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Part B

General guidelines on quality assurance for monitoring in the Baltic Sea

Annex B-13

Technical note on the determination of heavy metals and persistent organic compounds in marine sediments

Appendix 1
Technical note on the determination of polycyclic aromatic hydrocarbons (PAHs) in sediment

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ANNEX B-13 TECHNICAL NOTE ON THE DETERMINATION OF HEAVY METALS AND PERSISTENT ORGANIC COMPOUNDS IN MARINE SEDIMENTS

ANNEX B-13 APPENDIX 1. TECHNICAL NOTE ON THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN SEDIMENT

1. INTRODUCTION

This Technical Note provides advice on PAH analysis in total sediment, sieved fractions, and suspended particulate matter. The analysis of polycyclic aromatic hydrocarbons (PAHs) in sediments generally includes extraction with organic solvents, clean-up, and high performance liquid chromatography (HPLC) with ultraviolet or fluorescence detection or gas chromatographic separation (GC) with flame ionization (FID) or mass spectrometric (MS) detection (Fetzer and Vo-Dinh, 1989; Wise *et al.,* 1995). All steps in the procedure are susceptible to insufficient recovery and/or contamination. Quality control procedures are recommended in order to check the performance of the method. These guidelines are intended to encourage and assist analytical chemists to critically reconsider their methods and to improve their procedures and/or the associated quality control measures, where necessary.

These guidelines are not intended as a complete laboratory manual. If necessary, guidance should be sought from highly specialized research laboratories. Whichever procedure is adopted, each laboratory must demonstrate the validity of each step of its procedure. In addition, the use of a second (and different) method, carried out concurrently to the routine procedure, is recommended for validation. The analyses should be carried out by experienced staff.

2. SAMPLING AND STORAGE

The major criterion for successful sediment sampling is to guarantee a fairly undisturbed sample stratification. (For further details about sampling, see “Technical note on the determination of heavy metals in marine sediments”.) Plastic materials must not be used for sampling or storage owing to possible adsorption of the PAHs onto the container material. Samples should be transported in closed containers and at temperatures between 5 °C and 15 °C, preferably below 10 °C. If the samples are not analysed within 48 hours after collection, they must be stored at 4 °C (short-term storage). Storage over several months is only possible for frozen (i.e., below -20 °C) and/or dried samples (Law and de Boer, 1995).

As PAHs are sensitive to photo-degradation, exposure to direct sunlight or other strong light must be avoided during storage of the samples as well as during all steps of sample preparation, including extraction and storage of the extracts (Law and Biscaya, 1994). The use of amber glassware is strongly recommended.

3. BLANKS AND CONTAMINATION

The procedural detection limit is determined by the blank value. In order to keep the blank value as low as possible, PAHs or other interfering compounds should be removed from all glassware, solvents, chemicals, adsorption materials, etc., that are used in the analysis. The following procedures should be used:

- Glassware should be thoroughly washed with detergents and rinsed with an organic solvent prior to use. Further cleaning of the glassware, other than calibrated instruments, can be carried out by heating at temperatures > 250 °C.
- All solvents should be checked for impurities by concentrating the amount normally used to 10 % of the normal end volume. This concentrate can then be analysed by HPLC or GC and should not contain significant amounts of PAHs or other interfering compounds.
- All chemicals and adsorption materials should be checked 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. The storage of these supercleaned materials for a long period is not recommended, as laboratory air can contain PAHs that will be adsorbed by these materials. Blank values occurring despite all the above-mentioned precautions may be due to contamination from the air. The most volatile compounds will usually show the highest blanks (Gremm and Frimmel, 1990).

4. PRETREATMENT

Before taking a subsample for analysis, the samples should be sufficiently homogenized. The intake mass is dependent on the expected concentrations. For the marine environment, as a rule of thumb, the mass of sample taken for analysis can be equal to an amount representing 50–100 mg organic carbon.

PAHs can be extracted from wet or dried samples. However, storage, homogenization, and extraction are much easier when the samples are dry.

Drying the samples at ambient or elevated temperatures as well as freeze-drying may alter the concentrations, e.g., by contamination or by loss of compounds through evaporation (Law *et al.,* 1994). Possible losses and contamination have to be checked. Contamination can be checked by exposing 1–2 g CIS-bonded silica to drying conditions and analysing it as a sample (clean-up can be omitted) (Smedes and de Boer, 1998). Contamination during freeze-drying is reduced by placing a lid, with a hole about 3 mm in diameter, on the sample container, while evaporation of the water is not hindered.

Chemical drying of samples can be performed by grinding with Na2SO4, or MgSO4 until the sample reaches a sandy consistency. It is essential that at least 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). Since photo-degradation occurs more rapidly in the absence of a sample matrix, first of all the standard solution used for checking the recovery of the procedure will be affected, allowing a proper detection of the influence of light. The most photo-sensitive PAH is benzo[*a*]pyrene, followed by anthracene.

5.1 EXTRACTION OF WET SEDIMENTS

A commonly used and very efficient method for PAH extraction from sediments is alkaline saponification; apart from having a short extraction time (approximately 1.5 hrs under the reflux), it also eliminates organic sulphur and other interfering compounds such as lipids and yields an extract that is relatively 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. For sufficient extraction, at least three subsequent extractions are needed. The contact time with the solvent should be sufficient to complete the desorption of the PAHs out of the sediment pores. The contact time for the desorption of PAHs from sediments may vary with sediment type up to 24 hrs. If there is any doubt, a second extraction step should be performed and quantities of PAHs in the two extracts combined.

The contact time of the sediment with the solvent can be reduced by using microwave heating or a Soxhlet apparatus. When utilizing Soxhlet, the 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, then the flask is replaced and the extraction continued with a less polar solvent or solvent mixture (e.g., acetone/hexane). Thereafter, the extracts must be combined.

For both batch and Soxhlet extraction, water must be added to the combined extracts and the PAHs must be extracted to a non-polar solvent.

5.2 EXTRACTION OF DRY SEDIMENTS

Although all the methods mentioned above can also be used for dried sediments, Soxhlet extraction is the most frequently applied technique to extract PAHs from dried sediments. 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 favoured because of its high boiling point, it should be chosen as solvent when it is expected that sediment samples contain soot particles. For routine marine samples, the use of a mixture of a polar and a non-polar solvent (e.g., acetone/hexane (1/3, v/v)) is recommended.

The extraction can be carried out with a regular or a hot Soxhlet (Smedes and de Boer, 1998). A sufficient number of extraction cycles must be performed (approximately 8 hours for the hot Soxhlet and 12 to 24 hours for the normal Soxhlet). The extraction efficiency has to be checked for different types of sediments by a second extraction step. These extracts should be analysed separately. A recovery during the first extraction step of over 90 % is considered adequate.

All the methods described, both for wet and dry samples, are in principle suitable for the extraction of PAHs from sediments. However, Soxhlet extraction is recommended over mixing methods, especially for dry

samples. For naphthalene, which can easily be lost in several steps of the sample preparation, headspace or purge and trap analysis might provide a suitable alternative to extraction methods.

5.3 CLEAN-UP

The crude extract requires a clean-up to remove the many other compounds that are co-extracted (Wise *et al.,* 1995). Due to chlorophyll-like compounds extracted from the sediment, the raw extract will be coloured and will also contain sulphur and sulphur-containing compounds, oil, and many 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 in the extraction step should be removed. The recommended acetone/hexane mixture will end in hexane when evaporated because of the formation of an azeotrope. Evaporation can be done using either a Kuderna-Danish or a rotary evaporator. Especially for the latter, care should be taken to stop the evaporation in time at about 5 cm3. For further reducing the volume, a gentle stream of nitrogen should be applied. The extract should never be evaporated to dryness.

For removing more polar interferences from the extract, deactivated aluminium oxide (10 % water), eluted with hexane, as well as silica or modified silica columns, e.g., aminopropylsilane, eluted with toluene or a semipolar solvent mixture such as hexane/acetone (95/5, v/v) or hexane/dichloromethane (98/2, v/v) can be used. Gel permeation chromatography (GPC) can be used to remove high molecular weight material and sulphur from the extracts.

When using HPLC/fluorescence detection, for the majority of samples polar interferences can be removed from the extract using an aluminium oxide (deactivated with 10 % water) column that is eluted with hexane. If interferences appear to be present in the chromatogram, a clean-up combination of silica and a cyanopropyl phase, eluted with, e.g., hexane/acetone, is suitable. 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 Soxhlet extraction. Ultrasonic treatment might improve the removal of sulphur. As an alternative to copper, other methods can be used (Smedes and de Boer, 1998).

Analysis by GC 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. The first fraction eluting with hexane is rejected. The PAHs elute in a second fraction with a more polar solvent, e.g., diethylether or acetone/hexane. When applying fractionation, the elution pattern has to be checked frequently. This should be carried out in the presence of sample matrix, as that can partially deactivate the clean-up column, resulting in earlier elution of the PAHs 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 are 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 1–2 cm3. Concentrating the extract by evaporation, e.g., in a rotary evaporator, can easily result in losses of PAHs.

Care should be taken that the extracts are never evaporated to dryness and the water bath temperature should be carefully controlled (< 30 ºC).

HPLC and GC require different solvents for injection of the extract. The methods suggested above all yield an extract in which non-polar solvents are dominant. In HPLC, even small amounts of non-polar solvents result in a shift of retention time and broadening of the peaks (Reupert and Brausen, 1994). As for solvent exchange, evaporation to dryness must be avoided; hexane should be removed by the addition of 5 cm3 acetonitrile for each cm3 of extract and subsequent evaporation to 1–2 cm3. Azeotropic evaporation leaves only acetonitrile. Although this also works with methanol, acetonitrile is preferred because PAHs show a better stability when dissolved in acetonitrile. Azeotropic exchange can also be applied the other way round. In that case, 5 cm3 hexane must be added for each cm3 of acetonitrile. For GC methods, iso-octane or toluene are suitable solvents for injection and can already be added, before evaporation to the required volume, as a keeper.

5.4 EXTRACTION EFFICIENCY AND CLEAN-UP

A check on extraction efficiency and clean-up can be performed by analysing a reference material. To determine the recovery rates of the clean-up and concentration steps of each sample series, a standard solution should be put through the entire procedure. It is recommended to always use two, and preferably three, internal standards: hydrocarbons of small, medium, and high molecular weight, e.g., naphthalene-d8, phenanthrene-d10, perylene-d12, to check for recovery during the analytical procedures. If major losses have occurred, then the results obtained should not be reported.

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 the guidelines, both the HPLC-fluorescence and GC/MS methods are considered to be equally valid approaches. Although this may be the case for the parent PAHs, it is certainly not the case for alkylated species, as this range of compounds cannot be satisfactorily analysed using HPLC. This is particularly relevant for the future as additional PAHs, including both additional parent compounds of 5- and 6-rings, and the alkylated PAHs gain increasing interest.

6.1 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

For adequate HPLC analysis of PAHs, the equipment should meet some minimum requirements. At a minimum, a binary gradient is necessary to achieve proper separation. Using HPLC and measuring concentrations with the peak height, a 50 % valley should be considered as adequate separation. Solvents must be degassed in order to allow proper operation of the high pressure pump. Sample injection should be carried out with an autosampler.

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.

Columns with diameters smaller than 4.6 mm can be chosen in order to reduce the flow of the eluent and thus save solvents, if the dimensions of the detector cell and the tubings are appropriate. When using a smaller diameter column, the amount injected should also be reduced (e.g., 25–50 µl for a 4.6 mm column, 10 to 20 µl for a 3 mm column).

6.1.2 ELUTION

At a minimum, a binary gradient is necessary to allow for a proper separation. For elution, e.g., methanol/water or acetonitrile/water can be applied. Acetonitrile allows more rapid flow, but presents a greater health risk than methanol. A typical gradient (1–1.5 ml min-1 for a 4.6 mm column) starts at 50 % methanol/water or acetonitrile/water and runs to 100 % methanol or acetonitrile in 40 minutes, where it remains for 20 minutes and then returns to the initial conditions again for about 5 minutes. Prior to the next injection, the equilibrium time should be about 5–10 minutes (3–5 times the dead volume).

100 % methanol or acetonitrile may not be sufficient to elute all non-target compounds from the column, resulting in peaks that disturb the baseline in the subsequent chromatogram. To avoid this, 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. In addition, a thermostated column compartment (10–30 °C) should be used. Not only retention times but also the resolution between some PAHs can be affected by varying the temperature.

6.1.3 DETECTION

For the detection of PAHs, the more sensitive and selective fluorescence detector is preferred to 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. This can be done either by continuously passing a gentle stream of helium through the eluents or using a commercially available vacuum degasser. In addition, after degassing the eluents, they should not pass PTFE tubings, 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. A UV or diode-array detector can be used for detection.

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: 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. Below a diameter of 0.15 mm, the carrier gas pressure rises to values greater than 500 kPa, which are not compatible with normal GC equipment. Also, the risk of leakages increases.

6.2.2 CARRIER GAS

Preferably helium should be used as the carrier gas for GC/MS. When 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 20–40 cm s-1 and for 0.15 mm i.d. columns from 30–50 cm s-1.

6.2.3 INJECTION TECHNIQUES

An autosampler should be used for injection. 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, for PAHs on-column injection is recommended.

6.2.4 TEMPERATURE PROGRAMMING

The temperature program must be optimized for a sufficient separation of the PAH compounds. For GC/MS analysis peak area is generally used, and a 10 % valley would represent a good separation. Less resolved peaks may also be quantified (for instance, 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

A frequently used detector for PAH analysis is a mass spectrometric detector, used in the Selected Ion Monitoring (SIM) mode. Electron impact ionization (EI) may be used 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. As another technique of PAH identification, the full-scan MS using an ion trap can be mentioned; it operates with the same sensitivity as SIM but is a much more powerful analytical tool. The use of a flame ionization detector (FID) is also possible, but since the selectivity of the FID is low, it is not recommended.

6.3 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 analysed under the same conditions. In case of doubt, it is recommended to confirm the results by using a different wavelength for UV-absorption or a different combination of wavelengths for fluorescence detection. Using a GC/MS system, the molecular mass or characteristic mass fragments are a suitable way to prove the identification of the PAH compound. Using GC/MS on a modern instrument, the retention times should be reproducible to within ±0.05 minutes, and additionally there are deuterated analogues of many of the parent compounds present for comparative purposes. For HPLC, reproducibility of retention times may be less good, but should certainly be within ±1 minute.

6.4 QUANTIFICATION

PAH determinations should preferably be carried out using calibration solutions prepared from certified, crystalline PAHs. However, the laboratory should have the appropriate equipment and the expertise to handle these hazardous crystalline substances. Alternatively, certified PAH solutions, preferably from two different suppliers, can be used. Two independent stock solutions should always be prepared simultaneously to allow a cross-check to be made. Calibration solutions should be stored in ampoules in a cool, dark place. Weight loss during storage should be recorded for all standards.

Internal standards should be added to all standards and samples either in a fixed volume or by weight. The internal standards should preferably be non-natural PAHs which are not found in sediment samples and do not co-elute with the target PAHs. Several perdeuterated PAHs have proved to be suitable for GC/MS as well as for HPLC analysis. The use of several deuterated PAHs spanning the entire molecular weight range

as internal standards is encouraged. For example, for GC/MS it is recommended to add four internal standards representing different ring-sizes of PAHs.

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-dl2, perylene-dl2.

After clean-up and before GC analysis, an additional internal standard is added for volume correction.

A multilevel calibration with at least five concentration levels is recommended. For UV and fluorescence detection, the linear range is large. The calibration curve should be linear and should cover the working range.

Since the mass spectrometric detector often has no linear response curve, the use of stable, deuterated isotopes is a prerequisite. Furthermore, the response of PAHs in standard solutions is often much lower than in sample extracts. Only a combination of different techniques, e.g., the use of internal standard and standard addition, might give reliable quantitative results.

The calibration curve can be checked by recalculating the standards as if they were samples and comparing these results with the nominal values. Deviations from the nominal values should not exceed 5 %.

When chromatograms are processed using automated integrators, the baseline is not always set correctly, and always needs visual inspection. Because in HPLC analysis the separation of the peaks is often incomplete, the use of peak heights is recommended for quantification. Using GC techniques, either peak heights or peak areas can be used.

Prior to running a series of samples and standards, the GC or HPLC systems should be equilibrated by injecting at least one sample extract, the data of which should be ignored. In addition, standards used for multilevel calibration should be regularly distributed over the sample series so 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 that has been treated similarly to the samples (recovery determination).

The limit of determination should depend on the purpose of the investigation. A limit of 2 ng g-1 (dry weight) or better should be attained for single compounds. The method for calculating the limit of determination should reflect the advice in Part B-4.2.3 (COMBINE manual). The limit of determination that can be achieved depends on the blank, the sample matrix, concentrations of interfering compounds, and the mass of sediment taken for analysis.

6.5 SYSTEM PERFORMANCE

The performance of the HPLC or GC system can be monitored by regularly checking the resolution of two closely eluting PAHs. A decrease in resolution indicates deteriorating HPLC or GC conditions. The signal-to-noise ratio yields information on the condition of the mass spectrometric (MS) detector. A dirty MS-source can be recognized by the presence of a higher background signal, together with a reduced signal-to-noise ratio. Additionally, the peak shape can be affected.

6.6 LONG-TERM STABILITY

One laboratory reference sample should be included in each series of samples. A quality control chart should be recorded for selected PAHs, e.g., fluoranthene (stable results), pyrene (sensitive to quenching), benzo[*a*]pyrene (sensitive to light). If the warning limits are exceeded, the method including calibration solutions should be checked for possible errors. When alarm limits are exceeded, the results should not be reported. A Certified Reference Material should be analysed at least twice a year and each time the procedure is changed. Each laboratory analysing sediments should also participate in interlaboratory studies on the determination of PAHs in sediments on a regular basis.

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