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THE DETERMINATION OF PENTACHLOROPHENOL IN SEWAGE SLUDGE

A REPORT FOR THE DEPARTMENT OF THE ENVIRONMENT

FEBRUARY 1991

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1. Introduction

Pentachlorophenol (PCP) and its related esters are used as wood preservatives and have been reported at substantial levels in sewage sludges. The method of analysis measures the lauryl ester as well as free Pentachlorophenol and its salts. The objective of the present work was to test the draft SCA procedure and was carried out under contract to the Department of the Environment.

2. Source of samples

Sludge was removed from an anaerobic digester at Bedford Sewage Treatment Works and had a solids content of 2.0%.

3. Spiking procedure

10g samples of the sludge were spiked with pentachlorophenol at low (0.1 mg/l) and high (1.0 mg/l) levels using a stock solution of PCP in acetone. The same stock solution was used to prepare the working standards.

4. Apparatus and Reagents

A description of the apparatus reagents is given in the appendix. For the present work the instrument conditions used were:-

GC	Philips 4400
Injector	Split 10:1
Oven	140 to 225°C at 4°C per min
Detector	Electron capture
Make up	Nitrogen 50 ml/min
Carrier Gas	Hydrogen, 2ml/min
Column	SE54, fused silica 25m
Injection volume	2ul
Integrator	Hewlett Packard 3390A

5. Results

10 ml digesting sludge was used with a solids content of 2.0%.

Blanks	0.012 mg/l	
	0.010 mg/l	
	0.009 mg/l	
	0.010 mg/l	
	0.012 mg/l	
	0.006 mg/l	
	0.009 mg/l	
	0.010 mg/l	
	0.007 mg/l	
	0.009 mg/l	
Mean	0.0094 mg/l	Sd = 0.0019 mg/l

Low spikes (0.1 um/l)

Day 1	Day 2	Day 3
0.012	0.095	0.094
0.14	0.14	0.11

Mean = 0.116

High spikes (1.0 mg/l)

Day 1	Day 2	Day 3
1.03	0.88	0.86
1.02	0.94	0.71

Mean = 0.91

7. Conclusions

The method suffers from problems of emulsification during the sample preparation stages and the chromatograms obtained showed many extraneous peaks and late eluting compounds, necessitating the use of a temperature programme. The results however were satisfactory and the method is suitable for an SCA method.

APPENDIX

THE DETERMINATION OF TOTAL PENTACHLOROPHENOL IN SEWAGE SLUDGES

1. Performance characteristic of the method

1.1	Substances Determined	Pentachlorophenol (PCP) Tri and tetrachlorophenols may also be determined by the method. Pentachlorophenyl laurate has been found in river samples and the method measures this and other PCP esters as PCP.
1.2	Type of sample	Sewage sludges.
1.3	Basis of the method	Extraction of the alkaline sample to remove potentially interfering compounds. Acidification of the sample. Extraction into diethyl ether methylation and determination by,gas chromatography using an Electron capture detector (EC-GC)
1.4	Range of application	0-5 mg/l/ The range may be extended by dilution of the extract.
1.5	Calibration curve	The range of linearity depends on the detector in use.
1.6	Standard deviation	See table I
1.7	Limit of detection	0.009 mg/litre
1.8	Sensitivity	Dependent upon the instrument in use.
1.9	Bias	Extraction efficiencies are less than 100% This will lead to results consistently lower than the true value.

1.10 Interferences

Any co-extracted material or its derivative which has a similar GC retention time to PCP methyl ester will interfere. The methyl derivative of Pentachlorophenol may elute close to or be unresolved from dieldrin on OV1 columns.

1.11 Time required for analysis.

2. Principle

The sample, after preliminary ether extraction of the alkaline sample remove interfering compounds is acidified with sulphuric acid and extracted with diethyl ether in a Soxhlet apparatus. After concentration, the extract is methylated with diazomethane and analysed by Electron capture gas chromatography (EC-GC).

Phenolic esters such as Pentachlorophenol laurate are hydrolysed by standing in alkali solution at room temperature overnight.

3. Interferences

The detector is sensitive to many compounds. Gas chromatography using two or more columns may assist in differentiating Pentachlorophenol and other chlorinated phenol derivatives from interference peaks on the chromatogram.

4. Hazards

Diethyl ether and methanol are toxic narcotic and flammable. All electrical equipment should be flameproof. Pentachlorophenol especially in the undiluted state is toxic. Caution must be exercised when preparing the stock solutions. Diazomethane is toxic. carcinogenic and potentially explosive. The sulphonamide reagent used has been shown to induce tumours in laboratory animals. Skin contact ingestion and inhalation must be avoided. Ethers can form peroxides on storage or oxidation, which are explosive. Sodium hydroxide is caustic

5. Reagents — All reagents must be sufficient purity that they do not give rise to significant interfering peaks in the chromatograms ultimately obtained. This should be verified by running procedural blanks with each batch of samples analysed. Reagents should be stored in all glass containers

5.1 Dilute Sulphuric acid — Add 250ml concentrated sulphuric acid (AR grade) to 600 ml distilled water with swirling and cooling. Cool to ambient temperature and dilute to one litre with distilled water.

5.2 Sodium hydroxide solution 5M — Dissolve 200g $\pm$ 20 g sodium hydroxide in 600ml of distilled water with swirling and cooling. Cool to ambient temperature and dilute to one litre with distilled distilled water.

5.3 Diethyl ether — Freshly re-distilled from a mixture of 5 $\pm$ 1g of potassium hydroxide and 1 $\pm$ 0.2g of quinol per litre in all-Glass apparatus.

5.4 Methanol — Analytical Reagent Grade.

5.5 N-methyl-N-nitrosotoluene-4-sulphonamide Analytical Reagent grade.

5.6 Potassium Hydroxide — Dissolve 60 $\pm$ 0.5g potassium hydroxide in 100 $\pm$ 5ml distilled water.

5.7 Glacial acetic acid — Laboratory Reagent Grade.

5.8 Standard solutions of Pentachlorophenol

5.8.1 Stock solution — These may be prepared by dissolving pure or certified materials in methanol. A suitable concentration is 100 mg/100ml methanol.

5.8.2 Working standard — These may be prepared by diluting aliquot of the stock solution with ether (5.9) using microlitre syringe or calibrated pipettes which are reserved solely for this purpose. Some useful working standards are:-

0.1 ug/l	(1ul 5.8.1 diluted to 100ml)
0.5 ug/l	(5ul 5.8.1 diluted to 10ml)
1.0 ug/l	(10ul 5.8.1 diluted to 10ml)
5.0 ug/l	(50ul 5.8.1 diluted to 10ml)
10.0 ug/l	(100ul 5.8.1 diluted to 10ml)

5.9 Water saturated ether	Vigorously shake 200ml distilled water with 2L of distilled diethyl ether (5.3) in a glass stoppered taking care to release any built-up of pressure.
5.10 Roasted sodium Sulphate	Heat at $500^{o}C \pm 20^{o}C$ for 4 hr $\pm$ 30 min. Allow to cool to $200^{o}C$ in the muffle furnace and then to ambient temperature in a desiccator containing magnesium perchlorate or equivalent alternative.
5.11 Nitrogen	Dry, clean.
6. Apparatus	Glassware should be clean and dry. Rinsing with diethyl ether (5.3) just before use. Assists in freeing apparatus from possible contaminants.
6.1 Sample bottles	These should be of all-glass construction or with a teflon-lined screw cap. 100ml capacity is suitable.
6.2 Glass beakers	150ml capacity
6.3 Soxlet apparatus	250ml flask capacity and 80ml thimble holder.
6.4 Kuderna-Danish evaporators	250ml
6.5 Graduated centrifuge tubes	Glass 10 ml 0.1 ml graduations, glass stoppered, tapered.
6.6 Methylation apparatus suitable.	Any commercial diazomethane generator is The whole apparatus should be mounted in a fume cupboard.
6.7 Gas liquid chromatograph	GC fitted with an electron capture detector, is required,to be operated in accordance with the manufacturers instructions. Capillary columns or packed columns may be used, coated with mixed methyl/phenyl silicone.

7. Sample Storage

Samples should be extracted as soon as possible after sampling, as PCP is degraded in sludge. Phenolic esters can be hydrolysed by standing in alkali solution at room temperature overnight, but first remove approximately 10g for a dry weight determination (8.1.1.). Samples must then be stored in a freezer or if immediate analysis is impractical. NaoH can be added to pH12 to assist in preservation of the sample. The sample bottles should be protected from contamination by covering the top and shoulders with aluminium foil. Samples should not be placed in the proximity of concentration solutions of phenols.

8. Analytical Procedure

Step	Procedure	Notes
8.1	Extraction of Pentachlorophenol.	
8.1.1.	Stir the sample and remove approximately 10 $\pm$ 0.1g for a dry weight determination.	
8.1.2	Stir the sample and transfer 10 $\pm$ 1ml of wet sludge to a tarred 150ml beaker and record q the weight of sample taken (note a)	(a) if the result is to be expressed on a weight volume basis the exact volume of sample taken is recorded.
8.1.3	Ester Hydrolysis To the sample in the beaker add sodium hydroxide solution (5.2) until the pH is 11-12. Stir with a glass rod and leave the sample to stand overnight.	(b) PCP may be present in the form of its laurate should be left in contact with the alkali overnight to allow the hydro- lysis to the free phenol. The ester will not be determined if the sample is extracted immediately.
8.1.4	Add 50ml diethyl ether and stir with a glass rod. Leave to settle Decant off the ether and discard. Add a further 50ml diethyl ether and repeat.(note c)	(c) This process removes potentially interfering compounds. The PCB remaining on the sludge in the form of the sodium salt. If emulsions may occur the sample may be centrifuged if necessary.
8.1.5	Add sulphuric acid (5.1) with with stirring until the pH is <2. Note (d)	(d) pH indicator paper is suitable.
8.1.6	Add sodium sulphate and stir until a dry powder is obtained on which the sludge is adsorbed. The mixture should not be allowed to stand for prolonged periods as the whole mass may set solid.	

8.1.7 Transfer the solids from the beaker into a Soxhlet thimble (80ml capacity). Add diethyl ether to the apparatus and extract for 4 hours.

8.2 Concentration

8.2.1 Evaporate the extract from the the Soxlet using a Kuderna Danish evaporator. Add an anti-bumping granule and concentrate the extract to 2 or 3ml on a steam bath.

8.3 Methylation

8.3.1 Using a suitable apparatus and the reagents listed (5.3 to 5.6) generate a stream of diazomethane Dissolve the gas in diethyl ether until the solution is bright yellow (note e)

(e) This entire operation must be carried out in a fume cupboard.

8.3.2 Add 2 $\pm$ 0.2ml of diazomethane saturated ether from (8.3.1) to the sample extract (8.2.1). Mix thoroughly and leave for 15 minutes.

8.3.3 Using a stream of purified nitrogen remove the excess reagent and concentrate back down to the 1ml graduation mark. The methylated is extract is now ready for GC analysis.

8.4 Calibration Standards

8.4.1 Repeat steps (8.3.2) to (8.3.3) using 2 $\pm$ 0.1ml of each of the prepared working standards (5.8.2). Procedural blanks and spiked samples should also be run for AQC purposes.

8.5 Gas Chromatography

Inject a suitable volume of the extract into the GC. Inject the same volume of similarly derivatized standards into the GC and compare the retention times and peak heights (areas) of the standards and samples.

(f) An integrator or laboratory data system may be used.

8.6 Calculations

Plot the concentration of PCP in the standards (mg/l) against the response (peak height of area) Read off the concentration (A) of PCP in the sample from the calibration graph.

Then $C = \frac{A}{10}$

Where C = concentration in the sludge (mg/l)

A = concentration in the extract (mg/l)

TABLE 1

Means, standard deviations and recoveries

Sample	Mean Found	Sw	Sb	St	% recovery
Unspiked	0.009			0.0019	
Low spike (0.1 mg/l)	0.116	0.021(3)	0(2)	0.021 (5)	116
High spike (1.0 mg/l)	0.91	0.066(3)	ns	0.129(3)	91

Spiked samples results are not blank subtracted
Numbers in brackets are degrees of freedom.

Limit of detection (4.65 x St for unspiked sludge = 0.009 mg/litre.