ENVIRONMENT AGENCY

The determination of polycyclic aromatic hydrocarbons in soil by dichloromethane extraction using gas chromatography with mass spectrometric detection (2003)

Methods for the Examination of Waters and Associated Materials

The determination of polycyclic aromatic hydrocarbons in soil by dichloromethane extraction using gas chromatography with mass spectrometric detection (2003)

Methods for the Examination of Waters and Associated Materials

This booklet contains a method for determining polycyclic aromatic hydrocarbons in soil. The method is based on dichloromethane extraction using gas chromatography with mass spectrometric detection. Limited performance data are reported.

Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of materials and apparatus used. This booklet reports the materials actually used in the performance tests. However, this does not endorse these products as being superior to other similar materials. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate this method in their own laboratories.

Contents

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soil (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results encompassing at least ten degrees of freedom from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available. An indication of the status of the method is shown at the front of this publication on whether the method has undergone full performance testing.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials" and their continuing revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are

1 General principles of sampling and accuracy of results
2 Microbiological methods
3 Empirical and physical methods
4 Metals and metalloids
5 General non-metallic substances
6 Organic impurities
7 Biological methods
8 Biodegradability and inhibition methods
9 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with this method are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. An index of methods is available from the Secretary.

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

Dr D Westwood
Secretary

September 2002

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 1999 (SI 1999/437). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; "Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory", 1992, produced by the Royal Society of Chemistry; "Guidelines for Microbiological Safety", 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and "Safety Precautions, Notes for Guidance" produced by the Public Health Laboratory Service. Another useful publication is "Good Laboratory Practice" produced by the Department of Health.

The determination of polycyclic aromatic hydrocarbons in soil by dichloromethane extraction using gas chromatography with mass spectrometric detection

1 Introduction

This method describes the determination of a small selection of the many polycyclic aromatic hydrocarbons (PAHs) which may be found in soil. The method is based on solvent extraction using dichloromethane and gas chromatography with mass spectrometric detection. Other methods are available for the determination of PAHs in soil using gas chromatography with flame ionisation detection. However, these methods are susceptible to interferences and should be used with caution.

PAHs occur ubiquitously in the environment and can be found in sediments, soils and waters either in solution or adsorbed onto particulate material. In addition, PAHs enter the environment as a result of fossil fuel burning, the combustion of other organic material or via oil exploration and production processes. Substituted PAHs, mainly in the form of alkyl-substituted compounds, for example methyl, ethyl, propyl and butyl derivative PAHs are known to be produced biogenically. It is reported that a number of PAHs are carcinogenic.

The method described in this booklet has been shown to be suitable for the determination of a small number (19) of the PAHs found in contaminated soil, using five deuterated PAH internal standards and a deuterated surrogate standard. These PAHs are shown in Appendix A and Table 2 together with corresponding structures and molecular masses. Other PAHs, of which there are many in the environment, may also be determined by this method following suitable validation.

The method has been performance tested on air-dried soils, and as such, may not be suitable for soils containing significant quantities of moisture. Whilst a clean-up procedure has been described, it may not be necessary to carry out this procedure on all types of samples. In addition, great care should be taken to ensure that the sub-sample is homogeneous, and representative of the bulk material sampled.

2 Performance characteristics of the method

2.1 Substances determined	See Appendices A and B.
2.2 Type of sample	Contaminated soils.
2.3 Basis of method	Samples are Soxhlet-extracted with dichloromethane and determined by gas chromatography with mass spectrometric detection.
2.4 Range of application	This varies with individual PAHs, but is typically, up to about 250 mg kg^{-1}. Where samples contain a variety of PAHs at vastly different concentrations, the range may be significantly above this value for individual PAHs. Incomplete extraction can occur with

		samples that contain PAHs above this value. In these cases, the mass of sample should be reduced accordingly. Dilution of the sample extract with additional solvent is not recommended, as the efficiency of the extraction process is a function of the total extractable organic material present.
2.5	**Calibration curve**	All calibrations are linear up to 250 mg kg^{-1}.
2.6	**Interferences**	Any substance which is co-extracted under the conditions used, which exhibits similar chromatographic behaviour to any of the PAHs being determined and which has a similar mass will interfere.
2.7	**Standard deviation**	See Appendix B.
2.8	**Limit of detection**	See Appendix B.
2.9	**Sensitivity**	This is instrument dependent.
2.10	**Bias**	See Appendix B.

3 Principle

This method is based on an air-dried, ground and homogenised soil sample which is Soxhlet-extracted with dichloromethane. The extracted PAHs are determined by gas chromatography with mass spectrometric detection with electron impact ionisation, and quantified using internal standard addition after extraction. The mass spectrometer should be set to detect nominal molecular masses of the PAHs (see Appendix A and Table 2). Alternatively, if a high-resolution mass spectrometer is available, accurate molecular masses can be monitored.

PAHs exhibit relatively simple mass spectra, for example see Figure 1, with the molecular ion often the most intense ion. Standard solutions of PAHs are determined by gas chromatography with mass spectrometric detection before samples are analysed in order to assign retention times to individual PAHs, to calculate relative response factors, and for constructing calibration graphs. Response factors are calculated using appropriate deuterated PAH internal standards.

4 Hazards warning and safety precautions

Certain PAHs are carcinogenic and should be handled with extreme care. Skin contact with solid materials, solvent extracts and solutions of PAHs should be avoided. PAHs may become deposited on the outside surface of glassware that contains solutions of PAHs. Glassware should, therefore, always be handled using gloves that are solvent-resistant and preferably, disposable. PAH contamination of the outside surface of vessels may be detected by ultra violet irradiation at 366 nm. Care should be taken during this procedure to avoid irradiating

the bulk of the solution within the vessel, as certain PAHs are susceptible to photo-degradation. As well as being hazardous, such deposits may indicate that a change has taken place in the concentration of the solution contained in the vessel. Glassware containing solutions of PAHs should be stored under refrigeration, and upright in beakers in order to contain any spillage that may occur in the case of breakage.

Solid PAHs may give rise to dust hazards due to crystals becoming electrostatically charged. The solids should be handled only where proper facilities are available (for example adequate fume cupboards, protective clothing, dust masks etc). In order to minimise exposure when solid PAHs are weighed, it is prudent to do so in a single step; i.e. repeated adjustments of the amount of PAH (in order to achieve a specific quantity) should be avoided. Any necessary adjustment, if required, can be performed on solutions of the PAHs. It is strongly advised that standard solutions are prepared centrally in suitably equipped laboratories or are purchased from suppliers specialising in their preparation.

Highly contaminated samples, concentrated solutions of PAHs and used gloves etc, should be disposed of in an appropriate manner approved for the disposal of toxic waste. Dichloromethane is a presumptive carcinogen and should be handled with appropriate precautions.

5 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interfering peaks in the chromatographic analysis. This should be checked for each batch of chemicals and reagents and verified by running procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography or pesticide use and analytical grade materials are normally suitable unless otherwise stated and details of preparation are given, where appropriate. Where dilutions are prepared, it may be necessary, to avoid adsorption of PAHs onto the surface of glassware and loss by volatilisation, to add small volumes of the standard solutions to appropriate amounts of solvent, prior to making to volume. Reagents may become contaminated by contact with air and/or other materials, particularly plastics, or by degradation caused by the action of light. Reagents should be stored in tightly sealed containers or other suitable vessels and kept in the dark, if necessary.

To avoid excessive evaporation of solvent, standard solutions should be stored in a refrigerator. However, prior to use, all solutions and solvents should be allowed to reach ambient room temperature before volumetric measurements are made. When a standard solution is required for use, the flask and contents can be weighed, the stopper removed and a portion of the solution transferred to a clean, dry container of low, but sufficient volume. The stopper is then replaced and the flask and its (reduced) contents weighed again. If after appropriate storage, any significant difference occurs in the weight of the flask and its contents since it was last used, then this might indicate a possible change in the concentration of the standard solution. Standard solutions of PAHs are available from a number of suppliers and as an aid to the analyst, a list of suppliers is given below. Other suitable sources may be available and reference to these suppliers does not constitute an endorsement of products supplied.

Community Bureau of Reference, Directorate General XII, Commission of the European Communities, 200 rue de la Loi, B-1049 Brussels, Belgium.

Supelco (Sigma-Aldrich), Fancy Road, Poole, Dorset, BH17 7NH.

LGC Promochem, Queens Road, Teddington, Middlesex, TW11 0LY.

Greyhound Chromatography and Allied Chemicals, 88 Grange Road West, Birkenhead, Merseyside, L43 4XF.

QMx Laboratories Ltd, 4 Bolford Street, Thaxted, Essex, CM6 2 PY.

5.1 Dichloromethane.

5.2 PAH standard solution. A mixture of the PAHs to be determined, each at a concentration of 100 μg ml^{-1}.

5.3 Stock deuterated PAH internal standard solution. Naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} have been found suitable, each at a concentration of 2000 μg ml^{-1}.

5.4 Working deuterated PAH internal standard solution. Pipette 1.00 ± 0.05 ml of stock deuterated PAH internal standard solution (5.3) into a 25 ml volumetric flask. Make to volume with dichloromethane (5.1). The concentration of this solution is 80 μg ml^{-1} for individual deuterated PAHs. This solution is stable for up to six months if stored correctly under refrigerated conditions.

5.5 Stock deuterated surrogate standard solution. Accurately weigh out, and quantitatively transfer about 500 mg of deuterated *p*-terphenyl to a 500 ml volumetric flask. Make to volume with dichloromethane (5.1). The concentration of this solution is about 1000 μg ml^{-1}. This solution is stable for up to six months if stored correctly under refrigerated conditions.

5.6 Working deuterated surrogate standard solution. Pipette 10.0 ± 0.05 ml of the stock deuterated surrogate standard solution (5.5) into a 100 ml volumetric flask. Make to volume with dichloromethane (5.1). The concentration of this solution is about 100 μg ml^{-1}. This solution is stable for up to six months if stored correctly under refrigerated conditions. Equal volumes of this standard solution are added to all calibration solutions and spiked additions made to all sub-samples taken for analysis.

5.7 Working calibration mixed standard solutions. Five calibration standard solutions are prepared by adding to separate GC vilas, 200 ± 2 μl of the working deuterated PAH internal standard solution (5.4), 100 ± 1 μl of the working deuterated surrogate standard solution (5.6) and a volume of the PAH standard solution (5.2). Table 1 gives details of typical examples of the amounts of PAHs present in the GC vials. The final volumes of all the solutions and the concentrations of the deuterated internal and surrogate standard solutions should be the same and identical as those of the sample extracts, but see section 8.2.4, note k.

5.8 **Low level check standard**. Prepare a low level check standard by adding 500 ± 5 µl of PAH standard solution (5.2) to a 50 ml volumetric flask. Make to volume with dichloromethane (5.1) and mix well. Pipette 1.00 ± 0.05 ml of this solution into a GC vial containing 200 ± 2 µl of the working deuterated PAH internal standard solution (5.4) and 100 ± 1 µl of the working deuterated surrogate standard solution (5.6). This solution is used to determine limits of detection for individual PAHs where appropriate blank samples cannot be used.

5.9 **Alumina** (neutral) 100-250 mesh. Activated by drying for 24 hours at 150 ^{o}C.

5.10 **Silica gel**. Chromatography grade, 30-70 mesh, pore size 40 µm. Activated by drying for 16 hours at 250 ^{o}C.

5.11 **n-Pentane**.

Table 1 **Typical calibration standard solutions**

Laboratories should determine their own volumes and concentration range depending on the samples being analysed.

Vial number	Mass of working deuterated PAH internal standard solution (5.4) in vial (µg)	Mass of working deuterated surrogate standard solution (5.6) in vial (µg)	Volume of PAH standard solution (5.2) in vial (µl)	Volume of dichloro-methane (5.1) in vial (µl)	Mass of PAH in vial (µg)
0	16	10	0	1000	0
1	16	10	10	990	1
2	16	10	50	950	5
3	16	10	100	900	10
4	16	10	250	750	25
5	16	10	500	500	50

6 Apparatus

Apparatus should be free from contamination before use. Glassware should be thoroughly cleaned, rinsed with suitable solvent before use and allowed to dry.

6.1 **Sample bottles**. Sample containers should be carefully cleaned before use and contamination of lids with dirty soil residues should be avoided. Containers can be rinsed out and washed, manually, in hot water with detergents, or in an automatic glass washer. After an optional dilute acetic acid wash, containers should be thoroughly rinsed in deionised water. After draining, they can be heated slowly in an oven to 500 ^{o}C, maintained at that temperature for 1 hour and carefully cooled. Alternatively, containers can be rinsed with dichloromethane. Container-lids, polytetrafluoroethylene liners and aluminium liners should be considered disposable and new ones fitted.

6.2 **Analytical balance**. Capable of weighing to four decimal places, in grams.

6.3 **Extraction thimbles**. With beakers to contain thimbles whilst weighing.

6.4 **Soxhlet apparatus**. With associated glassware and heating mantles.

6.5 **Rotary evaporation apparatus**. Nitrogen blow-down apparatus with a supply of nitrogen (99.9 %) may also be used.

6.6 **Glass GC vials**. With crimp top and crimper tool.

6.7 **Syringes**. For example, 0-50, 100, 200, 250 and 500 µl.

6.8 **Glass-fritted chromatography column**. For example, 20 cm x 10 mm.

6.9 **Gas chromatography**. A gas chromatograph fitted with a capillary column with mass spectrometric detection. It is recognised that different instruments will require different operating conditions, but typical chromatographic conditions used in the generation of performance data were as follows:

Column:	30 m x 0.32 mm internal diameter, 0.1 µm film thickness, DB-5MS. Equivalent columns may also be used.
Injector temperature:	300 °C.
Injector:	Split/splitless type.
Column temperature:	Programmable at 75 ^{o}C for 3 minutes, ramped to 300 ^{o}C at a rate of 6 ^{o}C per minute and then held at this temperature for 10 minutes.
Transfer line temperature:	300 °C.
Carrier gas:	Helium at 1.2 ml per minute.
Mode:	Selective ion monitoring (SIM) or total ion current with extracted molecular ion for quantification, see Table 2.
Injection volume:	1 µl.

Typical chromatograms are shown in Figures 2 and 3.

7 Sample collection and storage

Samples should be collected in clean, wide-necked, amber glass containers with screw caps and polytetrafluorethylene liners or lids lined with aluminium foil. Samples should be stored in the dark, under refrigerated conditions and analysed as soon as possible after collection. The method as described has been performance tested using air-dried samples and may not be suitable for samples containing significant amounts of water. The procedures used to prepare

air-dried samples may, however, adversely affect the more volatile PAHs present in the original sample prior to air-drying. For example, naphthalene (and possibly other PAHs) is known to be volatilised at low temperatures. Analysts should, therefore, ascertain whether the procedures used to prepare air-dried samples affect the resulting determination of PAH concentrations. See "The preparation and pre-treatment of contaminated soil samples prior to chemical analysis", in preparation within this series. Alternatively, it may be possible to add a suitable drying agent to a non-air-dried sample, thus reducing the effects of moisture, prior to extraction. All procedures should, however, be validated before routine use.

8 Analytical procedure

Step	Procedure	Note
8.1	**Extraction procedure**	
8.1.1	Accurately weigh 10.0 ± 0.2 g of a crushed, air-dried and homogenised soil sample into a Soxhlet extraction thimble and record the weight (M_1 g). See note a.	(a) For ease of weighing, the extraction thimble may be placed into a small clean beaker. For high-level contaminated soil samples, smaller quantities may need to be taken, see sections 1 and 2.4.
8.1.2	Cautiously spike the sample by adding 1.00 ± 0.05 ml of working deuterated surrogate standard solution (5.6) (i.e. 100 μg of deuterated *p*-terphenyl) to the soil contained in the thimble, see note b.	(b) A small piece of white tissue paper placed above the sample will ensure the soil remains in the thimble.
8.1.3	Place the extraction thimble into a clean Soxhlet funnel. Add 120 ± 5 ml of dichloromethane (5.1) to a round-bottomed flask. Assemble the Soxhlet apparatus and extract the spiked soil for 6 hours, see note c.	(c) After 6 hours, the solvent in the reflux tube should be colourless. If after 6 hours, the solvent remains coloured, reflux for a further 1 hour. If the solvent in the reflux tube is still coloured after 7 hours of refluxing, then the solvent, thimble and extracted spiked soil are discarded and the extraction procedure is repeated using a smaller quantity of sample, see sections 1 and 2.4.
8.1.4	Allow the Soxhlet apparatus to cool to room temperature before removing the solvent.	
8.1.4.1	For high-level contaminated samples: Carefully, quantitatively transfer the solvent in the round-bottomed flask to a stoppered measuring cylinder. Rinse the flask with a small volume of dichloromethane (5.1) and	(d) This volume is used in the calculation.

add the solvent to the measuring cylinder. Stopper the cylinder and thoroughly mix the contents. Note the volume (V_1 ml). See note d. Alternatively, quantitatively transfer the solvent in the round-bottomed flask to a 100 ml volumetric flask. Rinse the round-bottomed flask with a small volume of dichloromethane and add the solvent to the volumetric flask. Make the volume to 100 ml with dichloromethane (5.1). Mix well. (In this case, V_1 = 100 ml). Go to section 8.2.1.

8.1.4.2 For low-level contaminated samples: Quantitatively transfer the solvent in the round-bottomed flask to a rotary evaporation apparatus (6.5). Rinse the flask with a small volume of dichloromethane (5.1) and add the solvent to the rotary evaporation apparatus. See note e. Reduce the volume to about 5 ml. See note f.

(e) An equivalent system may also be used.

(f) Do not allow the extract to become completely dry.

8.2 Clean-up procedure

8.2.1 A suitable aliquot of the extract solution is now transferred to a small clean glass beaker, see note g.

(g) Whilst the following procedures are well established, other procedures can be used provided the performance has been validated. Extract solutions, especially those contaminated with mineral oils, will require clean-up prior to GC analysis. However, it may not be necessary to carry out clean-up procedures on all samples.

8.2.1.1 For high-level contaminated samples: Pipette 5.00 ± 0.05 ml of the extract solution into a small clean glass beaker. A different volume may be used, but record the volume (V_2 ml). Go to section 8.2.2.

8.2.1.2 For low-level contaminated samples: Quantitatively transfer all of the extract solution from section 8.1.4.2 to a small clean glass beaker. Rinse the rotary evaporation apparatus with a small volume of dichloromethane (5.1) and add the solvent to the beaker.

8.2.2 Add 0.5 g of activated alumina (5.9) to the

(h) The following procedures and

beaker, see note h, and swirl the contents. Allow the solvent to evaporate. Set up a glass-fritted chromatography column (6.8) containing activated silica gel (5.10) to a depth of 60 mm, covered by activated alumina (5.9) to a depth of 30 mm. Condition the column by passing 20 ml of pentane (5.11) through the column, see note i. Discard the eluate.

respective amounts are based on 5 ml volumes being taken. If larger volumes are used the quantities of alumina and silica gel should be increased proportionately.

(i) At this stage do not allow the meniscus of the pentane to run below the surface of the alumina.

8.2.3 Transfer the alumina residue from the beaker to the top of the column (6.8) containing the alumina and silica gel and elute with 20 ml of pentane, see note i. Discard the eluate. Place a clean glass rotary evaporation flask beneath the column and elute the PAHs from the column with 25 ml of dichloromethane (5.1). Collect the eluate. Quantitatively transfer the extract solution to a rotary evaporation apparatus (6.5). Rinse the flask with a small volume of dichloromethane (5.1) and add the solvent to the apparatus, see note e, and reduce the volume to 1.00 ml (i.e. V_3 = 1 ml). Alternatively, reduce the volume to an appropriate volume greater than 1 ml and record the volume, V_3 ml, see note j.

(j) The volume of the evaporated solution is used in the calculation.

8.2.4 If the solution has been evaporated to 1.00 ml, quantitatively transfer all of it a GC vial (6.5). If not, transfer 1.00 ± 0.01 ml of the evaporated solution to a GC vial (6.5). Add 200 ± 2 µl of working deuterated PAH internal standard (5.4) to the GC vial, see note k. Seal the vial tightly with a crimp top. Thoroughly mix the resulting solution.

(k) The optional addition of 100 ± 1 µl of dichloromethane (5.1) ensures that the total volume is equivalent to the volumes of the calibration solutions, although this is not strictly necessary as internal standard ratios are used.

8.2.5 The extract solutions are now ready for the chromatographic determination.

8.3 Calibration

8.3.1 A calibration graph of the ratio of PAH determined to internal standard peak height or peak area against mass of PAH in sample injected is constructed either manually or via the data handling system. The original sample concentration is calculated from the graph taking into account the sample volume

(m) Since the deuterated PAH internal standard solution is added after extraction, correction for incomplete recoveries may need to be made, where appropriate. See section 9 and Appendix C.

extracted, sample volume injected and any dilutions that may have been used, see note m.

8.4 Analytical quality control

8.4.1 Blank samples:
For blank samples follow the procedures described in sections 8.1.2 to 8.2.5, but using an appropriate material, ideally, similar in nature to the soil matrix being determined and containing negligible amounts of PAHs.

8.4.2 Analytical quality assurance samples:
For analytical quality assurance samples follow the procedures described in sections 8.1.2 to 8.2.5, but using an appropriate certified reference material or an in-house reference material, ideally, similar in nature to the soil matrix being determined and containing similar amounts of PAHs.

---

9 Calculations

The mass chromatograms for individual PAHs are used to establish retention times and appropriate retention time windows. The mass chromatograms are then integrated and the peak area/mass/time data used for subsequent calibration and quantification.

In order to obtain correct integration of the chromatographic peaks, adequate resolution of all the individual PAHs should be achieved. A calibration solution should be used to demonstrate suitable chromatographic separation, especially with respect to, for example, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene. A typical chromatogram of selected PAHs showing their peak separation is shown in Figure 2. A typical chromatogram for an extracted soil sample is shown in Figure 3.

The recovery of the added deuterated *p*-terphenyl surrogate standard is determined for each sample. If the recovery falls outside an acceptable range a further sub-sample should be extracted and analysed. If the recovery repeatedly falls below the acceptable range, further investigations should be undertaken to ascertain the cause, or a different method considered. If recovery correction were to be considered, recoveries based solely on the use of added deuterated *p*-terphenyl should not be employed to establish recoveries of all the PAHs determined. See Appendix C.

9.1 Relative response factors

Relative response factors (RRF) for each PAH are calculated using the following equation:

$$RRF = \frac{\text{Peak area of PAH x mass of internal standard in GC vial}}{\text{Peak area of internal standard x mass of PAH in GC vial}}$$

The average relative response factor is then calculated as the mean of the response factors obtained for each of the calibration standard solutions. The percentage relative standard deviation should also be determined and be within acceptable limits for the calibration to be deemed valid.

Alternatively, the data handling system may be used to produce a calibration graph for individual PAHs.

9.2 PAHs in samples

If the procedures described in section 8 are followed and M_1 g of soil are taken and made to V_1 ml, and V_2 ml are taken for clean-up and reduced to V_3 ml, then the equivalent amount of soil (M_e) in the GC vial is given by

$$M_e = \frac{M_1 \times V_2 \times V_3}{V_1} \quad g$$

Depending upon the amounts taken, the value of M_e may be between 0.5 - 10 g.

The amount of PAH (A_{PAH} µg) in the GC vial can be obtained from the calibration graph; hence the concentration, C, of PAH in the soil taken for analysis is given by

$$C = A_{PAH} / M_e \quad \mu g\ g^{-1} \quad (\text{or } mg\ kg^{-1})$$

This value may then need to be converted and expressed on the basis of the sample submitted to the laboratory or on a dry-weight basis.

9.3 Recovery of deuterated surrogate standard

In a similar manner, the per cent recovery of the deuterated surrogate standard can be determined. Following the procedures described in section 8, the equivalent amount of deuterated surrogate standard (S_e) in the GC vial is given by

$$S_e = \frac{100 \times V_2 \times V_3}{V_1} \quad \mu g$$

Where the spiking amount from section 8.1.3 is 100 µg. Depending upon the volumes taken, the value of S_e may be between 5 - 100 µg.

The amount of deuterated surrogate standard (As µg) in the GC vial can be obtained from the calibration graph, hence the percent recovery of surrogate standard, Rs, is given by

$$Rs = As \times 100 / S_e$$

Table 2 List of compound numbers and molecular masses

Compound	Compound number*	Molecular mass (Daltons)
naphthalene-d_8	IS1	136.1128
naphthalene	1	128.0624
acenaphthene-d_{10}	IS2	164.1410
acenaphthylene	2	152.0625
acenaphthene	3	154.0782
fluorene	4	166.0782
phenanthrene-d_{10}	IS3	188.1410
phenanthrene	5	178.0782
anthracene	6	178.0782
fluoranthene	7	202.0782
pyrene	8	202.0782
cyclopenta[*c*,*d*]pyrene	9	226.0782
chrysene-d_{12}	IS4	240.1692
benz[*a*]anthracene	10	228.0936
chrysene	11	228.0936
perylene-d_{12}	IS5	264.1692
benzo[*b*]fluoranthene	12	252.0936
benzo[*k*]fluoranthene	13	252.0936
benzo[*e*]pyrene	14	252.0936
benzo[*a*]pyrene	15	252.0936
indeno[*1,2,3-cd*]pyrene	16	276.0939
dibenz[*a,h*]anthracene	17	278.1095
benzo[*g,h,i*]perylene	18	276.0939
anthanthrene	19	276.0939
p-terphenyl-d_{14}	S	230.1974

* This number is used in the chromatograms and Appendices A and B.
IS = internal standard.
S = surrogate standard.

Figure 1 Mass spectrum of benzo[*a*]pyrene

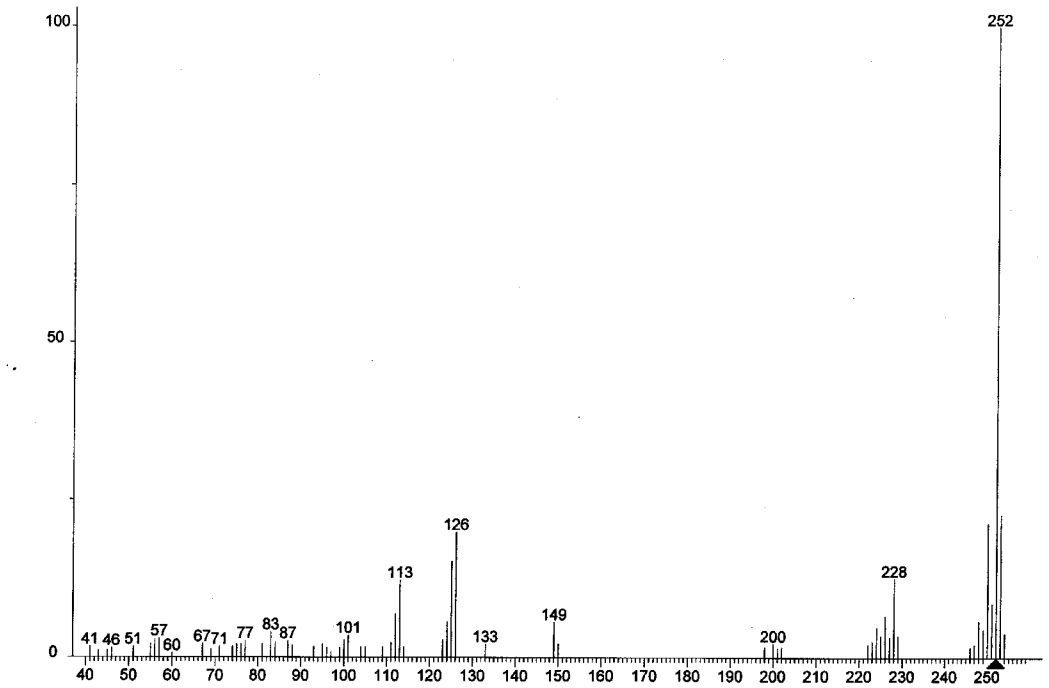


Figure 2 Gas chromatogram of selected PAHs with deuterated internal standard demonstrating peak separation

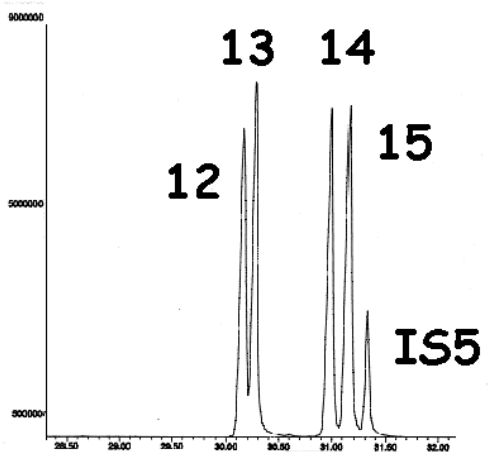
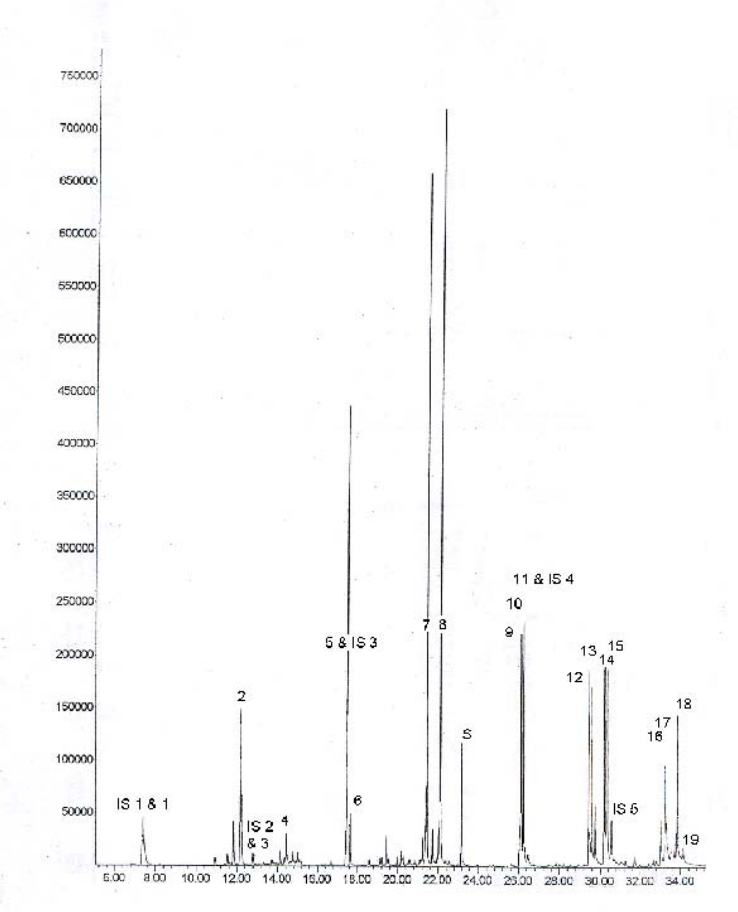
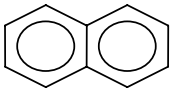


Figure 3 Typical gas chromatogram of an extracted sample

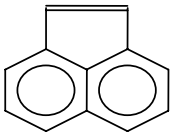


Appendix A Structures of PAHs determined by this method

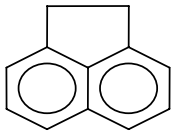
(See Table 2 for compound numbers and identification)



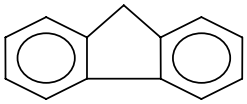
1



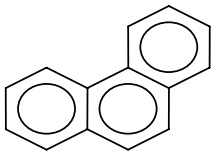
2



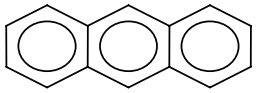
3



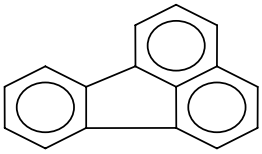
4



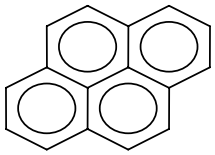
5



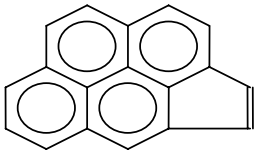
6



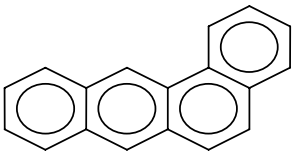
7



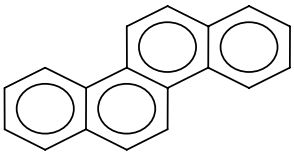
8



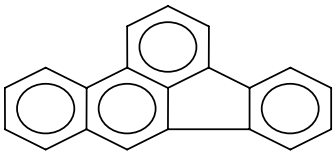
9



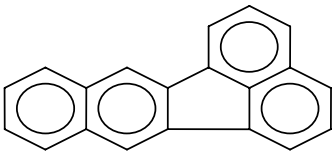
10



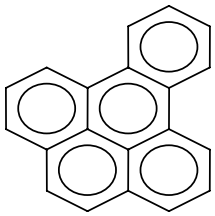
11



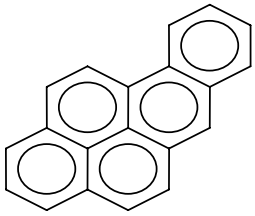
12



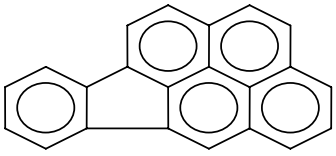
13



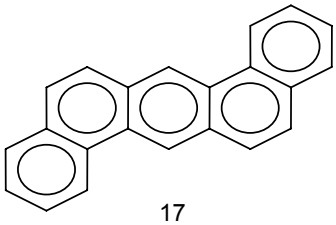
14



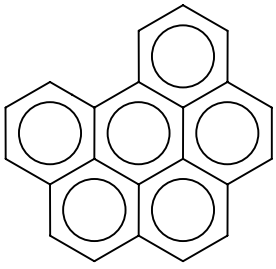
15



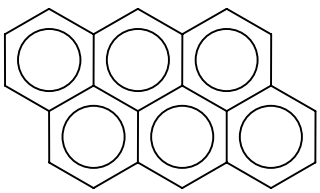
16



17



18



19

Appendix B Performance data

The performance data are based on the analysis of 20 replicate determinations using a proficiency-testing scheme air-dried contaminated soil. Sample extracts were not subjected to the clean-up procedure described in section 8.2. In addition, statistical outlier tests were not performed on the data.

Number	PAH	Concentration range (mg kg^{-1})	Mean concentration (mg kg^{-1})	Standard deviation (mg kg^{-1})	Relative standard deviation (%)
1	naphthalene	15.2 – 24.0	18.5	2.8	15
2	acenaphthylene	39.4 –71.2	54.6	8.9	16
3	acenaphthene	0.0 – 1.4	0.7	0.4	59
4	fluorene	10.2 – 15.2	12.3	1.2	10
5	phenanthrene	130.8 – 178.7	145.5	12.1	8
6	anthracene	36.2 – 59.5	46.2	6.3	14
7	fluoranthene	187.8 – 278.0	222.0	30.0	14
8	pyrene	235.3 – 329.5	262.2	22.3	8
9	cyclopenta[*c,d*]pyrene	14.4 – 19.3	16.7	1.2	7
10	benz[*a*]anthracene	86.6 – 120.3	98.3	8.7	9
11	chrysene	119.6 – 165.8	135.8	11.2	8
12	benzo[*b*]fluoranthene	150.2 – 206.6	170.7	14.3	8
13	benzo[*k*]fluoranthene	52.8 – 78.6	61.1	6.5	11
14	benzo[*e*]pyrene	87.5 – 118.3	98.0	8.0	8
15	benzo[*a*]pyrene	95.9 – 132.9	107.9	9.3	9
16	indeno[*1,2,3-cd*]pyrene	93.6 – 126.2	105.4	8.8	8
17	dibenz[*a,h*]anthracene	22.8 – 30.1	25.7	1.9	8
18	benzo[*g,h,i*]perylene	87.4 – 120.0	99.8	9.0	9
19	anthanthrene	19.0 – 27.0	21.2	1.9	9

Data provided by Ruth Woodhead of Advantica Technologies Ltd, Loughborough.

True or absolute concentrations of individual PAHs were not known, and hence an estimate of bias was not determined. However, results based on the analysis of a similar sample, using very similar procedures, gave the following values

PAH	**Value*** ($mg\ kg^{-1}$)	**Mean determined value** ($mg\ kg^{-1}$)	**Bias** (%)
naphthalene	31.3	28.94	8
acenaphthylene	(123)	121.67	1
acenaphthene	50.4	39.84	21
fluorene	235	198.39	16
phenanthrene	1040	1139.84	10
anthracene	205	185.99	9
fluoranthene	538	546.9	2
pyrene	592	619.69	5
benz[*a*]anthracene	181	186.35	3
chrysene	191	194.62	2
benzo[*b*]fluoranthene	(191)	174.04	9
benzo[*k*]fluoranthene	(75)	71.56	5
benzo[*a*]pyrene	161	138.79	14
indeno[*1,2,3-cd*]pyrene	95	126.11	33
dibenz[*a,h*]anthracene	(23)	21.11	8
benzo[*g,h,i*]perylene	99	104.42	6

* Figure in brackets is an indicative value, figure not in brackets is an assessed value.
Data provided by AES Ltd.

It is recognised that this sample comprises only one matrix, containing the PAHs listed, but possibly others not determined, at one concentration level and that other matrices containing different levels of concentrations may give different bias values.

Based on the analysis of the low level check sample (5.8) the method has been shown to achieve limits of detection lower than 1 $mg\ kg^{-1}$ for the majority of PAHs listed. However, laboratories should determine their own limits of detection.

Appendix C Quantification

In order to determine performance data it is important that the method described in this booklet and used by a laboratory is validated in that laboratory by examining samples of the matrix of interest. The recovery of the PAHs determined by this method is generally high. Data are available to show that recoveries for *p*-terphenyl vary between 72 - 80 %, with a mean of 76 % and a standard deviation of 6%. It is recognised that this method will produce different values of recovery for different soil matrices.

The analysis of an appropriate certified reference material enables an estimate of bias to be determined. A certified reference material should be analysed using the entire method as used for samples. In addition, the certified reference material should be appropriate to the matrix and concentration of PAHs in the sample, and ideally contain all PAHs of interest.

Where appropriate certified reference materials are not available, or when recovery information is required on different sample matrices, an alternative approach can be adopted. This approach may involve spiking a sample, prior to extraction, with individual (deuterated) PAHs and calculating the recoveries, based on the comparison of results from the extracted PAH-spiked matrix with those of an un-extracted calibration solution. The PAHs used should be reflective of the PAHs being determined. With the recovery values determined, consideration can then be given to ascertaining whether recovery corrections should be carried out.

The specific or individual PAHs should be of similar structure and possess similar properties to the PAHs being determined. They should also possess chromatographic properties similar to the PAHs being determined and should be readily discernible from the PAHs of interest. In addition, they should not be present in the samples being analysed. Typically, deuterated PAHs are suitable and Table 2 includes a selection found to be suitable.

Address for correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts at the address given below.

Standing Committee of Analysts
Environment Agency (National Laboratory Service)
Wheatcroft Office Park
Landmere Lane, Edwalton
Nottingham, NG12 4DG

Standing Committee of Analysts
Members assisting with this method

M Ashmore
R Arya
I Barnabas
F Bilby
D Davidson
H Davidson
S Gardner
J Green
D McMullan
S P Owen
M Rose
S P Scott
D Smith
P J Whittle
J Williams
D Wood
R J Woodhead
J Quick

CONTACTS:

ENVIRONMENT AGENCY HEAD OFFICE

Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol BS32 4UD
Tel: 01454 624 400 Fax: 01454 624 409

www.environment-agency.gov.uk
www.environment-agency.wales.gov.uk

ENVIRONMENT AGENCY REGIONAL OFFICES

ANGLIAN
Kingfisher House
Goldhay Way
Orton Goldhay
Peterborough PE2 5ZR
Tel: 01733 371 811
Fax: 01733 231 840

MIDLANDS
Sapphire East
550 Streetsbrook Road
Solihull B91 1QT
Tel: 0121 711 2324
Fax: 0121 711 5824

NORTH EAST
Rivers House
21 Park Square South
Leeds LS1 2QG
Tel: 0113 244 0191
Fax: 0113 246 1889

NORTH WEST
PO Box 12
Richard Fairclough House
Knutsford Road
Warrington WA4 1HG
Tel: 01925 653 999
Fax: 01925 415 961

SOUTHERN
Guildbourne House
Chatsworth Road
Worthing
West Sussex BN11 1LD
Tel: 01903 832 000
Fax: 01903 821 832

SOUTH WEST
Manley House
Kestrel Way
Exeter EX2 7LQ
Tel: 01392 444 000
Fax: 01392 444 238

THAMES
Kings Meadow House
Kings Meadow Road
Reading RG1 8DQ
Tel: 0118 953 5000
Fax: 0118 950 0388

WALES
Rivers House/Plas-yr-Afon
St Mellons Business Park
Fortran Road
St Mellons
Cardiff CF3 0EY
Tel: 029 2077 0088
Fax: 029 2079 8555

ENVIRONMENT AGENCY
GENERAL ENQUIRY LINE
0845 9 333 111

ENVIRONMENT AGENCY
FLOODLINE
0845 988 1188

ENVIRONMENT AGENCY
EMERGENCY HOTLINE
0800 80 70 60

ENVIRONMENT AGENCY