

# Efficient isolation of polyaromatic fraction from aliphatic compounds in complex extracts using dimethylformamide–pentane partitionings

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## Abstract

A liquid–liquid partitioning method was optimized for the rapid and quantitative separation of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from aliphatic hydrocarbons in complex primary extracts. This technique was based on the selective extraction of PAHs and PCBs from an aliphatic solvent into dimethylformamide (DMF). Partition experiments demonstrated that the optimal performance was achieved with a DMF (5% H<sub>2</sub>O)–*n*-pentane binary system. The optimized application of two consecutive DMF (5% H<sub>2</sub>O)–*n*-pentane treatments to extracts from two different polluted sediments facilitated the elimination of alkanes and unresolved complex mixture by more than 94% while the average recoveries of spiked deuterated-PAHs and <sup>13</sup>C labeled PCBs ranged from 84 to 94 and 75 to 96%, respectively.

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## 1. Introduction

During the last decades, the interest in hydrophobic organic contaminants, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans has significantly increased. Hazards associated with these compounds are mainly due to their persistence, their hydrophobic and thereby bioaccumulating character and their potentially toxic, carcinogenic, and/or mutagenic effects on animals and humans [1,2].

The analysis of PCBs, PAHs and other aromatic compounds in environmental samples requires a preliminary separation from the co-extracted interfering compounds (e.g. aliphatics, lipids, fatty acids). Although, chromatographic techniques, such as adsorption chromatography [3,4], gel permeation chromatography [5], high-performance liquid chromatography [6,7] are commonly used for this purpose, there are cases where these clean-up methods might be in-

efficient. For instance, during the purification of extracts derived from samples with high organic content (e.g. sewage sludge), improper separation, overloading, and/or clogging of the chromatographic column may occur and subsequently affect the quantification of the analytes. This case may be even worse during the separation of individual PAHs or other aromatic compounds from huge amounts of environmental matrix (e.g. often several kilograms of sediment) required to perform compound-specific isotope analysis [8], NMR analysis or bioassay tests.

Liquid–liquid extraction [9–12] and countercurrent chromatography [13] are two alternative methods which can simplify the isolation of polyaromatic compounds from complex matrices. Some of the inherent advantages of both techniques are large sample capacity and small solvent consumption. Moreover, liquid–liquid extraction is cheap, fast, simple in use, and does not require any special equipment. In fact, several waterless biphasic systems were developed for the cleanup of PAHs in the mid-1980s [9–12], but nowadays, liquid–liquid extraction continues to be used in only a few laboratories.

In a previous study, it was demonstrated that the partitioning between dimethylsulfoxide (DMSO) and *n*-pentane can

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be a simple and efficient procedure for the cleanup of PAHs and substituted-PAHs from aerosol samples [10]. However, a later study showed that the partition coefficients of PAHs between dimethylformamide (DMF) and an aliphatic solvent are about two times higher than the corresponding coefficients for DMSO [13]. Consequently, the isolation of polyaromatic compounds by liquid–liquid extraction is expected to be more efficient when DMF is used in that biphasic system. Although liquid–liquid extraction with DMF has been previously used [11,13], the efficiency of this procedure has never been published. The goal of this study was the optimization and the evaluation of this method for the isolation of PAHs and PCBs from co-extracted aliphatic components.

## 2. Experimental

### 2.1. Materials

All the experiments for the optimization of DMF liquid–liquid partition were performed by using standard solutions of PAHs (17 compounds), PCBs (13 congeners) and *n*-alkanes (10 compounds). The mixture of PAHs was a standard reference material (SRM 2260) prepared by the National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA). The mixtures of PCBs and *n*-alkanes were prepared from pure substances which were purchased from Dr. Ehrenstorfer (Augsburg, Germany) and Sigma–Aldrich (St. Louis, MO, USA), respectively. Deuterated-PAHs and <sup>13</sup>C labeled PCBs used in the present study were purchased from Dr. Ehrenstorfer (Augsburg, Germany) and Cambridge Isotope Laboratories (Andover, MA, USA), respectively. All solvents were obtained from Riedel de Haen (Seelze, Germany).

### 2.2. Procedure

Initially, the partition ratios of PAHs, PCBs and *n*-alkanes between DMF and several aliphatic solvents were determined by batch equilibrium experiments. In brief, a certain amount of PCBs (18 ng per congener), PAHs (252 ng per compound), and *n*-alkanes (500 ng per compound) were placed into a glass centrifuge tube and equal volumes of DMF (3 ml) and the aliphatic hydrocarbon solvent (3 ml) were then added. The tube was capped, vigorously shaken for 3 min and subsequently centrifuged at 2500 rpm for 3 min. After centrifugation, 2 ml of the aliphatic solvent were carefully removed and transferred to a glass vial. This fraction was spiked with a certain amount of the internal standards (chrysene-*d*<sub>12</sub>, <sup>13</sup>C labeled CB 153), it was evaporated to 200 μl and 2 μl were injected on a Fisons 8060 gas chromatograph (GC) equipped with a PTE-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Supelco Inc.) with a Fisons MD 800 mass spectrometer (MS) operated in the electron impact mode. The amounts of PAHs, PCBs and *n*-alkanes retained

in the aliphatic solvent layer were subsequently calculated.

The amount of the analytes that remained in the DMF phase after the equilibration experiments were also quantified. For this reason, a portion of DMF (2 ml) was transferred in a separate tube and mixed with 4 ml of *n*-hexane and 2 ml of water. The hexane was separated and the stripping procedure was repeated with another 4 ml of hexane. All hexane fractions were combined in a tube, spiked with a certain amount of internal standards and analyzed in the same way as mentioned above.

The partition ratio  $K_D$  of each compound was calculated by using the equation:

$$K_D = \frac{A_{\text{DMF}}}{A_{\text{solvent}}} \times \frac{V_{\text{solvent}}}{V_{\text{DMF}}} \quad (1)$$

where  $A_{\text{DMF}}$  and  $A_{\text{solvent}}$  are the amounts of the analyte in the DMF and aliphatic solvents, respectively, while  $V_{\text{DMF}}$  and  $V_{\text{solvent}}$  the volumes of DMF and aliphatic solvents, respectively, during the equilibration experiments. Furthermore, the fraction  $F_n$  of a solute that was recovered in the DMF phase after  $n$  discrete partitions is readily calculated by the following equation:

$$F_n = 1 - \left[ \frac{V_{\text{solvent}}}{(V_{\text{solvent}} + K_D V_{\text{DMF}})} \right]^n \quad (2)$$

The deactivation of DMF by addition of water and its effect on the partition ratios was also investigated. For this reason, the partition ratios of PCBs, PAHs and *n*-alkanes were determined for the case of DMF deactivated with a range of water fractions. Namely, equilibration experiments were performed in the same way as previously reported by using *n*-pentane as an aliphatic solvent and DMF deactivated with 2.5, 5, 7.5, 10 and 15% water. The effect of temperature was not investigated since it has been reported that it will have a minimum effect upon liquid–liquid partition ratios [10,14].

## 3. Results and discussion

### 3.1. Effect of solvent type

The partition ratios of PAHs were measured in triplicate for the different biphasic systems (Fig. 1). The results obtained from these experiments were highly reproducible and the relative standard deviation for  $K_D$  values was on average 13%. In general, partition ratios exhibited an exponential increase with the molecular mass ( $M_r$ ) of PAHs. Regardless of the aliphatic solvent used, the PAH members up to fluorene ( $M_r$  up to 166) provided the lowest  $K_D$  values (2.1–9.5), while benzo[ghi]perylene exhibited the highest ones (20.2–76.8). This behavior was expected since PAHs with more aromatic rings possess more  $\pi$ -electrons and, therefore, can exhibit more extensive interaction with the unshared electrons of oxygen atoms of DMF molecules. In

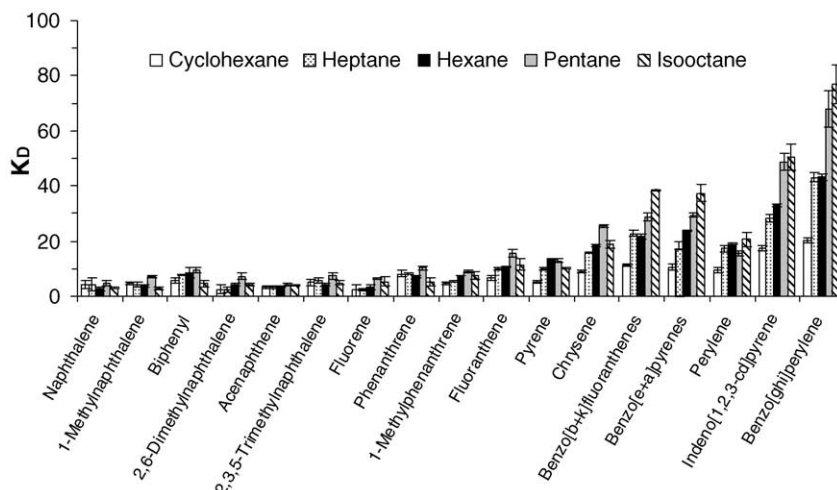


Fig. 1. Partition ratios for polycyclic aromatic hydrocarbons distributed between dimethylformamide and several aliphatic hydrocarbon solvents. The error bars correspond to  $\pm 1$  standard deviation ( $n = 3$ ).

general, compounds with higher degree of aromaticity will tend to shift from the aliphatic solvent toward the DMF layer during partition experiments.

The aliphatic solvent used in the biphasic system also affected the partition ratios of individual PAHs. In fact, higher  $K_D$  values were achieved by using DMF–pentane and DMF–*iso*-octane systems, while much lower values were observed for DMF–cyclohexane. For the case of pentane, the partition ratios of PAHs with up to four aromatic rings were about 25% higher than in any other solvent. On the other hand, the  $K_D$  values of PAHs with more than four aromatic rings were almost 17% higher in DMF–*iso*-octane system (Fig. 1). Based on Eq. (2), it can be deduced that both pentane and *iso*-octane will enable quantitative extraction of all PAHs after two equivolume partitions.

The partition ratios of PCBs were also measured in triplicate and the relative standard deviation of  $K_D$  values was on average 8%. The  $K_D$  values of PCBs were always lower than those of PAHs regardless of the aliphatic solvent, and tended to decrease with the degree of chlorination (Fig. 2).

The highest values were observed for CB 18 (2.4–6.9) and the lowest for CB 199 (0.9–2.7). The decreasing trend can be explained by the fact that an increasing number of chlorine atoms on the biphenyl skeleton causes larger steric hindrance and obstruct the dispersive interactions between DMF and PCB molecules. The cyclohexane–DMF system provided the lowest partition ratios, while the highest  $K_D$  values were achieved for PCBs when the DMF–pentane biphasic system was used (Fig. 2).

The partition ratios measured for *n*-alkanes were also characterized by high reproducibility (relative standard deviation was on average 14%), but they were at least two orders of magnitude lower than those observed for PCBs and PAHs. Although the  $K_D$  values of *n*-alkanes obtained from heptane–DMF system were somewhat lower compared with the other biphasic systems, the type of aliphatic solvent did not significantly affect the partition ratios of alkanes. Regardless of the aliphatic solvent used, the partition ratios of *n*-alkanes ranged between 0.011 and 0.047 and provided a gradual decrease with increasing molecular mass.

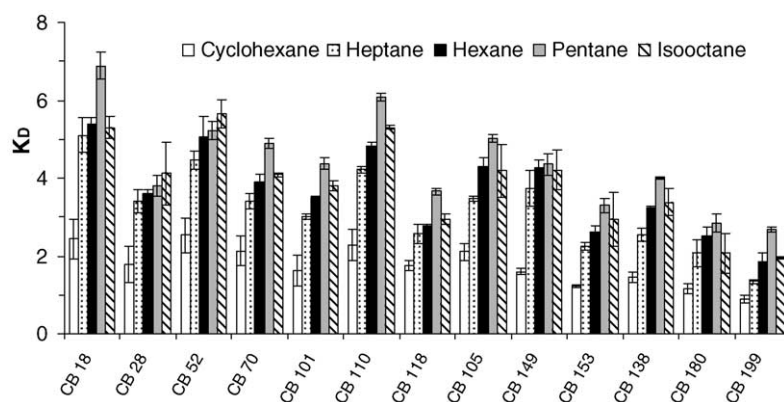


Fig. 2. Partition ratios for polychlorinated biphenyls distributed between dimethylformamide and several aliphatic hydrocarbon solvents. The error bars correspond to  $\pm 1$  standard deviation ( $n = 3$ ).

Table 1

Enrichment factors of PAHs and PCBs against *n*-alkanes for different biphasic systems composed of an aliphatic solvent and dimethylformamide

	Cyclohexane	Heptane	Hexane	Pentane	<i>iso</i> -Octane
ER(PAHs/alkanes)	296 ± 18	624 ± 43	496 ± 18	707 ± 16	760 ± 11
ER(PCBs/alkanes)	68 ± 5	162 ± 5	136 ± 3	170 ± 9	162 ± 5

The errors correspond to ±1 standard deviation ( $n = 3$ ).

The especially low  $K_D$  values of *n*-alkanes demonstrated that these compounds are poorly associated with dimethylformamide and tend to be retained in the aliphatic solvent. This was expected since *n*-alkanes do not possess any  $\pi$ -electrons and their interactions with other organic molecules are only based on van der Waals forces. The gradual decrease of  $K_D$  values with increasing molecular mass of *n*-alkanes can also be explained by this type of forces. The van der Waals interactions between *n*-alkanes and the aliphatic solvent become larger as the molecular size of *n*-alkanes increases, and thus the dissolution into the aliphatic solvent should be easier for *n*-alkanes of higher molecular size.

The solvent that should be selected as the most appropriate for the application of this binary phase partition as a clean-up method, should promote the selective enrichment of PAHs and PCBs against *n*-alkanes in the DMF layer. Thus, the enrichment factor of PAHs (or PCBs) against *n*-alkanes was calculated for each biphasic system based on the following equation:

$$ER_X = \frac{K_{D,X}}{K_{D,alkanes}} \quad (3)$$

where  $ER_X$  and  $K_{D,X}$  is the enrichment factor and the average partition ratio of PAHs (or PCBs), respectively, and  $K_{D,alkanes}$  is the average partition ratio of *n*-alkanes. The high enrichment factors calculated for PAHs and PCBs for the case of pentane and *iso*-octane (Table 1) confirm that either of these solvents may favorably be used in conjunction with dimethylformamide. Since *iso*-octane is less volatile and thus more difficult to evaporate during the concentration of the samples, *n*-pentane was finally selected as the most appropriate.

### 3.2. Effect of $H_2O$ deactivation

Although the extraction of PAHs and PCBs with the DMF–pentane biphasic system will be quantitative after two equivolume partitions, the  $K_D$  values of *n*-alkanes show that a small portion of these compounds will also be extracted in the DMF layer. In order to further improve the performance of the liquid–liquid extraction method

we investigated the partition behavior of PAHs, PCBs and *n*-alkanes with deactivation of the DMF phase with water.

The partition ratios of PAHs and PCBs linearly decreased with increasing amount of water in the dimethylformamide phase. The  $K_D$  values of PAHs and PCBs decreased by approximately 65 and 85%, respectively, when the fraction of water in DMF increased from 2.5 to 15%. This decrease can be attributed to the stronger interactions between DMF and  $H_2O$  molecules due to the formation of hydrogen bonds and the decreased ability of DMF to interact with the aromatic compounds. In addition, the  $K_D$  values of *n*-alkanes exhibited a significant decrease (approximately 50%) as the water content in DMF increased from 2.5 to 15%.

The enrichment factor of PAHs and PCBs against *n*-alkanes were subsequently calculated (Eq. (3)) for different amounts of  $H_2O$  in the DMF phase (Table 2). The enrichment factors of both PAHs and PCBs against *n*-alkanes, gradually increased as the water content in DMF increased from 0 to 5%, while they decreased for higher proportions of water. Based on these results it was concluded that DMF with 5% of water is the optimum mixture for the selective extraction of PAHs and PCBs from the *n*-pentane phase. Overall, the enrichment factors of PAHs and PCBs achieved with the deactivation of DMF with 5% water (Table 2) were improved by 50 and 10%, respectively, compared with those found when using a biphasic system of *n*-pentane with pure DMF (see Table 1).

### 3.3. Optimal number of partitions

Based on the partition ratios of PAHs and PCBs, it was estimated (Eq. (2)) that, on average, 97% of PAHs and 90% of PCBs should be recovered in DMF (5%  $H_2O$ ) after two discrete partitions with *n*-pentane. This estimation was further evaluated by the application of the optimized method to a mixture of PAHs (~100 ng per compound) and PCBs (~10 ng per congener). The solution of the analytes (in *n*-pentane) was partitioned with equal volume of DMF(5% $H_2O$ ) for three consecutive times and the amount of PAHs and PCBs recovered in each step was further quan-

Table 2

Enrichment factors of PAHs and PCBs against *n*-alkanes for different amounts of  $H_2O$  in DMF–pentane biphasic system

	DMF–2.5% $H_2O$	DMF–5% $H_2O$	DMF–7.5% $H_2O$	DMF–10% $H_2O$	DMF–15% $H_2O$
ER(PAHs/alkanes)	892 ± 16	1059 ± 38	979 ± 31	804 ± 2	704 ± 27
ER(PCBs/alkanes)	179 ± 4	186 ± 13	146 ± 14	82 ± 3	54 ± 2

Table 3  
Percentage amount of PAHs and PCBs recovered in DMF–5% H<sub>2</sub>O during three consecutive partitions with *n*-pentane

Compound <sup>a</sup>	Amount (%)		
	First step	Second step	Third step
Naphthalene	74	20	6
Acenaphthene	65	25	10
Fluorene	64	26	10
Phenanthrene	89	9	2
Fluoranthene	92	7	1
Pyrene	89	10	1
Chrysene	92	8	0
Benzo[ <i>b</i> ]fluoranthene	95	5	0
Benzo[ <i>e</i> ]pyrene	88	11	0
Perylene	97	3	0
Indeno[1,2,3- <i>cd</i> ]pyrene	97	3	0
Benzo[ <i>ghi</i> ]perylene	95	5	0
CB 18	80	17	3
CB 70	74	20	5
CB 101	68	25	7
CB 118	70	23	7
CB 149	66	24	9
CB 153	61	29	10
CB 180	57	30	13
CB 199	49	36	15

<sup>a</sup> The amounts of PAHs and PCBs used in the partition experiments were approximately 100 and 10 ng per compound, respectively.

tified. Each portion of DMF (5% H<sub>2</sub>O) was separately analyzed as described in Section 2.2.

The results were normalized against the total amount of each compound recovered during all three extraction steps and they are presented in Table 3. It was confirmed that most of the PAHs and PCBs indeed were efficiently extracted after two discrete partitions with DMF–5% H<sub>2</sub>O. The cumulative fraction of PAHs and PCBs isolated during the first two extraction steps was on average 97 and 91%, respectively. The application of more than two extraction steps should be avoided because the recoveries of PAHs and PCBs would not be substantially improved, while this would mainly cause contamination of the DMF layer with *n*-alkanes and other non-aromatic compounds.

### 3.4. Performance evaluation of the liquid–liquid extraction method

The performance of the optimized liquid–liquid extraction technique was tested for two heavily contaminated sediment samples collected from Slussen, Sweden (heavily polluted area of the Stockholm Waterways close to the city center) and Lake Ketelmeer, the Netherlands (polluted sedimentation area of Rhine River). These samples (about 0.5 g from each) were Soxhlet extracted with toluene for 24 h and the extracts were evaporated to almost dryness. Solvent extracts were then spiked with deuterated PAHs (~500 ng per compound) and <sup>13</sup>C labeled PCBs (~35 ng per compound) and the solvent of this mixture was exchanged to *n*-pentane.

Subsequently, the optimized liquid–liquid extraction method was applied. In brief, the pentane solution (2 ml) was partitioned two times with equal volumes of DMF–5% H<sub>2</sub>O and the layers of dimethylformamide were combined in a glass tube. After the addition of 4 ml of water, PAHs and PCBs were back-extracted in 4 ml of hexane. Back extraction was repeated one more time with another 4 ml of hexane. The volume of the hexane phase was then reduced and the sample was analyzed by GC–MS as described above. The chromatograms obtained from Slussen sediment extract before the clean-up procedure (Fig. 3a) demonstrated high peaks of aliphatic hydrocarbons (between C<sub>24</sub> and C<sub>35</sub>) superimposed on a typical UCM (unresolved complex mixture) pattern. It is interesting to note that the peaks of deuterated-PAHs and <sup>13</sup>C labeled PCBs were completely obscured by the extensive hump of UCM.

Recently, UCM was thoroughly investigated by using comprehensive two-dimensional gas chromatography and it was shown that branched alkanes, one- and two-ring alkylcycloalkanes dominate its composition [15]. Since the liquid–liquid extraction with DMF was specially optimized in order to separate aromatic compounds from *n*-alkanes, a significant fraction of the UCM should also be removed during the clean-up procedure. The chromatogram of the sediment sample after the application of the liquid–liquid extraction (Fig. 3b) demonstrates the complete removal of *n*-alkanes (between C<sub>24</sub> and C<sub>35</sub>) and the partial removal of the UCM. Based on the total ion chromatograms, we further estimated that about 94% of the UCM was eliminated from the original sample during the cleanup with DMF. Most of the dominant peaks shown in Fig. 3b correspond to native PAHs, deuterated-PAHs and <sup>13</sup>C labeled PCBs. The efficient cleanup of the sediment extract enabled the quantification of native PAHs and PCBs and the concentrations of ∑ PAHs (sum of 17 PAHs) and ∑ PCBs (sum of 13 PCBs) were 16.7 μg/gdw and 380 ng/gdw, respectively. Similar results were observed during the treatment of Ketelmeer sediment. Alkanes were completely removed after the application of DMF clean-up procedure, while the removal of

Table 4  
Absolute recoveries for selected PAHs (252 ng per compound) and PCBs (18 ng per compound) after two consecutive treatments with a DMF (5% H<sub>2</sub>O)–*n*-pentane binary system

Compound	Recovery (%)	Compound	Recovery (%)
Biphenyl	84 ± 10	CB 18	81 ± 2
Acenaphthene	83 ± 9	CB 28	80 ± 3
Fluorene	84 ± 11	CB 52	82 ± 2
Phenanthrene	86 ± 11	CB 70	82 ± 3
Pyrene	83 ± 7	CB 110	84 ± 4
Chrysene	93 ± 7	CB 118	83 ± 5
Benzo[ <i>k</i> ]fluoranthene	97 ± 11	CB 149	88 ± 8
Benzo[ <i>e</i> ]pyrene	97 ± 11	CB 138	89 ± 7
Perylene	96 ± 11	CB 180	91 ± 11
Indeno[1,2,3- <i>cd</i> ]pyrene	100 ± 10	CB 199	94 ± 25

The errors correspond to ±1 standard deviation (*n* = 3).

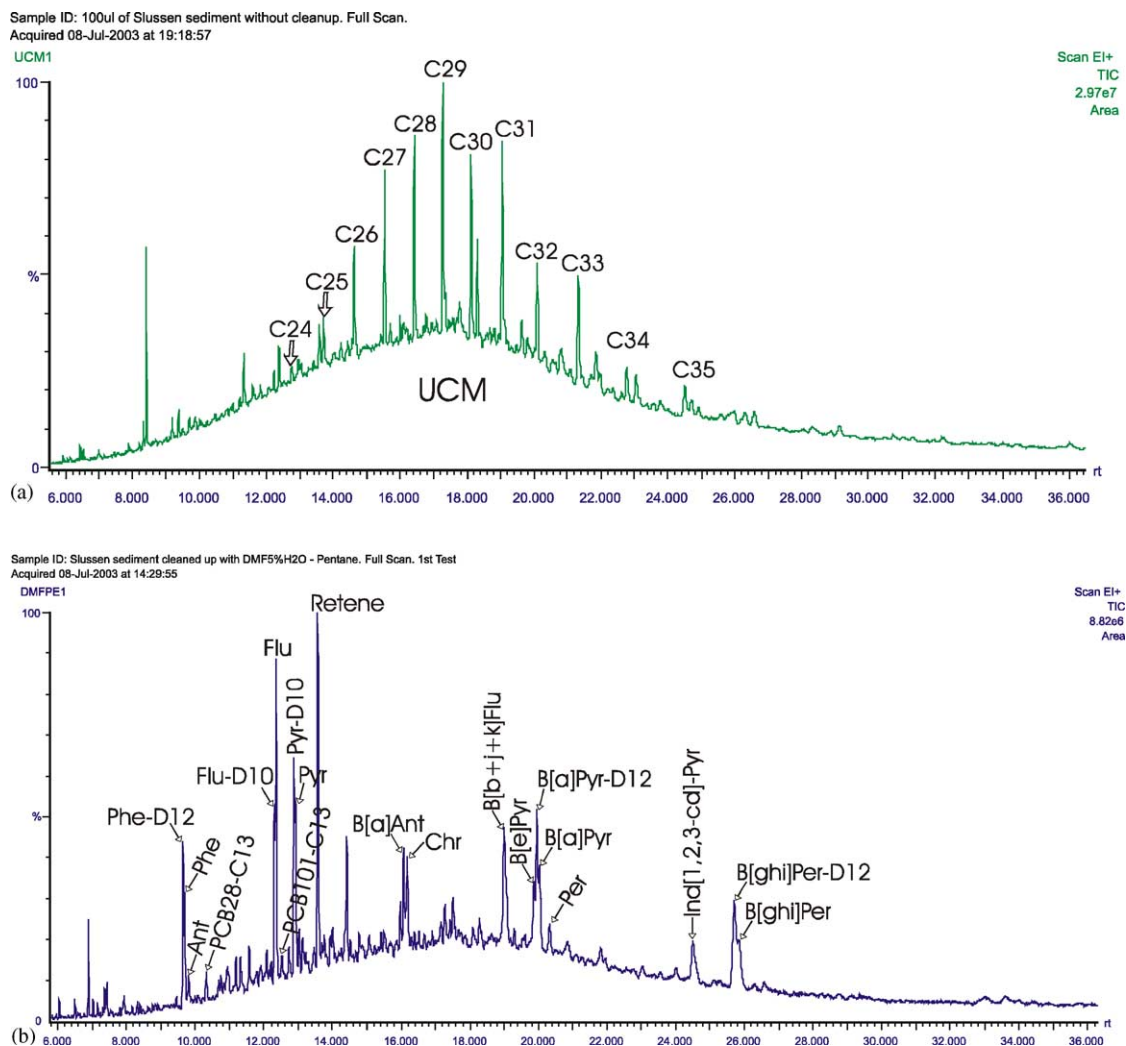


Fig. 3. Gas chromatograms of Slussen sediment extract spiked with deuterated PAHs ( $\sim 500$  ng per compound) and  $^{13}C$  labeled PCBs ( $\sim 35$  ng per compound): (a) before (original extract) and (b) after two consecutive DMF (5%  $H_2O$ )– $n$ -pentane treatments.

the UCM approached 96%. The concentrations of  $\sum$  PAHs and  $\sum$  PCBs in Ketelmeer sediment were  $23.8 \mu\text{g/gdw}$  and  $1020 \text{ ng/gdw}$ , respectively. The recoveries of individual deuterated PAHs and  $^{13}C$  labeled PCBs obtained from both sediments ranged from 84 to 94 and 75 to 96%, respectively.

The optimized clean-up method was also applied to standard mixtures of native PAHs (252 ng per compound) and PCBs (18 ng per compound) in order to assess their absolute recoveries and the repeatability of the method. In general, the average recoveries of PAHs (83–100%) were slightly higher than those of PCBs (80–94%), but for both groups of compounds the recoveries were higher than 80% (Table 4). Moreover, the repeatability of the liquid–liquid extraction method was fairly good for a variety of PAH members (relative standard deviation was between 7 and 13%) and PCB congeners (relative standard deviation was between 3 and 26%).

#### 4. Conclusions

In order to optimize a liquid–liquid partitioning method for the separation of PAHs and PCBs from aliphatic hydrocarbons, batch equilibrium experiments were performed in different biphasic systems of dimethylformamide with several aliphatic solvents. The partition ratios of these compounds demonstrated that the optimal separation can be achieved by using two consecutive treatments with a DMF (5%  $H_2O$ )– $n$ -pentane binary system.

The optimized method was applied to polluted sediment extracts and high recoveries were obtained for deuterated PAHs (84–94%) and  $^{13}C$  labeled PCBs (75–96%), while  $n$ -alkanes were quantitatively removed ( $>99\%$ ) and the unresolved complex mixtures (UCM) were reduced by more than 94%. The same procedure was applied in triplicate for a standard mixture of PAHs (252 ng per compound) and PCBs (18 ng per compound) and the average recoveries of

several PAH and PCB congeners ranged from 83 to 100% and 80 to 94%, respectively. In addition, the repeatability of the method was sufficient for both PAHs and PCBs (relative standard deviation: <26%). Our results suggest that liquid–liquid extraction with DMF can be applied as an alternative, simple clean-up method for the isolation of PAHs, PCBs and other polyaromatic compounds from complex environmental samples.

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