respectively.

All the results given in Tables I–III are averages of at least two independent experiments.

First the effect of the treatment of the water sample on the overall recovery of phenols was investigated. The following treatments of the water sample were compared: (1) no treatment; (2) 15 ml of a saturated solution of sodium chloride added; (3) pH adjusted to 1 and simultaneously 15 ml of a saturated solution of sodium chloride added; and (4) pH adjusted to 1 and simultaneously 60 g of solid sodium

TABLE I

EFFECT OF TREATMENT OF THE WATER SAMPLE ON THE OVERALL RECOVERY OF PHENOLS (%)

Time of distillation–extraction: 1 h for treatments 1 and 2, 1.5 h for treatments 3 and 4.

Phenol	*Treatment No.*			
	1	*2*	*3*	*4*
Phenol	29.1	28.3	47.8	91.1
o-Cresol	79.9	85.9	97.0	96.3
p-Cresol	45.3	49.4	69.3	99.4
2,4-Dimethylphenol	43.8	50.2	66.3	85.7
o-Nitrophenol	11.9	7.1	98.7	94.6

chloride were added (the addition of 60 g of solid sodium chloride corresponds to saturated sodium chloride solution in the water sample at 100°C).

Normally 1.5 h is a sufficient time to reach equilibrium in the apparatus, as verified by a kinetic test with sample treatment 3. For this reason, 1.5 h of steam distillation–extraction was also chosen for sample treatments 1, 2 and 4 in most instances.

The results are summarized in Table I. Because the best results were obtained using both salting methods combined with acidification, further work was carried out using treatments 3 and 4.

As the comparison of different treatments was made with relatively high concentrations of phenols (26 mg l^{-1} of each), the recovery was also measured at lower concentrations.

The recoveries obtained for concentrations of 26, 2.6, 0.26 and 0.065 mg l^{-1} of each phenol with treatment 3 are given in Table II. It can be seen that the recovery decreases strongly with decreasing concentration of phenols. For instance, with 2,4-dimethylphenol, at a concentration of 0.065 mg l^{-1} the recovery is only one tenth of that at a concentration of 26 mg l^{-1}. This undesirable phenomenon will result not only in a decrease in response at lower concentrations of phenols, but also in non-linear calibration graphs.

TABLE II

EFFECT OF CONCENTRATION ON THE OVERALL RECOVERY OF PHENOLS (%) WITH TREATMENT 3

Time of distillation–extraction: 1.5 h.

Phenol	*Concentration in water (mg l^{-1})*			
	26	*2.6*	*0.26*	*0.065*
Phenol	47.8	37.4	32.5	14.3
o-Cresol	97.0	87.7	55.9	36.8
p-Cresol	69.3	62.0	38.9	33.0
2,4-Dimethylphenol	66.3	56.0	16.7	8.9
o-Nitrophenol	98.7	88.0	65.8	52.5

TABLE III

EFFECT OF CONCENTRATION ON THE OVERALL RECOVERY OF PHENOLS (%) WITH TREATMENT 4

Time of distillation–extraction: 1.5 h.

Phenol	*Concentration in water (mg l^{-1})*			
	26	*2.6*	*0.26*	*0.13*
Phenol	91.1	89.9	93.3	86.4
o-Cresol	96.3	95.1	94.6	88.1
p-Cresol	99.4	92.8	86.8	92.6
2,4-Dimethylphenol	85.7	87.9	82.2	81.6
o-Nitrophenol	94.6	95.0	95.0	96.1

The recoveries obtained for concentrations of 26, 2.6, 0.26 and 0.13 mg l^{-1} of each phenol with treatment 4 are given in Table III. After 1.5 h of steam distillation–extraction almost all of the phenols added to water were present in the extract. This results in a good detection limit and in linear calibration graphs.

CONCLUSION

The following outline method can be recommended for the isolation of phenols from water: volume of the water sample, 150 ml; volume of diethyl ether, 3 ml; acidification and strong salting of the water sample; time of distillation–extraction, 1.5 h; and analysis of the extract by splitless capillary GC.

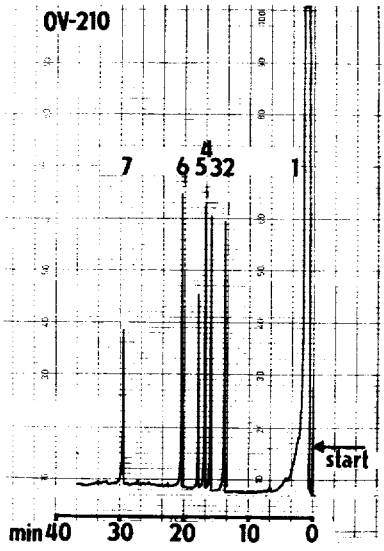

Fig. 2. Separation of phenols. Column: glass capillary (18 m × 0.25 mm I.D.), OV-210; carrier gas, nitrogen, p = 0.11 MPa; column temperature, programmed from 25 to 140°C at 5°C/min; splitless injection (1 μl); flame-ionization detector. Peaks: 1 = solvent (diethyl ether); 2 = phenol; 3 = *o*-cresol; 4 = *p*-cresol; 5 = *o*-nitrophenol; 6 = 2,4-dimethylphenol; 7 = α-naphthol.

The separation of small amounts of phenols with a glass capillary column coated with OV-210 is shown in Fig. 2.

The proposed method offers several advantages:

(1) The recovery for a concentration range of about 0.1–30 mg l^{-1} approaches 100% when acidification combined with strong salting is used.

(2) The phenols are isolated in a relatively small amount of diethyl ether, so that before the GC analysis itself no concentration of the extract is needed, which could lead to concentration of the impurities from diethyl ether.

(3) With the procedure proposed here, there is a dual isolation of phenols from water: by distillation and by extraction. Hence the probability of the simultaneous isolation of compounds that could interfere in the GC analysis is decreased.

(4) Phenols could also be isolated into diethyl ether from suspensions and from water with a high content of suspended solids.

(5) The detection limit of the method using splitless injection and glass capillary columns is approximately 10 $\mu g\ l^{-1}$ of each phenol tested.

REFERENCES

1 American Public Health Association, American Water Works Association and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA, WPCF, Washington, DC, 14th ed., 1975.
2 Environmental Protection Agency, *Fed. Regist.*, 44 (1979) 69464.
3 Q. V. Thomas, J. R. Stork and S. L. Lammert, *J. Chromatogr. Sci.*, 18 (1980) 583.
4 M. Štekláč, *PhD Thesis*, Universita Komenského, Bratislava, 1981.
5 G. A. Junk, J. J. Richard, M. D. Greiser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
6 Z. Vozňáková and M. Popl, *J. Chromatogr. Sci.*, 16 (1978) 123.
7 C. D. Chriswell, R. C. Chang and J. S. Fritz, *Anal. Chem.*, 47 (1975) 1325.
8 K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
9 R. T. Coutts, E. E. Hargesheimer and F. M. Pasutto, *J. Chromatogr.*, 179 (1979) 291.
10 L.Renberg, *Chemosphere*, 10 (1981) 767.
11 E. Fogelquist, B. Josefsson and C. Raas, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 568.
12 P. J. Rennie, *Analyst (London)*, 107 (1982) 327.
13 K. A. Pinkerton, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 33.
14 L.Renberg, in A. Bjorseth and G. Angeletti, (Editors), *Analysis of Organic Micropollutants in Water*, D. Reidel, Dordrecht, 1982, p. 286.
15 M. Goderfroot, M. Stechele, P. Sandra and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 75.