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Review

Solid-phase extraction of phenols

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Abstract

Sample preparation for phenol analysis using solid-phase extraction (SPE) is reviewed. The scope of the review has been restricted to the literature dealing with the analysis of phenols as the main objective. The use, advantages and disadvantages of silica sorbents, polymeric, functionalised, carbon-based and mixed available sorbents, when applied to the separation and preconcentration of phenols, as well as the available experimental devices, are discussed. Other aspects such as phenol derivatisation prior to SPE, solid-phase microextraction, matrix effects and the storage of phenols in SPE cartridges, have been also discussed.

Keywords: Solid-phase extraction; Sorbents; Derivatisation; Matrix effects; Reviews; Phenols

Contents

1. Introduction. Aims and scope

Phenolic compounds are presented in the aquatic environment as a result of their industrial applications. These compounds are generated in the pro-

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duction of plastics, dyes, drugs, pesticides, antioxidants and paper and in the petrochemical industry [1]. Pentachlorophenol (PCP) is used as wood preservative [2]. Phenol is generated from lignin degradation in the production of paper [3] and chlorophenols could be generated from phenols in the chlorinating of drinking water. Nitrophenols are formed photochemically in the atmosphere from vehicle exhausts [4].

Because of their toxicity and unpleasant organoleptic properties (concentrations as low as a few μg/l of phenols affect the taste and odour of water and fish), phenols have been included in the US Environmental Protection Agency (EPA) (Methods 604, 625 and 8041) list of priority pollutants [5–7]. Also, the European Union (EU) has classified several phenols as priority contaminants and the 80/778/EC directive states a maximum concentration of 0.5 μg/l for total phenols in drinking water. Individual concentration should be under 0.1 μg/l.

Analytical techniques used in the determination of phenols are mainly high-performance liquid chromatography (HPLC) and also capillary electrophoresis (CE) in combination with ultraviolet detection (UV), fluorescence detection, electrochemical detection or mass spectroscopy (MS) [8]. Also gas chromatography (GC), usually after phenol derivatisation, with flame ionisation detection (FID), electron-capture detection (ECD), MS or microwave-induced plasma atomic emission spectroscopy (MIP-AES) is a common tool for the analysis of phenols [9–11]. However, none of these combinations can achieve quantification limits required for the direct determination of phenols in drinking water, making a preconcentration step necessary in the analytical scheme.

Liquid–liquid extraction (LLE) is still used as preconcentration step, in standard and official methods for determination of phenols in water [5–7]. Nevertheless, there is an increasing tendency to replace LLE by solid-phase extraction (SPE) and solid-phase microextraction (SPME). Among the reasons of this evolution are the large volume of organic solvents, foam formation, length of analysis time and difficulties in the automation of LLE procedures. On the other hand, SPE requires smaller amounts of organic solvents (no solvent in SPME), it is easy to automate and possible to integrate into on-line dedicated systems. Even in the off-line mode, it is less time consuming, and more efficient than LLE when a single organic extraction is carried out [12].

The goals of SPE of phenols in water are:

- The concentration of large volumes of water with quantitative recoveries (high breakthrough volumes).
- The elution of retained phenols with minimum amounts of organic solvents.
- The compatibility of the solid-phase eluent with the analytical system. This task is especially important in on-line systems.
- The selectivity in the concentration and elution steps.

Achieving these requirements is not an easy task because the different behaviour of the phenols in terms of acidity and polarity (Table 1). Phenol, 2-chloro- and 2-nitrophenol are hydrophilic compounds with lower affinity for non-polar sorbents and low breakthrough volumes in comparison with tri-, tetra- and pentachlorophenol. On the other hand, the variability of pK_a values makes a selective isolation even for the 11 EPA priority phenols (US EPA Method 604) from acid and neutral interfering species difficult. These difficulties, added to the environmental interest in the analysis of phenols at low levels, probably contribute to the huge number of publications dealing with SPE of phenols in water. Nowadays, development of SPE procedures, which

Table 1
Partition coefficients (octanol–water) for phenols, and pK_a values for the 11 phenols included in the EPA-604 list (taken from Refs. [38,41,94])

Compound	Log K_{OW}	pK_a
Phenol	1.50	9.99
2,4-Dinitrophenol	1.53	4.09
2-Nitrophenol	1.78	7.21
4-Nitrophenol	1.90	7.16
2-Methyl-4,6-dinitrophenol	2.12	4.34
2-Chlorophenol	2.15	8.55
4-Chlorophenol	2.41	
2,4-Dimethylphenol	2.42	10.6
3-Chlorophenol	2.50	
2,4-Dichlorophenol	3.08	7.85
4-Chloro-3-methylphenol	3.10	9.55
2,4,6-Trichlorophenol	3.69	7.42
Pentachlorophenol	5.01	4.93

are able to concentrate 500–1000 ml of water, with quantitative recoveries for the 11 EPA-604 priority phenols, is still an elusive goal.

Some phenols have been systematically included in test and evaluation mixtures for chromatographic columns and SPE cartridges and/or materials as representative polar analytes. Thus, phenols are ubiquitous not only in the environment but also in the analytical literature. However, in many cases, isolated data on the retention and separation of phenols from other compounds are only useful with the aim of evaluating the chromatographic material performance but far less useful in the determination of environmental impact of phenols. We have, therefore concentrated on literature which has, as its main objective the analysis of phenols rather than on papers and application notes that include partial data on the isolation of phenols. Since other papers in this issue will deal with basic aspects, mechanisms and new materials for SPE, which are also applicable in the case of phenols, we limited the object of this paper to give a summarised overview of the state of art in the SPE of phenols in water samples. This information should prove useful to those analysing phenols in water samples for first time, and should also help to consolidate knowledge on SPE of phenols, for those with a previous background in the subject.

Recent published papers in SPE of phenol compounds in water deal with several subjects:

- New stationary phases and devices. Apart from carbon and silica based materials, there is a boom in the production of polymeric and modified polymeric sorbents from different suppliers, which usually give only brief information about the sorbents, but claim to improve the efficiency in the concentration of phenols. The number of publications on the use of membranes instead of cartridges and SPME has also increased exponentially.
- Development of fully automated *on-line concentration and analysis* protocols.
- *Derivatisation of phenols previously to concentration.*
- Influence of other matrix components in the efficiency of the SPE procedure, are also typical subjects in the bibliography related with SPE studies of phenols.

2. Sorbents for solid-phase extraction of phenols. Mechanisms

2.1. Silica sorbents

Non-polar reversed-phase sorbents with silica base were the first materials tested in SPE of phenols in water [13,14], of which, C_{18} is the most popular.

Retention of phenols from water samples by a C_{18} material is the result of a reversed-phase mechanism (apolar Van der Waals interactions between analytes and sorbent). Therefore, given the acidic behaviour of pentachloro- and dinitrophenols (Table 1), pH of the sample should be adjusted to 2–3 to minimise ionisation and so trifunctional bonded sorbents should be used to avoid hydrolysis of the C_{18} phase [12]. It is necessary, when dealing with aqueous samples to wet the hydrophobic surface of the C_{18} phase with a water miscible solvent, usually methanol, otherwise mass transfer between water and sorbent will be limited. Because the partitioning process involves the differences in solubility of the analytes between the aqueous and the solid apolar phase, the polarity (Table 1) of the analyte plays a crucial role in determining how effective the sorbent will be. In addition, increase in carbon loading will increase sorbent capacity. Therefore, the capacity of a given sorbent for the analytes is a function of the analyte concentration in the aqueous phase. This means that for dilute solutions (natural or drinking water samples) the capacity (mass sorbed) will be considerably less than for concentrated model solutions. All these factors have to be taken into account when selecting the most appropriate C_{18} sorbent for trapping of phenols. Currently, mono- and trifunctional, endcapped and non-endcapped C_{18} sorbents with carbon loading ranging from 12 to 18% are commercially available. Another important factor is pore diameter. Most commercially available materials have 60 Å average pore diameter but materials with 125 Å pore diameters are also common. The smaller the pores size the larger the available surface area. Furthermore, larger molecules such as humic substances, which would interfere with phenols in later analytical steps, will be excluded from entering the pore matrix.

Although the distribution coefficient (K_d) of solutes can be used to predict sorbent suitability,

experimentally determined breakthrough volumes are much more common in practice. For phenol compounds on C_{18}, and for hydrophobic sorbents in general, breakthrough volumes are related to the octanol–water partition coefficients (Table 1). Since phenol, nitro and 2-chlorophenol display the smallest values, they represent practical limits and can be used to evaluate the efficacy of a given sorbent for phenol trapping. Addition of sodium chloride to water samples [15,16], is a common technique to increase breakthrough volumes. In conclusion, it has been found that, using 500 mg of sorbent, its is impossible to get quantitative recoveries for phenol in a 100 ml sample (Table 2).

It is possible to concentrate higher sample volumes without breakthrough of phenol, by the use of sorbents with free silanol groups (non-endcapped sorbents). This allows the formation of hydrogen bonds between sorbent and phenols [17], but it could lead to irreversible sorption and extra difficulties in cartridge elution.

Elution of retained phenols is done after removing residual water from the sorbent. Different solvents such as ethyl acetate [18], methanol [16,19], acetonitrile [20] or acetone [13,14] are used to desorb retained phenols. Elution volume depends on: kind of solvent, amount of sorbent, SPE device (cartridge or membrane) and polarity of each phenol.

C_8, cyclohexyl, phenyl and cyano are other silica-based sorbents, which have also been used for SPE of phenols in water samples [16,21]. Cyclohexyl and phenyl sorbents have shown increased ability to sorb phenols when compared to C_{18} sorbents. However, in the off-line mode, none of them gives a breakthrough volume for phenol higher that 100 ml. Small columns (10×2 mm I.D.) filled with these materials

Table 2
Breakthrough volumes for phenol with different stationary phases

Phase	Commercial name/supplier	Amount (g)	Device	Sample	Flow (ml/min)	Breakthrough volume (ml)	Ref.
Silica sorbents							
C_{18}	J&W Scientific	0.50	Cartridge	Sea water	–	20	[20]
C_{18}	J.T. Baker	0.50	Membrane[a,b]	Sea water	20–25	<50	[20]
C_{18}	Varian	0.50	Membrane[a]	Milli-Q water	–	<100	[19]
Phenyl	J.T. Baker	0.50	Cartridge	Milli-Q water	4	<100	[16]
Polymeric materials							
PS–DVB	LiChrolut EN, Merck	0.20	Cartridge	Tertiary treated sewage	5	>400	[28]
PS–DVB	LiChrolut EN, Merck	0.25	Cartridge	Drinking water	–	>1000	[27]
PS–DVB	ENVI-Chrom P, Supelco	0.50	Cartridge	Milli-Q water	–	>200	[29]
PS–DVB	Analytichem International	0.50	Membrane[a,b]	Sea water	20–25	250	[20]
PS–DVB	Amberlite XAD-4	0.20	Cartridge	Distilled water	–	200	[23]
Graphitised carbon							
Carbon	Carbochimica Romana	1.0	Cartridge	Drinking water	70	2000	[54]
Carbon	Vulcan, Supelco	0.25	Cartridge	Surface water	32	180	[50]
Carbon	Carbograph 4, Carbochimica Romana	0.50	Cartridge	Drinking water	100	4000	[51]
Carbon	Carbopack B, Supelco	0.50	Cartridge	Milli-Q water		200	[42]
Functional sorbents							
PS–DVB acetylated	Laboratory-made	0.50	Membrane	Distilled water	200	500	[33]
PS–DVB acetylated	Laboratory-made	0.25	Cartridge	Milli-Q water	5	800	[42]
PS–DVB sulphonated	IST	0.20	Cartridge	Milli-Q water	100	1000	[45]
C_{18} positively charged	Laboratory-made	0.50	Cartridge	Milli-Q water	15	500	[41]

[a] 47×0.5 mm membranes.
[b] Two membranes were used.

have been used in on-line devices. In this approach, phenol breakthrough takes place for less than 10 ml of water [22].

2.2. Polymeric materials

Polymeric sorbents have been developed by modification of earlier used XAD resins [3,23–25], and incorporated in commercial SPE devices: cartridges, membranes and microextraction fibres. They comprise a polystyrene–divinylbenzene (PS–DVB) hydrophobic structure and different particle sizes, superficial areas and crosslinked grades depending on the supplier (Table 3).

The strategy to concentrate phenols in PS–DVB sorbents is similar to the procedure followed with C_{18} materials: sorbent activation, concentration of water sample (at pH 2–3), drying of the sorbent bed and elution using: methanol [22,23,26], acetonitrile [20,27], methanol–acetonitrile [28], ethyl acetate [18] or *tert*.-butyl methyl ether [29,30]. Retention of phenols is the result of a reversed-phase mechanism and $\pi-\pi$ interactions among electrons from the aromatic ring in the sorbent and in phenol molecules.

In comparison with silica base sorbents, PS–DVB is more stable at acid pH values, normally used in the concentration of phenols, and according to Hennion and Pichon [31] it has higher capacity for polar analytes. This can be attributed to a much large carbon content (nearly 90% as compared to the maximum 18% of C_{18} sorbents) but specially to the higher surface-area exhibited by polymers (many of commercial available ones have areas of >1000 m^2/g as compared to 200–600 m^2/g for C_{18} sorbents). The breakthrough volume obtained for phenol, using different polymeric sorbents, is in good agreement with this prediction, (Table 2). In particular the LiChrolut EN material allows to concentrate at least 1 l of water with quantitative recoveries for phenol. We should note that this is the polymeric sorbent with the highest superficial area (Table 3).

2.3. Functionalised sorbents

Retention of polar phenols on PS–DVB sorbents can be improved by the introduction of polar groups into the polymer. Resulting materials still retain the high capacities to trap less polar phenols, but, in addition, the hydrophilic character of the introduced functional group, improves their wetting characteristics and, consequently aids mass transfer of most polar phenols from the water solution to the sorbent. Most common groups used to modify polymeric sorbents are acetyl [32,33], hydroxymethyl [34], benzoyl [35], *o*-carboxybenzoyl [36,37], carboxylic [38,39] and sulphonic acid [40]. C_{18} sorbents have also been modified with quaternary ammonium salts [41].

Sorption of phenols in modified resins, is due to the polymeric skeleton (reversed-phase mechanism and $\pi-\pi$ interactions), and facilitated by the introduced functional group. Sorbents with carboxylic or sulphonic acid groups have a cationic exchanger character and form hydrogen bonds with protonated phenols. Sorbents with quaternary ammonium sites work as anion exchangers and are used to retain phenols in water samples adjusted to basic pH.

Table 3
Characteristics of some polymeric sorbents used in solid-phase extraction of phenols

Commercial name	Supplier	Particle size (μm)	Superficial area (m^2/g)
Amberchrome 161	Supelco	50–100	720
Sarasep	Sarasep	10	415
PLRP-S	Spark Holland	15–25	500
ENVI-Chrom P	Supelco	80–160	900
LiChrolut EN	Merck	40–120	1200
HYSphere-1	Spark Holland	5	>1000
ISOLUTE Env+[a]	IST	40–140	1000–1100
Bond Elut PPL	Varian	125	600

[a] Sulphonated PS–DVB.

Comparisons between these functionalised phases are not easy since many of them are not commercial, and the detailed description of the derivatisation is not given in most of published literature. Just a few articles describe in detail, the influence of the polymer modification in the retention of phenols:

– Piangerelli et al. [42] have reported recoveries obtained for 12 phenol compounds in 1 l of water, using both an acetyl functionalised and non-modified styrene–divinylbenzene copolymeric resin. Recoveries of 95% and 60% were obtained for phenol, respectively. Quantitative retention of pentachlorophenol was achieved with the non-functionalised resin. A 20:80 mixture of acetylated and non-acetylated resin gave recoveries from 90 to 95% for all the phenols studied.

– Fritz and co-workers [40,43] have studied the effect of sulphonation on the retention of phenol in a polystyrene–divinylbenzene (PS–DVB) sorbent. A maximum retention factor (k') of 457 was achieved for a material with 0.6 mequiv./g of sulphonic groups (a k' value of 22.3 was reported for phenol on a C_{18} sorbent [44]). According to these papers, sulphonic groups in this functionalised sorbent are presented only in the surface of the polymer particles, improving phenol transfer from water to the hydrophobic interior.

– Buchmeiser and co-workers [38,39] have also described the preparation of carboxylic acid-modified resins. Maximum efficiency corresponded to sorbents with 3–4 mequiv./g of carboxylic groups.

Breakthrough volumes for phenol using different modified sorbents are given in Table 2. With the exception of LiChrolut EN, modified materials allow concentration of higher volumes of sample than do bonded silica and polymeric materials. In particular, a sulphonated resin from IST (degree of sulphonation is not declared by the supplier), achieved quantitative recoveries for phenol in 1 l of water [45]; recoveries from 90 to 95% were obtained, using the same material, for several chlorophenols (from 2-chloro- to pentachlorophenol) in 2 l of water [46].

2.4. Carbon

Graphitised carbons are the third kind of sorbents used in SPE of phenol species. Retention of phenols on these materials results from the combination of several process: (1) reversed-phase sorption of non-polar compounds (larger capacities results from increased surface area of graphitised carbons which in turn increases the possibilities of reversed-phase interactions), (2) $\pi-\pi$ interactions between sorbent and aromatic analytes and (3) the anion-exchange behaviour of carbon. The latter mechanism was described by Di Corcia et al. [47], and it is the consequence of the benzpyrylium salts with positive charge present, as impurities, in the surface of graphitised carbon. Therefore, due to a combination of the three mechanisms, carbon presents a high efficiency for trace enrichment of neutral and acid pesticides in water samples [48].

When a carbon sorbent is used for the concentration of phenols, it is not necessary to acidify water samples. Under these conditions retention factors (k') for more acid species (pentachloro- and dinitrophenols) are very high in comparison with those for a non-polar sorbent as C_{18} [49], because of the strong interactions of phenolates with the positively charged sites on the carbon surface.

Retention of polar and non-acidic phenols, depends significantly on the kind of carbon sorbent used. Breakthrough volumes as different as 180 [50] and 4000 ml [51] have been reported by Di Corcia and co-workers, for phenol, using two different types of carbon adsorbents (Table 2). For 2-chlorophenol, even with the first carbon adsorbent, breakthrough volume was higher than 2000 ml [50], and in good agreement with results reported by other authors [52].

Not surprisingly, elution of phenols from carbon sorbents it is not an easy task. Phenol is desorbed with dichlorometane–methanol (90:10) or (80:20) mixtures [47,53]. Nevertheless mixtures of dichlorometane–methanol doped with trifluoroacetic acid [54] or better with a tetrabutyl ammonium salt [47,51,53,55], are necessary to desorb most acidic phenols. Even using these complex mixtures, pentachloro- and dinitrophenols are slowly eluted, so a backflush elution is advisable to decrease the volume of the final extract and to achieve, in this way, high concentration factors.

Apart from the strong retention of most acidic phenols, carbon sorbents present other drawbacks:

– Di Corcia and Marchetti [56] have pointed out the presence of quinone groups on the carbon

surface, which are responsible for irreversible adsorption of some species, especially when working at very low concentrations. To avoid this unwelcome effect it is necessary to wash the sorbent with an ascorbic acid solution, which reduces quinones to the less reactive hydroquinones.

– Carbon is a non-porous sorbent, so cartridges filled with this material have a high resistance to the passage of water. Initially high flow-rates are attainable, but carbon bed gradually compacts and the flow of water through the cartridge decreases steadily. We have checked that when 1 l of water, filtered through a 0.45-μm membrane, is concentrated, average flow-rates were in the range of 25–30 ml/min [46,52]. Nevertheless, Di Corcia and co-workers have reported attainable flow-rates of 100 ml/min [51]. However, they reported a diminution in the permeability of the sorbent when the same cartridges was used several times [54].

3. Mixed sorbents

As can be seen from the previous paragraphs, the different physical properties of phenols makes it difficult concentrate large volumes of 1 l or more, of real water samples with quantitative recoveries and interference elimination using a single sorbent.

Di Corcia et al. [57] achieved a selective concentration of several phenol species, in water samples containing linear alkyl benzenesulphonates (LASs), using a tandem of graphitised carbon and an anion exchanger sorbent (SAX). Once the water sample was forced through the carbon bed, the second cartridge was connected. First, 8 ml of dichloromethane–methanol (60:40) was passed through both sorbents and the eluent was discharged. Non-acidic species were removed with this solvent while most of the acidic phenols are retained in the carbon and the rest pass to the SAX sorbent. Elution of phenols was done with 8 ml of dichloromethane–methanol (90:10) 0.25 *M* in formic acid. This mixture allowed quantitative desorption of retained phenols, but was not strong enough to remove the most acid LAS from the SAX sorbent.

In preference to the use of two cartridges, other authors have proposed a single cartridge with mixed or layered sorbents to improve SPE of phenols, in terms of both recoveries and selectivity:

– Piangerelli et al. [42] mixed acetylated and non-functionalised Amberchrome 161, to achieve maximum breakthrough volumes for a mixture of 12 phenols with different polarities. Phenol was better retained in the acetylated resin and pentachlorophenol in the non-polar polymer. A 20:80 mixture of acetylated-non-functionalised sorbent gave quantitative recoveries for the studied species in 800 ml of water.

– Mixtures of Amberlite XAD-4 and carbon have also been proposed to improve breakthrough volumes of phenol species [58].

– Layered cartridges, containing acetyl functionalised resin and an amino-bonded silica sorbent, were also described for determination of trace levels of organic pollutants, including several phenol species, in water samples [59]. Nevertheless, reported recoveries, in 1 l of water, were clearly non-satisfactory.

4. Phenol derivatisation before solid-phase extraction

GC is a popular technique for the analysis of phenol compounds. However, because of their high polarity, phenols tend to give broad, tailed peaks, and the effect increases as the chromatographic column ages [18]. To avoid this drawback, several derivatisation reactions have been proposed to transform phenols to less polar compounds, with better chromatographic characteristics. Some of these reactions can also be used to improve efficiency of SPE procedures by enhancing reversed-phase interactions.

4.1. Acetylation

Phenol acetylation with acetic anhydride in presence of carbonate or hydrogencarbonate, is one of the most studied derivatisation procedures [13]. The reaction can be performed in aqueous samples, in a few minutes, with high efficiency and using low cost reagents [60]. Corresponding acetates are more easily extracted from water samples, using hydrophobic sorbents, than non-derivatised phenols.

C_{18} materials in cartridges [61,62] and membranes [63] have been used for the concentration of acetylated phenols and chlorophenols in water samples. Breakthrough volumes for phenol are close to 500 ml (Table 4), and higher that 1000 ml for cresols [64] and chlorophenols [62,63]. Aqueous acetylation has also been applied to increase breakthrough volumes of 2-chlorophenol in graphitised carbon cartridges, and to reduce solvent volume for desorption of pentachlorophenol and other acidic phenols [9,46,52].

The main limitation of SPE of acetylated phenolic compounds is the very low efficiency of the reaction with nitro and dinitrophenols [60,63]. In addition, CO_2 is formed in the reaction, which could disturb the efficiency of the extraction, especially when the sorbent is packed in a cartridge [62,63] and poor compatibility of acetylated species with HPLC or CE separation techniques, limits this approach in practice.

4.2. Ion-pair formation

Another way to decrease the polarity of phenol compounds is the formation of ion-pairs between phenolates and quaternary ammonium salts. In this case, water samples are adjusted to pH 9 and tetrabutylammonium bromide is added at a concentration of 5 m*M* in water [1,65,66]. The capacity of polymeric and carbon materials to concentrate the resulting ion-pairs have been tested, obtaining good recoveries for the 11 phenols considered in EPA Method 604, with the exception of phenol, which presented very low breakthrough volumes in carbon sorbents (Table 4). Elution of compounds is performed with methanol doped with 1% of acetic acid, to break the ion-pairs. The final extract is compatible with HPLC, CE and GC separation techniques.

In fact, retention of these ion-paired compounds on hydrophobic sorbents is very close to the already mentioned use of C_{18} sorbent modified with different quaternary ammonium compounds, to retain phenolates, as a result of an anion-exchange mechanism [41]. The only difference is that ion-pairs in this technique are formed in solution and not on the surface of the sorbent.

5. Devices for solid-phase extraction of phenols

Cartridges, columns and syringes are classic presentations of SPE sorbents. In all three cases, stationary phase is placed between two 20 μm polypropylene frits. Sorbent amounts from 200 to 1000 mg, are typically used in off-line extraction of phenols from water samples, and smaller microcolumns (10–30 mm×2–3 mm I.D.) in automated on-line SPE, coupled mainly with HPLC systems [32,35,36,67–69], and in less extension to GC techniques [70]. In both cases the amount of sorbent is quite low, in comparison with those used in off-line extraction, to make possible desorption of retained phenols with a small volume of an organic solvent or mobile phase, which is totally introduced into the chromatographic column. Therefore, the choice of sorbents with high retention factors for phenolic species is of vital importance.

Carbon [37,68,71], polymeric [69,72,73] and func-

Table 4
Breakthrough volumes for phenol (as acetylated compound) in Milli-Q water, using different sorbents

Phase	Commercial name/supplier	Derivatisation[a]	Amount (g)	Device	Flow (ml/min)	Breakthrough volume (ml)	Ref.
C_{18}	J.T. Baker	1	0.50	Membrane	50	<500	[63]
C_{18}	IST	1	0.50	Cartridge	10	<500	[63]
Carbon	ENVI-Carb, Supelco	1	0.25	Cartridge	25	1000 (2-Cl)	[46]
Carbon	Carbopack B, Supelco	2	0.30	Cartridge	–	<25	[66]
PS–DVB	ENVI-Chrom P, Supelco	2	0.50	Cartridge	–	500	[66]
PS–DVB	PLRP-S, Spark Holland	2	0.50	Cartridge	–	100	[65]

[a] 1=Acetylation, 2=ionic pair with TBABr.

tionalised polymeric materials [32,35,36,67] are normally used in SPE microcolumns. Breakthrough volumes for phenol in different sorbents used in on-line systems are given in Table 5; the best results correspond, as in the off-line approach, to LiChrolut EN and the sulphonated polymer ISOLUTE Env+.

Membranes – small particles of sorbent (from 8 to 12 μm in diameter), are imbedded into an inert matrix of polytetrafluoroethylene (PTFE) fibrils or in a glass–fibre matrix [74]. 47×0.5 mm membranes, with 500 mg of sorbent, are used in off-line processes to extract phenol compounds from water samples [19,20,22,33,63]. Small disks (4–10 mm× 0.5 mm), are also available in the market, and could be used in combination with high sensitivity techniques, such as GC–MS–MS [10], for which only a few millilitres of sample should be concentrated.

Small and homogeneous size of sorbent particles in a SPE membrane allow one to achieve theoretical plate heights of about 0.1 mm, five-times less than in a cartridge filled with particles from 40 to 60 μm [75]. In addition, sorbent surface, in a 47 mm membrane, is 20-times higher than in a conventional cartridge. As a consequence of these properties, capacity of a 500 mg membrane is similar in capacity to a cartridge with the same amount of sorbent, but higher sample flow-rates, up to 100 ml/min, are easily achieved without affecting recoveries of phenol compounds [20,33].

A drawback associated with membranes, is the high volume of solvent necessary to elute retained compounds; in the case of phenols, from 10 to 20 ml of methanol [20,22], acetonitrile [20] and ethyl acetate [63] are reported in the literature to elute these compounds from polymeric and C_{18}, 500 mg membranes. A further evaporative step, to reduce the volume of organic eluent and to improve concentration factors, often lead to loses of the most volatile phenols [9,52]. An adjustment of pH to basic values, is recommend by some authors to decrease evaporation loss [50]; nevertheless, this could lead to degradation of nitrophenols.

Table 5
Breakthrough volume for phenol in on-line solid-phase extraction[a]

Sorbent	Breakthrough volume (ml)	Ref.
Carbopack B	2	[68]
Envi-Carb	2	[37]
PLRP-S	4	[35]
Envi-Chrom P	7	[35]
LiChrolut EN	30	[35]
Amberchrome	8	[36]
Amberchrome acetylated	13	[35]
Bond Elut PPL	14	[37]
ISOLUTE Env+	40	[72]

[a] Results given for 10×3 mm I.D. microcolumns.

Another experimental configuration is the SPME device [76–78]. It consists of a fused-silica fibre coated with different polymers, which is housed in the needle of a syringe. By pushing down the plunger of the syringe, the fibre is exposed to the sample. SPME is not based on exhaustive extraction of analytes from the sample, but on an equilibrium between the analyte concentration on the sample and that in the fibre coating. This process can also be stopped before equilibrium, quantification can be made if sampling time, and agitation conditions are carefully controlled. After adsorption, analytes are thermally desorbed by introducing the needle into a heated injector of a GC system. Automation of SPME–GC analysis is available from Varian. Recently, Supelco has developed an interface to couple SPME and HPLC. In this case, introduction of analytes in the chromatographic system is by solvent desorption.

To date, the commercially available SPME coatings include: three polydimethylsiloxane (PDMS) films of different thickness (7, 30 and 100 μm), a polyacrylate (PA) coating of 85 μm and four mixed phases: polydimethylsiloxane–divinylbenzene (PDMS–DVB) of 65 μm and 60 μm for GC analysis and HPLC analysis, respectively, polyethylene glycol–divinylbenzene (Carbowax–DVB) of 65 μm for GC analysis, polyethylene glycol–template polydivinylbenzene (Carbowax–TPR) of 50 μm for HPLC and carboxen–polydimethylsiloxane (carboxen–PDMS) of 75 μm for GC analysis.

In the analysis of phenols only two kind of coating have been tested, PDMS [79,80] and PA [79–83], and final analysis of the adsorbed compounds has been performed by GC. PDMS is a liquid polymeric phase that has been successfully applied to a great number of applications [77,78,84–89]. Nevertheless, results obtained with this polymer for the analysis of phenols were not satisfactory [79]. The low partition coefficients between PDMS and water for most of

the phenols are due to the relatively non-polar nature of PDMS. For the SPME of phenols it is necessary to use a more polar phase such as PA or to derivatise these compounds in order to reduce their polarity.

The PA coating is a solid polymeric phase, which has an affinity for both polar and non-polar compounds since its structure consists of a hydrocarbon chain backbone with relatively polar ester side chains. This coating can successfully extract phenols from water [81–83]. The affinity of the PA film for the analytes is related with the octanol–water partition coefficient K_{ow} and with the solubility of phenols in water [79]. The higher the K_{ow} value and the lower the solubility, the higher the acrylate K values. In this way, phenol, the compound with the lowest K_{ow} value and the highest solubility, presents the lowest affinity for this polymeric phase. As the number of chlorine substituents on the molecule increases, so does the compounds' affinity for the coating, with PCP the compound with the highest acrylate K value. The efficiency of the extraction of phenols with PA fibre can be enhanced at a low pH and in a saturated salt environment. As we have previously discussed, at neutral pH the most acidic phenols are still largely deprotonated. At pH of 2 or lower, the percentage of ionised form is insignificant and, therefore, the amount of analyte extracted by the fibre increases. On the other hand, the addition of salt decreases the solubility of the compounds in water and forces more of these analytes into the fibre. Equilibrium for all phenols is reached in less than 1 h of direct SPME sampling. For the desorption of phenols was necessary to work at high injector temperatures to avoid carryover of pentachlorophenol [79,82,83].

Buchholz and Pawliszyn [79,81] developed an SPME–GC method for the determination of phenols from water samples. They used PA coated fibres with 95 μm thickness that were exposed directly to the water samples at a pH of 2, saturated with NaCl and magnetically stirred. Equilibrium for all target compounds was reached within 60 min and, when fibre was desorbed at 200°C carryover was 1% or less for all the compounds with the exception of PCP. They also demonstrated [79] that by derivatisation with acetic anhydride the efficiency of the SPME with PDMS fibres increases significantly. As we previously have mentioned, the limitation of the derivatised SPME method is the analysis of nitrophenols. They also run out some experiments to extract the acetate derivatives with the PA fibre. The extraction efficiency was essentially the same as for the free phenols.

In SPME, the fibre can be exposed to the headspace (HS) over the sample. HS-SPME is especially convenient in the analysis of samples containing large molecules that could irreversibly contaminate the fibre coating, and in the analysis of solid samples. Phenols could be extracted by HS-SPME [79], but the time to reach equilibrium was far larger than for direct sampling, due to the slow transfer of phenols from the aqueous layer through the headspace to the fibre.

Bartak and Cap [80] studied the SPME of free phenols in waters. They compared the results obtained with the 100 μm PDMS and 85 μm PA fibres. The recoveries obtained were about one-order the magnitude higher with the second fibre. They also investigated SPME, HS-SPME, and in situ acetylation of the samples using PA fibres. Optimum conditions for the concentration of phenols in PA coated fibres using the HS-SPME technique were at pH of 1 with saturation by sodium chloride. Extraction time was set at 60 min.

Although the number of studies dealing the SPME of phenols is still quite low and almost semiquantitative data have been reported, this technique appears to be promising for the determination of phenols in water and soils. Lee et al. [82] used PA fibres to extract chlorophenols in landfill leaches and soils. They optimised some parameters affecting the water extraction efficiency and applied the method to a landfill leachate sample contaminated with pentachlorophenol and to a chlorophenols contaminated soil. For this last sample the results obtained by SPME were quite close to the ones obtained by Soxhlet extraction. Llompart et al. [83] have recently developed a HS-SPME GC–MS method for the determination of phenols in soils using PDMS fibres. The samples were suspended in water and phenols were acetylated in situ. Effect of different parameters affecting the absorption process as well as the extraction kinetics at 25 and 100°C were studied. The procedure exhibited good linearity and precision and detection limits in the sub-ng/g level. The method was applied to a real contaminated soils and

the results obtained were in good agreement with the certified phenol values.

6. Matrix effects

As has been mentioned before, many published results on SPE of phenols correspond to model or synthetic water samples, so matrix effects were not sufficiently addressed. Drawbacks associated with SPE of phenol compounds from large volumes of real water samples (tap, surface and river water) are mainly two:

First, a decreasing of recoveries and breakthrough values, in comparison with results obtained for artificial samples prepared in the laboratory with ultrapure water [41]. This diminution in the efficiency of the extraction procedure, is related to the presence of other species, usually at higher levels than target analytes, which can saturate the load capacity of the sorbent. Fulvic and humic acids are normally responsible for this behaviour [41,54]. Second, the lack of selectivity in the concentration step, which leads to complex chromatograms (or electropherograms), when universal detection methods such as FID and UV are used.

In spite of the huge number of papers dealing with SPE of phenols from water samples, very few articles study, in a systematic way, the influence of the matrix in the performance of SPE procedure. However, it is possible to collect some comments from published literature:

(i) In the analysis of tap water, it is necessary to add a reducing agent (sodium thiosulphate [52] or sodium sulphite [66,69]) to eliminate free chlorine, which could react with phenols and produce chlorophenols.

(ii) Potential interference, from basic and non-polar species retained in extraction devices, can be removed by washing C_{18} and polymeric sorbents with a small volume of non-polar solvents, or non-modified mixtures of methanol–formic acid, in case of graphitised sorbents [53].

However, selective removal of polar interferences (mainly humic acids and surfactants) is a more difficult task, because of the variability in the octanol–water distribution coefficient of phenols (Table 1):

- Surface and river water, containing fulvic and humic acids at levels of a few mg/l, give brown extracts after concentration over polymeric and C_{18} sorbents. When these extracts are analysed using HPLC with UV [53,67], or electrochemical detection [69,90], a huge peak is observed at the beginning of chromatograms that hampers quantification of less retained species, such as phenol and 2-chlorophenol.
- Masqué et al. [67], have compared the use of several reagents (sodium sulphite, sodium thiosulphate, oxalic acid and potassium permanganate) to reduce these interferences. Best results were obtained with sodium sulphite. The optimal amount was related with the charge of humic substances in water.
- Influence of humic and fulvic acids in SPE of phenols over carbonaceous materials, has been systematically studied by Di Corcia and co-workers, using real and simulated river water [51,53,57]. They pointed out that these species are more retained in carbon, C_{18} and polymeric sorbents at lower pH values. As carbon is able to retain phenol species at neutral pH values, the extraction procedure is less prone to the interference of humic substances [53]. Nevertheless, even for carbon cartridges, a diminution in the recovery for phenol and 2-chlorophenol (the less retained species), was reported for samples spiked with fulvic acids at the level of 10 mg/l [54,57], which is normally higher than levels found in surface water.
- Strong anionic surfactants, as LASs, also could lead to the presence of potential interfering peaks in HPLC–UV chromatograms, for water samples concentrated using carbon sorbents. Typically concentrations of LASs in surface water range from 5 to 50 μg/l, which are not great enough to saturate positively charged sites in carbon surface and so to decrease recoveries for most acidic phenols. Moreover, a certain selective elution of phenols and LASs, from carbonaceous sorbents, could be achieved using dichlorometane–methanol modified with formic acid, instead of with tetrametylammonium hydroxide [47].
- Acetylation of phenol compounds in presence of carbonate or hydrogencarbonate and further preconcentration using hydrophobic sorbents, could

lead to a more selective extraction of phenols in presence of humic acids and LASs.

- As has been mentioned before, sorbents having small pore diameters, specially high-surface area PS–DVB polymers significantly exclude humic substances. It is expected that layered SPE sorbents would provide efficient procedures to deal routinely with real samples.
- Mölder et al. [84] applied SPME to the determination of phenols in wastewater. They used high desorption temperatures in order to prevent the carryover of PCP. After 5 min of desorption at 300°C PCP could be completely removed from the PA coating. However, after 10 SPME runs a drastic loss of performance was observed. Using less stringent desorption conditions (5 min at 280°C), a small carryover of PCP was still observed. They also proved that the presence of humic acids and surfactants in the samples decreased significantly the extraction efficiency.

7. Storage of phenols in solid-phase etxraction

Once a SPE procedure for phenol species have been optimised, it seems reasonable to use it in monitoring programmes involving, normally, the analysis of a huge number of samples. In this situation, a lot of space is saved in the laboratory and risk of degradation is minimised, if samples are preconcentrated in the field and then SPE cartridges transported and stored in the laboratory. This supposes that no degradation of phenol species happens while they are in contact with the extraction sorbent, and efficiency of the elution procedure does not change with time of storage. However, although this is an important practical aspect in environmental analytical campaigns, very few papers deal with this subject.

– Stability of pentachlorophenol, extracted from tap and river water, in polymeric PLRP-S cartridges, have been studied under different conditions of temperature and humidity [91]. After 7 weeks of storage at room temperature, a diminution around 20% of the signal obtained for PCP was noticed. Samples kept at 4°C show negligible diminution in the PCP peak, with independence of the moisture level in the environment.

– Frebortova and Tatarkovicova [92], have compared recoveries for several phenols using a C_{18} sorbent. Similar values were obtained for cartridges eluted immediately after sample loading and for those stored for 28 days at 3°C.

Systematic studies need to be conducted in order to produce validated and efficient strategic approaches involving SPE and SPME storage of practical usefulness in environmental screening studies.

SPE and SPME, as today fundamental parts of sample preparation technologies are continuously developed and a number of new products are continuously presented by manufactures in a strongly competing market. Majors [93] has recently reported 34 new sample preparation products (mainly SPE and SPME) exhibited at the Pittcon ‘99. Both enhancements of traditional formats (cartridges and discs) as well as new very thin packed beds; new and specialised sorbent materials together with the latest technology in sample process automation are readily available and should be tested.

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