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Review

Solid-phase extraction of polycyclic aromatic compounds

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Abstract

Solid-phase extraction (SPE) for two groups of polyaromatic compounds — polycyclic aromatic hydrocarbons and naphthalenesulfonates — with completely different problems in the extraction process are reviewed. The sorbents used in each case and the different steps of SPE are studied. Particular problems encountered in the SPE of each group are described. Adsorption problems of PAHs which require an organic solvent or a surfactant to be added to the sample are explained. The need of ion-pair solid-phase extraction for extracting naphthalenesulfonates and the influence of the inorganic species in the extraction are discussed. The on-line systems are described for both group of compounds. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Solid-phase extraction; Water analysis; Polynuclear aromatic hydrocarbons; Naphthalenesulfonates

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1. Introduction

Polycyclic aromatic compounds include different groups of compounds which have two or more benzenoid groups in their structure and various functional groups which may contain several elements. There is a considerable variety of groups of compounds but, from the environmental point of view, only a few of these are the most important.

An important group of polycyclic aromatic compounds are the polycyclic aromatic hydrocarbons (PAHs) which have two or more fused benzenoid rings and no elements other than carbon and hydrogen. PAHs are one of the most contaminating groups of pollutants in the environment because of their mutagenic and carcinogenic activity, and they can enter the environment from natural or anthropogenic sources [1]. They may be eliminated or transformed to even more toxic compounds by chemical reactions such as sulfonation, nitration or photooxidation. For instance, in some conditions, traces of nitric acid can transform some PAHs into nitro-PAHs [2]. Fig. 1 shows the structure of the 16 PAHs considered as priority by the American Environmental Protection Agency (EPA).

Naphthalenesulfonates (NS) are also an important group of compounds which can be amino-, alkyl- or/and hydroxy-substituted. Fig. 2 shows the structure of some naphthalenesulfonates. They are used as intermediates in day production, suspending and wetting agents, dispersants and stabilisers [3]. Condensation products, also known as sulphonated polyphenols, are applied as synthetic tanning agents, and sulfonated naphthalene formaldehyde condensates as plasticisers for cement [4]. The low biodegradability of some of these compounds and the fact that it is difficult to eliminate them by water treatment, since they can only be removed by means of frequently regenerated activated carbon, means that they may be present in environmental samples and their presence should be controlled [5–7].

These compounds are usually determined by a chromatographic technique because of the wide range of different compounds with similar characteristics. All these compounds are determined in several kinds of samples and a sample pre-treatment is usually required for cleaning the sample and/or preconcentrating it.

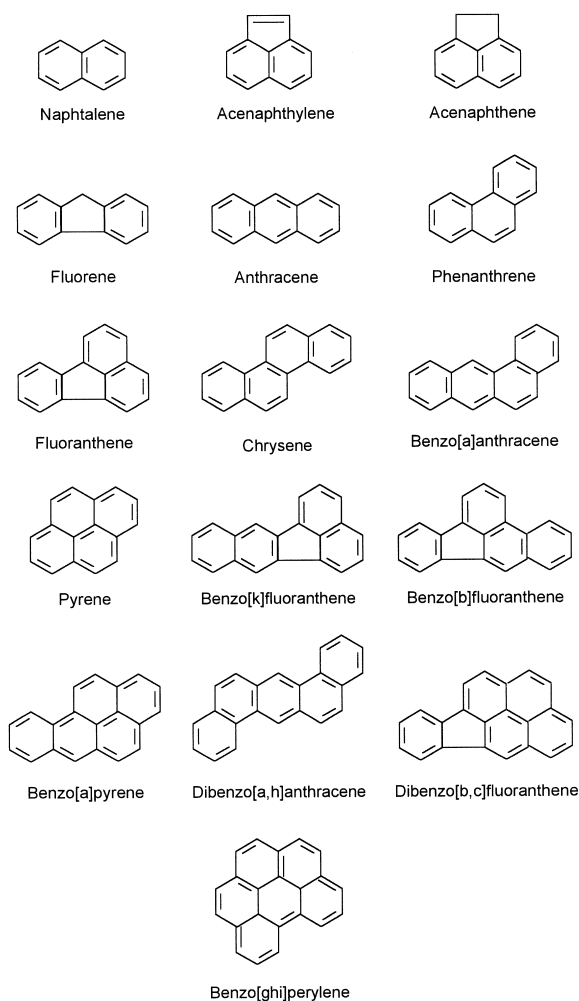


Fig. 1. Chemical structure of the PAHs considered as priority by the American Environmental Protection Agency.

Solid-phase extraction is a sample treatment technique which passes a liquid sample through a sorbent. Both the analytes to be determined or the interferences of the samples are retained on the sorbent by different mechanisms. In the first case, the analytes are eluted in a small volume of a solvent and so, the analytes are concentrated; in the second case the function of the solid-phase extraction is to clean the sample. The first case is mainly used for liquid samples and the second for solids, gases or liquids, usually after another sample-treatment tech-

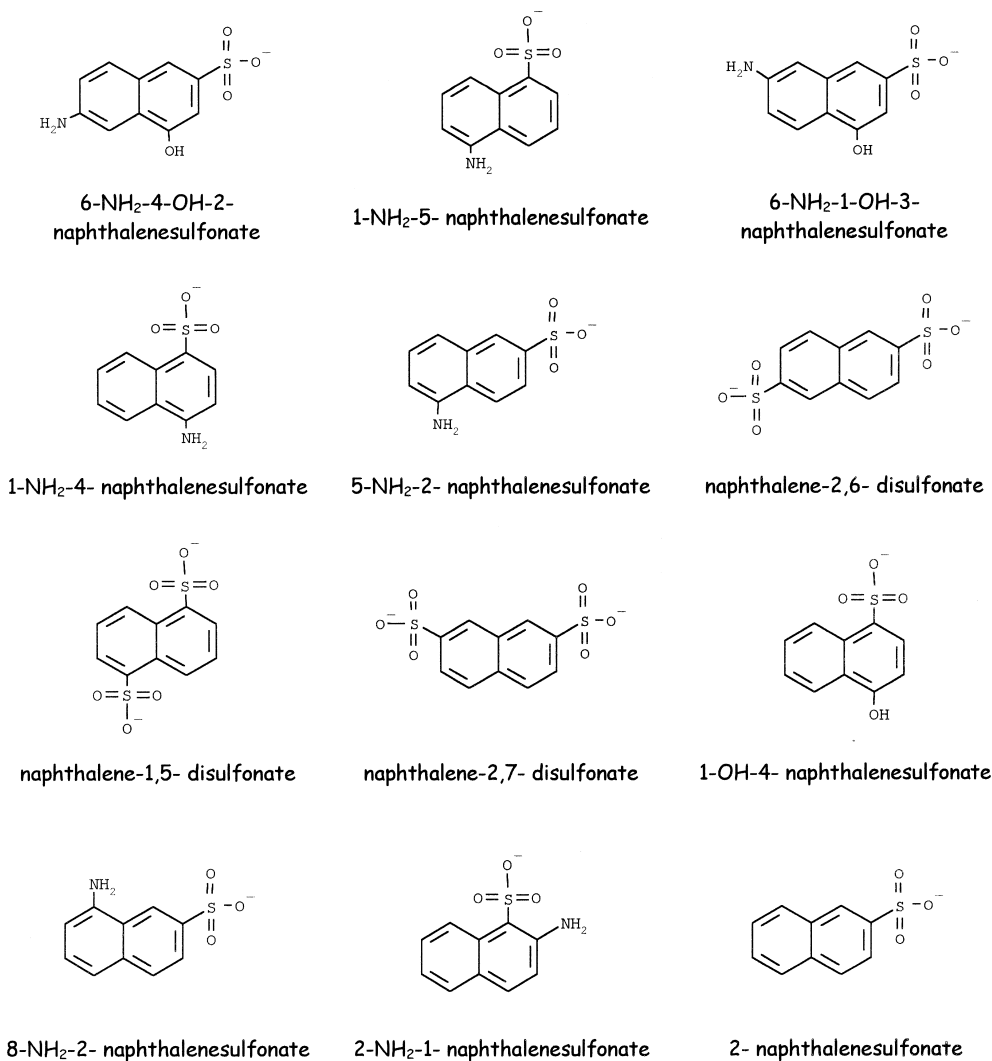


Fig. 2. Chemical structure of some naphthalenesulfonates.

nique. So, SPE is extremely versatile in the sense that it can be applied to a wide range of samples [8,9].

SPE is a technique that is increasingly popular, because unlike LLE it does not require large volumes of (toxic) organic solvents, analysis times can be decreased significantly and on-line and/or automated procedures are easily designed. Another advantage is the wide variety of extraction conditions which may be used to achieve the desired separation and pre-

concentration. The increasingly number of types of sorbents commercially available has increased its use.

SPE is used alone or in combination with other techniques. For instance, for determining PAHs in solid samples such as soil, sludge, sediment or tissue, SPE has been used after Soxhlet extraction [10], ultrasonic extraction [10,11] or accelerated solvent extraction [10]. For liquid samples, Solid-phase extraction has also been used in combination with

other techniques for the extraction of analytes in liquid samples [12]. For instance, Sargenti et al. [13] compare four different extraction techniques (solid-phase extraction, supercritical fluid extraction (SFE), solid-phase extraction followed by supercritical fluid extraction (SPE/SFE) and liquid–liquid extraction (LLE)) for the extraction of 16 PAHs from drinking water. The results showed that recoveries were good for SPE and for SPE/SFE for all compounds, recoveries for SFE were worse than SPE/SFE, and LLE had the worst recovery and reproducibility.

This review focuses on the application of solid-phase extraction to polycyclic aromatic compounds, paying special attention to the polycyclic aromatic hydrocarbons and naphthalenesulfonate compounds, because of their environmental interest. As will be seen, the problems for the solid-phase extraction of PAHs are completely different from those of naphthalenesulfonates because of their chemical structure. Firstly, the mostly applied chromatographic techniques will be briefly reviewed.

2. Chromatographic analysis

Chromatographic techniques are often used to determine compounds because they can determine individual concentrations. PAHs can be determined by high-performance liquid chromatography (HPLC) [1,14,15], gas chromatography (GC) [1,16,17], supercritical fluid chromatography (SFC) [1,18,19] and capillary electrophoresis (CE) [20,21].

By gas chromatography several PAH isomers are not resolved and although gas chromatography-mass spectrometry is a good technique [13], it requires using surrogate standards to quantify and clean-up after extraction of both liquid (effluent or waste water) and solid samples [10].

Supercritical fluid chromatography has also been used, the main advantages of which are its high separation efficiencies and short analysis time. UV absorbance, fluorescence and mass spectrometric detectors have all been used to determine PAHs [18,19].

Capillary electrophoresis can also be used but, since the molecules are uncharged and hydrophobic, micellar electrokinetic capillary chromatography (MECC) or capillary electrochromatography (CEC)

are recommended. Sixteen PAHs can be satisfactorily separated under 20 min [20,21] by MECC. Despite the advantages in resolution power the main drawback is its sensitivity.

Liquid chromatography with fluorescence detection is a very sensitive technique and more adapted to the analysis of several isomers. It is selective and requires much less clean up than GC-MS because it is easy to equip the analytical column of a guard precolumn. No clean-up is required for the analysis of surface water extracts. The identification is based on the retention time and fluorescence properties [22] and the availability of new detector providing the fluorescence spectra is very interesting [23]. DAD detector may also be used but less sensitivity is obtained and more clean-up is required for identification through UV spectra.

Naphthalenesulfonates are strong acids and they are difficult to derivatize, particularly in the presence of other functional groups, so gas chromatography is not recommended [24]. Liquid chromatography methods have been described by some authors and apart from some methods based on ion-exchange chromatography [25,26] the most general approach is ion-pair chromatography [4,27,28]. UV detection is suitable but fluorescence detection is also widely used because it is more sensitive and selective [4,28]. Mass spectrometry is also used, and the electrospray interface is the most suitable for determining naphthalenesulfonates [29,30], although particle beam has also been tested [26]. Capillary electrophoresis can also be used but its low sensitivity is a considerable drawback [31], although wavelength-resolved laser induced fluorescence detector has proved to give higher sensitivity [32].

3. Solid-phase extraction

The application of SPE to the polycyclic aromatic compounds studied in this review has two specific problems. On the one hand, PAHs are very hydrophobic compounds and there should be no problems in extracting them with typical reversed-phase sorbents but there are adsorption problems which must be taken into account [33–35]. These will be explained in detail. On the other hand, naphthalenesulfonates are strong acids which can be ex-

tracted by ion-exchange sorbents but there are serious limitations [36]. Their breakthrough volume in the most commonly used sorbents, such as modified-silica or polymeric sorbents, is low so ion-pair extraction with these sorbents is usually recommended [4].

Several kinds of sorbents in either cartridges or disks may be used for SPE although cartridges are more common used because only a few sorbents are commercially available in discs. The sorbents used for each group of compounds will be discussed in the relevant paragraph. One similarity between the groups is that they both have aromatic rings which can have π - π interactions with the aromatic groups of the sorbent. This is important in polymeric sorbents such as styrene-divinylbenzene copolymer (SDB) where the aromatic rings of the matrix network permit electron-donor interactions between the sorbent and the π bonds of the analyte. This further increases analyte-sorbent interactions [8].

SPE is usually carried out in the off-line mode but the on-line mode does have some advantages and recently has been used more and more. SPE systems coupled to high-performance liquid chromatography [37,38] and coupling to GC or SFC has also been described for PAHs [18].

A special device in SPE is solid-phase microextraction (SPME), which consists of a fused-silica fiber mounted in a syringe-like device. The fiber is coated by a sorbent, usually other than those used for SPE [39]. The following sorbents, or a mixture of any two of them, can be used for SPME: polydimethylsiloxane, polyacrylate, carboxen, carbowax and divinylbenzene. The SPME can be easily coupled to GC and also to HPLC with a special device. The main advantage of this technique is that it is solvent free and it requires a small volume of sample.

3.1. Solid-phase extraction of polycyclic aromatic compounds

3.1.1. Sample preparation

The solid-phase extraction of PAHs may seem to be a simple process because they are very hydrophobic and no breakthrough problems are expected when a typical reversed-phase sorbent is used.

However, the low solubility of PAHs, which decreases when molecular weight increases, does present a problem because it may lead to adsorption problems during sampling and storage. To increase the solubility, an organic solvent, such as methanol, acetonitrile or 2-propanol, or a surfactant is usually added to the sample. The concentration of the organic solvent is a critical parameter because if it is low it may not be enough to solubilize the high molecular weight PAHs (HMW) whereas if it is high the breakthrough volume will be low for the low molecular weight PAHs (LMW) [14,40]. So for each kind of sorbent and organic solvent this parameter must be optimized. For instance, Nirmaier et al. [41] added 75 ml of 2-propanol to 500 ml of water sample in a SPE glass column of 1 g of C_{18} and obtained recoveries higher than 75% for the eight PAHs studied. El Harrak et al. [40] studied the influence of the percentage of 2-propanol added to the samples when they are extracted in membrane discs of C_{18} and styrene-divinylbenzene are used, and results were best for 10% of 2-propanol because at lower percentages the recoveries for the HMW PAHs were low and at higher percentages, the recoveries for the LMW PAHs were low. Table 1 shows the influence of the percentage of the 2-propanol in 200 ml-sample on PAH recoveries using C_{18} and styrene-divinylbenzene membrane extraction.

Kiss et al. [14] studied the different parameters which affect the SPE of PAHs with C_{18} cartridges. An organic solvent, they said, needed to be added to keep the octadecyl chains activated because a large amount of water would remove the activating organic solvent from the hydrocarbonaceous layer of the packing and the alkyl chains, because of their hydrophobic character, would collapse to a tight film. As a consequence, the solute molecules have difficulty in penetrating between the bonded octadecyl chains, the retention is weak and recoveries of PAHs may be low. They added solvents such as methanol, acetonitrile and 2-propanol and results were best for 25% of 2-propanol when 50 ml of sample was analysed. When volume increased, however, the recovery of the LMW PAHs decreases considerably. Other factors affecting the recovery of PAHs were also studied (e.g. conditioning of the SPE cartridge, flow-rate of the sample loaded on the cartridge,

Table 1

Influence of the percentage of 2-propanol in the sample of PAHs using C₁₈ and SDB membrane extraction. (Results are the mean of three determinations) (Reprinted with permission from [40])

Compound ^a	Recovery and RSD (%) in the presence of 2-propanol					
	0%		10%		15%	
	C ₁₈	SDB	C ₁₈	SDB	C ₁₈	SDB
Naphthalene	86±3	89±3	80±5	75±8	70±7	62±9
Acenaphthylene	83±4	85±3	80±6	80±4	75±6	65±8
Acenaphthene	85±3	87±4	83±4	82±4	81±6	70±6
Fluorene	87±4	85±4	85±4	80±6	86±6	73±6
Phenanthrene	84±4	88±3	92±3	90±3	95±3	78±6
Anthracene	79±5	81±3	85±3	75±4	93±3	78±6
Fluoranthene	75±5	70±5	92±3	80±5	97±3	79±5
Pyrene	74±6	70±5	92±3	75±6	97±3	71±6
Benzo[<i>a</i>]anthracene	64±8	52±8	72±5	82±5	98±3	85±4
Chrysene	71±7	53±8	75±5	80±4	99±3	84±4
Benzo[<i>b</i>]fluoranthene	66±7	45±9	74±6	77±5	99±3	85±4
Benzo[<i>k</i>]fluoranthene	74±7	50±8	85±4	78±6	95±3	88±4
Benzo[<i>a</i>]pyrene	54±9	44±9	75±5	69±8	95±4	85±4
Dibenz[<i>a,h</i>]anthracene	59±9	39±9	77±6	73±8	97±3	72±6
Benzo[<i>ghi</i>]perylene	60±8	37±10	81±5	70±8	97±3	82±5
Indeno[<i>1,2,3-cd</i>]pyrene	63±8	40±9	90±3	75±8	93±3	80±6

^a Sample volume: 200 ml.

concentration of PAHs in the sample, drying after sample loading and elution of the analytes from the cartridge with different organic solvents).

A surfactant has also been added so that an organic solvent need not be used and different results have been published [34,35,42]. Surfactant molecules are amphiphilic — that is to say they have a polar and non-polar moiety — and so they can dissolve in water as monomers or be incorporated with other surfactant to form a micelle. The concentration at which they start to form a micelle is termed the critical micelle concentration (CMC) and depends on various factors. When the hydrophobic part of the amphiphile is a hydrocarbon chain, the micelles will consist of a hydrocarbon core with polar groups at the surface, which serve to maintain solubility in water. Brouwer et al. [43] have tested Brij-35 as surfactant and Table 2 shows the influence of surfactant concentration on the recovery. The recoveries are low because of the sorbent used but higher recoveries were obtained with other sorbent as will be seen. In another study [40] in which Brij-35 was also tested, recoveries were better when 2-propanol was added.

3.1.2. Sorbents and devices

In SPE, either cartridges or membrane discs can be used to extract PAHs. The main advantage of membrane discs is the considerable reduction in the extraction time and the higher surface of extraction which means fewer clogging problems for the sorbent [8]. The membrane discs which have been used most are the PTFE matrix discs [40] but another type of membrane, the glass fiber matrix (GFM) has been shown to considerably reduce the extraction time. For instance, Urbe et al. [44] compared three SPE systems — glass columns, PTFE discs and GFM discs — with the same amount of C₁₈ sorbent and they found that the time for extracting 1 l of real sample was about 4 h for columns, about 1 h for PTFE discs and about 15 min for the GFM discs. Recovery values were quite similar.

Several sorbents have been used in the SPE of PAHs, and the sorbent which has been used most is the C₁₈-bonded silica [4,13,41,44]. C₈ has also been used with good results [45,46]. Sargenti et al. [13] compared three different bonded silica sorbents — C₁₈, cyano and phenyl — and results were best for C₁₈ (see Table 3).

Table 2

Influence of surfactant concentration on recovery of PAHs, after 10 ml preconcentration on a 10×3 mm I.D. Boos silica precolumn. (Reprinted with permission from [43])

Compound	Analyte recovery (%; $n=2$) at Brij-35 concentration ($\times 10^{-4}$ M) of				
	0.0	0.5	1.1	3.0	6.0
Naphthalene	18	15	13	12	12
Acenaphthene	55	53	55	39	32
Fluorene	73	75	83	54	38
Phenanthrene	42	37	52	84	75
Anthracene	41	38	55	80	69
Fluoranthene	21	23	48	91	84
Pyrene	17	20	46	99	88
Benzo[<i>a</i>]anthracene	16	20	46	94	64
Chrysene	16	19	45	94	62
Benzo[<i>b</i>]fluoranthene	14	26	49	82	54
Benzo[<i>k</i>]fluoranthene	14	23	48	81	54
Benzo[<i>a</i>]pyrene	14	24	49	81	52
Dibenz[<i>a,h</i>]anthracene	11	30	53	62	31
Benzo[<i>ghi</i>]perylene	7	29	32	50	31
Indeno[1,2,3- <i>cd</i>]pyrene	7	28	32	50	31

Table 3

Comparison of recoveries for different solid-phases with CH₂Cl₂ or CH₃CN. Reprinted with permission from [13]

PAH ^a	Octadecyl solid-phase				Cyano solid-phase				Phenyl solid-phase			
	CH ₂ Cl ₂		CH ₃ CN		CH ₂ Cl ₂		CH ₃ CN		CH ₂ Cl ₂		CH ₃ CN	
	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
1	108	7	71	29	32	14	19	32	72	3	45	22
2	97	3	67	32	57	12	30	27	81	12	68	11
3	112	3	71	39	82	8	34	19	90	11	64	20
4	109	4	68	50	96	7	39	31	90	12	54	21
5	23	6	57	66	94	14	38	54	88	7	35	9
6	85	6	53	73	88	16	36	64	80	6	31	12
7	73	11	46	89	73	35	28	86	105	3	23	8
8	72	13	45	95	73	34	27	90	105	2	22	10
9	51	13	46	57	44	41	38	54	65	11	40	31
10	63	10	54	34	49	40	45	39	66	11	51	19
11	53	12	50	68	46	49	44	46	60	23	48	29
12	27	12	55	53	46	15	42	54	60	16	52	30
13	57	18	47	75	49	27	46	47	60	25	47	54
14	61	13	61	57	58	26	58	39	62	36	60	22
15	53	26	53	60	51	31	51	51	56	45	54	33
16	57	19	56	81	52	33	51	36	59	32	57	36

^a Volatile PAHs: 1, naphthalene; 2, acenaphthylene; 3, acenaphthene; 4, fluorene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene. High-molecular PAHs: 9, benzo[*a*]anthracene; 10, chrysene; 11, benzo[*b*]fluoranthene; 12, benzo[*k*]fluoranthene; 13, benzo[*a*]pyrene; 14, indeno[1,2,3-*cd*]pyrene; 15, dibenz[*a,h*]anthracene; 16, benzo[*ghi*]perylene. Sample volume: 100 ml. Amount of sorbent: 100 mg.

El Harrak et al. [40] compared C₁₈ and SDB membrane discs and found similar results at low sample volumes but SDB gave better results, mainly for LMW PAHs, when the volume of sample was 1000 ml.

Brouwer et al. [43] studied various selective sorbents, some of which are not commercially available, for extracting PAHs by an on-line SPE system. They were a diol-modified porous glass support with a particle diameter of 30–60 µm chemically modified with a copper phthalocyanine trisulphonic acid derivative (called Boos glass), a diol-modified silica with a particle diameter of 20 µm chemically modified with the same copper phthalocyanine trisulphonic acid moiety (called Boos silica), a copper phthalocyanine trisulphate-modified polymethacrylamide (called Blue Pearls), Chromspher π and C₁₈-bonded silica with a particle diameter of 40 µm. The results showed that Boos silica is very useful for the polyaromatic compounds containing three or more fused benzene rings but conventional C₁₈-bonded silica and Chromspher π have better recoveries for the smaller PAHs although their selectivity is lower. Table 4 shows the recoveries obtained for some of the sorbents tested.

Other authors also studied these selective sorbents [47–49], predominantly the copper phthalocyanine trisulfonate type, for extracting PAHs.

Other authors say [50] that for preconcentration of PAHs from drinking water best results were obtained for combined C₁₈-NH₂ solid-phase cartridges whereas for enrichment of PAHs from soil samples was best achieved with silica-cyano or C₁₈-CN combinations.

SPE has also been used before SFE for extracting PAHs from water and C₁₈-bonded silica is the sorbent most preferred. For instance, Messer et al. [12] used C₁₈ discs and obtained good results and Sargenti et al. [13] used cartridges of C₁₈ and results are better than when only SPE is used.

A clean-up step is often recommended before the analytical determination of PAHs in sample extracts when the sample is considerably contaminated while clean-up might be unnecessary for a relatively clean sample matrix. Moreover, the degree to which clean-up is necessary depends on the selectivity of the final detection step. The clean-up is usually performed by SPE using normal-phase sorbents or C₁₈-bonded silica, due to the low polarity of PAHs [11]. For instance silica and alumina have been used for extraction from soils [10], food [51] and oyster tissues [52]. Other frequently used sorbents are aminopropyl, cyanopropyl and fluorisil [53,54]. The solvent used for reconstituting the extract before application of the clean-up step must be carefully selected.

Table 4

Recovery data for different sorbents after preconcentration of 10 ml micelle-mediated surface water samples, spiked with PAHs (100 ng l⁻¹), with disruption of micelles. Reprinted with permission from [43]

Compound	Recovery (% , n=2)		
	C ₁₈	Boos silica	Chromspher π
Naphthalene	96	4	78
Acenaphthene	100	22	97
Fluorene	97	26	97
Phenanthrene	100	94	97
Anthracene	100	97	99
Fluoranthene	99	94	95
Pyrene	99	100	90
Benzo[<i>a</i>]anthracene	100	93	100
Chrysene	100	94	100
Benzo[<i>b</i>]fluoranthene	91	92	90
Benzo[<i>k</i>]fluoranthene	93	92	92
Benzo[<i>a</i>]pyrene	90	94	93
Dibenzo[<i>a,h</i>]anthracene	92	100	100
Benzo[<i>ghi</i>]perylene	94	100	100
Indeno[1,2,3- <i>cd</i>]pyrene	94	100	100

The choice of SPE sorbent is often dictated by the chromatographic method used for PAHs separation and identification. For instance, a study [55] showed that for determining PAHs in lake sediments, C_{18} and silica columns could be used satisfactorily to clean-up extracts when HPLC and fluorescence detection are used, but they could not be used for GC–MS for PAHs greater than chrysene because of the interferences from aliphatic waxes and then fully activated silicic acid and neutral alumina columns were recommended.

Sorbents recently developed, the immunosorbents (IS), based on antigen-antibody interactions have also been used for selective isolation of PAHs from complex environmental samples [56,57]. IS were used for determining PAHs in river samples [58]. Pérez et al. [59] used sonication with dichloromethane/methanol and an anti-fluorene immunosorbent followed by HPLC and diode array detection for determining PAHs from environmental sediments and a sludge reference material containing PAHs. Results showed a better selectivity since the chromatograms presented a clear baseline allowing the determination of PAHs at ppb levels. Good results were obtained when IS were used after SFE in order to increase the selectivity when soot samples were analysed [60].

Solid-phase microextraction (SPME) has rapidly been established among the practical alternatives for sample preparation for GC. However, PAHs are more effectively monitored by HPLC and lastly a new SPME-HPLC was developed which enables one to take advantages of the time and solvent saving offered by SPME [39]. Different chemically bonded silica stationary phases (phenyl, C_8 and monomeric and polymeric C_{18}) were tested for SPME of PAHs and results showed that polymeric C_{18} had higher selectivity for large PAHs whereas phenyl bonded silica had it for benzene and naphthalene [61]. Negrao et al. [62] used commercialised 7- and 100- μm polydimethylsiloxane (PDMS) fibers and although 100- μm provided highest extraction levels, different results were obtained for two different 100- μm PDMS fibers.

3.1.3. Elution of PAHs

Once the analytes are retained on the cartridges or discs, they are eluted by an organic solvent such as

acetonitrile [13,14,45], tetrahydrofuran [45,63], methanol [14], 2-propanol [14], acetone [11], n-hexane [44], dichloromethane [13], ethyl acetate [40] and ethyl ether or mixtures of them [11,40,41]. Recoveries of the LMW PAHs are higher with non-volatile solvents but recoveries for most of the PAHs with 4–6 aromatic rings are higher when a non-polar solvent is used. So, to ensure higher recoveries of all the PAHs, mixtures of solvents are usually recommended. For instance, Sargenti et al. [13] compared acetonitrile and dichloromethane and obtained better results for dichloromethane as can be seen in Table 3.

Sun et al. [11] used C_{18} -bonded silica as clean-up step after ultrasonic solvent extraction of soil samples and tested dichloromethane, acetone and acetone:tetrahydrofuran (THF) (1:1). Results showed that recoveries for the best volatile PAHs were lower when dichloromethane was used because of the evaporation of the eluates; recoveries for most of the 4–6 aromatic rings PAHs were lower than those obtained by dichloromethane. They explained this fact because the polarity of acetone is higher than the polarity of dichloromethane but polarities of PAHs with 4–6 rings are very low. Finally they decided to use acetone–THF (1:1) because polarity of THF is lower than that of acetone and it can also be miscible with the mobile phase ($\text{ACN-H}_2\text{O}$) omitting the step of the evaporation of eluates to near dryness. Recoveries for all the 16 PAHs were between 90 and 108%. Fig. 3 shows the results obtained by eluting the PAHs with the three solvents mentioned.

Solvents with low polarity are disadvantageous for reversed-phase HPLC separation. If PAHs are determined directly from the eluate (dissolved in dichloromethane or THF) considerable band broadening will hinder the separation and reliable quantitative analysis. Therefore polarity of the eluate must be increased before HPLC analysis. This is usually done by partial or complete evaporation of the eluate and dilution back of the compounds in a more polar solvent, but evaporation down to a volume not less than 50–100 μl can be suggested when the more volatile two and three ring PAHs are also determined because complete evaporation may lead to a remarkable loss of these compounds [14].

Other authors [40,44] dehydrated the eluate by

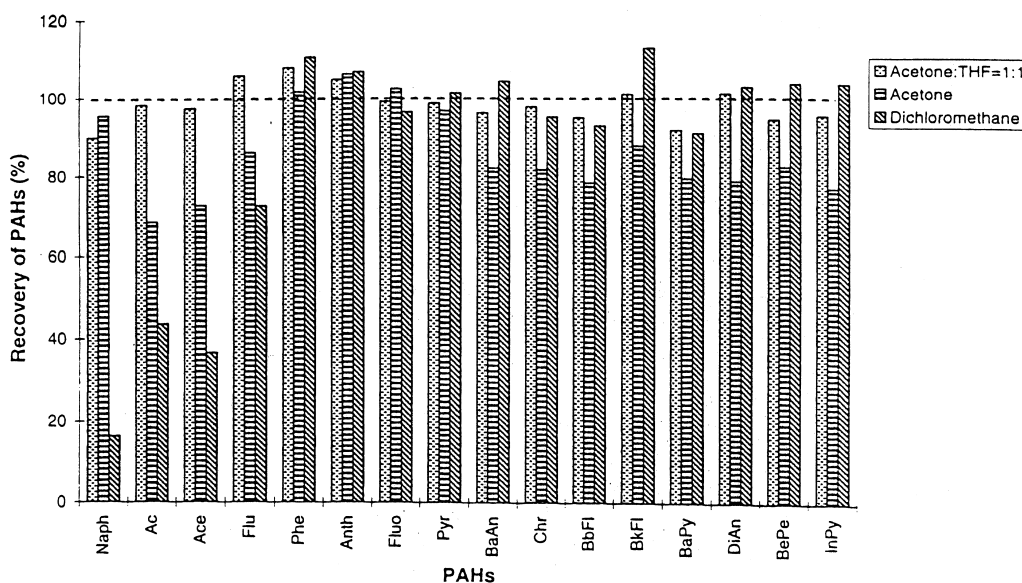


Fig. 3. Selection of elution solution for 16 PAHs from C_{18} -bonded silica SPE cartridge sorbent. Sample: extract from soil in 40% acetone in water. Volume of elution solvent: 3×1 ml of acetone or acetone-THF, 3×2 ml dichloromethane (reprinted with permission from [11]).

passing them through anhydrous sodium sulphate to eliminate residual water before the evaporation at room temperature with a rotatory evaporator or a current of N_2 . The evaporation step involves a concentration of the analytes and enables low levels of PAHs to be determined.

Drying of the SPE cartridge after sample loading is also an important aspect to be taken into account when an apolar solvent is used to elute the PAHs [14]. Water should be removed from the cartridge before elution otherwise lower recovery and lower

repeatability may be obtained. Kiss et al. [14] compared the elution with THF and dichloromethane and with drying and without drying, and drying step influenced more the elution with dichloromethane and with this solvent if the cartridge was not dried, lower recoveries and higher relative deviation were obtained. Table 5 shows the effect of drying the cartridge when tetrahydrofuran and dichloromethane are used.

Some authors [37,45] studied to extract the sample at high temperatures because high temperatures

Table 5
Effect of drying on recovery of PAHs. Reprinted with permission from [14]

Compound ^a	Elution with tetrahydrofuran				Elution with dichloromethane			
	With drying		Without drying		With drying		Without drying	
	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)
Acenaphthylene	78	5	67	4	81	7	46	25
Anthracene	92	6	79	6	92	3	75	15
Fluoranthene	93	4	92	4	93	5	87	9
Pyrene	92	4	87	5	92	4	87	9
Benzo[<i>a</i>]anthracene	91	5	84	4	89	3	83	14
Benzo[<i>a</i>]pyrene	91	5	77	5	90	3	82	16
Dibenz[<i>a,h</i>]anthracene	90	5	74	5	90	4	63	34
Benzo[<i>ghi</i>]perylene	92	5	84	4	91	6	71	31

^a Conditions: $n=4$; 50-ml sample; 25% (v/v) 2-propanol as organic modifier.

increases solvent strength, reduces retention factor and retention volume and therefore might improve recoveries of strongly retained solutes. Recoveries were by 10–30% higher for four PAHs (naphthalene, fluorene, anthracene and fluorethene) at 50°C than at 25°C but standard deviations at 50°C were not as good as that at 25°C and they concluded that temperature was a valuable parameter for SPE although it should be further investigated [45].

The SPE has also been applied for direct determination of PAHs with an spectroscopic technique. Hagestuen et al. [64] studied the solid-phase room-temperature phosphorimetry (SS-RTP) for determining PAHs adsorbed on three different solid-phase extraction membranes that were commercially available. They demonstrated that the capacity of SPE for isolation and enrichment of target compounds associated with the selectivity and sensitivity of the SS-RTP may be a rapid, simple and inexpensive procedure for routine determination of PAHs although some drawbacks still are not completely resolved.

3.1.4. On-line systems

SPE can be coupled to various chromatographic techniques to determine PAH. The main advantages of the on-line systems are that they are automatic, which means that the sample has to be manipulated less, they reduce the analysis time, they consume less organic solvent and they need less sample volume [65].

HPLC is the most used for determining PAHs and SPE-HPLC is the most straightforward coupling method and therefore the most used. The sample preparation and conditioning steps are similar to those in the off-line mode but only the mobile phase is required to elute the compounds retained in the precolumn, which contained the sorbent, on-line connected to the analytical column. Precolumns with sorbents or membrane discs can also be used.

Either C₁₈-bonded silica [37,43,66] and SDB [66] have been used for determining PAHs. Selective sorbents, already mentioned, such as Boos silica, Boos Glass [43] have been on-line coupled to HPLC. The high selectivity of these sorbents is demonstrated in Fig. 4, although, as mentioned, recoveries were not good for all the PAHs and better results were obtained with C₁₈-bonded silica.

One problem of the on-line systems is the peak broadening which can appear when the sorbent is much different than the stationary phase of the analytical column. This also may occur when a surfactant is used as modifier [43] because of the distribution of the analyte over the precolumn and the strong interaction of some analytes with the micelles. In this case, the authors [43] proposed to add water in order to disrupt the micelle since the concentration of surfactant is below the CMC.

El Harrak et al. [66] used discs of SDB and tested MeOH, ACN and 2-propanol. Results are in Table 6. When 15% of MeOH or 2-propanol was added to the sample, several peaks appeared at the same retention time as some LMW PAHs. However, when acetonitrile was used, the blank was much cleaner and no interferences appeared in the chromatogram. But, it was necessary to increase the percentage of acetonitrile to increase the recovery of HMW PAHs. An increase in the percentage of acetonitrile distorted the peaks of the LMW compounds and so they could not be quantified. For this reason, 15% is the highest percentage of acetonitrile that can be used. That is why the authors recommended that PAHs be analysed in two separate runs: 15% of acetonitrile and 20% of 2-propanol should be used, respectively, for the LMW PAHs (from naphthalene to pyrene) and HMW PAHs if recovery are to be good.

Immunosorbent have also been coupled to liquid chromatography for determining PAHs [56,67] but problems were encountered with recoveries on the anti-fluorene IS because of the addition of an organic solvent to avoid adsorption of PAHs on vessels or tubings. With a sample volume of 20 ml, levels between 2 and 10 ng l⁻¹ were determined in real samples.

SPE can also be coupled to GC or SFC but an additional step of drying the precolumn before elution of the analytes retained in the precolumn is always required. Bernal et al. [18] coupled SPE to SFC for determining PAHs in water and results were better with C₁₈ discs than with SDB discs.

3.2. Solid-phase extraction of naphthalenesulfonates

Due to the polar groups in NS chemical structure, these compounds exhibit very low retention on the

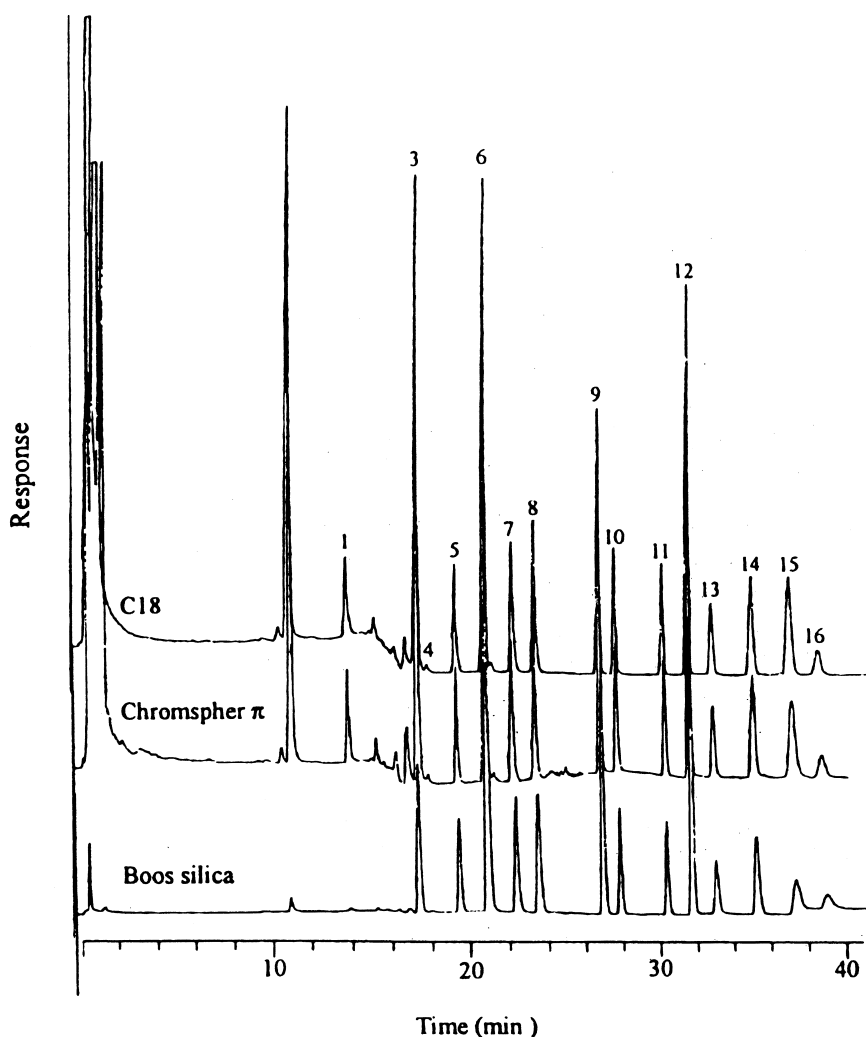


Fig. 4. On-line trace enrichment-LC-fluorescence chromatograms of 10 ml surface water, containing $3 \cdot 10^{-4}$ M Brij-35, spiked at the 100 ng l^{-1} level with all PAHs, using a Boos silica, Chromspher, or C_{18} -bonded silica in a 10×3 mm I.D. precolumn. Peak assignment: (1) naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benzo[*a*]pyrene, (10) chrysene, (11) benzo[*b*]fluoranthene, (12) benzo[*k*]fluoranthene, (13) benzo[*a*]pyrene, (14) dibenzo[*a,h*]anthracene, (15) benzo[*ghi*]perylene, (16) indeno[1,2,3-*cd*]pyrene (reprinted with permission from [43]).

common reversed-phase sorbents. However, if NS are paired with an organic cation such as tetraalkylammonium, the recoveries increase considerably. It should be mentioned that ion-pair SPE suffers from some drawbacks [4]. Recently highly cross-linked copolymers have also been used [29,68].

3.2.1. Ion-pair reagent

The most used ion-pair reagents are the tetra-

butylammonium (TBA) [3,69] and cetyltrimethylammonium (CTMA). Some authors said that with CTMA, which is more hydrophobic, aminosubstituted sulfonates appeared to be more effectively extracted [24].

The ion-pair reagent is usually added to the aqueous sample prior to extraction. Zerbinati et al. [28] saturated the solid-phase with octyltrimethyl ammonium acetate, thereby producing an ion-ex-

Table 6

Recovery values obtained in the analysis of 50 ml of a standard solution of $0.4 \mu\text{g l}^{-1}$ using nine STDVB disks at several percentages of ACN and IPA

Compounds	Percentage of ACN%				Percentages of IPA%		
	10	15	25	35	10	20	30
Naphthalene	81	77	– ^a	–	85	78	70
Acenaphthene	77	74	–	–	87	81	68
Fluorene	72	84	–	–	82	80	70
Phenanthrene	50	78	74	–	85	83	80
Anthracene	52	72	76	–	80	96	77
Fluoranthene	42	82	85	–	91	87	82
Pyrene	46	86	92	–	80	82	90
Benzo[<i>a</i>]anthracene	45	55	90	98	74	82	92
Chrysene	44	53	87	92	76	85	90
Benzo[<i>b</i>]fluoranthene	32	48	71	82	72	83	92
Benzo[<i>k</i>]fluoranthene	44	57	76	88	74	82	95
Benzo[<i>a</i>]pyrene	42	52	65	85	72	80	90
Dibenzo[<i>a,h</i>]anthracene	31	59	63	82	70	78	85
Benzo[<i>ghi</i>]perylene	28	58	69	78	68	82	89
Indeno[1,2,3- <i>cd</i>]pyrene	25	54	62	72	62	81	82

^a (–) not quantified.

change column. Good recoveries were obtained but the ion-exchange capacity and the breakthrough volume were low.

The influence of the pH and TBA concentration in the ion-pair was studied by El Harrak et al. [3] and the best results for a SDB sorbent were pH 7 and 3 mM TBA. Similar values are used by other authors [69] who used pH 6.5 and 5 mM TBA. Triethyl-

amine (TEA) has also been used when NS are determined by HPLC–MS, because problems were encountered when TBA was used [70]. A 5 mM TEA concentration and pH of sample adjusted to 6.5 were used in this case [70].

3.2.2. Sorbents

C_{18} -bonded silica is a widely used sorbent but

Table 7

Recoveries of naphthalenesulfonates versus volume of sample preconcentrated using 10×2 mm I.D. precolumn with C_{18} -bonded silica or PLRP-S and a standard solution of $10 \mu\text{g l}^{-1}$

Compound ^c	10 ml ^b		20 ml ^b		50 ml ^b		100 ml ^b	
	C_{18}	PLRP-S	C_{18}	PLRP-S	C_{18}	PLRP-S	C_{18}	PLRP-S
6-NH ₂ -4-OH-2-NS	68	92	52	88	14	75	n.d. ^a	60
6-NH ₂ -1-OH-3-NS	65	90	54	85	16	70	n.d.	62
5-NH ₂ -2NS	75	95	60	88	22	80	n.d.	74
8-NH ₂ -1-OH-3,6DNS	80	91	74	82	39	75	15	69
2,6-NDS	88	91	79	86	57	83	23	75
1,5-NDS	86	90	77	87	49	82	33	78
1-OH-3,6-NDS	93	89	80	86	68	82	23	75
2-OH-3,6-NDS	82	90	75	87	50	83	13	79
2-NH ₂ -1-NS	94	89	83	87	45	82	32	75
1-NS	90	97	82	92	48	85	30	77
2-NS	92	98	84	95	50	87	33	80

^a n.d. not detected.

^b RSD < 13% ($n=4$).

^c Sample conditions: pH 7 and 3 mM TBA.

Table 8

Mean percent recoveries and precision as percent relative standard deviation (%RSD) ($n=6$) for benzene and naphthalenesulfonates at the $50 \mu\text{g l}^{-1}$ level when 150 ml of ground water was processed. Reprinted with permission from [29]

Compound	Rec (%RSD)
2-amino-1,5-naphthalenedisulfonate	27 (3)
1,5-naphthalenedisulfonate	42 (9)
2,6-naphthalenedisulfonate	87 (8)
1-hydroxy-3,6-naphthalenedisulfonate	71 (8)
1-amino-4-naphthalenesulfonate	94 (10)
2-hydroxy-3,6-naphthalenedisulfonate	86 (6)
1-hydroxy-6-amino-3-naphthalenesulfonate	75 (8)
3-nitrobenzenesulfonate	93 (1)
1-amino-6-naphthalenesulfonate	91 (8)
1-hydroxy-4-naphthalenesulfonate	103 (8)
4-methylbenzenesulfonate	99 (11)
4-chlorobenzenesulfonate	102 (11)
1-amino-7-naphthalenesulfonate	85 (3)
2-naphthalenesulfonate	101 (2)

SDB has shown to give better results. For instance, El Harrak et al. [3] compared C_{18} and PLRP-S (a styrene-divinylbenzene copolymer) in on-line SPE–HPLC system and recoveries were much higher with PLRP-s. Results are shown in Table 7. When the method was applied to river water, recovery decreased considerably and 20 ml was selected as value to extracted. The most problematic compounds are those with OH and NH_2 groups because of its higher polarity.

Other polymeric compounds, recently developed, have been used by Alonso et al. [29,68]. They

compare two highly crosslinked styrene-divinylbenzene, Isolute ENV+ and Lichrolut EN. These sorbents have a higher degree of crosslinking and so a higher specific surface area, which allows greater π – π interactions between aromatic analytes and the sorbent [73]. Best recoveries were obtained with Isolute ENV+ sorbent mainly for the naphthalenesulfonates with more than one SO_3^- groups [68]. In these cases, the ion-pair reagent was not added to the sample and the sample is adjusted at pH 2.5–3. The sample volume was 150 ml and the elution step was performed by adding 1 ml of water containing 5 mM TEA as ion-pair reagent and 4 ml of methanol [29]. Table 8 shows the recoveries and precision obtained and, as can be seen, low recovery values were still found for some compounds.

An alternative approach which does not use the ion-pair reagent consisted on using graphitized carbon black [71]. In this case, ionic interactions are suggested to be responsible for the specific adsorption of anionic species, thereby reducing the interference from humic substances [71,72]. Recoveries were higher than 90% for 100 ml except for the amino-substituted compounds [71].

It is important to note that the SPE of NS has still some problems and new sorbents need to be developed. In this sense, chemically modified polymers [73] may be a solution although have not been demonstrated yet. The recent application of molecular imprinted sorbents to SPE [74,75] can also be a solution even this has not been tested for NS.

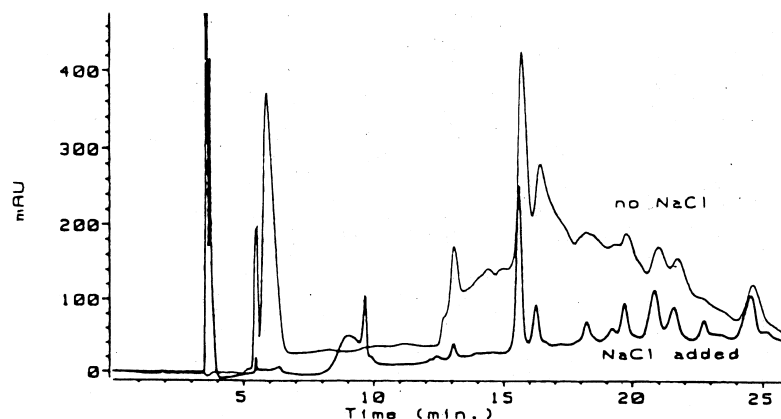


Fig. 5. Influence of sample ionic strength (no NaCl or 0.5 M NaCl added) on the removal of humic substances. Sample volume: 30 ml (pH 7) containing 10 mM MTBA. Precolumn: 10×4 mm I.D. packed with PLRP-S (reprinted with permission from [76]).

3.2.3. Influence of the ionic strength

While a salting-out effect is observed in conventional reversed-phase SPE, higher contents of inorganic salts might substantially affect the recoveries when ion-pair SPE is used, because inorganic anions compete with the sulfonate anions for the organic

cation, thereby decreasing the extent of ion-pair formation of the NS and their extraction efficiency [4].

Different effects have been described in literature. Brouwer et al. [76] studied the influence of the ionic strength on the rather large interfering peaks in the

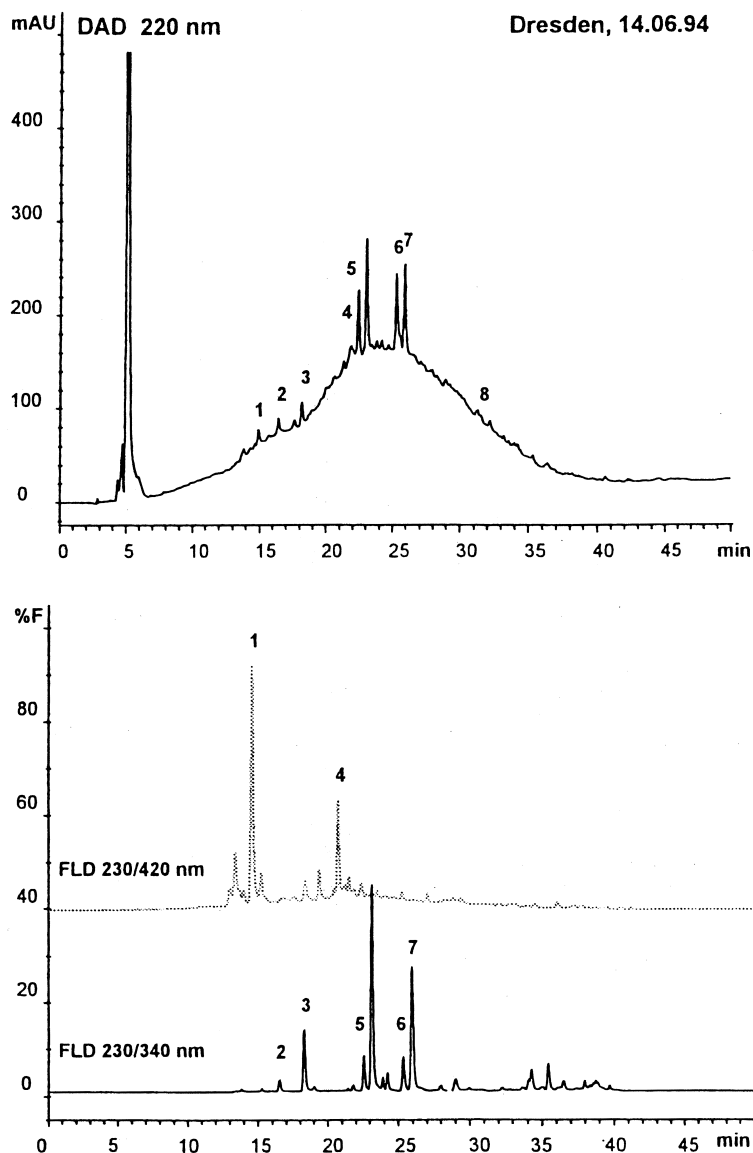


Fig. 6. UV and fluorescence chromatograms of a river Elbe spot check sampled in Dresden. Sample volume: 20 ml (1 mM TBABr, pH 6.5). Precolumn: 10× 2 mm I.D. C₁₈-bonded silica. Identified substances: (1) 2-aminonaphthalene-4,8-disulfonate, (2) naphthalene-1,5-disulfonate, (3) naphthalene-2,7-disulfonate, (4) 2-hydroxynaphthalene-3,6-disulfonate, (5) naphthalene-1,3,6-trisulfonate, (6) naphthalene-1-sulfonate, (7) naphthalene-2-sulfonate, (8) 4,4'-dinitrostilbene-2,2'-disulfonate (reprinted with permission from [38]).

LC–DAD chromatogram of the analysis of 30 ml surface water. They proposed that the addition of TBA probably aggravated the problem of interference of humic/fulvic acids because the charged groups on the humic/fulvic acids were neutralised by TBA and the negatively charged ions are converted into less polar ion-pair. They added sodium chloride to the sample in order to eliminate part of the humic/fulvic hump from the chromatogram since a decreased retention of charged compounds was observed when ionic strength increased because of the competition between the added ions and the analyte ions for the ion-pair. When 0.5 M NaCl was added, about 75% of interfering peaks disappeared but recoveries for the sulfonic acids studied did not decrease significantly for most of compounds. Fig. 5 shows chromatograms obtained with and without adding NaCl.

Different results were obtained by other authors [77,78] who found that inorganic anions compete with the sulfonate anions for the organic cation, thereby decreasing the extent of the ion-pair formation and the extraction efficiency. This is important for the analysis of industrial water and sea water. El Harrak et al. [77] found that the most influential inorganic species were nitrate and chloride and the influence was more significant for the compounds eluted first.

3.2.4. On-line systems

SPE–HPLC has been widely used for determining NS in water samples [3,5,69,76,77]. Either C₁₈-bonded silica and PLRP-S has been used but, as already mentioned, PLRP-S gave better recoveries [3]. Another study by the same group [77] recommended a 10×3 mm ID precolumn instead of a 10×2 mm previously used [3] because good recoveries were obtained for most compounds at higher sample volumes (100 ml) and no peak broadening was observed. In fact, Brouwer et al. [76] used a 10×4 mm ID precolumn filled with PLRP-S.

TEA as ion-pair has also been used in on-line systems with a 10×3 mm ID precolumn packed with PLRP-S but to obtain good recoveries for most naphthalenesulfonates only 15 ml were preconcentrated [70]. In this case, since electrospray-mass spectrometry was used, detection limits were low enough.

As mentioned, recoveries in real samples may vary from those obtained with Milli-Q water and so, the recoveries of the method must always be checked for real samples. Fig. 6 shows the chromatogram of the on-line SPE–HPLC with DAD and fluorescence detector of 20 ml of a river Elbe sample.

4. Conclusions

The SPE of polycyclic aromatic compounds is partially resolved because some problems have still to be solved. As regards the PAHs different sorbents may be used since no significant problems arise because of its higher hydrophobicity. However, it should be mentioned that the sorbents mainly used are not selective and there can be interferences from the samples. Care must be taken with the sorption problems (in both on-line and off-line modes) and depending on the sorbent used the concentration of organic solvent or surfactant must be optimized.

As regards the naphthalenesulfonates, there are significant problems with the recovery of more polar compounds, and with the interference of ionic species present in the samples. Different sorbents have been tested but still much research is needed to overcome these problems.

On-line systems have been applied to both groups of compounds and no additional problems have been detected.

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