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Multi-residue analysis of polycyclic aromatic hydrocarbons, polychlorobiphenyls, and organochlorine pesticides in marine sediments

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Abstract A multi-residue analysis procedure using microwave-assisted extraction and pre-purification has been developed for the combined analysis of polycyclic aromatic hydrocarbons (PAH), polychlorobiphenyls (PCB), and organochlorine pesticides (OCP) in marine sediments. This procedure has been validated with certified marine sediment. Several surrogate standards have been employed and the use of octachloronaphthalene (OCN) as a surrogate standard for organochlorine determination in this matrix is discussed. The recoveries of all compounds were high (>70%) and the relative standard deviations are of the same order as the certified values. Different analytical problems are discussed, including DDT degradation in gas chromatography and laboratory PCB background levels. Quantification problems encountered for two pesticides (*cis*-chlordane and *trans*-nonachlor) were attributed to PAH interference in the GC–ECD chromatogram.

Keywords Aromatic compounds · Organochlorine compounds · Multi-residue analysis

Introduction

Polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and organochlorine pesticides (OCP) such as γ-hexachlorocyclohexane (HCH) and DDT, are three classes of persistent and ubiquitous organic contaminants. These compounds have similar physicochemical properties such as hydrophobicity, low degradability, and high affinity for lipids. Because of these properties, these contaminants are readily accumulated by living organisms. They are often found together in environmental samples, because they are mostly generated by anthropogenic activity. Industrial activity and combustion of fossil fuels are the main sources of PAH in the environment. PCB were widely used in the electrical industry and as additives in a variety of materials such as plastics, inks, and carbon copy paper. OCP were used as insecticides, although most have been withdrawn because of their environmental persistence. Atmospheric or fluvial processes can transport these contaminants into the marine environment, where they can be adsorbed on to particulate matter and sediment.

To evaluate the impact of pollution on living organisms, a variety of biomarkers [1, 2] has been developed for rapid screening of exposure to environmental contaminants. These techniques analyse the enzyme activity (ethylresorufine-*O*-deethylase, EROD, acetylcholinesterase AChE) induced by the mechanism of metabolism of xenobiotics. Such activity is not, however, compound-specific and synergetic or antagonistic effects can be observed. For example, planar compounds such as PAH and certain PCB [3] both induce EROD activity. To validate the use of biomarkers in environmental evaluation detailed chemical analysis should be performed and there is, therefore, a need for a single analytical procedure which enables the determination of several classes of contaminants.

Several environmental monitoring programmes (National Status and Trends Program [4], Reseau National d'Observation [5]) specify the routine analysis of marine sediments and many environmental studies evaluate a large number of samples. To satisfy the demand for increased productivity and faster analysis of these contaminants an analytical procedure has been developed in this work which enables the determination of the three classes from the same purified extract of sediment.

Quantitative analysis of these compounds remains a challenging task, because they often occur at very low concentrations (ng g^{-1}) compared with endogenous material, and several purification steps may be necessary to obtain a chromatogram free from interference. Gas chromatographic separation of all of the PCB is currently impossible. As Larsen [6] pointed out, no single column is capable of separating even the seven priority PCB (28, 52, 101, 118, 138, 153, and 180). Indeed, several congeners can

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coelute in gas chromatography and they cannot be distinguished by electron capture detection (ECD). Compounds of other classes can also interfere, e.g. OCP, which also give an ECD signal.

Sample-preparation procedures result in losses of the compounds to be analysed. Surrogate standards that have physicochemical properties similar to those of the studied compounds will be subject to the same losses and thus enable accurate determination of the original concentrations. Octachloronaphthalene (OCN) is often used as a surrogate standard for PCB quantification [7, 8, 9], although it does not have the same chemical structure as PCB. Also some authors have reported the presence of polychlorinated naphthalenes (PCN), also called chlorowaxes, in environmental samples [10, 11]. Although used to a lesser extent than PCB, PCN industrial formulations have been used since the beginning of the century, and are also present in PCB industrial mixtures. PCB congeners which are absent from technical mixtures because of their thermodynamically unstable substitution patterns seem more suitable as surrogate standards, because they are also absent from environmental samples and their physicochemical properties are similar to the other PCB congeners.

Some authors have recently published results from measurements of PCB in indoor air [12, 13, 14, 15, 16], which can be high because of the extensive use of PCB in the past. Background levels of PCB in indoor air can be high enough to interfere with measurements and even contaminate samples [14], and as such must necessarily be determined in analytical procedures. Blank measurements reveal levels of PCB, which can bias results.

Similarly, the analysis of DDT by gas chromatographic methods can be a challenging task [17, 18]. DDT is a relatively thermolabile compound and the high injector temperatures used in gas chromatography can cause degradation during the analysis. Our laboratory has studied this problem and the chromatographic conditions have been optimised to limit DDT degradation.

Quality-control procedures are important to ensure correct quantification, and the use of certified reference materials enables determination of the accuracy of an analytical procedure. The precision of a method can be determined by replicate analyses of a homogeneous material. The developed procedure has been validated with the reference material SRM 1941.a from the National Institute of Standards and Technology, Gaithersburg, MD, USA (NIST), a marine sediment. The recoveries and repeatability for PAH, PCB, and pesticide analysis are reported. The results obtained for the PCB are compared with those calculated with OCN as a surrogate and the suitability of this compound for PCB quantification is discussed. PCB blank levels are also discussed with regard to possible sources of indoor contamination.

Experimental

The experimental procedure is summarised in Fig. 1. The samples were treated by microwave-assisted extraction and after filtration were purified with sulfuric acid under a microwave field. A second purification was performed on silica gel, after which the extract was submitted to a liquid chromatographic step to yield two fractions.

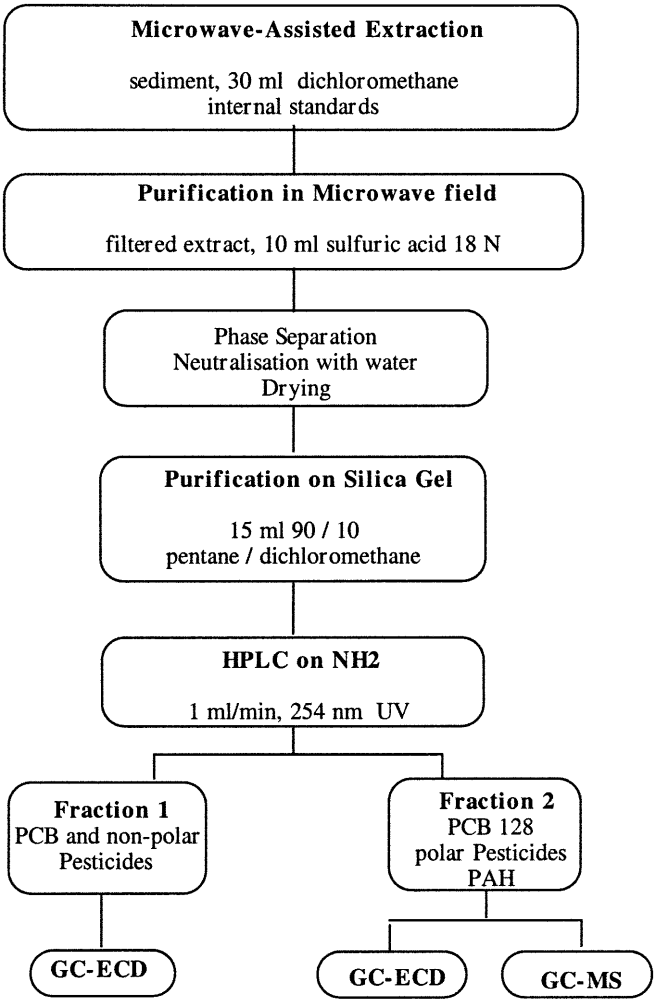

Fig. 1 The sample-preparation procedure

Sample preparation

The surrogate standards PCB 30, 103, 155, 198 and OCN, 4,4'-DDT d8 and the perdeuterated PAH were added to the sediment before extraction. The sample (2 g mass of dry sediment) was extracted by microwave-assisted extraction with dichloromethane (30 mL) by use of the Maxidigest 350 Prolabo apparatus (Prolabo, Paris, France), which operates with open cells under atmospheric pressure. The extraction conditions were: 30% (w/w) moisture; time 10 min; power 30 W. These microwave-assisted extraction conditions were optimised previously [19, 20].

After extraction, the sample was filtered and purified with sulfuric acid (9 mol L^{-1}, 10 mL) under a microwave field (operating conditions: time 10 min; power 30 W) [21]. The organic and acid phases were separated and the organic extract was neutralised with de-ionised water, and dried with anhydrous sodium sulfate. The extract was concentrated under a gentle flow of nitrogen, and purified a second time on a column (10 cm×1 cm i.d.) containing 9 cm activated silica on top of 1 cm activated copper for elimination of elemental sulfur. The PAH, PCB, and OCP were eluted from this column with 10: 90 dichloromethane–pentane (15 mL). The extract was concentrated under nitrogen and transferred to 0.5 mL

isooctane. The solution was further re-concentrated to 0.05 mL in a conical injection vial.

Liquid chromatography

The extract was further purified by HPLC with an aminosilane column (NH_2 5 μm, 250 mm; 4.6 mm i.d.; Stagroma, Switzerland) with pentane as mobile phase at a flow rate of 1 mL min^{-1} and UV detection at 254 nm. The sample was introduced into the sample loop (100 μL) by means of a single injection of 0.05 mL. Two fractions were collected. The first was collected from the solvent peak at a retention time of 3.5 min until the retention time corresponding to PCB 128. This PCB was the last of the studied PCB to elute. This first fraction contains the PCB and the least polar pesticides. The second fraction was collected from the cut off point of the first fraction until the last eluting PAH – dibenz[*a*,*h*]anthracene (retention time 22 min). The second fraction contains the PAH from phenanthrene to dibenz[*a*,*h*]anthracene and the polar pesticides. The HPLC column was calibrated for retention times by use of a standard solution of PCB 128 and dibenz[*a*,*h*]anthracene.

Gas chromatography

Fraction 1, which contained organochlorine compounds only, was analysed by GC–ECD and Fraction 2 was analysed by GC–ECD for the remaining organochlorine compounds and by GC–MS for PAH determination.

GC–ECD analyses were performed on an Hewlett–Packard (HP; Avondale, MA, USA) 5890 series II gas chromatograph equipped with a ^{63}Ni electron-capture detector, an automatic HP 7673 injector, and a 60 m×0.25 mm i.d.×0.25 μm film thickness HP5-Trace (5% phenyl methylsiloxane) capillary column (Hewlett–Packard). The GC conditions were: splitless injection (1 μL); purge off at injection and on after 1.5 min; injector temperature, 280 °C for Fraction 1, 250 °C for Fraction 2; detector temperature, 290 °C; initial oven temperature, 60 °C; held for 2 min, heated to 120 °C at 6 ° min^{-1} and held for 5 min, then heated to 280 °C at 2° min^{-1} and held for 20 min, total time 117 min. Helium was used as the carrier gas at a column head pressure of 140 kPa for Fraction 1 and 190 kPa for Fraction 2, and the ECD make-up gas was nitrogen at 60 mL min^{-1}. The anode purge gas used was helium at a flow rate of 12 mL min^{-1}. The relative response factors of the different compounds were determined by injecting a standard solution (SRM) spiked with the same solution of surrogate standards as that used for spiking the sediments. The response factors were determined after each four samples. Blank injections of isooctane were performed between each injection of a sample to ensure the cleanliness of the injector.

Electron ionisation (70 eV) GC–MS analyses were performed on an HP 5890 series II GC equipped with an automatic HP 7673 injector and a 60 m×0.25 mm i.d.×0.25 μm film thickness HP5 (5% phenyl methylsiloxane) capillary column (Hewlett-Packard). The injector was maintained at 270 °C. The temperature program was: 50 °C (2 min) to 290 °C (20 min) at 5 ° min^{-1}. The carrier gas was helium at a constant flow rate of 1 mL min^{-1}. The GC was coupled to an HP 5972 mass selective detector. Single-ion-monitoring mode was employed and the signal was acquired on the molecular ions at 1.4 scan s^{-1} with the electron multiplier at 1500 V. The ions acquired were: m/z=178, 188, 202, 212, 228, 240, 252, 264, 276, 278, 288. The interface temperature was 240 °C. The PAH studied ranged from tri-aromatic (phenanthrene, anthracene) to hexa-aromatic (benzo[*ghi*]perylene) and included: phenanthrene; anthracene; fluoranthene; pyrene; benzo[*a*]anthracene; chrysene; triphenylene; benzo[*b*]fluoranthene; benzo[*j*]fluoranthene; benzo[*k*]fluoranthene; benzo[*e*]pyrene; benzo[*a*]pyrene; perylene; indeno[1,2,3-*cd*]pyrene; benzo[*ghi*]perylene; dibenz[*a*,*h*]-anthracene; dibenz[*a*,*c*]anthracene. Response factors were determined relative to surrogate standards by injecting SRM 2260 preparations of PAH. Some of the PAH co-eluted; for these the results are given as the sum of the compounds.

Chemicals and reagents

The compounds used as surrogate standards for PAH determination were perdeuterated PAH. P-d_{10}, BaP-d_{12} and Bper-d_{12} were purchased from Cambridge Isotope Laboratories (CIL, Cambridge, MA, USA), Fluo-d_{12}, and Chyr-d_{12} from MSD Isotopes (Division of Merck Frost Canada, Montreal, Canada) and Py-d_{12} from NIST (Gaithersburg, MD, USA). The Standard Reference Material SRM 2260, a standard solution of 24 aromatic hydrocarbons was provided by the NIST.

The PCB were analysed as individual congeners and the standards were purchased from Promochem, (Promochem, Molsheim, France) in solution at 99%+ purity. The surrogate standards PCB 30, 103, 155, and 198 and OCN were also obtained from Promochem (Molsheim, France) as crystals of 99%+ purity. A certified solution of PCB, SRM 2262 "PCB in Hexane" was obtained from NIST.

The surrogate standard for pesticide analysis was 4,4'-DDT d8 obtained from CIL, (Cambridge, MA, USA). The Standard Reference Material SRM 2261, a standard solution of chlorinated pesticides was provided by the NIST (Gaithersburg, MD, USA).

All glassware was rigorously cleaned with detergent, then by overnight heating at 450 °C. The anhydrous sodium sulfate and the concentrated sulfuric acid was from Fluka Chemie (Buchs, Switzerland), and the silica gel (particle size 0.063–0.2 mm) from Merck (Darmstadt, Germany). The sodium sulfate and silica gel were pre-extracted with dichloromethane (Prolabo, Fontenay sous Bois, France, pesticide grade) in an ultrasonic bath, dried and were rinsed with dichloromethane just before use. The silica gel was activated by overnight storage in an oven at 140 °C. The copper (40 mesh, 95.5% purity, Aldrich, Strasbourg, France) was activated with hydrochloric acid (1 mol L^{-1}), neutralised with water, and rinsed with acetone and dichloromethane. Isooctane of spectroscopy grade quality, and pentane and acetone of HPLC grade were from Scharlau, ICS (St. Médard en Jalles, France).

Procedural blanks were conducted in different laboratories and buildings with exactly the same material and glassware under the same conditions as the samples but with no matrix added to the solvent for the extraction. The solvent tests were conducted by evaporating 24 mL solvent under a gentle flow of nitrogen.

Results and discussion

Surrogate standards for PCB determination

The principle of surrogate standard quantification is well known and described elsewhere [22, 23]. The standards are added to the sample matrix and are taken through the entire analytical procedure – extraction, clean-up, chromatography. This method assumes that the recoveries of the surrogate standard and the analyte are equivalent and enables estimation of handling efficiency. The choice of surrogate standard thus depends on the similarity of its physicochemical properties with those of the analyte. The ideal surrogate standards must also be absent from the environment, and free from interference in the chromatogram.

For this study, we have investigated the use of several surrogate standards for the determination of PCB – PCB 30, (2,4,6-trichlorobiphenyl), PCB 103, (2,2'-,4,5'-,6-pentachlorobiphenyl), PCB 155, (2,2'-,4,4'-,6,6'-hexachlorobiphenyl), and PCB 198, (2,2'-,3,3'-,4,5,5'-,6-octachlorobiphenyl). All of these have a thermodynamically unfavourable 2,4,6 chloro-substitution pattern and have never been identified in technical mixtures [24]. These standards

Table 1 The organic compounds analysed, the surrogate standard used for each, and the HPLC Fraction

Compound	Internal Standard	Fraction
Phenanthrene	Phenanthrene d10	2
Anthracene	Phenanthrene d10	2
Fluoranthene	Fluoranthene d10	2
Pyrene	Pyrene d12	2
Benzo[*a*]anthracene	Chrysene d12	2
Chrysene	Chrysene d12	2
Triphenylene	Chrysene d12	2
Benzo[*b*]fluoranthene	Benzo[*b*]fluoranthene d12	2
Benzo[*k*]fluoranthene	Benzo[*b*]fluoranthene d12	2
Benzo[*j*]fluoranthene	Benzo[*b*]fluoranthene d12	2
Benzo[*e*]pyrene	Benzo[*e*]pyrene d12	2
Benzo[*a*]pyrene	Benzo[*a*]pyrene d12	2
Perylene	Benzo[*a*]pyrene d12	2
Indeno[1,2,3-*cd*]pyrene	Benzo[*g,h,i*]perylene d12	2
Dibenz[*a,h*]anthracene	Benzo[*g,h,i*]perylene d12	2
Dibenz[*a,c*]anthracene	Benzo[*g,h,i*]perylene d12	2
Benzo[*g,h,i*]pyrene	Benzo[*g,h,i*]perylene d12	2
PCB 28	PCB 30	1
PCB 44	PCB 103	1
PCB 52	PCB 103	1
PCB 66	PCB 155	1
PCB 87	PCB 155	1
PCB 101	PCB 155	1
PCB 105	PCB 198	1
PCB 118	PCB 198	1
PCB 128	PCB 198	2
PCB 138	PCB 198	1
PCB 170	PCB 198	1
PCB 180	PCB 198	1
PCB 206	PCB 198	1
PCB 209	PCB 198	1
Hexachlorobenzene (HCB)	PCB 198	1
2,4'-DDE	PCB 198	1
4,4'-DDE	PCB 198	1
4,4'-DDD	4,4'-DDT d3	2
4,4'-DDT	4,4'-DDT d3	2
cis-Chlordane	4,4'-DDT d3	2
trans-Nanochlor	4,4'-DDT d3	2

represent the full range of PCB both in degree of chlorine substitution and in the range of elution times in the gas chromatogram. Octachloronaphthalene was also investigated for comparison purposes. This study considered individual PCB, and the congeners studied are shown in Table 1.

The PCB surrogate standards were used to quantify a standard solution of PCB, SRM 2262 "PCB in Hexane", which had undergone an evaporation step only. This experiment mimics volatilisation/adsorption that might occur during re-concentration of a sample. The dependence of the error (%) of the quantified value of a few selected PCB, representative of the full range of PCB studied, on the surrogate standard used for their determination is shown in Fig. 2. PCB 30 results in the lowest error for the trichloro- and tetrachloro-congeners and a larger error for

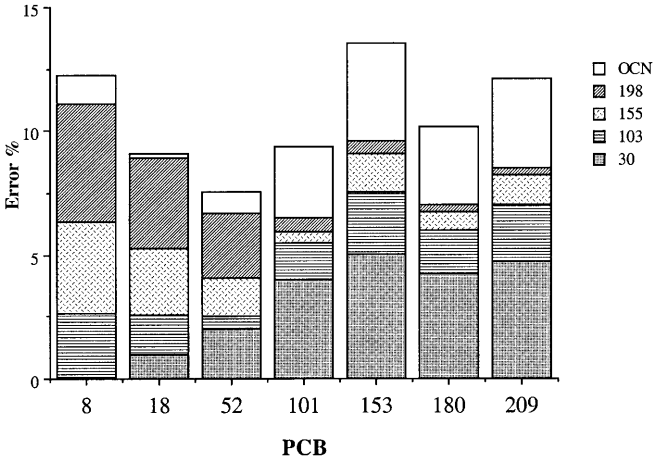

Fig. 2 Percentage error in the quantification of some PCB with different surrogate standards

the more chlorinated congeners. The less chlorinated congeners are more volatile than the higher chlorinated congeners, as seen by comparing Henry's Law constant, H, for the different congeners [25] and will be more subject to loss during the analytical procedure. Thus a surrogate standard with similar physicochemical properties, such as number of chlorine atoms or volatility, should be lost to a similar extent. Similarly the other surrogate standards are highly suitable for the higher chlorinated congeners. PCB 198 gives good results for a large range of PCB, from hexachlorobiphenyl to decachlorobiphenyl. OCN also gives reasonable values for the range of PCB.

As a consequence of these results PCB 30 was used to quantify, in elution order, PCB 8 to PCB 28, PCB 103 to quantify PCB 52 to PCB 44, PCB 155 to quantify PCB 66 to PCB 77 and PCB 198 to quantify PCB 118 to PCB 209 (Table 1). The use of several surrogate standards in a natural sample also enables determination of whether there is an interference problem with one of the standards. For example, if there is a large difference between the value of an analyte calculated by use of two different surrogate standards there might be a co-elution problem with one of the standards.

OCN as surrogate standard for PCB determination in SRM 1941.a

Quantification using OCN as surrogate standard for the marine sediment SRM 1941.a gave very poor results. Recovery was approximately 200% for all the compounds, which suggests either that the area of the chromatographic peak for OCN is too large or that the concentration assigned is too low.

A sample of SRM 1941.a was qualitatively extracted without addition of surrogate standards. The extract was then spiked with the standards one by one and analysed by GC–ECD to reveal any possible matrix interference in the chromatogram. All the PCB congeners were free from interference but OCN co-eluted with an unknown impurity

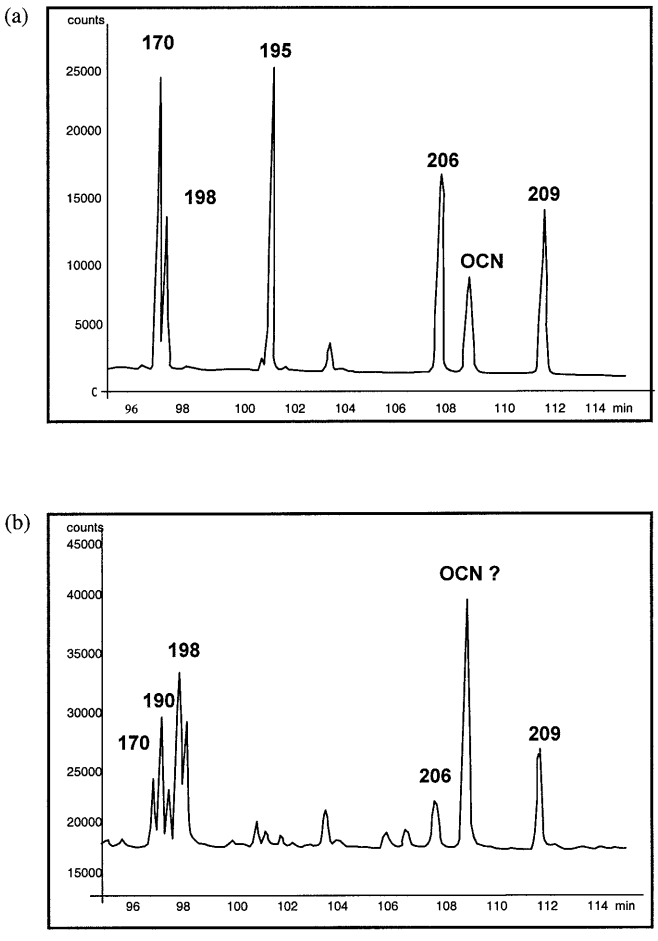

Fig. 3 (**a**) GC–ECD Chromatogram obtained from a standard solution, showing OCN. (**b**) GC–ECD chromatogram obtained from a marine sediment extract before spiking with OCN

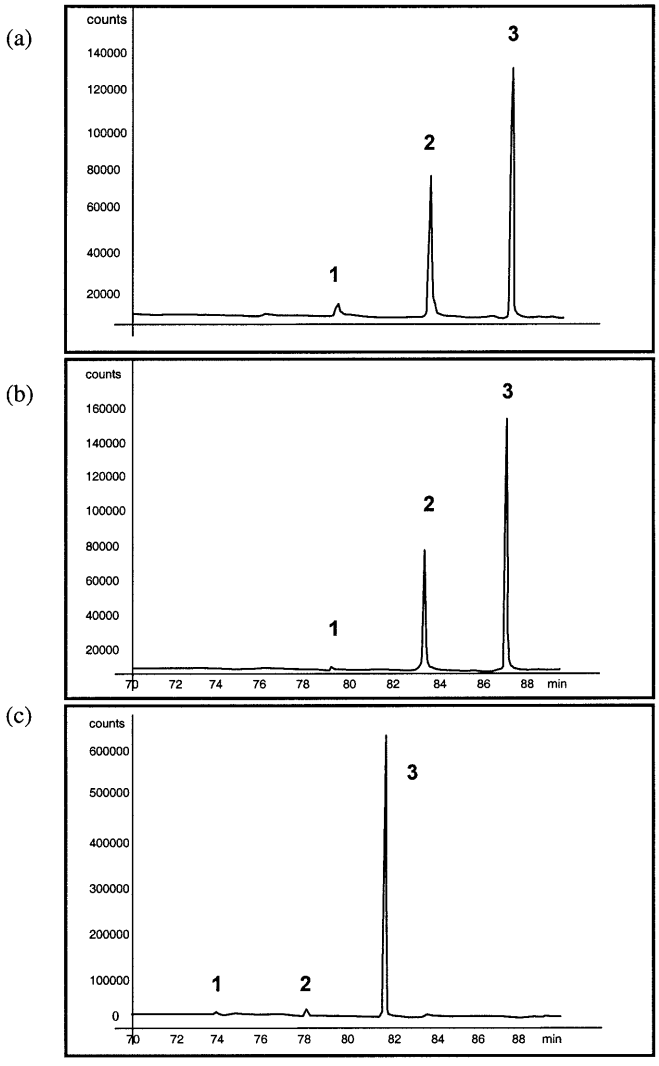

Fig. 4 GC–ECD Chromatograms of 4,4'-DDT d8 under different chromatographic conditions. (**a**) Injector temperature=280 °C; column head pressure=140 kPa. (**b**) Injector temperature=250 °C; column head pressure=140 kPa. (**c**) Injector temperature=250 °C; column head pressure=190 kPa

which resulted in a large peak (Fig. 3). OCN cannot be used as an surrogate standard for this matrix because its use will result in systematic overestimation of the concentrations of the analytes (area of the standard too high).

Optimisation of gas chromatographic injector conditions for the analysis of DDT

DDT is a thermolabile compound that can be degraded during gas chromatographic analysis [17, 18]. For example, the analysis of 4,4'-DDT-d_8, the surrogate standard used for the quantification of chlorinated pesticides under the conditions used for the analysis of PCB leads to the detection of three peaks (Fig. 4). These peaks have retention times corresponding to 4,4'-DDE-d_8, 4,4'-DDD-d_8 and 4,4'-DDT-d_8. The DDT compound represents only 60% of the total area of the three peaks. The analysis was performed at different injector temperatures to determine the optimum conditions for the GC analysis of 4,4'-DDT-d_8. Reduction of the injector temperature to 250 °C increases the area of the 4,4'-DDT-d_8 peak to 67%. The gas flow through the injector can be increased so that the compound spends less time in the hot glass insert of the injector and is rapidly deposited in the cooler (oven at 60 °C) column head. Under these conditions (injector temperature=250 °C, and column head pressure=190 kPa) the degradation is minimal, 4,4'-DDT-d_8 represents 96% of the total area. For this sample-preparation procedure the degradation of DDT can be determined, because the deuterated standard will also be degraded and will lead to the corresponding deuterated degradation product peaks, which are not present in the environmental sample.

PAH interference in GC–ECD chromatograms

The ECD is a highly sensitive detector that responds to electronegative compounds; the signal is proportional to the electron affinity of the analyte. the signal from organo-

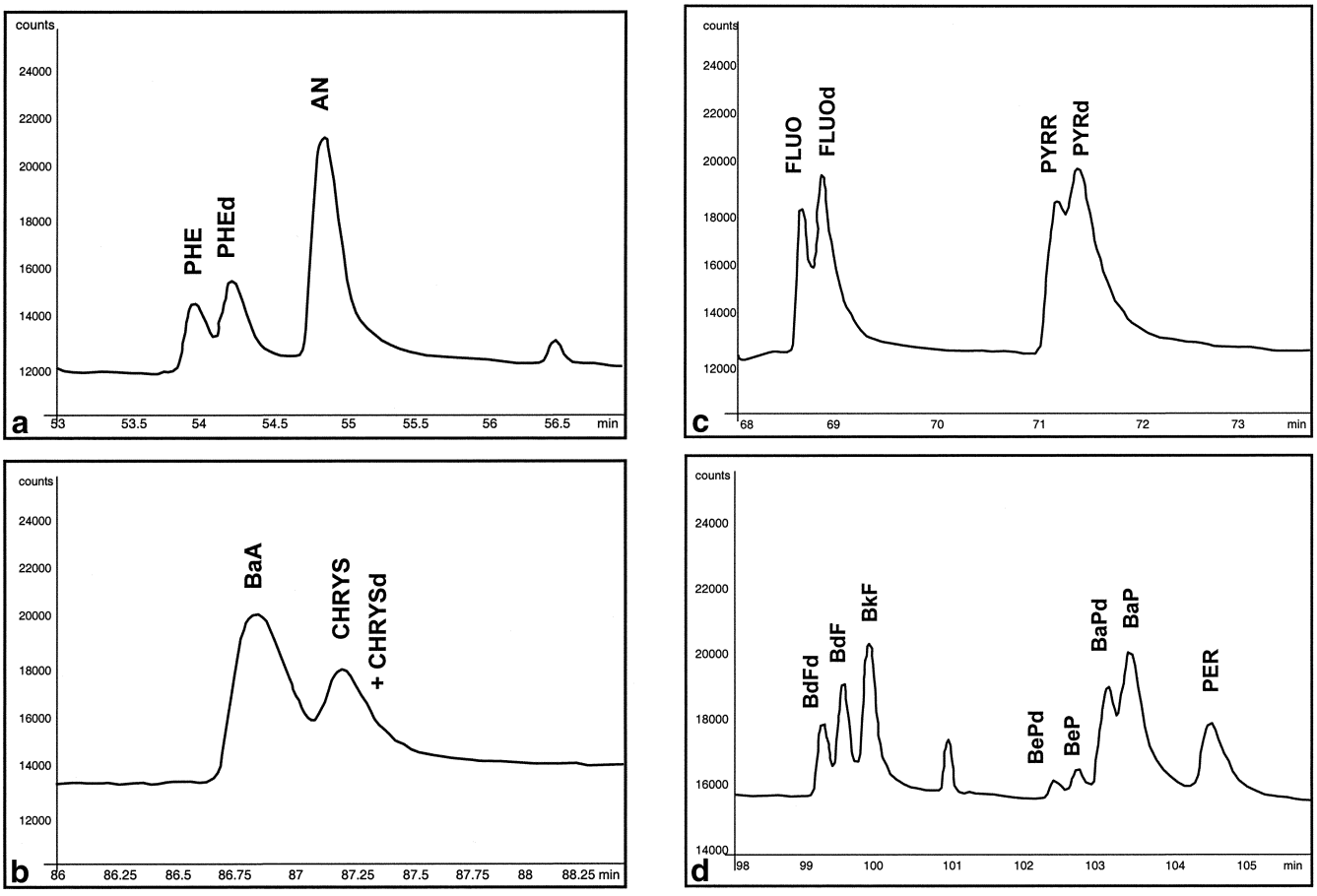

Fig. 5 GC–ECD Chromatogram of SRM 2260 "PAH in Toluene"

chlorine compounds such as PCB and the chlorinated pesticides depends on the degree of chlorination. On a normalised scale, hydrocarbons have a relative sensitivity of 1, monochlorinated compounds 100 and polychlorinated compounds 10^6 [26]. The electron affinities of condensed aromatic compounds are, however, much greater than those of aliphatic hydrocarbons, and the ECD has been proposed as a selective detector for the PAH [27, 28], because there are large differences between the electron affinities of the different isomers. For example, benzo[*a*]pyrene has a relative response factor more than twice that of benzo[*e*]pyrene. Indeed, this electron-accepting property is thought to be responsible for their toxic behaviour [29].

A GC–ECD chromatogram obtained from an SRM 2260 standard solution of PAH is presented in Fig. 5. The average individual compound concentration in this solution is 50 ng μL^{-1}. The peaks of the PAH are not very intense, but the areas are significant compared with those of the peaks resulting from low concentrations of organochlorine compounds. Comparison of the retention times of the standards of the three classes of contaminant reveals that several co-elutions are possible. Because the HPLC step in the sample preparation separates the PCB from the PAH, however, only the pesticides that remain in Fraction 2 are affected. Quantification problems were encountered for two pesticides, *cis*-chlordane and *trans*-nonachlor, in GC–ECD analysis. These two chlorinated pesticides can co-elute with pyrene and deuterated pyrene. Other authors have reported the interference of pyrene with chlorinated pesticides in gas chromatographic analysis [30]. Although PAH have low response factors compared with organochlorine compounds, because the PAH can be present at concentrations 100 times greater, their signal can be sufficient to create interference.

Procedural blanks

Procedural blanks are a standard procedure in analytical chemistry and are a necessary step for exact quantification. The procedural blanks performed during these validation experiments revealed a background level of PCB. There were no significant peaks in the pesticide and PAH fraction. The results obtained are shown in Table 2 in ng/sample and the overall standard deviation is low (<5%). The chromatographic profile of these analyses is also constant. There are few tri-chlorinated congeners that are typical of an air source of PCB. The distribution is dominated by tetra- to hexachlorinated PCB, which suggests an indoor source such as sealant [15] or capacitors [13]. PCB were used in building material (insulators, electrical transformer fluids) until the 1970s and, as other authors have demonstrated [14], it is probable that the air of the laboratory is

Table 2 Results (ng/sample) obtained for procedural blanks of PCB

PCB	Laboratory	RSD	Chemistry school
8	0.27	29.6	0.36
18	0.29	3.4	0.2
28	0.53	64.2	0.0
44	1.31	29.0	0.39
52	2.62	18.7	0.0
66	4.27	3.3	1.47
87	1.66	13.3	0.66
101	3.41	20.8	1.51
105	1.36	15.4	0.58
118	3.42	6.1	1.85
128	0.47	27.6	0.24
138	2.37	26.2	1.54
153	1.98	25.3	1.72
170	0.16	18.7	0.07
180	0.29	33.3	0.25
187	0.15	20.0	0.09
Total	24.56	6.8	11.09

contaminated. The laboratory is situated in the Department of Chemistry building that was constructed in the early 1960s, the period during which PCB were extensively employed. Procedural blanks were performed in other laboratories in the same building, where no PCB research had been performed. The results showed that background levels were the same, with the same chromatographic profile, thus the contamination was not caused by the manipulation of PCB.

It was suggested by Wallace et al. [12] that contamination of procedural blanks occurs during clean-up and treatment of the sample. This is demonstrated by comparing the values obtained for solvent, 0.14 ng mL^{-1} for the sum of 18 PCB, compared with 24.6 ng/sample for a procedural blank (purification steps included), in which a maximum of 30 mL solvent were used.

To verify these results a procedural blank was performed in another building on the University campus (School of Chemistry) the construction of which dates from approximately 1990. No research has been conducted on PCB in this building. All the material (glassware, silica gel, sodium sulfate) was prepared in our laboratory but was washed with dichloromethane just before use in the Chemistry School. The results are shown in Table 2, the level of PCB is approximately a third of that in laboratory in the Department of Chemistry (11 ng/sample compared with 28 ng/sample). Because the glassware and material was prepared in the contaminated laboratory, it is not surprising traces of PCB were found, but the difference is significant. The chromatographic profile is different, however. Although the penta- and hexachlorobiphenyls still dominate, the tri- and tetra-chlorinated congeners were absent. This could be explained by the stronger adsorption of heavier PCB congeners (penta- and hexachlorobiphenyls) by glassware compared with the lighter PCB.

These results demonstrate that PCB persist in indoor environments even after about 15 years since they were banned. Indoor sources seem to be the cause of the high levels of PCB, as shown by the distribution of congeners. This contamination particularly affects buildings that date from before the PCB ban (1930–1980), i.e. most public buildings.

Validation of the analytical procedure

The reference material, SRM 1941.a "Organics in Marine Sediment" was analysed to determine the precision of the procedure. Three separate extractions were performed according to the sample-preparation procedure (Fig. 1), enabling calculation of the standard deviation of the measurements. The recoveries were corrected for the values obtained in the procedural blanks.

PAH

Sixteen PAH were found in Fraction 2; their concentrations and recoveries are given in Table 3. Some of the

Table 3 Recoveries and relative standard deviations for polycyclic aromatic hydrocarbons in SRM 1941.a

PAH	SRM 1941.a (ng g^{-1})	RSD (%)	Experimental (ng g^{-1})	Recovery (%)	RSD (%)
PHE	489± 23	4.7	432±146	88.3	33.8
AN	184± 14	7.5	108± 23	58.4	21.3
FLUO	981± 78	8.0	847±149	86.3	17.6
PYR	811± 24	3.0	665±114	82.1	18.2
BaA	427± 25	5.9	299± 51	70.0	17.1
CHRY+TRIPH	577± 35	6.1	567± 43	98.4	7.6
BbF+BkF+BjF	1442±150	10.4	1160± 56	80.4	4.8
BeP	553± 59	10.7	462± 41	83.6	8.9
BaP	628+ 52	8.3	463± 21	73.7	4.5
PER	452+ 58	12.8	366± 23	81.0	6.3
IP	501± 72	14.4	572± 30	114.3	5.2
BP	525+ 67	12.8	509± 25	97.0	4.9
DaA	117+ 13	11.1	77± 6	65.8	7.8
Total	7687±650	8.5	6527±728	85.0	11.2

Table 4 Recoveries and relative standard deviations for polychlorinated biphenyls in SRM 1941.a

PCB	SRM 1941.a (ng g^{-1})	RSD (%)	Experimental (ng g^{-1})	Recovery (%)	RSD (%)
28[a]	9.80± 3.70	37.8	10.56±1.35	107.8	12.8
44	4.80± 0.62	12.9	4.82±1.43	100.5	29.9
52	6.89± 0.56	8.1	8.56±0.82	124.3	9.3
66	6.80± 1.40	20.6	6.52±0.62	95.9	9.5
87	6.70± 0.37	5.5	3.55±0.34	53.0	9.6
101	11.00± 1.60	14.5	11.73±0.35	106.7	3.0
105	3.65± 0.27	7.4	3.60±0.05	98.6	1.4
118	10.00± 1.10	11.0	10.64±0.51	106.4	4.8
128	1.87± 0.32	17.1	1.60±0.19	85.6	11.9
138+163+164	13.38± 0.97	7.2	11.01±0.79	82.3	7.2
153	17.60± 1.90	10.8	16.02±0.36	91.0	2.2
170+190	3.00± 0.46	15.3	4.32±0.09	143.9	2.1
180	5.83± 0.58	9.9	8.68±0.42	148.9	4.8
206	3.67± 0.87	23.7	4.30±0.41	117.3	9.5
209	8.34± 0.49	5.9	10.18±0.63	122.0	6.2
Total	113.53±15.21	13.4	116.09±8.36	102.4	7.2

[a]Indicative concentration only

compounds are given as sums of two or three individual compounds because of co-elution from the gas chromatographic column (chrysene + triphenylene; benzo[*b*]fluoranthene + benzo[*j*]fluoranthene + benzo[*k*]fluoranthene; dibenz[*a*,*h*]anthracene + dibenz[*a*,*c*]anthracene). Recoveries range from 58% to 114%, with an average of 85% for all the compounds (Table 3). Relative standard deviations are quite high for the lighter compounds (phenanthrene, anthracene, fluoranthene, and pyrene) ranging from 17 to 34%, for phenanthrene. The heavier compounds, from chrysene to benzo[*g*,*h*,*i*]perylene have relative standard deviations equivalent to or lower than those given with the certified values. It is possible that the acid purification step leads to slight degradation of the smaller tri-aromatic PAH, leading to the low recovery for anthracene. The lowest recoveries were found for the PAH anthracene and dibenzanthracenes. These compounds are also the least abundant in the matrix with concentrations of only 117 and 184 ng g^{-1}. The recoveries of the PAH are, however, comparable with those in other studies [17, 18], and the results are reasonable for environmental analysis.

PCB

All the PCB are found in Fraction 1 except for PCB 128, which is in Fraction 2. For most of the PCB, and using the surrogate standards described, the recoveries are high (usually >80%); the results are presented in Table 4. The average recovery of all the PCB is 102.4%. Only for PCB 87 is the recovery low – 53%; the relative standard deviation of 10% is, however, not very high compared with those of the other PCB congeners. The recovery of PCB 52 is high – 124%; this can be explained by the close elution of a large interfering peak which is not removed by the HPLC purification step. High recoveries, approximately 120% to 150%, were obtained for PCB 170 to PCB 209. The peaks of these congeners are well-resolved in the chromatogram and co-eluting impurities do not seem to be present. Their quantification by use of other surrogate standards does not significantly change the result. The standard deviations calculated on three measures are comparable with those of the certified concentrations, except for PCB 44. The results are an improvement on previously published results [21] for some congeners, because of the extra HPLC purification step. This removes the polar pesticides which can interfere with the PCB, e.g. 4,4'-DDT which co-elutes with PCB 138.

Pesticides

Six chlorinated pesticides are certified in the marine sediment SRM 1941.a, and an indicative concentration is given for 4,4'-DDT. The recoveries and relative standard deviations are shown in Table 5. The recoveries of hexachlorobenzene, 4,4'-DDE, 4,4'-DDD and 4,4'-DDT were good, and ranged from 102% to 124%.

The relative standard deviations are quite high for this class of compound, except for hexachlorobenzene. This is probably because of the low concentrations of some of these pesticides in this matrix. The average recovery for the sum of the pesticides is 118.5%. The recovery of 2,4'-DDE is too high at 278%. This compound is not totally separated from interference, and its low concentration in this matrix, 0.73 ng g^{-1}, leads to a chromatographic peak which is small relative to those of other closely eluting compounds such as PCB 101, the concentration of which is 11.0 ng g^{-1}. To improve the recovery of this compound a larger amount of certified material should be extracted.

Recovery of *cis*-chlordane and *trans*-nonachlor from this matrix are very high, 420% and 250%, respectively. When analysed without addition of PAH surrogates recoveries of these compounds are much improved – 130% and 70%, respectively. *cis*-Chlordane and *trans*-nonachlor are not entirely separated in the chromatogram and are co-eluted with deuterated pyrene and pyrene. The certified values of these compounds are determined by mass spec-

Table 5 Recoveries and relative standard deviations for pesticides in SRM 1941.a

Pesticide	SRM 1941.a (ng g^{-1})	RSD (%)	Experimental (ng g^{-1})	Recovery (%)	RSD (%)
HCB	70 ±25	35.7	83.0 ±1.7	118.6	2.0
2,4'-DDE	0.73± 0.11	15.1	2.03±0.35	278.1	17.2
4,4'-DDE	6.59± 0.56	8.5	6.78±1.90	102.9	28.0
4,4'-DDD	5.06± 0.58	11.5	6.28±1.40	124.1	22.3
4,4'-DDT[a]	1.25± 0.10	8.0	1.28±0.40	102.4	31.3
cis-Chlordane	2.33± 0.56	24.0	9.78±2.43	419.7	24.8
			3.07±0.18[b]	131.8	5.9
trans-Nanochlor	1.26± 0.13	10.3	3.18±0.42	252.4	13.2
			0.90±0.04[b]	71.4	4.4
Total	87.22±27.04	31.0	103.34±5.97[b]	118.5	5.8

[a]Indicative concentration only
[b]Concentration determined without addition of PAH deuterated standards

trometry, which can clearly distinguish between the compounds as a result of their different molecular mass, m/z= 202, pyrene; 212, pyrene-d_{12}; 373, *cis*-chlordane; 409, *trans*-nonachlor. In this matrix pyrene is present at a concentration of 811±24 ng g^{-1}, compared with 2.33±0.56 ng g^{-1} for *cis*-chlordane and 1.26±0.13 ng g^{-1} for *trans*-nonachlor. To avoid interference problems GC–MS is the preferred method for detection of these compounds, although the higher detection limits of GC–MS are not always practical for environmental samples. The determination of these pesticides with the developed sample preparation procedure and analysis by GC–ECD remains a suitable technique which leads to good recoveries, with the condition that deuterated pyrene is not used as an surrogate standard.

Conclusion

The analytical procedure combining microwave-assisted extraction and pre-purification steps developed for the determination of PAH, PCB, and chlorinated pesticides in sediment matrices enables the precise determination of most of these compounds. This procedure enables the determination of the three classes of contaminant in the same extract and is thus a timesaving method.

Some problems persist however for certain compounds in these matrices, notably for the two pesticides *cis*-chlordane and *trans*-nonachlor. The interference of PAH in the GC–ECD chromatogram can lead to over-estimation of organochlorine compounds. Although the response factors of the PAH are low compared with those of chlorinated compounds, the PAH are often present at concentrations 100 times greater. Elimination of deuterated pyrene as an surrogate standard for PAH determination limits the interference and enables good recovery of these compounds.

The use of PCB congeners which are absent from environmental samples as surrogate standards improves the precision of PCB quantification. Similarly the use of several surrogate standards simultaneously enables the analyst to identify possible co-elutions with the standards, as can be shown by the example of OCN for SRM 1941.a. Care should be taken with the use of OCN as an surrogate standard for PCB analysis – the possible presence of interference should always be investigated.

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