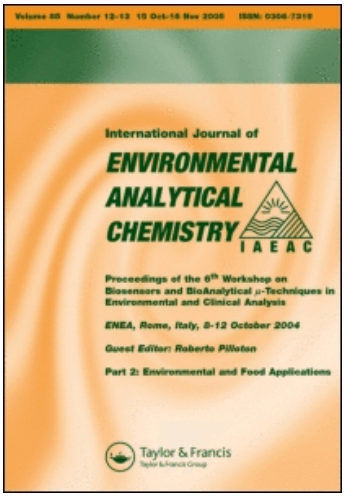

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Determination of Pentachlorophenol by Exhaustive Methylation and Capillary Gas Chromatography in Sewage Sludge, Contaminated Water and Suspended Particulates

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DETERMINATION OF PENTACHLOROPHENOL BY EXHAUSTIVE METHYLATION AND CAPILLARY GAS CHROMATOGRAPHY IN SEWAGE SLUDGE, CONTAMINATED WATER AND SUSPENDED PARTICULATES

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A method for the determination of pentachlorophenol (PCP) in large volumes of sea water and suspended particulate matter is described. PCP is methylated using methyl iodide in the presence of tetrabutylammonium hydroxide (TBA). The methyl derivative, pentachloroanisole, is quantified by capillary gas chromatography using electron-capture detection. Recovery and the coefficient of variation of the analytical method are found to be: 78% and 4.6% respectively, ($n = 17$).

The PCP is extracted from the sea water by liquid-liquid partition with pentane and sulphuric acid, and by soxhlet extraction with hexane:acetone, 40:60, plus sulphuric acid from the particulate matter. These extraction procedures are also effective for a wide range of other organic contaminants including sterols, chlorinated pesticides and PCBs.

The sample clean-up and PCP separation are achieved by liquid-liquid extraction with alkali to isolate the acidic compounds. The PCP is back-extracted into organic solvent after acidifying the aqueous phase and raising the ionic strength. No further clean-up is needed.

Following the method validation samples were taken after sewage sludge dumping operations and analysed for PCP in the water and particulate fractions. These results are reported.

KEY WORDS: Pentachlorophenol, methylation, sewage sludge, sea water, particles, gas chromatography

INTRODUCTION

Pentachlorophenol (PCP) was introduced in the late 1930s as a wood preservative, and since then its application has extended, together with other chlorophenols, for use as a fungicide, bactericide, herbicide, moluscicide, algicide, and insecticide[1]. Chlorophenols and PCP, in particular, are toxic to aquatic life and bioaccumulate in the tissue of biota exposed to contaminated waters.

Phenolic and chlorophenolic compounds can enter the aquatic environment directly via industrial effluents, and indirectly as transformation products from the chlorination of natural and synthetic chemicals, in potable water supplies[2] or from the pulp bleaching processes[3]. Residues of phenolics and chlorophenolics have been found in industrial wastewaters and sludges[1], and they are known to cause odour and taint problems in drinking water[5]. PCP is corrosive, toxic and volatile, it is easily

degraded by sunlight[1], but is largely adsorbed onto municipal solid wastes, contaminating landfill leachates, and sediments[6,7].

A suitable analytical method was required for the determination of PCP in sea water, suspended particulates and sewage sludge, as part of a study of physicochemical processes controlling the dispersion and degradation of persistent hydrophobic contaminants in the sea, resulting from contaminated sewage sludge dumping operations. A sample intake of *ca* 30 l was required to obtain the necessary sensitivity of 1 pg l^{-1} PCP. This technique should also be suitable to incorporate other organochlorine contaminants[8] into the analytical scheme.

The determination of chlorophenols in environmental samples can be separated in three or four stages: (a) an extraction followed by; (b) clean-up with or without a derivatisation stage and; (c) the final determination by capillary gas chromatography.

Chlorophenols do not have the most favourable gas chromatographic properties owing to their high polarity, chemical reactivity, and low vapour pressures[9], causing adsorption and tailing of the chromatographic peaks. This can be overcome to a large extent by derivatisation and there are four main methods which have been developed to determine pentachlorophenol in environmental samples by capillary GC-ECD.

Pyrolytic ethylation with triethylsulphonium hydroxide has been used to determine PCP in sediments and clams[10], and in human serum and urine[11]. This method involves the extraction of lyophilised samples with toluene under acidic conditions and the back extraction of the chlorophenols into a methanol/water solution of triethylsulphonium hydroxide. Upon injection of the methanol/water phase into the gas chromatograph a pyrolytic ethylation occurs in the hot injection port. This method is clearly unsuitable for cold on-column injection and capillary column chromatography, where thermal degradation is minimised.

Pentafluorobenzylation has been used as a derivative step to determine PCP in raw and potable waters[5]. The PCP is extracted from water with dichloromethane. The solvent is changed to acetone and pentafluorobenzyl bromide added. The mixture is heated at 60°C for 30 min, and when the derivatisation is complete the volume is reduced to 2 ml and the product cleaned-up on a silica column. Good sensitivity and chromatography is obtained with this method with only minor interferences from the reagent blank. However, a substantial number of coextracted compounds were also derivatised and extensive interferences occurred when environmental samples were analysed, even after silica column clean-up. This method was considered unsuitable for environmental samples without extensive and time consuming additional clean-up.

PCP has been determined as the acetylated derivative in biological tissues and water extracts[12,6], or sediment[2,4,13]. The phenolic compounds are acetylated in aqueous solution by adding acetic anhydride and extracting the reaction products into an organic solvent.

An alternative to forming the acetylated derivative is the methylation reaction to form pentachloroanisole. Methylation occurs by the ion-pair alkylation of PCP with methyl iodide or by reaction with diazomethane. The diazomethane is good methylating reagent, but care is required on handling. It has been used to derivatise PCP

prior to the determination in foods[14,15] animal tissues and water extracts[15] and in tallow[1].

After reviewing the methods of derivatisation currently available, and their suitability to the environmental matrices, acetylation and methylation techniques were selected for further investigation. Acetylation is a simple method with the advantage of direct extraction of the phenolic fraction from the sample matrix under certain circumstances[13]. Methylation could also be an appropriate derivatisation technique since PCP is metabolically converted in the environment to pentachloroanisole (PCA) which can cause taint in water, eggs and poultry[16]. The PCA is also determined in environmental samples where the presence of the parent compound, PCP, is suspected. It is, therefore, desirable to have a single method for both compounds. Pentachloroanisole also is stable in the dark at low temperatures, whereas PCP and the acetylated derivative are not, which makes the storage of calibration standards, samples and archived extracts easier if they are methylated.

EXPERIMENTAL

Reagents

Hexane and acetone were obtained as glass distilled grade and dichloromethane and *iso*-octane as HPLC grade. All solvents were supplied by Rathburn Chemicals (Walkerburn, UK).

The following chemicals were used:

—Sodium sulphate anhydrous granular, BDH, AnalaR grade. Dried at 200°C for four hours.

— Pentachlorophenol, Aldrich, gold label, 99+%. Standard solutions in *iso*-octane.

—Pentachloroanisole, Dr Ehrenstorfer, 99%. Standard solutions in *iso*-octane.

—Dichlorobenzyl hexyl ether (DCBE 6), D Wells[17], 99%. Standard solutions in *iso*-octane.

—Tetrabutylammonium hydroxide (TBA), 40% aqueous solution, Aldrich.

—Tetrabutylammonium hydroxide in ammonia solution, 0.05 M solution of TBA in 5 M ammonia.

— Methyl iodide (gold label) and acetic anhydride Aldrich.

—Sodium hydroxide, sulphuric acid and sodium bicarbonate, BDH, Anal.

—Sodium chloride and sodium carbonate, Fison, SLR grade.

Instrumentation

Gas Chromatograph Varian 3500

—Column: CP SIL8CB, 50 m × 0.22 mm.

—Injector: on column injection, injection volume 0.5 μl.

—Injector temperature program: from 120°C to 260°C at 10 deg min^{-1}

—Column temperature program: from 120°C to 170°C at 3 deg min^{-1}, to 270°C at 20 deg min^{-1}.

—Detector: ECD at 330°C.

—Carrier gas: Hydrogen, 25 cm sec^{-1}

—Autosampler: Varian 8035.

Sampling and sample preparation

Samples were taken with a stainless steel filtration-extraction apparatus, specially designed to operate under pressure and vacuum and built for this study[19] (Figure 1). Sea water (30 l) was filtered through a 1 μm glass fibre filter, and the organic contaminants in the filtered water were extracted with pentane (500 ml) and 20 ml of 5 M sulphuric acid (to assist extraction of the pentachlorophenol). This sampling method separated the dissolved and absorbed organic contaminants prior to further clean-up and determination by GC-ECD.

The pentane extract was dried with Na_2SO_4 and the solvent volume reduced using a clean air stream prior to the clean-up, and group separation.

The filters retaining the particulate material were acidified with 0.2 M H_2SO_4 (1.5 ml) and extracted in a Soxhlet with hexane:acetone, 40:60, (100 ml) for 4 hours

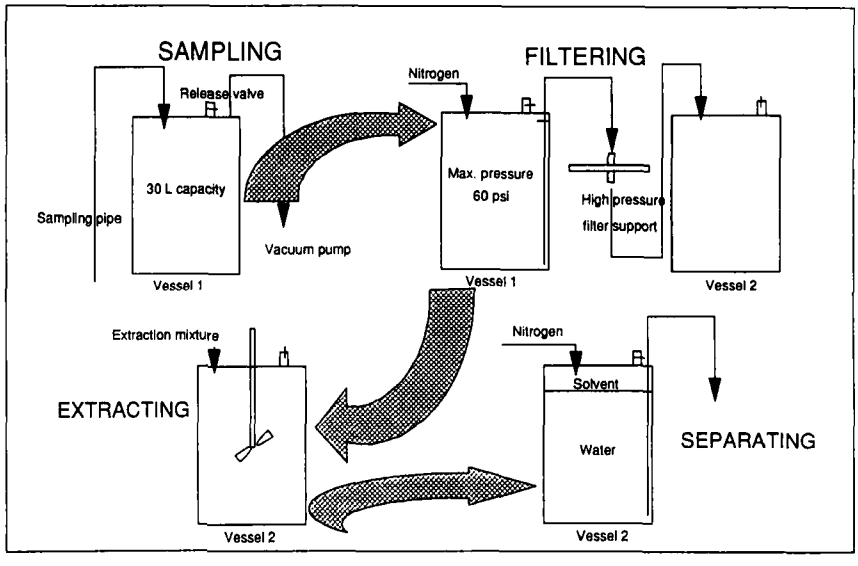

Figure 1 Sampling apparatus diagram. The sampling apparatus is designed to perform separation of the suspended particles from the water and extraction of organic compounds in the aqueous fraction into organic solvent. All the operations are carried out in the field just after sampling to avoid post-sampling interactions within the sample fractions. It is built of stainless steel and it is operated under high pressure conditions.

at a siphon rate of 20 cycles per hour. When the extraction cycle was completed the water/acetone phase was washed with dilute H_2SO_4 (pH = 2,250 ml), and the hexane separated and dried with Na_2SO_4. The extracts from the particles were then treated in the same manner as the water extracts.

PCP Extract Separation and Clean-up

A solution of PCP in hexane (30 ml) was extracted with 0.01 M NaOH aqueous solution (50 ml) in a separation funnel and re-extracted twice with the basic solution (30 ml). The aqueous phase, containing the pentachlorophenol, was acidified with H_2SO_4 to pH = 1.5 and back extracted into organic solvent with hexane (30 ml) three times[13].

Acetylation

The acetylation method investigated was based on a procedure described by Lee[4]. Hexane (50 ml) were spiked with a 1 ml of 360 ng g^{-1} PCP solution, in a separation funnel, and extracted into a 2% aqueous $NaHCO_3$ solution (50 ml). The extraction was repeated twice. Acetic anhydride (3 ml) and hexane (50 ml) were added to the aqueous layer to back-extract the acetylated chlorophenols into hexane. The mixture was shaken for 10 minutes, separated, and the aqueous phase was washed with hexane (20 ml). The volume of the organic phase was reduced in a rota-evaporator (Buchi R 110) and transferred to a test tube. The solvent was changed to *iso*-octane by reducing the hexane volume with a stream of warm, dry air to 0.5–1 ml. *Iso*-octane was added, (5–7 ml) and, again the volume was reduced to 1 ml.

Dichlorobenzyl hexyl ether (DCBE 6), 1 ml of 0.5 $\mu g\ g^{-1}$ solution in *iso*-octane, was used as internal standard[17].

The acetylated pentachlorophenol was determined by GC-ECD. Recoveries were estimated assuming that the ECD response to the acetylated pentachlorophenol is the same as that for the methlated derivative, pentachloroanisole, because the acetylated pentachlorophenol was not commercially available.

Methylation

One ml of a solution containing 230 ng g^{-1} PCP in hexane was treated with methyl iodide, (MeI), and tetrabutyl ammonia hydroxide, (TBAOH), and heated at 40°C[15]; or mechanically shaken for 30 minutes[18]. When reaction was completed the excess reagent was removed by addition of distilled water and shaking. The organic solution was separated and dried with sodium sulphate, the solvent changed to iso-octane, and internal standard added. The pentachloroanisole was determined by GC-ECD. Recoveries were estimated directly by comparison with pentachloroanisole calibration solution.

Table 1 Recovery and precision of the methods of the clean-up extraction and derivatisation of PCP

Method	*Recoveries*			*Comments*
	R	*CV*	*N*	
Acetylation	79.4%	5.5%	5	Acetylation of PCP standard solutions (50 ml). The handling is tedious and contamination interferes in the chromatogram.
	59%	45%		The sample volume was reduced before the acetylation, recoveries dropped because of losses when the CO_2 evolution. Chromatograms improved their quality.
Methylation	8%			Methylation is assisted by adding TBA and shaking
	4%			Methylation is assisted by adding TBA/ammonia solution and shaking.
	91%			Methylation is assisted by adding TBA and heating.
	23%			Methylation is assisted by adding TBA/ammonia solution and heating.
	81.5%	6.5%	16	Recoveries and reproducibility are satisfactory when PCP standards are methylated with MeI as the methylation reagent, TBA to assist the ionisation of the PCP, and the reaction solution is heated to provide the required reaction energy.
	73.5%	18.7%	13	The performance of the methylation decreases if the reagents are not added simultaneously.
Clean-up extraction	59.5%	8.7%	4	PCP is extracted with alkali and back-extracted into hexane by acidifying the aqueous phase.
	86.5%	5.9%	4	The liquid-liquid extraction is more effective by rising the ionic strength of the aqueous phase before back-extracting.
	66.6%	11.3%	5	Recoveries decrease if IPA is added, necessary when working with environmental samples.
	79.0%	3.5%	5	When the use of IPA is required the performance of the liquid-liquid extraction is satisfactory if the aqueous phase is re-extracted three times with 2 ml portions of organic solvent.

RESULTS AND DISCUSSION

Results for recovery trials for derivatisation and PCP separation from distilled water are listed in Table 1.

Although in the normal course of events a method proceeds from extraction through the separation, clean-up, derivatisation and final determination stages the order is reversed when developing a method. The results and discussion in this paper follow the order of development and testing.

Acetylation

Although the recovery of the PCP derivative is acceptable and the method is reproducible, there were some difficulties with the determination of this compound.

The derivatisation procedure gave some manipulation problems due to the large volumes used for the liquid-liquid extraction, and the evolution of CO_2 when the acetic anhydride is added to the carbonate solution. Considerable care was necessary to keep any losses to a minimum. In addition to some losses at the derivatisation step the chromatograms of the acetylated PCP following extraction from spiked distilled water contained many unknown peaks, indicating that a number of co-extracted polar compounds were also derivatised increasing the likelihood of interference with the measurement of PCP and other chlorophenols.

An attempt was made to work with a smaller volume of organic solvent and acetic anhydride prior to acetylation to make for easier manipulation. The recovery dropped noticeably, (59%, 45%), but there was an improvement in the quality of the chromatography.

Blank extracts from the water, solvent, glassware and reagents were checked to locate the source of contamination, which was identified as the acetic anhydride itself. This observation agrees with other literature accounts of acetylation procedures, causing most other workers to distill the commercial anhydride prior to use. These difficulties with contamination together with the unavailability and instability of the acetylated standards, led us to investigate an alternative method of derivatisation.

Methylation

Although diazomethane has been used extensively as methylating agent, it is a suspected carcinogen, the reaction can be explosive, and the reagent must be prepared fresh daily and stored in a freezer when not in use[1]. For these reasons methyl iodide was selected as an alternative methylating reagent.

Methyl iodide can be used as a methylating agent for acidic groups, forming the methyl ethers or esters in the presence of an alkali, to assist dissociation the weakly acidic molecules. Methyl iodide has been used for methylating the moth-proofing agent polychloro-2-(chloromethyl-sulphonamido)diphenyl ether extracted from fish tissue[18], and PCP in foods[14,15] by ion-pair reaction with tetrabutyl ammonium hydroxide (TBAOH).

The methylation conditions were examined by changing the conditions of the derivatisation reaction, by adding TBAOH in the commercial aqueous solution, or a more diluted solution in ammonia, and by heating or shaking the reaction mixture. Results for these experiments showed that the best recoveries were obtained when heating rather than when shaking, and by using commercial TBAOH solution directly rather than a reagent prepared from TBAOH and ammonia.

A method for the determination of PCP, based on the methylation procedure, was developed to meet the requirements of the environmental samples.

MeI (200 μl) and TBAOH (200 μl) were added simultaneously to 1 ml aliquots of the PCP solution in hexane, in 10 ml test tubes. The tubes were stoppered and the reaction mixture heated at 40°C for 90 minutes in a water bath. The excess of the

reagent was removed by shaking with water and separating the two layers. The solvent (hexane) was dried, replaced by *iso*-octane, and the internal standard added (1 ml of DCBE 6). The sample was transferred to an autosampler vial prior to determination by GC-ECD. The recoveries were calculated for spiked solutions prepared on different days and were reproducible.

If MeI and TBAOH were not added simultaneously then the recoveries decrease and were less consistent. This was probably due to a side reaction between the MeI and PCP in the absence of the TBAOH. This problem completely disappeared when both reagents were added simultaneously to each sample.

Different solvents such as acetone, hexane, *iso*-octane or dichloromethane appear to have little overall effect in the efficiency of methylation. Therefore hexane was chosen as the most convenient solvent for the method as a whole.

Since the ECD concentration-response curve for pentachloroanisole is not linear the working range was limited to a maximum deviation from linearity of 10%. The quantification limits were set between 5 and 105 pg PCP on column.

There was a large unidentified peak in the chromatograms which was directly related to the methylation performance, so a sample was examined by gas-chromatography-mass spectrometry (GC-MS). The impurity was identified as a methyl-m-bromo benzoate, arising from the original contaminant m-bromo-benzoic acid, in the sample. This compound has a much shorter retention time and it does not interfere in the PCP analysis.

Having optimised the derivatisation (Figure 2 part c) and final determination and obtaining recoveries from standard solutions of around 80%, the method was developed to include the separation from other interfering organochlorine compounds and extraction from sea water, suspended particles and sewage sludge. The target recovery of the method was set at 70% or better with a coefficient of variation not greater than $\pm 10\%$.

Pentachlorophenol separation

It is possible to separate the PCP from other co-extracted organic compounds in the initial pentane extract by making use of the acidic function and extracting with 0.01 M NaOH (Figure 2 part b). This liquid/liquid clean-up extraction technique was investigated with solutions of PCP in pentance followed by the described MeI methylation prior GC-ECD determination. The recovery was less than satisfactory although, the efficiency of the procedure was substantially improved by adding salt to the aqueous phase to raise the ionic strength[21].

Although, in principle, this extraction procedure is very simple the practicalities of multi-extraction manipulation using separation funnels can be tedious and inconvenient, especially if large number of samples are to be analysed. The scale of the extraction, using smaller volumes of the pentane extract in test-tubes, was tested.

The initial pentane extract of 500 ml was reduced to *ca* 5 ml in a stream of dry air and the PCP doubly extracted with an equal volume of 0.1 M NaOH. The efficiency of this step was independent of the volume of pentane between 50 and 5 ml. Since there was no loss in PCP by reducing the volume of pentane prior to the "clean-up" extraction the smaller volume of 5 ml was selected.

Modification of pentachlorophenol analysis procedure

If the organic content of the sea water was unusually higher than normal ie sampling immediately following sewage sludge dumping then emulsions would tend to be created at the clean-up extraction stage when the PCP was removed into the alkaline solution. When sea water samples were extracted by liquid-liquid extraction with pentane emulsions tended to form, making it difficult to separate the two phases. This was avoided by adding iso-propanol 1 ml[12]. However the addition of IPA did affect the extraction efficiency of the method, but the recovery was improved in the final step of the extraction by washing the aqueous phase with 2 ml portions of solvent three times (Table 1).

The liquid-liquid extraction, used in the first stage as a separation method, also provided a suitable clean-up procedure for contaminated sewage sludge extracts analysed without further clean-up by GC-ECD.

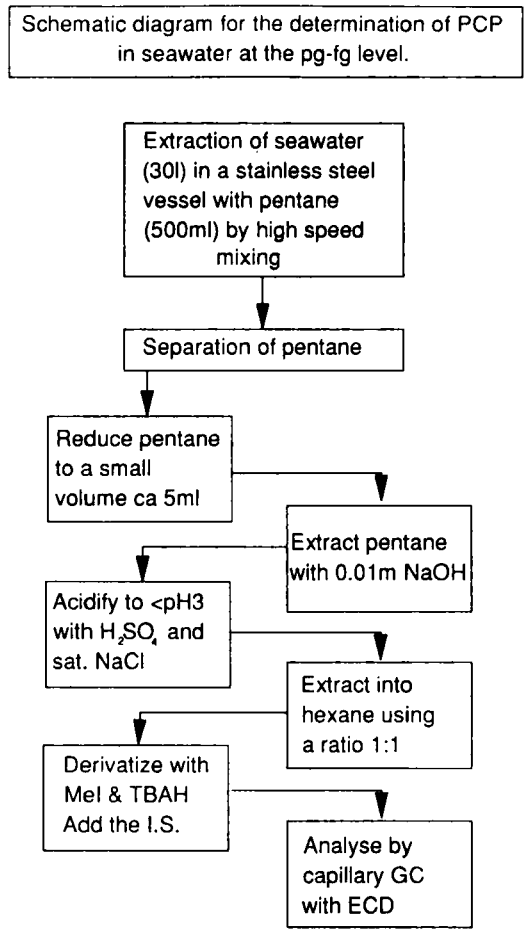

Figure 2 Schematic diagram of the extraction, clean-up and derivatisation of PCP in sea water.

Table 2 Recovery and precision of the method for the analysis of large volumes of sea water (30 l) for PCP

PCP concentration in water ng/kg	*Recovery*	*CV*	*n*
0.3–0.4	81%	19.9%	3
0.6–0.8	75%	19.8%	4
3.0–4.0	72%	19.0%	3

Recovery for the proposed method

The recovery of the whole PCP analysis procedure (Figure 2) and the efficiency of the sampling apparatus (Figure 1) to extract PCP from water were tested.

Sea water was filtered in the sampling apparatus[19] and spiked with a solution of PCP in methanol. Extraction of the organics from the water, separation of the phenolic fraction from other organics and derivatisation and determination of PCP were performedly methylation as discussed. Unspiked sea water blanks were also included for reference.

The study was carried out at three concentration levels covering an order of magnitude. The results from this spiking experiment are given in Table 2 and plotted in Figure 3. The recoveries for PCP range between 72% and 81% for the three levels with a CV% of around 20%. The limit of quantification (LOQ), based on 10 times the limit of detection, for this combined sampling and analytical procedure for the

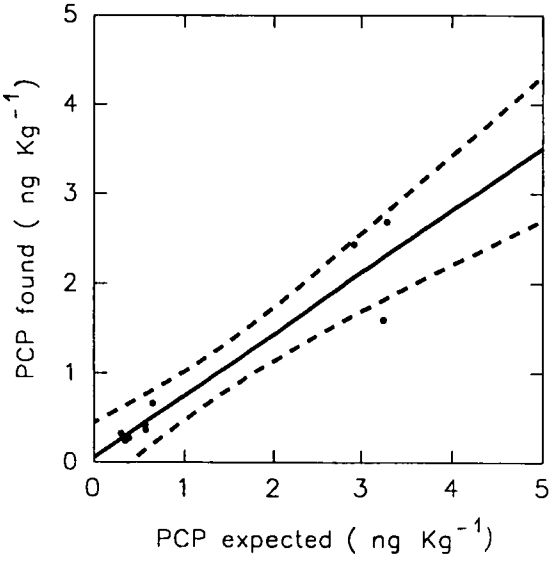

Figure 3 The obtained PCP concentrations vs the expected values. The best straight line is fitted and the confident limits assigned.

Table 3 Concentrations of PCP in sea water samples from Garroch Head following sludge dumping

Sample	*Time from dumping (h)*	*Concentration*	
		Water (ng l^{-1})	*Particles (ng kg^{-1})*
GH1	0.50	38.0	2,190
GH2	1.50	7.2	4,170
GH3	2.50	1.1	1,040
GH4	5.75	0.3	453
GH5	6.50	0.3	1,410

Table 4 Concentrations of PC in sewage sludge/sea water samples from bag experiment at Poolewe at 1 m depth

Sample	*Time from dosing (h)*	*Concentration*	
		Water (ng l^{-1})	*Particles (ng kg^{-1})*
PL1	1.0	11.3	616
PL2	3.0	11.6	236
PL3	8.0	9.6	215
PL4	22.0	8.7	924

determination of PCP in sea water is 0.2 ng kg^{-1}, giving a concentration factor of 60,000. Samples containing PCP below this concentration may be analysed by reducing the final volume to 50 μl and injecting the samplings manually in the GC. The LOQ using this final concentration is lowered to 35 pg kg^{-1}.

PCP Determination in environmental samples

This analytical method has been applied to samples taken at two different field experiments. The first was at the Garroch Head sewage sludge dumping site (Firth of the Cyde, Scotland). Samples were taken on board of the research vessel *Goldseeker* at 5 m depth just after dumping, following the sewage sludge plume with a drifting buoy.

The second field trial was undertaken at the Field Station at Loch Ewe, West Scotland. In May 1990 forty litres of sewage sludge, normally dumped at Garroch Head, was released into an experimental bag[22], 60,000 litre capacity, giving a dilution of $\times$ 15,000. Samples were taken at different depths and time and then filtered, extracted, cleaned-up, and the PCP determined according to the method given in this paper. The results are listed in Tables 3 and 4. The environmental implications of these results will be published elsewhere, as part of the study of partitioning and

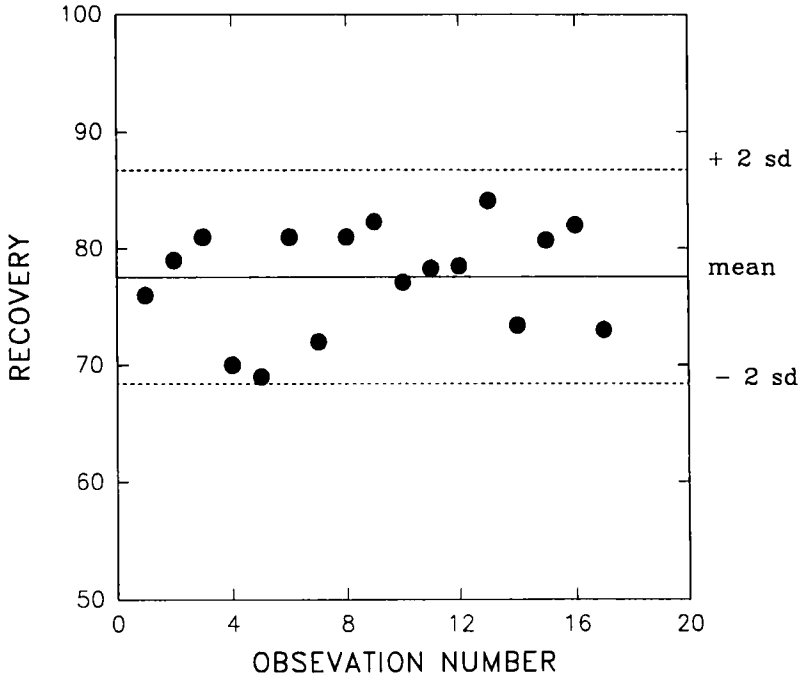

Figure 4 Methylation control chart. The long term reproducibility for the described method of separation and analysis has been studied for a period of 72 days and for PCP amounts ranging from 20 to 36 pg on column.

fate of chlorinated organic pollutants in the marine environment. However these results are given in this paper to demonstrate the suitability of the analytical method for this study.

In addition to the recovery experiments, the efficiency of the methylation was controlled by derivatising two aliquots of the PCP standard solution with each batch of environmental samples. Recoveries obtained from this quality control measure can be used to calculate the long term reproducibility of the methylation procedure (Figure 4). At present there are no certified reference, or laboratory reference materials available for PCP analysis in any matrix. Control of these methods will be made by a standard addition technique and recovery checks as illustrated in this paper.

CONCLUSIONS

An analytical method for the determination of PCP in organically rich sea water at the pg-fg level has been successfully developed and applied in field trials.

This method extraction of PCP from sea water and particulate matter is currently being applied to a wide range of other trace organic contaminants[22]. The samples are extracted with pentane for the sea water, and hexane:acetone (40:60) for the particles. Sulphuric acid is also added to improve the extraction on efficiency of PCP.

A single extraction with 500 ml pentane was sufficient for PCP and a number of other organochlorine compounds. The PCP is separated by the liquid-liquid extraction which isolates the acidic compounds from other non-polar organic contaminants and no further clean-up is required.

Methylation was found to be the most effective derivatisation procedure for the GC-ECD determination, giving acceptable recovery and good chromatographic characteristics. However to obtain good reproducible results it is necessary to control the following parameters. The temperature during the methylation step must be strictly controlled. It is important to maintain the temperature between 35–40°C for a fast reaction, but without loss of MeI. The reagents, MeI and TBAOH, must be added simultaneously to each sample, otherwise the efficiency and reproducibility of the derivatisation will deteriorate.

A sample containing a known amount of PCP should be methylated with each batch of samples to check the effectiveness of the derivatisation and to minimise possible errors, eg if the methylating reagent decomposes by oxidation. The methylating reagent should be stored at 4°C in a fridge and in a sealed container.

The sampling technique coupled with the method of analysis described in this paper has made it possible to determine PCP in sea water at the parts per quatrillion (pg kg^{-1}) level.

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References

1. B. E. Lee, M. D. Lacroix, G. A. J. Dupont and J. A. Scott. *J. Assoc. Off. Anal. Chem.*, **67**, 546–548 (1984).
2. R. C. C. Wegman and H. H. van den Broek. *Water Research*, **17**, 227–230 (1983).
3. I. O. O. Korhonen and J. Knuutinen. *J. Chromatogr.*, **256**, 135–142 (1983).
4. H. Lee, Y. D. Stokker and A. S. Chau. *J. Assoc. Off. Anal. Chem.*, **70**, 1003–1008 (1987).
5. B. B. Sithole, D. T. Williams, C. Lastoria and J. L. Robertson *J. Assoc. Off. Anal. Chem.*, **69**, 466–473 (1986).
6. H. Lee, L. Weng and A. Chau. *J. Assoc. Off. Anal. Chem.*, **67**, 789–794 (1984).
7. J. Paasivirta, K. Heinola, A. Karjalainen, J. Knuutinen, K. Mantykoski, T. Piiloloa, K. Surma-Aho, J. Tarhanen, L. Welling and J. Sarka. *Chemosphere*, **14**, 469–491 (1985).
8. D. E. Wells, A. A. Cowan and E. G. Christie. *J. Chromatogr.*, **328**, 372–377 (1985).
9. I. O. O. Korhonen and J. Knuutinen. *Chromatographia*, **17**, 154–156 (1983).
10. W. Butte, M. Kirsch and J. Denker. *Inter. J. Environ. Anal. Chem.*, **13**, 141–153 (1983).
11. W. Butte. *Fresenius J. Anal. Chem.*, **326**, 449–452 (1987).
12. L. Rudling. *Water Research*, **4**, 533–537 (1970).
13. Tian-Min Xie. *Chemosphere*, **12**, 1183–1191 (1983).
14. M. L. Hopper. *J. Agric. Food Chem.*, **35**, 265–269 (1987).
15. Food and Drug Administration. *Pesticide Analytical Manual*, Vol. 1, Section 221.1, page 1, (1989).
16. D. E. Mundy and A. F. Machin. *J. Chromatogr.*, **219**, 229–238 (1981).
17. D. E. Wells, M. J. Gillespie and E. A. Porter. *J. High Resol. Chromatogr. & C.C.*, **8**, 443–449 (1985).
18. D. E. Wells and A. A. Cowan. *Analyst*, **106**, 862–868 (1981).
19. A. G. Kelly, *SOAFD Internal Report*, (1990).
20. D. E. Wells, J. de Boer, L.G.M.T. Tuinstra and B. Griepink. *Fresenius J. Anal. Chem.*, **332**, 591–597 (1988).
21. G. W. Burns and R. A. Currie. *J. Assoc. Off. Anal. Chem.*, **63**, 56–60 (1980).
22. I. Cruz and A. G. Kelly. *Research Data.* SOAFD, (1991).