*Journal of Chromatography*, 279 (1983) 199 208
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 122

# DIRECT DETERMINATION OF TRACE AMOUNTS OF CHLOROPHENOLS IN FRESH WATER, WASTE WATER AND SEA WATER

K. ABRAHAMSSON* and T. M. XIE
*Department of Analytical and Marine Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg (Sweden)*

## SUMMARY

Chlorophenols were acetylated and the derivatives extracted by the simultaneous addition of acetic anhydride and hexane directly to the water sample. The extracts were then analysed by glass capillary column gas chromatography with electron-capture detection. Determination of chlorinated phenols at μg/l concentration levels requires only 5 ml of sample. At ng/l levels a 100-ml sample is sufficient. The total time of analysis is 18 min per sample. A comparison between pentafluorobenzoylation and acetylation showed that the acetylated derivatives of chlorophenol isomers separated better on the column. The method has been applied to drinking water, sea water and waste water from a sulphate pulp mill.

## INTRODUCTION

Chlorophenols are of environmental concern because of their toxicity and their wide distribution. Chlorination of drinking water may produce chlorophenols, which cause a disagreeable odour and taste, even at very low concentration levels. The waste water from pulp mills that use chlorine bleaching contains chlorinated phenols, guaiacols and catechols[1] and some of these phenols seem to accumulate in fish[2,3]. The distribution patterns of chlorophenols in heavily polluted rivers and lakes have been reported earlier[4,5].

There is a need for a simple and sensitive method for determining chlorophenols at very low concentration levels in water. For practical reasons, the preferred technique is gas chromatography (GC) with electron-capture detection. The chlorophenols are often converted into non-polar derivatives before GC analysis. Different procedures for derivatizing phenols directly in the water samples have been suggested, including extractive alkylation with pentafluorobenzyl bromide[6] and acylation with trichloroacetic anhydride[7], pentafluorobenzoyl chloride[8] or acetic anhydride[9]. Reagents containing halogens will yield electron-affinity products, even with non-halogenated phenols, thus diminishing the selectivity of the method.

The objective of this work was to develop a rapid and simple method, capable of resolving a wide range of chlorinated phenolic compounds at ng/l concentration levels. Glass capillary column chromatography with electron-capture detection con-

0021-9673/83/$03.00 

stitutes an efficient combination. The method should be suitable for studying the distribution patterns of chlorophenols in the sea far from the source.

## EXPERIMENTAL

### *Materials*

The standard solutions used were 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol (all from Merck), pentachlorophenol (Fluka), 4,5,6-trichloroguaiacol, tetrachloroguaiacol and tetrachlorocatechol, dissolved in acetone (Merck). The test solutions were prepared at different concentrations by spiking appropriate amounts of these stock solutions in doubly distilled water. 2,6-Dibromophenol (Merck) was acetylated and used as an internal standard. The other reagents used were disodium hydrogen phosphate ($Na_2HPO_4 \cdot 2H_2O$), sodium hydrogen carbonate, acetic anhydride and hexane (all from Merck). All reagents were of analytical-reagent grade.

### *Gas chromatography with electron-capture detection*

A Carlo Erba Fractovap 4160 and a Perkin-Elmer 3920 gas chromatograph were used, both equipped with a nickel-63 electron-capture detector and a Grob-type injector. The compounds were separated on a Duran 50 glass capillary column (30 m × 0.3 mm I.D.) coated with OV-73, prepared according to the procedures of Grob[10]. The GC conditions were as follows: hydrogen carrier gas flow-rate, 2 ml/min; argon–methane (95:5) make-up gas flow-rate, 30 ml/min; temperature programme, 100–260°C at 16°C/min; injector and detector temperature, 275°C. The interface in the Perkin-Elmer instrument was at 275°C. The sample size injected was 1 μl for the Carlo Erba and 2 μl for the Perkin-Elmer instrument. The injection was splitless for 45 sec.

### *Derivatization procedure*

Two different water to solvent ratios were used: for high concentrations (> 1 μg/l) of chlorinated phenols a 5:1 ratio was used, and for low concentrations (< 1 μg/l) 200:1 was used.

For high concentrations, to 4.5 ml of sample in a PTFE-lined screw-capped glas tube 0.5 ml of buffer solution (0.5 *M* $Na_2HPO_4$) was added. Derivatisation and extraction were performed by adding 1 ml of hexane containing the internal standard (i.s.) and 46 μl of acetic anhydride. After shaking the mixture for 3 min, the extract was injected onto the column.

For low concentrations, 0.8 g of $Na_2HPO_4 \cdot 2H_2O$ was dissolved in 100 ml of sample in a glass volumetric flask and 0.5 ml of hexane containing the i.s. and 0.8 ml of acetic anhydride was added. After 3 min, the extract was injected onto the column.

For sea water and water containing alkaline-earth metal ions, a sodium hydrogen carbonate buffer solution at the same molar concentration was used instead of $Na_2HPO_4$.

For acid waste water the pH was adjusted to 7 with sodium hydroxide prior to adding the buffer solution.

## RESULTS AND DISCUSSION

*Reaction conditions*

The pH dependence of the acetylation of the phenols tested is shown in Fig. 1. At a pH above 11.5 the hydrolysis of acetic anhydride is faster than acetylation. At a pH lower than 6 phenolate ions are not formed. This results in poor derivatization. The optimal pH differs for the various chlorinated phenols since their $pK_a$ values are different. The optimal compromise pH was 9.

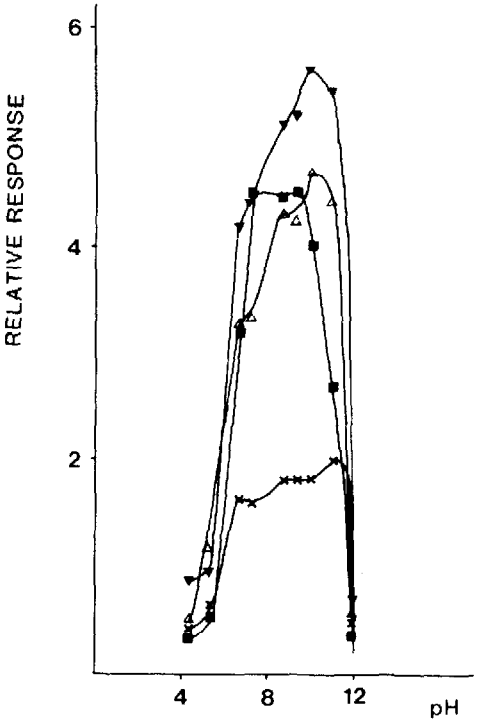


Fig. 1. pH dependence of the acetylation of phenols. × = 2,6-Dichlorophenol; ▼ = 2,3,4,6-tetrachlorophenol; △ = 4,5,6-trichloroguaiacol; ■ = tetrachlorocatechol.

The influence of different buffers and buffer concentrations was investigated. There were no obvious differences in acetylation yield between carbonate, hydrogen carbonate, and phosphate buffers. However, the problem of intense evolution of carbon dioxide during acetylation, described by Coutts *et al.*[9], can be overcome by using phosphate buffer or by using carbonate buffer at a low concentration of 0.05 *M*.

For the determination of chlorinated phenols in sea water and water containing alkaline-earth metal ions, the carbonate buffer system is preferable, because the precipitation of phosphates interferes with acetylation.

In previous reports acetic anhydride to buffer ratios ranged widely from 1:1 to 1:20[9,11]. We have found that a ratio of 2:1 resulted in the best acetylation yield.

A study of the reaction time showed that 2 min is sufficient for derivatization and extraction. However, a reaction time of 3 min is necessary for complete hydrolysis of the acetic anhydride, which otherwise interferes in the determination of 2-bromophenol.

*Extraction efficiency*

The extraction efficiency was determined by using consecutive extractions at water to hexane ratios ranging from 5:1 to 200:1. As shown in Fig. 2, at a low water to hexane ratio (5:1) the extraction efficiency for all the derivatives of the chlorinated phenols tested was essentially 100%.

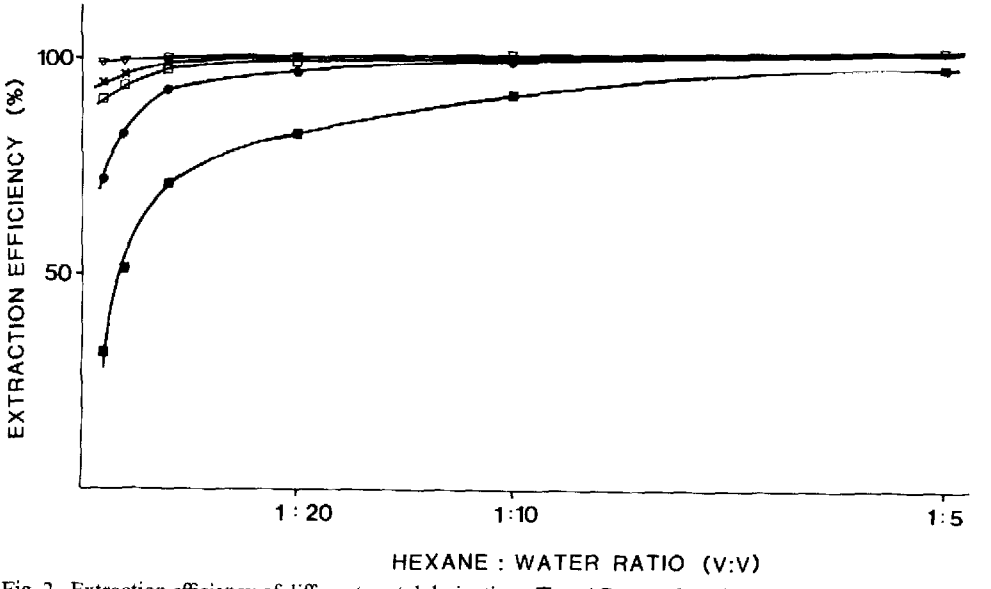


Fig. 2. Extraction efficiency of different acetyl derivatives. ■ = 4.Bromophenol; ● = 2,6-dichlorophenol; □ = 4,5,6-trichloroguaiacol; × = 2,4,6-trichlorophenol; ▽ = pentachlorophenol and tetrachlorocatechol.

TABLE I

EFFECT OF CONCENTRATION ON THE EXTRACTION EFFICIENCY (%) OF PHENOLIC ACETYL DERIVATIVES

Water to hexane ratio = 200:1.

| *Compound* | *Concentration (µg/l)* | | |
|---|---|---|---|
| | *10* | *0.5* | *0.05* |
| 4-Bromophenol | 32 | 66 | 69 |
| 2,6-Dichlorophenol | 71 | 83 | 87 |
| 2,4-Dichlorophenol | 71 | 82 | 84 |
| 2,4,6-Trichlorophenol | 93 | 95 | 95 |
| 2,3,4,6-Tetrachlorophenol | 98 | 96 | 97 |
| 4,5,6-Trichloroguaiacol | 90 | 90 | 91 |
| Tetrachlorocatechol | 99 | 99 | 99 |
| Pentachlorophenol | 99 | 99 | 99 |

Increasing the water to hexane ratio decreased the extraction efficiency. However, a high sensitivity can still be achieved. The extraction efficiency is higher for the phenols with more chlorine substituents. At a higher extraction ratio (200:1) the extraction efficiency for the more polar 4-bromophenol and 2,4- and 2,6-dichlorophenols varies with the concentration (see Table I).

Using dichloromethane, the extraction efficiency can be improved[11]. However, a high background from the solvent interferes.

*Gas chromatography*

A chromatogram of acetylated chlorophenols at a concentration of 100 ng/l

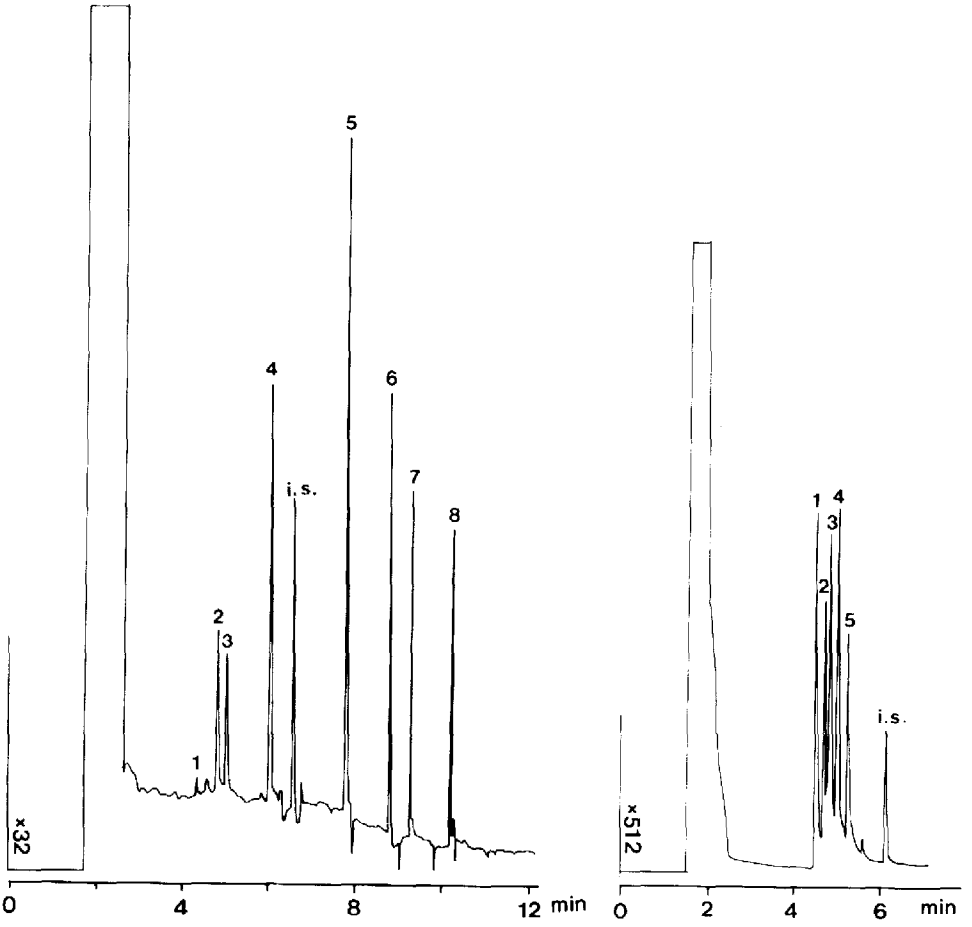


Fig. 3. Chromatogram of a standard mixture at a concentration level of 100 ng/l. Water to hexane ratio = 100:1. Peaks [concentrations of the compounds ($\mu$g/l) in parentheses]: 1 = 4-bromophenol (0.2); 2 = 2,6-dichlorophenol (0.2); 3 = 2,4-dichlorophenol (0.2); 4 = 2,4,6-trichlorophenol (0.1); 5 = 2,3,4,6-tetrachlorophenol (0.077); 6 = 4,5,6-trichloroguaiacol (0.1); 7 = pentachlorophenol (0.031); 8 = tetrachlorocatechol (0.1). GC conditions: stationary phase OV-73, 30 m × 0.3 mm I.D., injector temperature 275°C, temperature programmed from 100 to 260°C at 16°C/min, interface and detector temperature 275°C, hydrogen carrier gas flow-rate 2 ml/min, argon + 5% methane make-up gas flow-rate 30 ml/min, 2 $\mu$l injected, splitless injection period 45 sec.

Fig. 4. Separation of five dichlorophenol isomers. GC conditions as in Fig. 3. Peaks: 1 = 2,6-dichlorophenol; 2 = 2,4-, 2,5-dichlorophenol; 3 = 3,5-dichlorophenol; 4 = 2,3-dichlorophenol; 5 = 3,4-dichlorophenol.

is shown in Fig. 3. The identity of each chlorophenol was confirmed by gas chromatography–mass spectrometry (GC–MS).

The capillary column gave a good resolution of isomers. Five of six dichlorophenols could be separated within 6 min (see Fig. 4).

*Precision and linearity*

The precision and linearity of the method were determined on five standards each at seven concentrations ranging from 1–2 to 1000 ng/l. Except for tetrachlorocatechol the precision is in the range 1.0–8.9% (relative standard deviation) at concentrations higher than 10 ng/l, and 10–20% at concentrations of 1–5 ng/l. The linearity was good, as indicated by correlation coefficients of 0.999 for all the phenols, with the exception of tetrachlorocatechol (see Fig. 5). The yield was calculated by measuring peak heights.

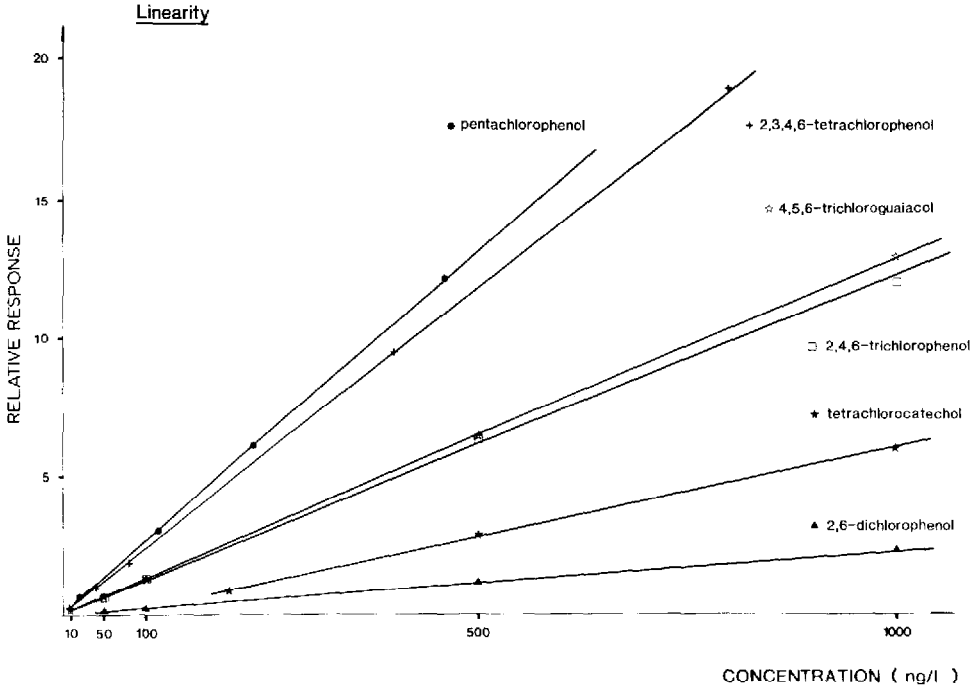


Fig. 5. Calibration graphs of chlorophenols in the concentration range 10 to 1000 ng/l.

*Recovery*

The recovery study was performed by adding known amounts of chlorinated phenols to drinking water and sea water. The results are shown in Table II. With the exception of tetrachlorocatechol, the recovery was 90% or better.

*Detection limit*

The detection limits of the method are 2 ng/l for 2,6- and 2,4-dichlorophenol, 1 ng/l for 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol and

TABLE II

RECOVERY OF CHLOROPHENOLS AS ACETYL DERIVATIVES FROM DRINKING WATER AND SEA WATER

| *Compound* | *Drinking water* | | | *Sea water* | | |
|---|---|---|---|---|---|---|
| | *Added (μg/l)* | *Recovery (%)* | *S.D. (%)* | *Added (μg/l)* | *Recovery (%)* | *S.D. (%)* |
| 4-Bromophenol | 0.20 | 95 | 12 | 2.0 | 100 | 7.4 |
| 2,6-Dichlorophenol | 0.20 | 100 | 4.2 | 2.0 | 100 | 3.2 |
| 2,4-Dichlorophenol | 0.20 | 100 | 6.6 | 2.0 | 100 | 0.8 |
| 2,4,6-Trichlorophenol | 0.10 | 105 | 1.4 | 1.0 | 99 | 1.2 |
| 2,3,4,6-Tetrachlorophenol* | 0.078 | 97 | 7.3 | 0.78 | 101 | 7.7 |
| 4,5,6-Trichloroguaiacol | 0.10 | 100 | 2.6 | 1.0 | 93 | 6.7 |
| Tetrachlorocatechol | 0.20 | 77 | 26 | 2.6 | 65 | 27 |
| Pentachlorophenol* | 0.031 | 100 | 3.1 | 0.31 | 98 | 6.7 |

* The amounts of 2,3,4,6-tetrachlorophenol and pentachlorophenol originally present in the water have been subtracted.

4,5,6-trichloroguaiacol and 100 ng/l for tetrachlorocatechol. The determination of these limits was based on the linearity of the method at the lowest concentrations where a correlation coefficient 0.999 can still be obtained. In qualitative analysis the detection limits could be lower.

*Comparison between pentafluorobenzoylation and acetylation*

Pentafluorobenzoyl chloride and acetic anhydride were compared as derivatizing agents. To reduce the high background observed when pentafluorobenzoyl chloride was used, a clean-up step with alkali solution was needed[8]. This resulted in an obvious loss of derivatives because of hydrolysis. In addition, isomers derivatized with pentafluorobenzoyl chloride were poorly resolved. The pentafluorobenzoylated 2,4- and 2,6-dichlorophenols were not separated. Better resolution of isomers was obtained in the form of acetyl derivatives (see Fig. 4). Moreover, because the electron affinity of the halogenated phenols is not affected by acetylation, the selectivity for these compounds is maintained. Also, no clean-up step is required, because of the low background.

*Determination of tetrachlorocatechol*

Unlike the other chlorophenols tetrachlorocatechol was not stable. It was stored in a glass flask with and without buffer to determine the loss as a function of time. After 18 h, the losses were 8.4% in water and 59% in buffer solution; after 48 h the losses had increased to 24% and 98%, respectively. This decrease was intensified when either the pH or temperature was raised. The possibility of adsorption of tetrachlorocatechol on the glass surface was also considered. However, a comparison between a normal glass flask and a silanized glass flask showed no differences. Thus, the loss was not caused by adsorption. It is important to derivatize the tetrachlorocatechol to its stable acetyl derivatives as soon as possible after sampling.

*Applications*

The method was used to determine chlorinated phenols in (a) local drinking water (Fig. 6), (b) sea water from the East coast of Sweden at a station 7 km from a sulphate pulp mill (Fig. 7) and (c) waste water from a sulphate pulp mill (Fig. 8). The different extraction conditions and the concentrations of chlorinated phenols are indicated in the figures.

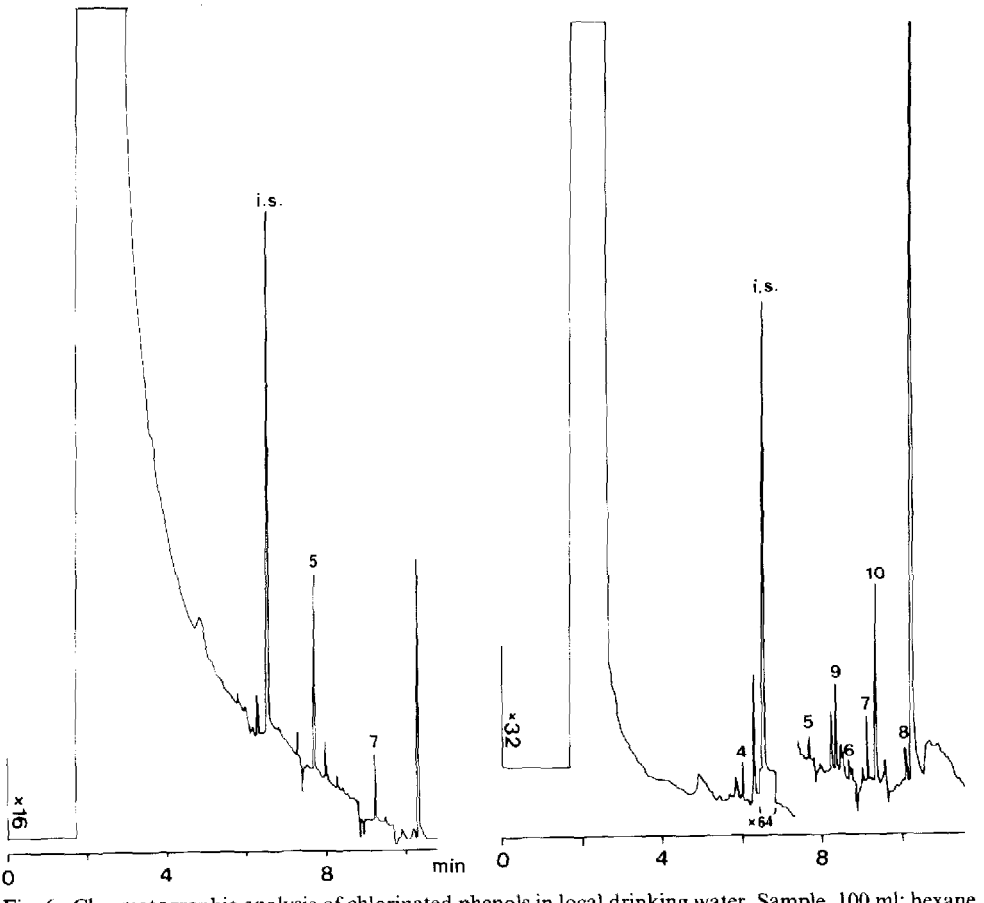


Fig. 6. Chromatographic analysis of chlorinated phenols in local drinking water. Sample, 100 ml; hexane, 0.5 ml. GC conditions as in Fig. 3. Peaks: 5 = 2,3,4,6-tetrachlorophenol (20 ng/l); 7 = pentachlorophenol (9 ng/l).

Fig. 7. Chromatographic analysis of chlorinated phenols in sea water, sampled at a depth of 5 m at a station 7 km from a sulphate pulp mill. Sample, 100 ml; hexane, 0.5 ml. GC conditions as in Fig. 3. Peaks: 4 = 2,4,6-trichlorophenol (6 ng/l); 5 = 2,3,4,6-tetrachlorophenol (2 ng/l); 6 = 4,5,6-trichloroguaiacol (2 ng/l); 7 = pentachlorophenol (6 ng/l); 8 = tetrachlorocatechol (< 10 ng/l); 9 = 3,4,5-trichloroguaiacol (12 ng/l); 10 = tetrachloroguaiacol (13 ng/l).

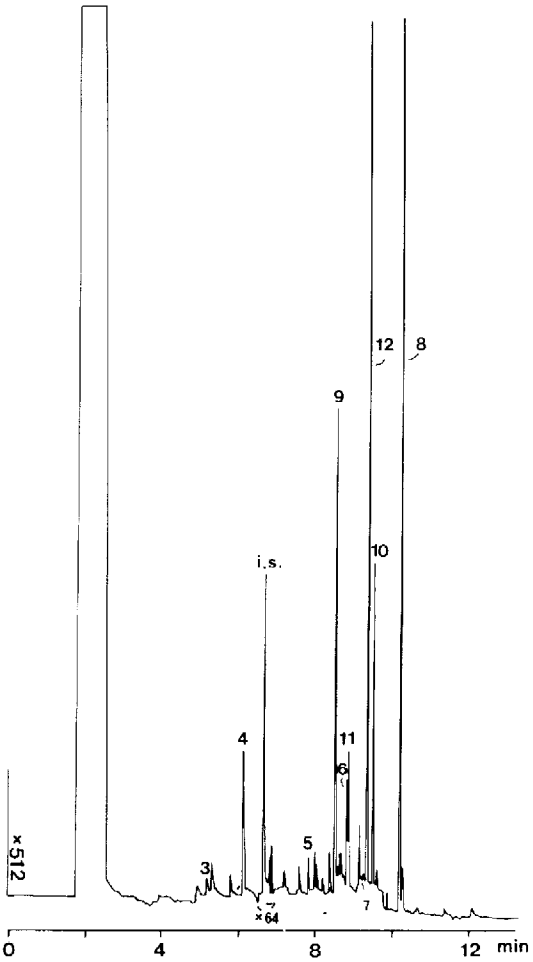


Fig. 8. Chromatographic analysis of chlorinated phenols in waste water from a sulphate pulp mill. Sample, 5 ml; hexane, 1 ml. GC conditions as in Fig. 3. Peaks: 3 = 2,4-dichlorophenol (7.2 μg/l); 4 = 2,4,6-trichlorophenol (15 μg/l); 5 = 2,3,4,6-tetrachlorophenol (2.5 μg/l); 6 = 4,5,6-trichloroguaiacol (10 μg/l); 7 = pentachlorophenol (< 0.2 μg/l); 8 = tetrachlorocatechol (87 μg/l); 9 = 3,4,5-trichloroguaiacol (50 μg/l); 10 = tetrachloroguaiacol (20 μg/l); 11 = 3,4,6-trichlorocatechol (≈ 10 μg/l); 12 = 3,4,5-trichlorocatechol (≈ 100 μg/l).

ACKNOWLEDGEMENTS

We thank B. Josefsson for instructive and stimulating discussions and criticism of the manuscript. The chlorinated guaiacols and the catechol were kindly supplied by G. Sundström and L. Rehnberg. We also thank B. Sundby for his help with language correction.

REFERENCES

1 K. Lindström and J. Nordin, *J. Chromatogr.*, 128 (1976) 13–26.

2 L. Landner, K. Lindström, M. Karlsson, J. Nordin and L. Sörensen, *Bull. Environ. Contamin. Toxicol.*, 6 (1977) 663–673.
3 J. Paasivirta, J. Särkkä, T. Leskijärvi and A. Roos, *Chemosphere*, 9 (1980) 441 454.
4 R. C. C. Wegman and A. W. M. Hofstel, *Water Res.*, 13 (1979) 651–657.
5 R. C. C. Wegman and H. H. van den Broek, *Water Res.*, 17 (1983) 227–230.
6 E. Fogelqvist, B. Josefsson and C. Roos, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 568–574.
7 R. J. Arganer, *Anal. Chem.*, 40 (1968) 122–124.
8 L. Renberg, *Chemosphere*, 10 (1981) 767–773.
9 R. T. Coutts, E. E. Hargesheimer and F. M. Pasutto, *J. Chromatogr.*, 179 (1979) 291–299.
10 K. Grob, G. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 31–35 and 677–678.
11 J. Matthew and A. W. Elzerman, *Anal. Lett.*, 14(A16) (1981) 1351–1361.