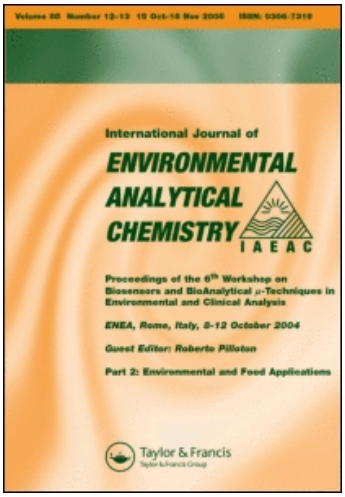

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Evaluation and optimization of extraction and clean-up methods for the analysis of polycyclic aromatic hydrocarbons in peat samples

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The analysis of PAH in peat samples is complicated by the high content of organic matter in peat which affects both extraction efficiency and analytical quality. Therefore, we evaluated the efficiencies of three extraction methods (accelerated solvent extraction (ASE), fluidized bed extraction, ultrasonic extraction) and several clean-up techniques in order to find the best set of methods. ASE proved to be the best extraction method. For clean-up, a procedure using aluminium oxide and silica gel showed the highest efficiency, whereas a method originally developed for soil samples failed to remove the peat matrix satisfactorily. With the optimized extraction and clean-up procedure, 170 samples from Canadian bogs were analysed for PAH. With overall recovery rates between 69 ± 14 and $89 \pm 16\%$ and an inaccuracy of $\leq 20\%$, the optimized method was a well suitable tool for the analysis of PAH in peat samples.

Keywords: ASE; Ultrasonic extraction; Fluidized bed extraction; Column chromatography; PAH

1. Introduction

For the investigation of historical atmospheric depositions of environmental contaminants, ombrotrophic bogs have turned out to be excellent archives [1–3]. However, the determination of organic contaminants such as polycyclic aromatic hydrocarbons (PAH) in peat can be difficult because of its high proportion of organic material: up to 95% of peat consists of organic matter. Due to the physical–chemical properties of PAH, strong adsorption of PAH to this matrix can be expected, leading to limited extractability of these compounds [4]. Moreover, another complication encountered in analysis of PAH is their isolation from a matrix that is rich in naturally occurring organic molecules like for example humic substances, lignins, pigments, or phenols [1]. Removal of these matrix compounds is essential in order to reduce interferences during analysis and thus to improve analytical quality.

Various extraction methods, solvents and clean-up techniques were and are used for the determination of PAH in matrices rich in organic matter. In the past, soxhlet

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extraction [3, 5–8] and ultrasonic extraction (USE) [9] were by far the extraction techniques most commonly used. Other extraction methods like shaking [1] or saponification were less commonly employed. Recently, modern extraction techniques – for example super-critical fluid extraction [10], accelerated solvent extraction (ASE) [11, 12], or fluidized bed extraction (FBE) [13] – were applied. It was found that these methods were as good as the more classical ones or even better, that they consume less solvent, and/or that they are more time-effective [14]. With respect to sample purification, column chromatography with florisil [3, 7], silica gel [9], and silica gel in combination with aluminium oxide (alox) [11] as stationary phase were widely used. Hexane, dichloromethane [7, 9], and dichloromethane/hexane in different mixtures [8, 15] were subsequently used for elution.

Several studies investigated the efficiency of different methods for the extraction of PAH from soil samples. Berset *et al.* [14] as well as Hollender *et al.* [16] found that ASE was more efficient than sonication, shaking extraction and/or soxhlet extraction. However, soxhlet extraction showed the smallest variations in the results compared to all other methods [14]. Both studies concluded that ASE was the preferable extraction method. Hollender *et al.* [16] also tested different extraction solvents. In general, the use of a mixture of two solvents with different properties led to higher recoveries. Obviously these mixtures were most suitable to disrupt the PAH–matrix interactions. Since none of these methods has been tested for peat samples, however, one aim of this study was to compare the extraction yields of ASE, FBE and USE for the determination of PAH in peat samples.

For the purification of extracts from highly organic matrices like soil samples, column chromatography with silica gel and aluminium oxide (alox) as stationary phases has proved to be effective [9, 12, 15]. Due to the exceptional high content of organic matter in peat, however, we encountered difficulties during sample clean-up and analysis with a method described by Wilcke *et al.* [15]. Therefore, the second aim of this study was to evaluate other methods for sample clean-up in order to improve the chromatographic separation and quantification of PAH. One method incorporated an additional clean-up step with a polymeric adsorption resin, whereas the third method – which had been used for aerosol samples [17] – utilized only alox-silica chromatography with different degrees of deactivation and different amounts of stationary phases compared to the first method. All methods were evaluated regarding their performance for the extraction of the 16 PAH from the EPA priority list; however, only PAH with molecular weight $MW \geq 178\,g\,mol^{-1}$ were considered in this study, since we were not interested in the more volatile compounds with lower molecular weight.

2. Experimental

2.1 *Peat sample*

Peat samples for the optimization of the analytical procedure were taken in April 2003 at the site 'Schlöppnerbrunnen' located in the Fichtelgebirge, Germany, a fen that is dominated by *Sphagnum* mosses. The soil has been classified as Fibric Histosol [18]. The samples were dried at 30°C for about two weeks. Afterwards they were ground, homogenized and stored at room temperature in amber glass bottles until analysis.

2.2 *Solvents, chemicals, standard solutions, and glassware treatment*

All solvents used were of picograde quality and purchased form Promochem (Wesel, Germany). PTFE Filters (FF 1.1, 10–20 µm) for FBE were from IKA (Staufen, Germany). Glass fibre filters (GF/B) for ASE were from Whatman (Maidstone, UK). Quartz sand (granular 1–2 mm from J. T. Baker, Griesheim, Germany) and celite (celite 545 coarse from Fluka, Buchs, Switzerland) were used as extraction additives for ASE. Na_2SO_4 (p.a.) was from Merck (Darmstadt, Germany). Before use it was activated at 250°C for 12 h. For column chromatography, silica gel (silica 60, 200 mesh), alox (alox 90, neutral, 70–230 mesh), and the adsorption resin Lichrolut EN were purchased from Merck (Darmstadt, Germany). Silica and alox were activated for 12 h at 250°C before use. Defined deactivation of silica and alox was done with exactly known weight percentages of ultrapure water after the material cooled down to room temperature. The PAH stock solution containing the 16 EPA–PAH (2000 µg mL^{-1}; for abbreviations used see the Appendix) was from Ultra Scientific (North Kingstown, USA). Pery and BeP were from Fluka and Sigma (Buchs, Switzerland). All deuterated PAH were purchased as solids (purity > 98%) from Cambridge Isotopes Laboratories (Andover, USA). Stock solutions were produced by dissolving a weighed amount of PAH in toluene. Calibration solutions were established by appropriate dilution of the stock solutions (concentration range: 0.2–10 µg mL^{-1}).

For the determination of recovery rates, samples were spiked with 100 µL of a solution containing several deuterated PAH (Naph-d_8, Fluo-d_{10}, Ace-d_{10}, Pyr-d_{10}, Pery-d_{12}, Chry-d_{12}; 5 µg mL^{-1} each) prior to extraction. In the following, this solution is called internal standard solution. Spiking was done after the sample was loaded into the extraction device; subsequently, the solvent was allowed to evaporate. As injection standard, 200 µL of a solution containing Ant-d_{10} and BaA-d_{12}, 2 µg mL^{-1} each, was used. The results reported here were calculated with Ant-d_{10}, since the quantification of BaA-d_{12} was sometimes affected by chromatographic interferences in peat extracts.

The entire glassware used was machine-washed and rinsed with cyclohexane/acetone 2 : 1 (v : v; p.a. quality) before it was baked at 250°C for 12 h.

2.3 *Ultrasonic extraction (USE)*

Peat samples (5 g dw) were weighed into 100 mL centrifuge glasses and spiked with the internal standard solution. Afterwards samples were extracted with 50 mL hexane/acetone 2 : 1 (v : v) for 15 min in an ultrasonic bath (Sonorex, Bandelin electronic GmbH & Co. KG, Berlin, Germany). Samples were centrifuged for 5 min at 2370 g (Labofuge Ae, Heraeus Sepatech). Water residues in the extracts were removed through filtration with Na_2SO_4, and the extract was transferred into 250 mL pointed flasks. This extraction cycle was repeated two times; the extracts were combined.

2.4 *Fluidized bed extraction (FBE)*

Peat samples (5 g dw) were weighed, loaded in the prepared extraction tubes and spiked with the internal standard solution. The samples were extracted with a solid–liquid extractor (fexIKA Vario Control, IKA, Staufen, Germany) with 150 mL hexane/acetone 2 : 1 (v : v). The solvent was heated to a temperature of 85°C which was held for 15 min. Once the heating time had elapsed, the solvent was cooled down to 30°C.

This cycle was carried out five times. Afterwards water residues were removed through filtration with Na_2SO_4 and the extracts were transferred into 250 mL pointed flasks.

2.5 *Accelerated solvent extraction (ASE)*

Peat samples (5 g dw) were filled in stainless steel extraction vessels and spiked with the internal standard solution. Samples were extracted with hexane/acetone 2 : 1 (v : v) in an accelerated solvent extractor (Dionex 200, Dionex Co. Sunnyvale, USA). Cells were filled with solvent, pressurized to 14 MPa, and heated to 120°C within 6 min. Pressure and heat were held for 5 min (static extraction) followed by rinsing with cold solvent (60% of the cell volume) and purging with argon for 90 s. This extraction cycle was repeated once again. Afterwards water residues were removed through filtration with Na_2SO_4 and the extracts were transferred into 250 mL pointed flasks.

2.6 *Sample clean-up for the comparison of extraction methods*

All extracts were treated in the same manner. Three drops of toluene were added as a keeper and the solvent was evaporated (Rotavapor R-134, Büchi, Flawil, Switzerland) to about 1 mL at 40°C. For clean-up of the extracts, the method of Wilcke *et al.* [15] was applied utilizing column chromatography with 2 g alox (5% deactivated) upon 2 g silica (5% deactivated). Samples were transferred to the columns (diameter $d \approx 1$ cm), which then were eluted with 15 mL hexane, 5 mL hexane/dichloromethane 9 : 1 (v : v) and 20 mL hexane/dichloromethane 4 : 1 (v : v), respectively. As we were not interested in the more volatile compounds, the combined extracts were evaporated to dryness with a rotary evaporator and finally under a stream of nitrogen.

2.7 *Comparison of clean-up procedures*

Peat samples were spiked with the internal standard solution and extracted with ASE (conditions see above). Three drops of toluene were added as a keeper and the solvent was reduced with a rotavapor to about 1 mL at 40°C. Two replicates were analysed per purification method.

2.7.1. Clean-up 1. 2 g alox (5% deactivated) upon 2 g silica (5% deactivated) were filled into a glass column ($d \approx 1$ cm) and conditioned with hexane. The sample was transferred to the column and eluted with 15 mL hexane, 5 mL hexane/dichloromethane 9 : 1 (v : v), and 20 mL hexane/dichloromethane 4 : 1 (v : v), respectively [15]. With three drops of toluene as keeper, the solvent was evaporated with a rotavapor to about 1 mL at 40°C.

2.7.2. Clean-up 2. This procedure consisted of an additional clean-up step preceded by clean-up method 1. The extracts obtained by clean-up 1 were evaporated to approx. 1 mL and then subjected to this procedure. Glass columns ($d \approx 1$ cm) were filled with 2 g of the highly versatile adsorption resin Lichrolut EN (Merck) and equilibrated with 20 mL hexane. The samples were transferred to the columns and eluted with 10 mL hexane. This fraction was discarded. The columns were allowed to dry for about 1 h and were subsequently eluted with 20 mL toluene. The eluted samples were evaporated with a rotavapor to about 1 mL at 40°C.

2.7.3. Clean-up 3. This purification method was used by Kaupp [17] for the clean-up of aerosol particles and plant samples. 3 g alox (15% deactivated) upon 5 g (silica 0% deactivated) were filled into glass columns ($d \approx 1$ cm) and equilibrated with hexane. The samples were transferred to the glass columns and eluted with 35 mL hexane and 30 mL hexane/dichloromethane 3 : 1 (v : v), respectively. The combined fractions were evaporated with a rotavapor to about 1 mL at 40°C.

2.8 *Analysis*

Samples were evaporated to dryness under a gentle stream of nitrogen. Prior to analysis, samples were redissolved in 200 µL of the injection standard solution. Samples were transferred to glass vials and the 16 PAH from the EPA priority list, BeP and Pery were measured using a Hewlett Packard 5890 Series II Gas Chromatograph equipped with a DB-5ms capillary column (30 m × 0.25 mm × 0.25 µm, J&W Scientific, Folsom, USA), coupled to a Hewlett Packard 5971A mass selective detector. The following instrumental parameters were used: injection volume: 1 µL; injector temperature: 280°C; detector temperature: 300°C; oven temperature program: initial temperature 80°C hold for 2 min, 10°C min^{-1} to 250°C hold for 4 min, 10°C min^{-1} to 300°C hold for 10 min, 15°C min^{-1} to 310°C hold for 5 min; carrier gas: helium. PAH were measured in the selected ion monitoring (SIM) mode. Benzo[b]fluoranthene and benzo[k]fluoranthene could not be separated satisfactorily and were subsequently integrated together. (Note: some isomeric PAH which occur in the environment like benzo[j]fluoranthene, triphenylene or dibenzo[a,c]anthracene will not be separated on DB-5ms-like capillary columns and may result in an overestimation of concentrations of some EPA-PAH [14].)

The operational limit of detection (LOD) was set at a signal to noise ratio of 3 : 1, the limit of quantification (LOQ) was set at a signal to noise ratio of 5 : 1. The calculated LOQ for the whole procedure was approx. 8 µg kg_{dw}^{-1}. Three fragment ions per compound were measured; one target ion which was used for quantification, and two qualifier ions. Quality assurance was done by the determining the ratios between qualifier and target ions. If the ion ratios in the samples were not within the range of ±20% of the average standard's ratios, a compound was considered as not detected.

PAH concentrations were calculated using the internal standard method using the deuterated compounds from the injection standard solution. The recovery was determined by the deuterated PAH from the internal standard solution that was spiked to the samples prior to extraction. The recovery of each deuterated PAH was assigned to one or more analytes of similar properties to determine the actual PAH content of the peat sample.

3. Results

3.1 *Extraction methods*

The concentrations of PAH in the peat sample determined with the three different extraction methods are presented in figure 1.

Generally, PAH concentrations in ASE and FBE extracts were up to 20% higher than in USE extracts (figure 1), except for some compounds like BaP and BeP where

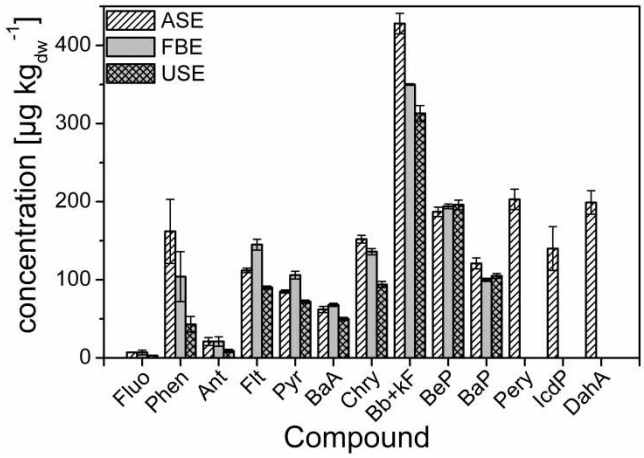

Figure 1. Mean concentrations and standard deviations ($n = 3$) of PAH in peat sample extracted with ASE, FBE and USE.

Table 1. Mean recovery rates [%] (±standard deviation; $n = 3$) of the internal standards for a peat sample extracted with ASE, FBE and USE.

	ASE	FBE	USE
Fluo-d_{10}	42 ± 13	39 ± 10	52 ± 8
Pyr-d_{10}	97 ± 9	63 ± 6	78 ± 2
Chry-d_{12}	78 ± 4	62 ± 3	70 ± 4
Pery-d_{12}	60 ± 2	56 ± 2	53 ± 1

the extraction yield of all methods was similar. The high molecular weight compounds IcdP, DahA and BghiP were only determined in ASE extracts. Both in FBE and USE extracts, these compounds were present, but their concentrations were below the LOD. As expected, the low molecular weight PAH Naph, Acy, and Ace could not be detected with any of these methods due to evaporation of the samples to dryness during clean-up. In general standard deviations of ASE were higher compared to those of the other methods. With respect to the recovery rates of the internal standards shown in table 1, ASE was the best method yielding average recovery rates between 60 and 97%, followed by USE and FBE. As expected, the recovery of the more volatile Fluo-d_{10} was much lower.

3.2 *Clean-up methods*

In figure 2, the PAH concentrations determined in the peat extracts after clean-up with the three clean-up procedures are shown. Generally, highest concentrations were determined in the extracts purified with clean-up 3. For some compounds, concentrations after clean-up 1 were similar to clean-up 3, whereas additional losses occurred during clean-up 2. The recovery rates of the internal standards were high and quite similar for procedures 1 and 3, whereas for clean-up 2, generally lower recovery rates for Pyr-d_{10}, Chry-d_{12} and Pery-d_{12} were determined (table 2). Again, as expected the recovery rates for Fluo-d_{10} were low.

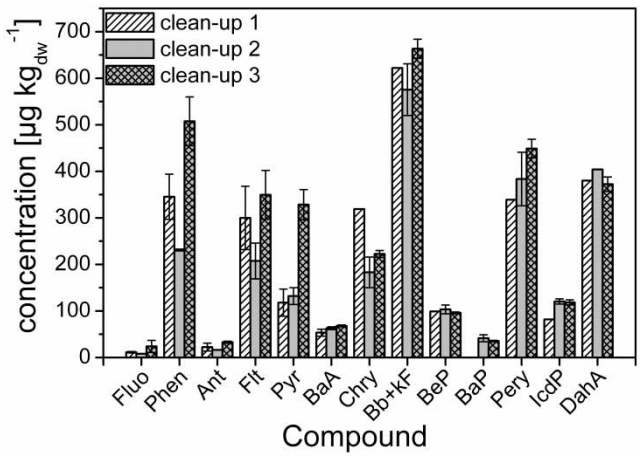

Figure 2. Comparison of different clean-up methods for the analysis of PAH in peat samples ($n = 2$; error bars represent the deviation of the samples). Missing error bars denote samples where a compound was not quantifiable due to analytical interferences.

Table 2. Mean recovery rates [%] (±deviance of the replicates; $n = 2$) of the internal standards in an ASE extract subjected to different clean-up procedures.

	Clean-up 1	Clean-up 2	Clean-up 3
Fluo-d_{10}	34 ± 14	36 ± 5	12 ± 0
Pyr-d_{10}	84 ± 5	79 ± 5	87 ± 6
Chry-d_{12}	99 ± 1	79 ± 3	94 ± 3
Pery-d_{12}	116[a]	76 ± 17	104 ± 5

[a]Quantifiable only in one sample.

With respect to the performance of the different clean-up methods, however, not only the recoveries or yields should be considered. In samples subjected to clean-up method 1, precipitation of waxes and other high-molecular weight matrix constituents that were not removed by column-chromatography occurred in the evaporated samples after elution and evaporation. This insufficient sample clean-up can be observed in the chromatograms (figure 3a), causing problems with the determination of individual compounds. For example, for BaP the quality criteria were usually not met due to interfering substances (insert in figure 3a) and therefore the compound could not be quantified.

The additional clean-up step with the adsorption resin (clean-up 2) led to an enhanced removal of matrix components. After evaporation of the solvent, there was less precipitation than with clean-up 1, but it was still present. The chromatograms also showed less interference (not shown). However, the concentrations of PAH as well as the recoveries of the deuterated PAH were lower than those obtained with the other methods. In contrast, samples purified with clean-up method 3 showed no precipitation, and the chromatograms had clearly separated peaks without much interference (figure 3b). For almost all PAH, concentrations and recoveries were higher than those of clean-up method 2. Compounds like BaP could clearly be identified and quantified due to the almost complete removal of interferences.

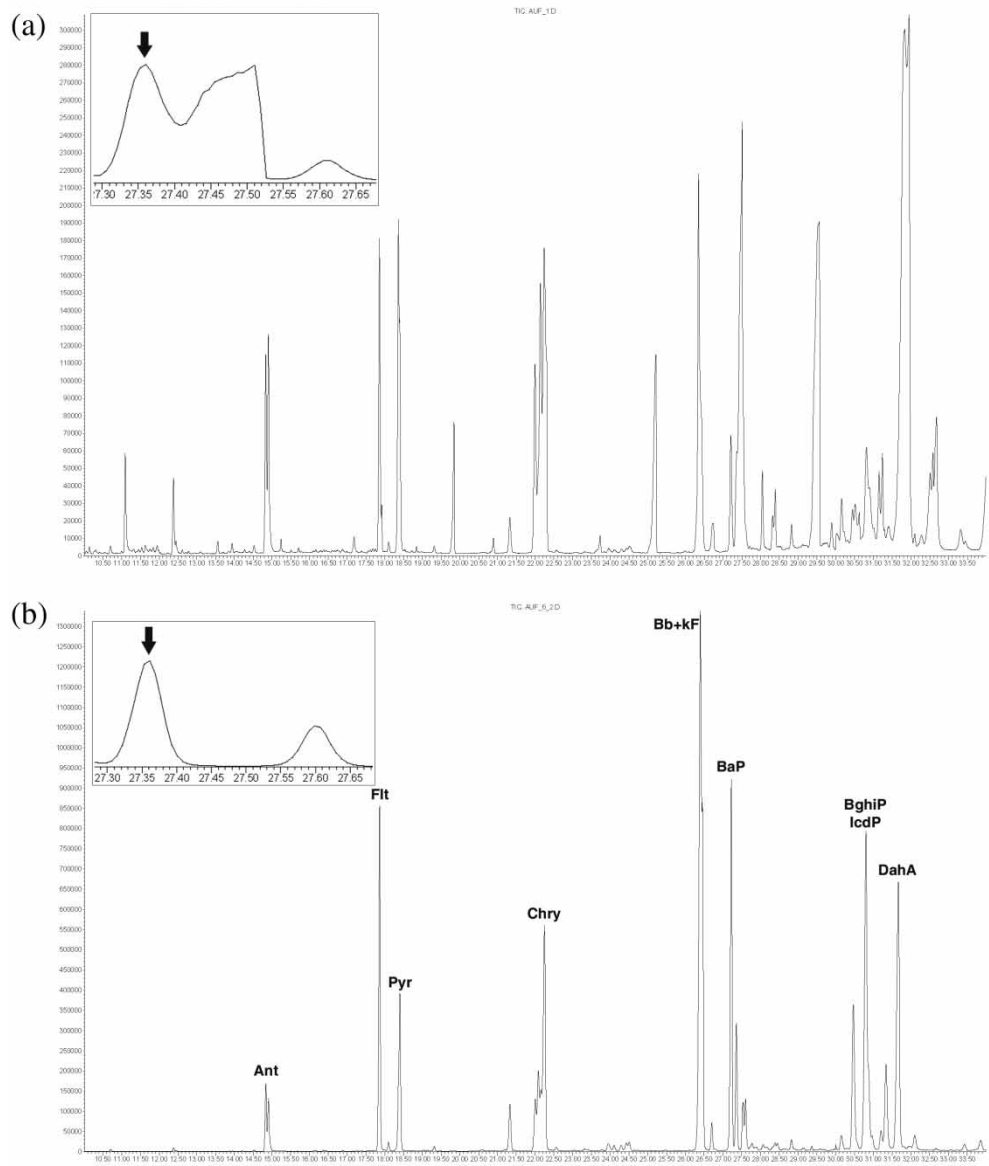

Figure 3. GC-MS chromatogram (total ion chromatogram, TIC) of a peat sample extracted with ASE and subsequently treated with clean-up 1 (a) and clean-up 3 (b) The insert shows the trace of BaP (m/z 252) which is marked by an arrow. For details see text.

4. Discussion

A good extraction technique can be defined as a procedure which extracts the highest amount of PAH from a soil sample for which no certified concentrations are available [14]. Based on this criterion, ASE was the most suitable method for the extraction of PAH from peat samples because of the highest extraction efficiency

Table 3. Average recovery rates [%] and standard deviations ($n = 170$) of internal standards for Canadian peat samples.

	Recovery rate
Fluo-d_{10}	53 ± 17
Pyr-d_{10}	81 ± 11
Chry-d_{12}	89 ± 16
Pery-d_{12}	69 ± 14

of PAH from peat samples, the much higher yields of IcdP, BghiP and DahA (figure 1) and the highest recoveries (table 1). This agrees with results attained for soil samples by Berset *et al.* [14] as well as by Hollender *et al.* [16].

The results of this study show that the selection of an appropriate extraction technique should not be based on the determination of recoveries of internal standards only. These were quite similar for USE and ASE (table 1), however, lower amounts of several PAH were extracted from peat by USE compared to ASE (figure 1). This is most probably due to stronger sorption of the target compounds in consequence of their longer residence time in peat samples compared to the internal standards, whereby the newly added internal standards were more easily extractable.

The comparison of the clean-up procedures gave a fairly clear result with clean-up 3 as the method of choice. Obviously, clean-up 1 which was developed and successfully applied for soil samples [15] was not suitable for peat samples. The additional purification step with the adsorption resin (clean-up 2) similar to that used by Krauss *et al.* [12] for the enrichment of PAH from forest soils was also not capable of removing matrix components without reducing the recovery of PAH. In contrast, by the method originally developed by Kaupp [17] for the purification of aerosol extracts, almost all interferences from the GC-MS-chromatogram were removed. Since the solvents used for elution were similar for both clean-up 1 and 3, the better performance of clean-up 3 was mainly due to the different degrees of deactivation of silica and alox.

In total 170 samples from 15 ombrotrophic bogs located in eastern Canada were analysed for PAH with the final method consisting of ASE extraction followed by clean-up procedure 3 [19]. The method yielded acceptable and reproducible recoveries of the internal standards between 69 and 89% (Pyr-d_{10}, Chry-d_{12}, Pery-d_{12}), and interestingly, for Fluo-d_{10} a relatively high recovery rate ($53 \pm 17\%$) was also determined (table 3). This higher recovery of Fluo-d_{10} compared to the values determined during method optimisation might be due to minor improvements during the extraction and clean-up procedures, for example slightly higher pressures during rotary evaporation. Based on the recoveries of the internal standards obtained in our study, we estimated the imprecision of the overall analytical procedure for the determination of PAH with $MW \geq 178\,g\,mol^{-1}$ to be $\leq 20\%$. In conclusion, the optimized method was a well suitable tool for the analysis of PAH in peat samples.

Appendix

Abbreviations used for the PAH: naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant),

fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chry), benzo [b+k]fluoranthenes (Bb+kF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), perylene (Pery), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), benzo[g,h,i] perylene (BghiP).

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