Guidelines for the determination of polycyclic aromatic hydrocarbons (PAH) in sediment

1. Introduction

This Technical note provides advice on the analysis of polycyclic aromatic hydrocarbons (PAH) in total marine sediments, sieved fractions, and suspended particulate matter. The analysis of PAH compounds in sediments basically includes extraction with organic solvents, clean-up, and separation through high performance liquid chromatography (HPLC) with ultraviolet (UV) or fluorescence detection or gas chromatographic separation (GC) with flame ionization (FID) or mass spectrometric (MS) detection (Kassim & Barcelo, 2009, 1989; Wise *et al.,* 1995).

All steps of the procedure are susceptible to insufficient recovery and contamination. Quality control measures are recommended in order to regularly monitor the performance of the method. These guidelines are intended to encourage and assist analytical chemists to critically review their methods and to improve their procedures and quality assurance measures, if necessary.

These guidelines are not intended as complete laboratory manual. If necessary, guidance should be sought from specialized laboratories. Laboratories should demonstrate validity of each methodological step.

Moreover, use of an alternative method, carried out concurrently to the routine procedure, is recommended for validation.

Contracting parties should follow the HELCOM monitoring guideline but minor deviations from this are acceptable if the method achieves comparable results. Validation of the adopted method needs to be performed on the relevant matrix and concentration range e.g. by taking part in intercomparison studies or proficiency testing schemes.

2. Sampling and storage

The major criterion for successful sediment sampling is to ensure undisturbed sample stratification. (For further details about sampling, see Annex B-13, Appendix 3 "Technical note on the determination of heavy metals in marine sediments" of the HELCOM COMBINE manual.)

Plastic materials should not be used for sampling and storage due to the risk of adsorption of PAH compounds onto the container material. Samples should be transported in closed containers and preferentially at temperatures below 10 °C. The samples should be stored at 4 °C as soon as possible, but at least if they have not been analysed within 48 hours after collection (short-term storage). For long-term storage over several months the samples should be frozen below -20 °C or dried (Law and de Boer, 1995). When drying, avoid methods with substantial risk of losing volatile substances (see Chapter 4: Pretreatment).

PAH compounds are sensitive to photo-degradation and, thus, exposure to direct sunlight or other light sources should be avoided during storage as well as during all steps of sample preparation (Law and Biscaya, 1994). The use of amber glassware is strongly recommended.

3. Blanks and contamination

Basically, care should be taken to avoid contaminations during all steps of the analytical chain, including sampling, extraction and clean-up.

In order to reduce blank and sample contaminations to a minimum it is strongly recommended to pretreat all used glassware, solvents, chemicals, adsorption materials, etc., as follows:

- Glassware should be thoroughly washed with detergents and can be furthered cleaned, other than calibrated instruments, by heating at temperatures > 250 °C. The glassware should be rinsed with an organic solvent prior to use.
- All solvents should be analyzed for impurities by concentrating to 10 % of the regular final volume. This concentrate is then analysed similarly to a sample by HPLC or GC. The solvent blank should not contain target analytes or other interfering compounds in higher concentrations than specified by the laboratory.
- All chemicals and adsorption materials should be analyzed for impurities and purified (e.g., by heating or extraction), if necessary. Soxhlet thimbles should be pre-extracted. Glass fiber thimbles are preferred over paper thimbles. Alternatively, full glass Soxhlet thimbles, with a G1 glass filter at the bottom, can be used.

Storage of these supercleaned materials for a longer period is not recommended, as laboratory air might contain PAH compounds which can adsorb onto these materials. Therefore, contaminated blank samples might occur despite precautionary measures due to contamination from the air. Volatile compounds, in particular naphthalene and phenanthrene, are usually the most common contaminants in blank samples (Gremm and Frimmel, 1990). Therefore, if possible, critical steps should be done in a clean bench.

4. Pretreatment

The samples should be thoroughly homogenized before subsampling for analysis. The amount of samples usually depends on the expected concentrations. For the marine environment, the amount of sample should be equal to an amount representing 50–100 mg of organic carbon.

PAHs can be extracted from wet or dried samples. However, storage, homogenization and extraction are easier to handle with dried samples.

Drying the samples at ambient or elevated temperatures as well as freeze-drying may alter the concentrations, e.g., by contamination or loss of compounds through evaporation (Law *et al.,* 1994). Therefore, potential losses and contaminations should be analyzed in advance, e.g. by exposing 1–2 g CIS-bonded silica to the drying conditions and subsequent extraction and analysis (clean-up can be omitted) (Smedes and de Boer, 1998). For evaluation of potential losses, analytes identical or similar to PAHs need to be added to the material. However, bear in mind that added analytes can behave differently from analytes that have interacted longer with the matrix material and therefore may be sorbed more strongly. To avoid contamination during freeze-drying, placing a lid with a hole of about 3 mm in diameter on the sample container is suggested.

Chemical drying of samples can be performed by grinding with Na_2SO_4, or $MgSO_4$ until the sample reaches a sandy consistency. It is essential that several hours elapse between grinding and extraction to allow for complete dehydration of the sample. Residual water will decrease extraction efficiency.

5. Extraction and clean-up

Exposure to light must be kept to a minimum during extraction and further handling of the extracts (Law and Biscaya, 1994). The most photo-sensitive PAH is benzo[*a*]pyrene, followed by anthracene. Photo-degradation occurs more rapidly in the absence of a sample matrix. Therefore, the PAH standard solution should be regularly analyzed for their PAH content.

Other extraction and clean-up methods than those described below may be used, provided that the methods have been tested and found equivalent to established methods regarding e.g. recovery. For naphthalene, which can easily be lost in several steps during sample preparation, headspace or purge and trap analysis might provide a suitable alternative to extraction methods.

5.1 Extraction of wet sediments

A commonly used and very efficient method for PAH extraction from sediments is alkaline saponification. This method requires only a short extraction time (approximately 1.5 hrs under the reflux) and it also eliminates organic sulphur and other interfering compounds such as lipids. The resulting extract is easy to clean up.

Wet sediments could also be extracted using a stepwise procedure by mixing with organic solvents. Extraction is enhanced by shaking, Ultra Turrax mixing, ball mill tumbling or ultrasonic treatment. Water-miscible solvents, such as acetone, methanol, or acetonitrile, are used in the first step. The extraction efficiency of the first step will be low as there is a considerable amount of water in the liquid phase. In a second step a less polar solvent / solvent mixture such as acetone/hexane should be used. It has to be kept in mind that hexane is a lot more toxic than similar solvents such as pentane, heptane, cyclohexane, isohexane. For sufficient extraction at least three subsequent extractions are needed. The contact time with the solvent should be long enough to allow complete desorption of the PAH compounds from the sediment pores. The contact time might be up to 24 hours which basically depends on the type of sediment.

The required contact time of the sediment with the solvent can be reduced by using microwave extraction, supercritical fluid extraction, Soxhlet extraction or pressured liquid extraction (e.g. ASE). Soxhlet or ASE extraction of wet sediments should be conducted in two steps. First, a polar solvent, such as acetone, is

used to extract the water from the sediment. In a second step the collecting flask is replaced and the extraction will be continued using a less polar solvent or solvent mixture such as acetone/hexane or toluene. Thereafter, the extracts will be combined.

To separate the water and keep the PAHs in a solvent that is compatible with the continued analysis different methods can be used. For example, water will be added to the combined extracts and the PAH compounds will be extracted to a non-polar solvent. Another possibility is to add Na_2SO_4 to bind water.

Extraction should be conducted with a sufficient number of extraction cycles. Extraction efficiency should be analyzed for different types of sediments through a second extraction step. The extracts will be analysed separately and compared. A recovery of more than 90 % during the first extraction step is considered adequate.

5.2 Extraction of dry sediments

The methods described above can also be used for dried sediments. However, pressurized liquid extraction (PLE) is the most frequently applied technique to extract PAH compounds from dried sediments and it is recommended over mixing methods, in particular for dry samples.

Medium-polar solvents such as dichloromethane or toluene or mixtures of polar and non-polar solvents can be used. When using dichloromethane, losses of PAHs have occasionally been observed. Although toluene is not favored due to its high boiling point, it should be chosen when sediment samples could contain soot particles. For routine marine samples, the use of a mixture of a polar and a non-polar solvent such as acetone/hexane (1/3, v/v) is recommended.

Extraction should be conducted with a sufficient number of extraction cycles. Extraction efficiency should be analyzed for different types of sediments through a second extraction step. The extracts will be analysed separately and compared. A recovery of more than 90 % during the first extraction step is considered adequate.

5.3 Clean-up

The crude extracts usually require clean-up to remove co-extracted compounds (Wise *et al.,* 1995). Due to chlorophyll-like compounds extracted from the sediment, the raw extract is usually colored and also contains sulphur and sulphur-containing compounds, oil and other natural and anthropogenic compounds. Selection of the appropriate clean-up method depends on the subsequent instrumental method to be used for analysis.

Prior to the clean-up, the sample must be concentrated and polar solvents used during extraction should be removed. The recommended acetone/hexane mixture will result in hexane after evaporation due to the formation of an azeotrope if hexane is abundant. Evaporation can be done using either a Kuderna-Danish,a rotary evaporator or other evaporation system (e.g. parallel evaporation). In particular, upon using rotary or parallel evaporation, ambient or mild vacuum conditions and a water bath temperature of not more than 30 °C should be applied and care should be taken to stop evaporation at a sample volume of about 2 ml or by using automatic systems. For further volume reduction a gentle stream of nitrogen can be applied. The extract should never be evaporated to dryness.

To remove polar interferences from the extract the following chromatographic procedures can be used:

- desactivated aluminium oxide (10 % water), eluted with hexane – in particular upon using HPLC-Fluorescence for subsequent analysis
- silica or modified silica columns, e.g., aminopropylsilane or cyanopropyl phase eluted with toluene or a semipolar solvent mixture such as hexane/acetone (95/5, v/v) or hexane/dichloromethane (98/2, v/v)

- Gel permeation chromatography (LC-GPC) can be used to remove high molecular weight material and sulphur from the extracts

For GC-MS analysis sulphur should be removed from the extracts in order to protect the detector. This can be achieved by the addition of copper powder, wire or gauze during or after organic solvent extraction. Ultrasonic treatment might improve the removal of sulphur. Alternative methods to the use of copper were reported by (Smedes and de Boer, 1998).

Analysis by GC-FID or HPLC-UV requires a more elaborate clean-up. Aliphatic hydrocarbons originating from mineral oil interfere with the flame ionization detection. They can be removed from the extract by fractionation over columns filled with activated aluminium oxide or silica as described above. However, a first fraction is eluted with only hexane and then rejected. The PAHs elute in the second fraction with a more polar solvent, e.g., diethylether or acetone/hexane. When applying fractionation, the elution pattern has to be checked frequently and in the presence of sample matrix, as this can partially deactivate the clean-up column resulting in earlier elution of the PAH compounds than in the standard solution.

Alkylated PAHs are difficult to remove from extracts by column clean-up. When excessive amounts of these compounds are present, they may interfere with HPLC analysis and such samples should be better analysed by GC-MS. An alternative could be preparative HPLC fractionation using a normal phase silica, cyanopropyl or aminopropyl column.

After clean-up, the eluate or fractions must be concentrated, to e.g. 1 ml. Any concentration method should be conducted carefully as described above as high volatility of the PAH compounds may result in losses during evaporation. HPLC and GC require different solvents for injection of the extract. With the methods suggested, obtained extracts are usually in non-polar solvents. However, for HPLC analysis even small amounts of non-polar solvents may result in a shift of retention time and broadening of the peaks (Reupert and Brausen, 1994). Acetonitrile should be used preferentially as the PAH exhibit higher stability in acetonitrile as compared to e.g., methanol. Hexane can be removed by the addition of 5 ml acetonitrile for each ml of extract and subsequent evaporation to 1–2 ml. Azeotropic evaporation leaves only acetonitrile. During solvent exchange, evaporation to dryness should be avoided.

Azeotropic exchange can also be applied the other way around. In that case, 5 ml hexane must be added for each ml of acetonitrile.

For GC methods, *iso*-octane or toluene are suitable solvents for injection and can be added as keeper before evaporation to the required volume.

6. Chromatographic determination

The separation of PAHs should be optimized for at least the compounds listed in Annex B-13 (Appendix 1, Table 1) (Keith and Telliard, 1979). Separation should not only be optimized for a standard solution but also for a sample, as samples often contain several non-target PAHs that should be separated from the target compounds, if possible. In addition, sample extracts can be affected by remaining matrix effects, despite clean-up.

Basically and in particular for the parent PAH both HPLC-Fluorescence and GC-MS analyses are considered to be equally valid methods. However, with respect to the alkylated PAH species satisfactory analysis is often not obtained using HPLC. This is particularly relevant as alkylated PAH compounds are of increasing interest. Therefore, use of GC-MS analysis is recommended.

Table 1 Compounds of interest for environmental monitoring for which the guideline applies.

Compound	MW	Compound	MW

Naphtalene	128	Fluoranthene	202
C1-Naphtalenes	142	Pyrene	202
C2-Naphtalenes	156	Benzo[a]anthracene	228
C3-Naphtalenes	170	Chrysene	228
Acenaphthylene	152	Benzo[a]pyrene	252
Acenaphthene	154	Perylene	252
Fluorene	166	Indeno[1,2,3-cd]pyrene	276
Phenanthrene	178	Benzo[k]fluoranthene	252
Anthracene	178	Benzo[ghi]perylene	276
C1-Phenanthrene/Anthracene	196	Dibenzo[ah]anthracene	278
C2-Phenanthrene/Anthracene	206		
C3-Phenanthrene/Anthracene	220		

6.1 High performance liquid chromatography

For HPLC analysis of PAH, a binary gradient is necessary to achieve proper compound separation.

Using HPLC and measuring concentrations with the peak height, a 50 % valley should be considered as adequate separation.

Solvents should be degassed through an online degassing system in order to allow proper operation of the high pressure pump. Sample injection should be carried out with an autosampler. In addition, a thermostated column compartment (10–30 °C) should be used as retention time and resolution can be affected by varying the temperature.

6.1.1 Columns

The column specifications are:

- stationary phases: e.g., octadecylsilane (RP-18), or special PAH column material;
- length: 15–25 cm;
- inner diameter: 4.6 mm or less;
- particle size: 5 µm or less.

If the dimensions of the detector cell and the tubings are appropriate, columns with diameters smaller than 4.6 mm can be chosen in order to reduce the flow of the eluent and, thus, to save solvent. In this case the amount of sample injected should also be reduced to e.g. 25–50 µl for a 4.6 mm column or 10 to 20 µl for a 3 mm column.

6.1.2 Gradient Elution

For elution, e.g. methanol/water or acetonitrile/water can be applied. The use of acetonitrile allows higher flow rates, with the disadvantage of having higher health risks than methanol.

A typical elution gradient with a flow rate of 1–1.5 ml min-1 for a 4.6 mm column is:

- start at initially 50 % methanol/water or acetonitrile/water

- run to 100 % methanol or acetonitrile in 40 minutes
- remain for 20 minutes
- back to the initial conditions for about 5 minutes
- equilibrium time of about 5 to10 minutes (3–5 times the dead volume) prior to the next injection,

100 % methanol or acetonitrile may not be sufficient to elute all non-target compounds from the column. In this respect, a further elution step using acetone/methanol (1/1) or acetonitrile/acetone (1/1) can be applied. A ternary gradient is then necessary.

In order to obtain reproducible retention times, the equilibrium time after each run should be constant. Therefore, automatic injection is strongly recommended.

6.1.3 Detection
For the detection of PAHs, the more sensitive and selective fluorescence detector is preferred over a UV detector. The excitation and emission wavelengths should be programmable to allow the detection of PAHs at their optimum wavelength (Reupert and Brausen, 1994; ISO, 1995).

However, when PAHs elute close to each other, wavelength switching cannot be carried out between these peaks and a wavelength pair appropriate for the respective compounds has to be chosen. The use of two detectors in series, or running the analysis twice with different wavelength programmes, can minimize the need for such compromises.

As the fluorescence signals of some PAHs can decrease by up to a factor of ten in the presence of oxygen, the eluents must be degassed thoroughly. Therefore, instruments with online degassing systems are strongly recommended. In addition, PTFE tubings should not be used as this material is permeable to oxygen and allows oxygen to enter the system again. The use of stainless steel or PEEK (polyetheretherketone) tubing is recommended.

Acenaphthylene is not detectable with fluorescence and, therefore, a UV or diode-array detector should be used for detection.

Another possible detection technique is mass spectrometry, where isotopically labeled compounds are used as internal standards.

6.1.4 Identification
The individual PAHs are identified by comparing the retention time of the substance in a sample with that of the respective compound in a standard solution analyzed under the same conditions. It is recommended to confirm the results by using other suitable wavelength for UV-absorption or excitation and emission wavelengths for fluorescence detection.For HPLC analysis, reproducibility of retention times should be within ±1 minute.

6.2 Gas chromatography

6.2.1 Columns
Column dimensions for the determination of PAHs should be the following:

- length: minimum 25 m;
- inner diameter (i. d.): maximum 0.25 mm;
- film thickness: between 0.2 μm and 0.4 μm;
- stationary phases: A wide range of non-polar or slightly polar stationary phases can be used for the separation of PAHs, e.g., a 5 % phenyl-substituted methyl polysiloxane phase.

Better resolution can be obtained by increasing the length and reducing the inner diameter to 0.20 mm or less. However, below a diameter of 0.15 mm, the carrier gas pressure rises to values above 500 kPa, which are often not compatible with regular GC equipment. Also, the risk of leakages increases.

6.2.2 Carrier gas

Preferentially, helium should be used as carrier gas for GC-MS. Upon using columns with very small inner diameters, the use of hydrogen is essential.

The linear gas velocity should be optimized. Appropriate settings for 0.25 mm i.d. columns range from 20 to 40 cm s^{-1} and for 0.15 mm i.d. columns from 30 to 50 cm s^{-1}.

6.2.3 Injection techniques

Sample injection should be carried out with an autosampler. The two systems commonly used are splitless and on-column injection. Other techniques such as temperature-programmed or pressure-programmed injection may have additional advantages, but should be thoroughly optimized before use. Due to their high boiling points, on-column injection is recommended for separation of the PAH compounds.

6.2.4 Temperature programming

The temperature program must be optimized for sufficient separation of the PAH compounds. For GC-MS analysis peak areas are generally used and a 10 % valley would represent a good separation. Less resolved peaks may also be quantified - e.g. by dropping perpendiculars to the baseline-, but increasing errors may result.

In addition to a reproducible temperature program, a fixed equilibration time is important for a correct analysis and constant retention times.

6.2.5 Detection

The most frequently used detector for GC analysis of the PAH compounds is a mass spectrometric detector operating in the Selected Ion Monitoring (SIM) mode and with electron impact ionization (EI) as the ionization method. The selectivity of a mass spectrometric detector is excellent and the chromatographic noise of a standard is similar to that of a sample. However, major drawbacks are the matrix-dependent response and the convex calibration curves that both often occur and make quantification difficult which, however, can be overcame with tandem mass spectrometry (GC-MS/MS).

 Another technique for PAH identification is the full-scan MS using an ion trap operating with the same sensitivity as SIM, but in full scan to give the best detection limits and compound identification for methylated PAHs, compared to quadrupole MS with multiple ion monitoring mode (Law et al, 2011). The use of a flame ionization detector (FID) is also possible, but since the selectivity of the FID is low, it is not recommended. In addition, isotopically labeled internal standards (see 8.5) cannot be used in combination with a FID.

6.2.6 Identification

For GC-MS analysis the presence of the characteristic mass fragments or mass transitions (GC-MS/MS) prove the presence of the particular PAH compound. Retention times should be reproducible within ±0.05 minutes.

7. Quantification

Automatically processed chromatograms should be reviewed if, e.g., the baseline is set correctly. Because the separation of the peaks is often incomplete in HPLC analysis, the use of peak heights is recommended for quantification. In case of GC techniques, the use of peak areas is recommended.

For calibration purposes a multilevel calibration with at least five concentration levels is recommended. The calibration curve should be linear and cover the working range. Usually, the response of FID, UV and fluorescence detectors exhibit linearity over a large range.

Since mass spectrometric detectors often lack sufficient linear response, the use of stable isotopes is a prerequisite. Furthermore, the response of PAHs in standard solutions is often much lower than in sample extracts. A combination of different methods, e.g., use of internal standards and standard addition, might give quantitative results.

Obtained calibrations should be regularly validated in terms of precision and accuracy.

Prior to running a series of samples and standards, the GC or HPLC systems should be equilibrated by injecting at least one sample extract. In addition, standards used for multilevel calibrations should be regularly distributed over the sample series so that matrix-and non-matrix-containing injections alternate. A sample series should include:

- a procedural blank;
- a laboratory reference material;
- at least five standards;
- one standard sample treated similarly to the samples for determination of the recovery.

The method for calculating the limit of determination should reflect the advice in Part B-4.2.3 (COMBINE manual).

The limit of quantification usually depends on the purpose of the investigation. The limit of quantification that can be achieved depends on the blank sample, the sample matrix, concentrations of interfering compounds, and the amount of sample. However, a limit of quantification of 2 ng g^{-1} (dry weight) or better should be attained for single compound analysis.

8. Quality Assurance

A number of measures should be taken to ensure sufficient quality of the analysis. Six main areas can be identified:

1. extraction efficiency and clean-up;
2. calibrant and calibration;
3. system performance;
4. long-term stability;
5. internal standards; and
6. Frequent participation in interlaboratory proficiency testing schemes (e.g. QUASIMEME two times a year, www.quasimeme.org).

8.1 Extraction efficiency and clean-up

Extraction efficiency and clean-up can be controlled by analysing reference materials (Annex B-7). To determine the recovery rates of the clean-up and concentration steps, it is recommended to pass a standard solution (see 8.5. INTERNAL STANDARDS) through the entire procedure. The addition of corresponding internal standards to the samples is preferred.

If major losses have occurred, the results should not be reported.

8.2 Calibrant and calibration

Basically, calibration solutions should be stored in ampoules at a cool, dark place. Weight loss during storage should be recorded for all standards.

For PAH determination preferentially calibration solutions from certified crystalline PAHs should be used. However, the laboratory should have the appropriate equipment and expertise to handle these hazardous crystalline substances. Alternatively, certified PAH solutions can be used. Preparation of two independent stock solutions allows cross-checks of the standard solutions if necessary.

8.3 System performance
The performance of the HPLC or GC system can be monitored through regularly analyzing the resolution of two closely eluting PAHs or chlorinated biphenyl compounds. A decrease in resolution indicates deteriorating HPLC or GC conditions.

The signal-to-noise ratio of a low concentrated standard can give information on the condition of the detector. For example, a dirty MS-source can be recognized by the presence of a higher background signal, together with a reduced signal-to-noise ratio if not used in the SIM mode.

8.4 Long-term stability
One laboratory reference sample should be included in each series of samples. A quality control chart should be recorded for selected PAH compounds, e.g., fluoranthene (stable results), pyrene (sensitive to quenching), benzo[a]pyrene (sensitive to light). If warning limits are exceeded, the method should be checked for possible errors and the obtained sample results should not be reported.

If available, a certified reference material (CRM) should be analysed regularly and in particular, if the procedure was changed.

8.5 Internal standards
Internal standards should be added to all standards and samples either in a fixed volume or by weight and should not interfere with the target analytes.

A number of deuterated PAH compounds were proven to be suitable for GC-MS as well as for HPLC analysis. For GC-MS analysis it is recommended to have internal standards corresponding to each analyte, e.g. by using isotopically labeled compounds. Otherwise, at least four internal standards representing the different ring-sizes of the PAH compounds should be added.

The following compounds can be used (Wise et al., 1995):

- for HPLC analysis: phenanthrene-d10, fluoranthene-d10, perylene-d12, 6-methyl-chrysene;
- for GC-MS analysis: naphthalene-d8, phenanthrene-d10, chrysene-d12, perylene-d12;
- for GC-FID analysis: 1-butylpropylene, m-tetraphenyl

After clean-up and before GC analysis, an additional internal standard can be added to evaluate the recovery of the internal standards added before clean-up.

8.6 Interlaboratory proficiency testing schemes
Each laboratory analysing sediments should participate in interlaboratory studies on the determination of PAH in sediments on a regular basis (e.g. QUASIMEME offers the possibility to take part twice a year, www.quasimeme.org).

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