Review: New materials in extraction techniques for polar compounds

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Keywords: polymeric sorbents; hydrophilic materials; novel coatings; sorptive techniques; polar compounds

Abstract

This paper provides an overview of the new developments in material and format technology that improve the extraction of polar compounds in several extraction techniques. They mainly include solid-phase extraction, but there are also other sorptive extraction techniques such as solid-phase microextraction that use either fibers, in-tube devices, or stir bars.

We focus on new synthesised materials that are both commercially available and “in-house”. Most novel materials that enhance the extraction of polar compounds are hydrophilic and have large specific surface area; however, we also cover other leading technologies such as sol-gel or monolith.

We describe the morphological and chemical properties of these new sorbents so that we can better understand them and relate them to their capability of retaining polar compounds. We discuss the extraction efficiency for polar compounds when these polymers are used as sorptive material and compare them to other materials. We also mention some representative examples of applications.

Contents

1. Introduction

Sample preparation is often considered to be a fundamental step in analytical procedures, because it helps not only to achieve detection limits that are as low as legislation requires but also to clean up the sample matrix. The most popular sample preparation technique for liquid samples is solid phase extraction (SPE), which has already replaced liquid-liquid extraction (LLE). SPE has been used extensively in the purification and concentration of several analytes from complex matrices such as environmental and biological. Of special interest are the achievements of SPE in the extraction of polar analytes in complex aqueous samples, because they are difficult to isolate and enrich. Solid-phase microextraction (SPME), which was ideally designed to be coupled to gas chromatography (GC), is gaining popularity for extracting polar compounds in liquid samples, after the last improvements, in both coating and format technology [1-4].

SPE and SPME are sorptive techniques, so retention is due to reversible hydrophobic, polar and ionic interactions between the analyte and the sorptive material. The type of sorbent or coating used in SPE and SPME, respectively, is, therefore, responsible for the efficiency of the extraction process. The availability of different materials is one of the advantages that sorptive techniques have over other extraction techniques. Proof of this is that it is a very active research field [1,5].

The classical sorbents in SPE are silica-based (C_2, C_8, C_{18}), carbons or polymeric (basically polystyrene-divinylbenzene (St-DVB)). More recently, hydrophilic polymeric sorbents have been used which, as a general rule, have a high specific surface area (that increases the points of interaction with the

analyte) and are hydrophilic (thus defining the type of interactions suitable for correlation with polar analytes) [6,7]. Molecularly imprinted polymers (MIPs) enhance selectivity. As well as selectively extracting the target compound, they are also helpful in cleaning up complex matrices [8,9]. Another advantage of SPE is the column-like format, which means that almost all types of sorbents (whatever their morphological or chemical structure) can be straightforwardly packed [6,10].

The initial SPME format, on the other hand, is a stationary phase coating onto an extraction fiber, which restricts the morphology and chemistry of the coatings to those that can be deposited onto the fiber. Thus, the applicability of this technique has always been subjected to a limited number of commercially available fibers. The coatings that are commercially available are polydimethylsiloxane (PDMS), polyacrylate (PA), carboxen (CAR) and carbowax (CW) and divinylbenzene (DVB) in different combinations, which just cover almost some range of polarity. The in-tube format of SPME (in which the phase coats a capillary column) increases the availability of coatings for this technique and also solves other drawbacks of the fiber format such as the advance in the coupling to liquid chromatography (LC) [11,12].

This article reviews the new commercially available or “in-house” materials that have been developed to improve the classical SPE sorbents and SPME coatings and, in turn, enhance the extraction of polar compounds. As well as the progress in material technology, this review also covers new formats in sorptive techniques that attempt to improve the extraction of polar analytes from complex aqueous matrices.

2. Sorbents for solid-phase extraction

Numerous materials can be used as SPE sorbents. Classically, they are divided into silica-based, carbon-based and macroporous polymeric sorbents. Of these, polymeric sorbents are the most suitable because of their chemical stability and broad range of physico-chemical characteristics. The type of sorbent, its structure and its interactions with the solute are clearly related to the efficiency of the extraction process. Thus, when new materials are being developed, it is equally important to define both their chemical structure, which determines the type of interactions, and their morphology (i.e. specific surface area, porosity, particle size, etc.), which determines the mechanical properties and, eventually, the stability of the resin. In this section, we describe polymeric sorbents, together with their chemical and morphological properties, which have been progressively developed in recent years to be used as SPE packing.

2.1 Hydrophobic polymeric sorbents

The traditional polymeric sorbent is macroporous St-DVB (see structure in Table 1), which has a hydrophobic structure with a specific surface area up to 800 $m^2 g^{-1}$. It interacts with the analytes (due to the hydrophobic character of the sorbent) basically through Van der Waals forces and the π-π sites of the aromatic rings that make up the sorbent structure. Some examples of commercial polymeric resins (also shown in Table 1) are: PLRP-S-10 (500 $m^2 g^{-1}$) and PLRP-S-30 (350 $m^2 g^{-1}$), both from Polymer Lab., and Amberlite XAD-2

(300 m^2 g^{-1}) and Amberlite XAD-4 (880 m^2 g^{-1}) from Supelco, and Strata SBD-L (500 m^2 g^{-1}) from Phenomenex.

In the extraction of polar compounds using these hydrophobic sorbents, one of the most important parameters to control is the specific surface area, as the higher the specific surface area, the higher the π-π sites available to interact with the compounds. Thus, one way to improve the extraction efficiency of these hydrophobic sorbents is to increase the specific surface area.

Highly crosslinked sorbents are macroporous St-DVB polymers that are prepared with conventional methods but with a high loading of crosslinking agent (DVB), which results in specific surface areas up to 800 m^2 g^{-1}. As an alternative, hypercrosslinked resins can increase specific surface areas to as high as 2000 m^2 g^{-1}. These resins are obtained by a novel method introduced by Davankov in the early 1970s which consists of extensive post-crosslinking of linear polystyrene chains by means of the Friedel-Crafts reaction. This produces various structural bridges between neighbouring phenyl groups in a highly swollen state [13-15].

Some of the commercial hypercrosslinked resins are Styrosorb 2m (910 m^2 g^{-1}), Styrosorb MN-150 (1070 m^2 g^{-1}) and Styrosorb MT-430 (1050 m^2 g^{-1}), all of which are from Purolite Int.; Lichrolut EN (1200 m^2 g^{-1}) from Merck; HySphere-SH (>1000 m^2 g^{-1}) from Spark Holland; Envi-Chrom P (800-950 m^2 g^{-1}) from Supelco; Bakerbond SBD1 (1060 m^2 g^{-1}) from J. T. Baker, and Amberchrom GC-161m (900 m^2 g^{-1}) from TosoHaas (Table 1).

Some studies have shown that recoveries are best when hypercrosslinked sorbents are used and not sorbents with a lower crosslinking degree (and therefore with a lower specific surface area). For instance, the hypercrosslinked

resin Hysphere-SH gave better recoveries than conventional macroporous resin PRLP-S in the on-line SPE of substituted phenols [16] and anilines [17].

2.2. Hydrophilic polymeric sorbents

Despite the high specific surface areas of these resins, their chemical nature and their interactions with the analytes are only hydrophobic, which leads to poor retention in the extraction of polar compounds. One solution to this problem is to introduce polarity into the resins, thus favouring the polar interaction between the sorbent and the analyte, and enhancing the recoveries for this type of analytes. In recent years, some of the research in the field of new SPE materials has focused on the development of new hydrophilic polymeric materials. In the section below, we discuss several ways of obtaining hydrophilic sorbents and describe how they can be applied in SPE. The hydrophilic sorbents can be prepared by copolymerising monomers that contain suitable functional groups or by chemically modifying the St-DVB hydrophobic polymers with a polar moiety.

2.2.1 Copolymers with a hydrophilic monomer

The first commercially available hydrophilic sorbents were the series of Amberlite XAD from Rohm & Haas, with the introduction of Amberlite XAD-7 and Amberlite XAD-8. Both sorbents are based on a methacrylate-divinylbenzene (MA-DVB) (Table 2) copolymeric structure with a specific surface area of 310 and 450 m^2 g^{-1}, respectively (see the details and some

applications of all the resins described in Table 2). These sorbents are characteristic because they combine a polar monomer (MA), which promotes hydrophilic interactions, and a crosslinking monomer (DVB), which helps to increase the specific surface area and enhance lipophilic interactions. Inserting a polar monomer into the resin, as Thurman et al. [18] described in their early study, where they compared the hydrophobic XAD resins (XAD-1, XAD-2 and XAD-4) with the hydrophilic resins (XAD-7 and XAD-8) in the concentration of fulvic acids in water samples, favours interaction with water, because the resin pores expand, and thus help the compounds penetrate the resin.

More recently, another MA-DVB resin has been marketed under the trademark of Abselut Nexus (Varian) (575 m^2 g^{-1}). This sorbent has been used to clean up complex matrices, such as blood [19], urine [19,20], plasma [21,22] and animal tissue [23]. An added feature of Abselut Nexus is that there is no need to condition the cartridge before extraction, which is a development known as non-conditioned SPE (NC-SPE) [24]. This approach was successfully applied [20] when Abselut Nexus was compared to another hydrophilic copolymeric sorbent, Oasis HLB (see information about this sorbent below), and silica-modified C_{18} in the extraction of methadone enantiomers and benzodiazepines from serum and urine. The performances of these two polymeric sorbents were not significantly different, and better than that of the silica-modified resin. However, Abselut Nexus was selected for this application because the sorbent did not need the column to be activated by methanol and water before use. On the other hand, some studies [19,21] have stated that the efficiency of the extraction with Abselut Nexus decreases when there is no conditioning step in the extraction protocol.

Varian also commercialises the sorbent Focus which, according to the information provided by the supplier, is a polar-enhanced sorbent. To the best of our knowledge, no studies have been published on Focus as a SPE sorbent.

Oasis HLB (Waters) was one of the first hydrophilic sorbents to be commercially available. It is a macroporous poly(N-vinylpyrrolidone-divinylbenzene) (PVP-DVB) copolymer and has a specific surface area of ~800 $m^2 g^{-1}$ (see the details in Table 2). Oasis HLB has been widely used in SPE and some of the applications can be seen in Table 2. Basically, it has been used to extract and clean up several analyte types from biological matrices [25-28] and to extract pollutants such as phenols [29], pesticides [30-32] and pharmaceuticals [33-36] from aqueous samples.

More interesting are the studies which compare Oasis HLB to other hydrophobic polymeric sorbents in extracting different group of compounds [37-43]. Most of the studies mentioned above show the potential of Oasis HLB for extracting compounds with high polarity. Oasis HLB will be compared with other similar hydrophilic sorbents throughout this section.

Most of the studies investigate the performance of Oasis HLB in off-line SPE using the different cartridge sizes available (from 30 mg to 500 mg). Nevertheless, other studies use it in other formats: for example, packed in a SPE precolumn [36] and leading to a completely automated system, packed in a turbulent flow column [44,45] or using a 96-well plate [46] which not only enables several extractions to be performed at the same time but also makes it possible to use microliters as the elution solvent, thus avoiding the evaporation and reconstitution steps.

Porapak RDX is another commercial sorbent from the Waters Corporation based on the same N-vinylpyrrolidone-divinylbenzene structure. In spite of having the same structure, Porapak RDX has not shown the same potential and satisfactory results as Oasis HLB, perhaps because of its lower specific surface area (550 $m^2 g^{-1}$ in contrast to 830 $m^2 g^{-1}$). For instance, on the one hand, Oasis HLB provided higher recoveries than Lichrolut EN when extracting a group of weak acid endocrine-disrupting compounds (ECDs) [47]. The authors attributed this to the hydrophilic-lipophilic balance of the Oasis HLB material, which allows a stronger retention of the ionised analytes. On the other hand, Lichrolut EN was preferred to Porapak RDX when extracting explosives, the structure of which is that of a nitrobenzene derivate, because its significantly increased surface area (1200 $m^2 g^{-1}$) led to better recoveries, which in this case favour the π- π interactions between the resin and the aromatic groups in the compounds [48].

Discovery DPA-6S (Supelco) (Table 2) is another hydrophilic sorbent based on polyamide but, unlike the sorbents described above, its specific surface area is only a few square meters per gram due to its linear polymeric structure. It was compared to other polymeric sorbents in the extraction of ECDs [49] and alkyl amines [50], but it was not the sorbent of choice in any of the studies because its recoveries were low, which might be because of the lack of specific surface area of the sorbent.

Apart from of the several commercial hydrophilic sorbents, mainly Oasis HLB, there are some research groups that have synthesised hydrophilic polymers to be used as SPE sorbents.

In this respect, Throchimczuk's group [51,52] synthesised a series of resins based on polar monomers. In the first study [51], these resins were based on either acrylonitrile (AN) or methacrylonitrile (MAN)) crosslinked with DVB (Table 3); and, in the recent study [52], they were based on cyanomethylstyrene (CMSt) also crosslinked with DVB (Table 3). In both studies [51,52], the resins were generated with different degrees of polarity and specific surface areas (their properties were related to the initial percentage of each monomer, i.e. polar or crosslinked). Then, these resins were tested in the sorption of phenols and it was found that the best sorption properties were for the resins with a 50:50 ratio; thus, the authors concluded that both effects (polarity and specific surface area) were equally important. And of the three 50:50 ratio resins, the best sorption properties were for the AN-DVB resin, since it combines a relatively high specific surface area (460 m^2 g^{-1}) and the highest nitrogen content (5.9 %N) of the three.

Another example is the conductive resins synthesised by Bagheri's group. They are based on polyaniline (PANI) [53,54], poly-N-methylaniline (PNMA) [55], polydiphenylaniline (PDPA) [55], and polypyrrole (PPy) [56,57] (Table 3). All these resins are hydrophilic and their specific surface areas are no higher than 40 m^2 g^{-1}, because they are linear polymers. After the synthesis, their SPE performance was tested in the extraction of phenol and a group of chlorophenols, and they were also compared to the commercial Lichrolut EN (St-DVB, 1200 m^2 g^{-1}) and Oasis HLB (PVP-DVB, 800 m^2 g^{-1}). The results of off-line SPE of chlorophenols were similar for Lichrolut EN and Oasis HLB; however, the results of extracting phenol were better with the commercial sorbents studied. This might be because of the low specific surface area of the

new sorbent synthesised, which leads to poor recoveries when a polar compound such as phenol is extracted.

In recent years, our research group has synthesised several SPE sorbents. They were prepared by polymerising a polar monomer and a crosslinking agent (DVB), and the resulting polymers combined hydrophilicity and a high specific surface area. These sorbents are based on 4-vinylpyridine-divinylbenzene (4VP-DVB) [58,59], N-vinylimidazole-divinylbenzene (NVIm-DVB) [60,61] and 4-vinylimidazole-divinylbenzene (4VIm-DVB) [62] (Table 3). During the preparation of each series of resins, several parameters of the synthetic procedure that affected the final balance of polarity and specific surface area were tested. The optimum properties of these resins, in terms of specific surface area and nitrogen content (which are directly related to the polarity of the resin), are shown in Table 3. All these sorbents were tested as SPE sorbents for extracting polar compounds. As an example, Figure 1 shows the recovery values of these hydrophilic resins and an St-DVB resin (728 m^2 g^{-1}) after 100 and 200 ml of standard solution spiked with phenol were percolated. As can be seen in Figure 1, the recoveries for the St-DVB sorbent are lower than those for the other sorbents (which have a hydrophilic part). These low recoveries indicate that the polar part of the sorbent plays an important role in the extraction of polar compounds. As Figure 1 shows, results are best for NVIm-DVB, which has both the highest specific area and the highest nitrogen content. Therefore, both parameters contribute equally to the enhanced retention of polar compounds.

In further synthesis, our research group also prepared hypercrosslinked resins [63], which have different hydroxyl group contents (depending on the

precursor) and specific surface areas (the characterisation details for each hypercrosslinked resin are also shown in Table 3). These hypercrosslinked resins were also evaluated as SPE sorbents for the extraction of polar compounds [64]. For example, Figure 1 shows that the recovery for 300 ml of extracted phenol when HXLGp (high hydroxyl content) was used as sorbent was 72%, whereas when HXLGmix (low hydroxyl content) was used, the recovery decreased to 33%. Of all the sorbents in Figure 1, HXLGp, which combines the highest number of hydroxyl groups and a high specific surface area, has the highest recoveries. Another of its features is that it can on-line preconcentrate up to 300 ml of sample with acceptable recoveries. Once again, the retention of polar analytes in SPE is enhanced when the sorbent has a suitable combination of polar and π-π interactions.

2.2.2 Chemically modified sorbents

Another approach, which is an alternative to copolymerising the sorbents, is to prepare functionalised polymers by chemical modification. The first chemically modified sorbents applied to the extraction of polar compounds were synthesised by Fritz, and the styrenic resins were functionalized with sulfonic [65,66], acetyl and hydroxymethyl [66-68] groups (Table 4 gives the information about all these resins). At the end of the 90s, Masque *et al.* modified the commercial Amberchrom GC-161m (St-DVB, 900 m^2 g^{-1}) with acetyl [69], benzoyl [70], o-carboxybenzoyl [71], 2,4-dicarboxibenzoyl and 2-carboxy-3/4-nitrobenzoyl [72]. In all instances, the extraction of polar compounds from the modified resins is more efficient than the unmodified analogues. This is

because the introduction of polar moieties enhances the polar interactions between the resin and the analytes and also because the presence of the polar groups increase the contact with the aqueous solution and also with the analytes.

Nowadays, there are also several commercially available modified sorbents. (Table 5). In most cases, due to a patent pending, it is not known the functional group that modifies these resins; nevertheless, the functional groups in all the resins must be polar.

Varian was the first to introduce a chemically modified sorbent under the trademark of Bond Elut PPL (700 m^2 g^{-1}). This sorbent gave better results than the classical carbon-based sorbents [73,74] but not better than the results achieved with highly crosslinked hydrophobic sorbents [74] or the chemically modified resin with o-carboxybenzoyl moieties [73]. Another well-known sorbent is Isolute ENV+ (St-DVB-OH, 1100 m^2 g^{-1}, IST), which is a hydroxylated St-DVB resin. The recoveries of Isolute ENV+ were similar to or slightly worse than those of Oasis HLB in the extraction of carbamates [75] and polybrominated diphenyl ethers (PBDEs) [28] or Oasis HLB and Abselut Nexus in the extraction of chlorinated pesticides [76].

More recently, Strata X (St-DVB-VP, 800 m^2 g^{-1}, Phenomenex), which has a styrenic skeleton and is modified with a pyrrolidone group, has been commercialised. Strata X has been applied in SPE to clean up biological samples such as plasma [77] or milk [78], or to enrich pesticides [62,79] or pharmaceuticals [80] in water samples. Some research studies have made a comparative evaluation of the efficiency of Strata X with other SPE sorbents. For instance, Posyniak *et al.* [81] compared Strata X with other silica-based

sorbents modified with C_{18} and C_8, and the polymeric sorbents Bakerbond SBD-1 (St-DVB, 1060 m^2 g^{-1}) and Oasis HLB (PVP-DVB, 830 m^2 g^{-1}) for the extraction of tetracyclines in pig kidney. The recoveries were better with the polymeric sorbents, and they finally chose Strata X as the extraction sorbent, because it gave cleaner extracts.

Spe-ed Advanta (Applied Separations) is another commercially available chemically modified sorbent, with a non specified functional group. However, after characterising it Sirvent *et al.* [82] deduced that it is a polymeric sorbent chemically modified with a carboxyl moiety. The same authors [82,83] also compared the SPE performance of Spe-ed Advanta with Isolute ENV+ in the extraction of phenolic compounds in aqueous samples, and they found that the recoveries of Spe-ed Advanta were better.

2.3. Mixed-mode ion-exchange sorbents

Other sorbents that are also chemically modified are ion-exchange sorbents. Of particular interest are the mixed-mode polymeric sorbents, which combine a polymeric skeleton with ion-exchange groups, so they can mix two types of interaction mechanisms: reversed-phase and ionic-exchange.

The first commercially available mixed-mode polymers were the Oasis MCX and Oasis MAX (Waters), which have Oasis HLB skeleton (polyvinylpyrrolidone-divinylbenzene, 830 m^2 g^{-1}) chemically modified with sulfonic and quaternary amines, respectively. Oasis MCX and Oasis MAX are classified as strong ion-exchange resins, because of the high acidic and basic, behaviour, respectively, of the ionic groups that modify each resin. More recently, the same company

commercialised the weak ion-exchange sorbents Oasis WCX and Oasis WAX, which have the same Oasis HLB skeleton, but modified with carboxylic acid and piperazine groups, respectively. Table 6 lists the chemical structures, properties and some applications of mixed-mode ion-exchange sorbents.

These mixed-mode sorbents are mainly applied to extract analytes (charged or not) from complex matrixes such as food [84-87], biological fluids [88-94], animal tissue [95,96], wastewater [97] and wood extracts [98,99]. The benefit of the ion-exchange capacity is that the analytes, the interferences in the sample or even the sorbent chargeability (in the case of weak-ion-exchange sorbents) can be switched during the different steps in the SPE, thus getting rid of the interferences in the washing step and eluting the analytes more selectively, just by using a suitable pH combination in each SPE step.

Mixed-mode ion exchange sorbents are specifically designed to interact with ionic species. However, they can also effectively retain non-charged species through hydrophobic and hydrophilic interactions. For instance, Jimenez-Lozano's group [95] studied the performance of several sorbents, including Isolute ENV+, Oasis HLB, Oasis MAX and SBD-RPS (ion-exchange resin based on a hydrophobic skeleton) in the extraction of quinolones from animal tissue. Oasis MAX showed the best recoveries and peak shapes in the following capillary electrophoresis (CE) analysis. Figure 2 shows the electropherograms of spiked chicken sample tissue using different sorbents. It can be seen that the peak shape is better when Oasis MAX was the sorbent. The peak shape is also better because the elution solvent used for Oasis MAX (2% formic acid in MeOH) was not the same as the one used for the other three sorbents (1% trifluoroacetic acid in 75:25 acetonitrile:H_2O). Another example is the

comparison of Oasis HLB with Oasis WAX in the extraction of fluorescent whitening agents in environmental waters [100]. These two sorbents behaved similarly when extracting the target from deionised water samples. However, the recoveries with Oasis HLB dropped off in the analysis of highly charged aqueous samples such as river water or wastewater, because salts and ionic species interfere during the extraction process. The recoveries for Oasis WAX, on the other hand, were almost constant in all of the samples, since most of the interferences can be effectively removed during the washing step using this mixed-mode sorbent.

Similarly, Strata X, which is an St-DVB resin that is chemically modified with a polar group, has been modified with ionic groups to convert the resin into a mixed-mode ion-exchange resin. In this case, the strong cation exchange Strata-X-C is modified with a sulfonic group, the weak cation exchange resin, Strata-X-CW, is modified with a carboxylic group, and the weak anion exchange resin, Strata-X-AW, is modified with a diamine group (see Table 6 for structural details and examples of applications). Because these resins are new, they are not in such widespread use as Oasis technology, but Strata X-C has also been applied in the analysis of plasma [101], food [102] and urine [103] samples. In the last of these applications, it was compared to Strata X for extracting the major metabolite of the active principle in marijuana, tetrahydrocannabinol-COOH, in urine sample. In this particular case, as the metabolite has no cation exchange sites available, the molecule must interact with Strata-X-C hydrophobically. In the same study, when Strata X and Strata-X-C were compared for extracting groups of paraben and phenolic compounds it was found that mixed-mode cation-exchange resin Strata-X-C showed better

hydrophobic and polar retention characteristics than the neutral polymer with the same backbone, Strata X. The authors concluded that the superior hydrophobic retention of Strata-X-C is due to the electron withdrawing nature of the sulfonic acid functionality, which induces a lot more electron polarisation in the neighbourhood of the aromatic ring to which it is attached. In view of the above, Strata-X-C was selected to extract the marijuana metabolite from urine samples, with satisfactory results [103].

To the best of our knowledge, no studies have described the application of Strata-X-AW and Strata-X-CW, presumably because of their novelty.

Chromabond EASY (Macherey-Nagel) is another chemically modified sorbent with a weak anion-exchange group (chemical structure not available), which, apart from allowing ion-exchange interactions, enhances the polarity of the resin. Chomabond EASY has been compared [104] to other hydrophobic (Lichrolut EN, Bakerbond SBD-1 and Chromabond HR-P) and hydrophilic resins (Oasis HLB, Abselut Nexus and Isolute ENV+) in the extraction of a group of pharmaceuticals that covers different ranges of acidicity and basicity. Unexpectedly, the recoveries for the acidic compounds were lower for Chromabond EASY than for the other hydrophilic resins. The authors explained that these results might be improved by using a more specific elution protocol for acidic compounds (i.e. a basic solution) rather than pure methanol.

Moving on to home-made sorbents, the NVIm-DVB sorbent (see section 2.2.1 for further details and Table 6 for the chemical structure), which was initially designed as a hydrophilic sorbent, has also an ion-exchange feature since, depending on the pH, the imidazole group can be protonated. In a recent study [105], the performance of the NVIm-DVB sorbent was compared to that of

the Oasis HLB (reversed-phase), Oasis WAX (weak anion-exchange) and Oasis MAX (strong anion-exchange) in the extraction of a group of pharmaceuticals and using the suitable SPE protocol in each case (reversed-phase, weak anion-exchange and strong anion-exchange, respectively). From this comparison, and because of the similarity of the NVIm-DVB and Oasis MAX results, the authors concluded that NVIm-DVB behaves like a strong anion-exchange sorbent. Nevertheless, by choosing the appropriate SPE protocol, which is crucial if the analyte recovery and selectivity are to be enhanced, these mixed-mode ion-exchange resins can be tuned to properly extract charged or non-charged species.

2.4 Other materials tested for SPE

Even though bead shaped polymeric sorbents are the most usual and the most studied in SPE, other materials have also been tested as SPE materials. In this section, we review some of these other materials that have been used as SPE sorbents in the extraction of polar compounds.

First of all, this review would not be complete without mentioning monolith technology. Monoliths are produced by direct polymerisation in situ in a mold. They are rigid structures with a proper balance of pores (small pores to increase the specific surface area and large to allow the liquid to flow without pressure). Monolith technology, also called “stationary phases of the fourth generation” has caused considerable impact in separation areas such as capillary electrochromatography (CEC) and micro- and nano-LC [106,107]. However, monoliths have not yet been applied very much as material for SPE. This might

be because monoliths need to have balanced pore structures, which mean that their specific surface areas are lower than those of packed materials. Only in one early study did the pioneers of the technology (Fréchet and Svec) [108] compare two monoliths used to extract phenolic compounds from aqueous samples, one was based on St-DVB and another the other on poly(2-hydroxyethylmethylacrylate-divinylbenzene) (p(HEMA-DVB) (Table 7), to extract phenolic compounds from aqueous samples. The results were better with the polar monolith. Apart from SPE, some other improvements regarding to monolith technology have been developed in other fields. These will be summarised in section 3.2 and section 4.

Much more can be expected of monolith technology in the future because, as F. Svec pointed out, monoliths are still teenagers compared to packed columns (mainly in LC, but also in SPE) [107].

Carbon nanotubes (CNTs) are fullerene structures (see Table 7) (carbon atoms clustering in spherical structures) which consist of graphene cylinders closed at their end with caps containing pentagonal rings. Multiwalled carbon nanotubes (MWCNTs) arise when there are many carbon atom layers in the wall of the nanotubes. The CNTs surfaces have a strong interaction with other molecules and atoms, which make a promising material in sorption fields, and substitute the active carbon. In spite of its great potential, only Cai *et al.* have used this material as a SPE sorbent for extracting organic compounds, in particular EDCs [109] and phtalates [110]. Their studies show that MWCNTs are similar to or more effective than silica-based sorbents and St-DVB sorbents.

Liu *et al.* [111] modified a silica-based sorbent with β-cyclodextrins. β-cyclodextrins (Table 7) combine the hydrophilicity of their outer part with the

hydrophobicity of their inner part. This special feature was exploited in the same study to extract a group of structurally complex compounds such as humic acids.

Supramolecular assemblies (hemimicelles/ admicelles) are formed by surfactants adsorbing on the surface of metal oxides. Surfactants and metal oxides form electrostatic interactions (hemimicelles) and, after the metal oxide has been saturated, hydrophobic interactions (admicelles). Supramolecular sorbents have interesting adsorbing characteristics, because they can be easily tuned by modifying the surfactant and the type of assembly formed (hemimicelles or admicelles). In the last few years, supramolecular sorbents have been applied to extract organic compounds such as phenolic compounds [112-114], herbicides [115] or surfactants [113,116] from aqueous samples.

Cigarette filter is an inexpensive sorbent that has been recently tested [117] to extract polycyclic aromatic hydrocarbons (PAHs), which are non-polar compounds, from aqueous samples. In this study, 70 mg of cigarette filter (the composition of which was not specified) was packed in a column on-line connected to LC-UV. In the comparison to C_{18} and XAD-4 sorbents, in general, cigarette filter gave better results than the conventional sorbent tested.

All the materials mentioned above should be alternatives for the extraction of polar analytes. However, much more research should be done before polymeric materials, well established in SPE fields, can be replaced.

3. Coatings for microextraction–related techniques

Of all the extraction techniques, SPE is the area in which most effort has been made to develop new sorbents that enhance the extraction of polar compounds. Considerably less research has been made for other sorptive extraction techniques, both regarding new commercial materials and new materials developed by research groups. Nevertheless, some research has focussed on the development of new materials for other sorption techniques that improve the extraction of polar analytes. In the sections below, we overview these last developments in sorbent technology for other sorptive extraction techniques.

3.1 New materials for solid-phase microextraction

The first commercially available fibers used in SPME used polymethylsiloxane (PDMS) and polyacrylate (PA) as coatings. PDMS is apolar and presents high affinity for the extraction of non-polar compounds. On the other hand, PA is polar and more suitable for extracting polar compounds. However, both phases are linear and lack specific surface area, which in turn means there is a lack of retention when polar compounds are extracted. More recently, coatings have been blended with DVB or Carbowax (CW): for example, PDMS-DVB, PDMS-carboxen, CW-DVB and CW-templated resin (CW-TPR) which present larger specific surface areas and have greater potential for extracting polar compounds. Supelco commercialises all these coatings, with different fiber thicknesses and assemblies. PA and CW-DVB are

the most suitable for extracting polar compounds, but they are still less efficient than other techniques such as SPE using hydrophilic sorbents [118].

In order to improve the retention of polar compounds, some research groups have focused on designing approaches to improve the extraction efficiency for polar compounds. In the development of new coatings for SPME, it is important to bear in mind that the coating or phase has to be attached to the fiber, and also the chemical and mechanical resistance of the coating (which during the desorption step could be exposed to high temperatures or strong organic solvents).

Two recent reviews [11,12] cover all the information, both in terms of synthesis and application, about new coatings for SPME. Briefly, there are two approaches to designing polar coatings. One approach is sol-gel technology, which deposits organic structures onto inorganic polymeric structures (fiber). If the organic components are properly selected, the selectivity of the coating can be tuned to extract more polar compounds. Crown-ether [119-124] and calyx[4]arenes [125,126] are examples of polar coatings prepared by sol-gel technology. Table 8 summarises the general structure of these new coatings as well as some their applications.

Several authors have prepared fibers modified with crown-ether of different chain sizes and chemistry. After these preparations all studies conclude that the fibers modified with crown-ether (whatever its structure was) showed better recoveries when determining phenols [122-124], amines [119,121] and organophosporous compounds [120] than the commercial PDMS, PA, CW-DVB or PDMS-DVB. In general, the fibers derived from crown-ether sol-gel have greater potential than the commercial ones because of, basically, three factors:

the three-dimensional network in the coating, which provides higher specific surface areas and sample capacity; the increase in the hydrogen-bond forces and, eventually, the polarity, and the high desorption temperature that solves the sample carryover problem. The better performance of the crown-ether fibers was demonstrated in the paper [119] in which three crown-ether-derived fibers and the commercial PDMS and PA were compared for the extraction of aliphatic amines (Figure 3). The three fibers had different substitutions and different numbers of oxygen atoms in the crown ether ring. They were 4'-allyldibenzo-18-crown-6, 3'-allylbenzo-15-crown-5 and allylethoxymethyl-18-crown-6 (Figure 3b). Subsequently, the performance of the same three fibers and the commercial PDMS and PA was compared in the headspace extraction of a group of tetrafluorobenzoic acid N-hydroxysuccinimide ester derivated amines. From this comparison (Figure 3a), it was concluded that the fiber derived with 4'-allyldibenzo-18-crown-6 gave the best results, because the benzyl rings favour π-π interactions, and the greater number of oxygen atoms in the crown ether ring favour polar interactions.

Another feature of the fibers prepared by sol-gel technology is that the chemical binding between the surface of the fiber and the coating makes them more chemically and thermally stable than fibers prepared by physical deposition of the coating on the surface. Thus, most of the crown-ether modified fibers [122-124] are stable over 350 °C, while the maximum temperatures for commercial fibers are lower (i.e. 280 °C for PDMS or 260 °C for PA). The high thermal stability can extend the SPME range towards compounds with higher boiling points. Another advantage of the robustness of crown-ether fibers is their longer lifetime and their stability in strong organic solvents, which might be used

in SPME-LC. For example, a sol-gel-derived bisbenzo crown-ether SPME coating can be used over 200 times without damaging the fiber surface while all the commercial fibers can only be used about 40-100 times [120].

More recently, sol-gel technology has been applied to the derivatization of fibers with calyx[4]arene [125,126] (see Table 8 for general structure), which posses well-defined cavities with polar and non-polar rims (upper and lower rims, respectively). Like the crown-ether derived fibers, the new calyx[4]arene fibers gave better results than the commercial ones in the extraction of benzene, toluene, ethylbenzene and xylenes (BTEX), PAHS (it is worth mentioning that these groups of analytes are non-polar, but to the best of our knowledge they are the only application for these calyx[4]arene fibers) [125] and aromatic amines [125,126], and they were also thermally and chemically stable.

Another way to overcome the polarity of the fibers is the electrodeposition of conductive polymers onto the fiber. Again, the selection of a polar electrochemical polymer means that the properties of the coating can be adjusted to enhance the affinity for extracting more polar compounds. For instance, fibers based on polyaniline (PANI) [127-131], polypyrrole (PPY) [129,132,133] and poly-N-phenylpyrrole (PPPY) [133] (Table 8) have been used to extract polar analytes in aqueous samples. All of these structures are expected to show different extraction efficiencies towards compounds with different functional groups, because they are capable of π-π, polar, hydrogen bonding and even ionic interactions. Ghassempour *et al.* [129] investigated the various interactions involved in different forms of aniline, which included the reduced form (presence of free NH), the ionic form and the oxidized form, in the extraction of anatoxin-a. They concluded that the reduced form of the

polyaniline is more effective at extracting this compound because the hydrogen bonding interacts with the analyte.

In the comparison with the commercial fibers, only one study [130] has compared, in the extraction of bisphenol A, 4-n-noylphenol and 4-tert-octyl phenol from water samples, the performance of the newly prepared polyaniline coating with that of the commercial CW-TRP, which has been reported to be the most suitable fiber for extract these analytes. The results show that polyaniline fibers are more sensitive than CW-TPR. The same study evaluated the lifetime of the polyaniline fibers and showed that the extraction ability decreased when the fiber was used more than 100 times. In view of this, and taking into account that none of the above studies claimed about the thermal stability of the fibers prepared by electrodeposition, it might be concluded that the fibers prepared by sol-gel technology are more robust. Nevertheless, electrodeposition technology performs better in other formats, such as in-tube SPME. The following section will cover this modification of the microextraction technique in more detail and discuss new developments in coatings.

3.2 New coatings for in-tube SPME

The main drawbacks of conventional SPME (using fibers) are its lack of capacity (because the fiber exposes little material, which affects the ability to extract compounds) and its the higher complexity to coupling with LC, which leads to the automation of SPME-LC. The in-tube configuration of SPME might solve the above drawbacks, since it is based on a capillary column instead of fibers. Thus, the length and thickness of the column are more easily tunable,

and also straightforwardly connected to LC. The first applications in in-tube SPME were by using part of GC capillary column, which used to be silica modified columns being more suitable for the analysis of groups of apolar compounds. The GC columns (all from Supelco) tested as extraction device for in-tube SPME mainly included silica modified with PDMS, such as SPB-1, PTE-5 and SPB-5, or polyethylene glycol (PEG), such as Omegawax 250 and Supelcowax or porous DVB, Supel-Q-Plot, or also using a retention gap made of polar silica tubing. Although the recoveries for polar compounds when the PEG-modified columns are used, are more acceptable than the ones for the apolar columns, they are still not sufficient and more polar coatings have to be used to improve the efficiency of extracting polar compounds [11].

Thus, as has been done with SPME fibers, some research groups have attempted to synthesise new materials and increase the affinity in the extraction of polar compounds. In this respect, Pawliszyn's group prepared a series of electrochemical coatings based on polypyrrol (PPY) [133,134] and poly-N-phenylpyrrole (PPPY) [133] (structures available in Table 8). Then, they evaluated them and compared them to some GC capillary columns (SPB-1, PTE-5 SPB-5, Omegawax 250 and Supel-Q-Plot) for the in-tube extraction of heterocyclic amines, groups of polar and non-polar aromatic compounds, organoarsenic compounds [133] and β-blockers [133,134]. In all instances, the PPY and PPPY coatings showed better extraction efficiency than the commercial GC columns, which can be easily explained by the numerous types of interactions between these multifunctional (i.e. π-π, polar, hydrogen bonding and ionic interactions) coatings and the analytes with different chemical properties. Another advantage of electrochemical polymer-coated capillaries

over commercial capillaries for in-tube SPME is that the extraction efficiency and selectivity can be easily manipulated by regulating the thickness of the coating (i.e. the number of electrochemical polymer cycles) [133].

Another way of increasing the thickness of the capillary, and thus improving the extraction efficiency, is to use monolithic capillaries with monolithic sorbents, which can be synthesised in situ and can provide monolithic structures with different kinds of functional groups.

Feng's research group prepared monolithic capillaries based on poly(methacrylic acid-ethylene glycol dimethacrylate) -p(MMA-EGDMA)- (see structure and application in Table 8) and then applied them to in-tube SPME-LC for the extraction of drugs from complex sample matrices, such as human body fluids [135-139], animal tissue [140] or food [135]. The hydrophobic polymer bone structure and the acidic pendant groups (from the MAA monomer) make this monolithic polymer suitable for extracting basic analytes, such as most of the drugs studied. Moreover, as some studies have reported [135,136,139], the biocompatibility of this monolithic structure led to biological samples being effectively applied with no other manipulation except dilution and/or centrifugation, which simplified the whole determination procedure. Figure 4 shows a typical chromatogram for whole egg and egg albumina samples spiked with five fluoroquinolones and analysed by p(MMA-EGDMA) monolithic capillary in-tube SPME-LC-UV [135], where the matrix peaks at the beginning of the chromatogram do not interfere with the separation of the five fluoroquinolones, even though the detector used (UV) was non-selective for fluoroquinolones.

The same group also synthesised a monolithic capillary based on poly(acrylamide-vinylpyridine-*N, N'*-methylene bisacrylamide) (AA-VP-Bis)

(Table 8), from which is expected to show greatest ion-exchange interactions with acidic compounds through the pyridyl group. The authors confirmed this hypothesis by using in-tube SPME-LC-UV to extract a group of analytes, including acidic drugs, phenols and ECDs. The extraction yield for 2,4-dinitrophenol (the most acidic phenolic compound analysed) was 87%, while for phenol (the least acidic and least hydrophobic compound) it was 6%.

The same authors simplified the in-tube monolithic SPME device by developing the novel technique called polymer monolith microextraction (PMME). The extraction device consisted of a regular 1 mL syringe, a poly(MAA-EGDMA) monolithic capillary (2 cm X 530 μm ID) and a plastic pinhead, which connected the former two components seamlessly [141]. PPME has been successfully used to extract several angiotensin II receptor antagonists in urine samples [141] and low aliphatic aldehyde derivatives in human saliva [142]. The authors claimed that PMME was easier to prepare and had a greater extraction capacity than other microextraction devices [141].

3.3 Stir bar sorptive extraction (SBSE)

SBSE is another sorptive technique that also overcomes the lack of capacity of SPME with fibers. In SBSE, the coating covers a magnetic stir bar, which means that the phase is 50-250 times greater than in SPME [143]. However, the main drawback of the SBSE technique is the desorption step, especially to LC.

The only commercially available phase for SBSE is PDMS, which is commercialised under the trademark of Twister (Gerstel), although recently, the

variant dual-phase twisters were also commercialised. They consist of a short PDMS tube closed at both ends with two magnets, and packed with sorbent. So far, this dual-phase twister has only been applied with carbon as the sorbent, and the recovery is better than that of the conventional PDMS-coated SBSE when polar compounds are extracted [144].

It should be mentioned that Liu *et al.* [145] used sol-gel technology in stir bars to generate a partially hydroxyterminated-PDMS coated stir bar, which was then successfully applied to extract a group of PAHs and organophosporous compounds. Unfortunately, they did not compare the novel coated stir bar with the conventional PDMS stir bar.

4. New sorptive extraction formats

In recent years, interest in miniaturised systems, which integrate sample treatment, separation and detection in a single device, has been growing. Here, we briefly describe some strategies used to integrate SPE into these miniaturised systems.

Monolith technology has been applied in microscale preparation, developing on-chip SPE [146-148] or µSPE [149], which can be also directly integrated in the mass spectrometer through a tip [147-149]. So far, these high-tech devices have been applied to clean up complex samples [148] or concentrate peptides [149], rather than concentrate polar compounds.

Another example of µSPE device consists of electropolymerisation of PPY on a stainless steel frit was coupled on-line to pulsed-eluted (PE) - LC. This µdevice is capable of extracting 20 µl of sample spiked at 10 µg l^{-1} of ochratoxin

A. Recoveries range between 65% and 80% depending on the pH and the complexity of the sample matrix [150].

Abdel-Rehim and co-workers patented a SPE variation called microextraction in packed syringe (MEPS), which differs from SPE in that the sorbent (normally 1 mg) is packed into a syringe (100-250 µl) as a plug. Then, this syringe is connected to the instrument autosampler, which controls all the SPE steps. Thus, MEPS needs no additional instrumentation for the extraction procedure. This research group has coupled MEPS to LC-MS-MS to extract drugs from human plasma [151-155] and to GC-MS to extract non-polar PAHs from water [156]. The sorbent packed in MEPS can be the same as for SPE. In one of their studies [152], for instance, they compared how three sorbents extracted drugs from biological fluids: Isolute ENV+, silica modified with C_8 and a hydrophilic monolith prepared “in-situ” prepared. The results showed that Isolute ENV+ performed better than C_8, and that the monolithic sorbent was the worst of the three.

The formats described in this section are expected to be better established in the near future because of growing interest and their suitability for miniaturised systems.

5. Conclusions

The development of new materials and formats that improve the extraction of polar compounds is a growing research topic in sorptive techniques. The range of commercially available materials is extensive and numerous research groups are working in the field.

One of the main focuses of attention is the development of polymer-based materials that can be easily packed and used as SPE sorbents, since their chemical and morphological properties can be easily modified. Also of considerable significance, however, is the research into new strategies for preparing coatings for microextraction-based techniques or novel formats suitable for miniaturised systems.

Despite all the research in this field lasting recent years, we can still expect further improvements in materials and formats that continue to simplify the sample preparation step of polar compounds in complex matrices

6. References

[1] D.E. Raynie, Anal. Chem. 78 (2006) 3997.

[2] C.J. Koester, A. Moulik, Anal. Chem. 77 (2005) 3737.

[3] R.K. Gilpin, L.A. Pachla, Anal. Chem. 77 (2005) 3755.

[4] S.D. Richardson, Anal. Chem. 78 (2006) 4021.

[5] J.S. Fritz, M. Macka, J. Chromatogr. A 902 (2000) 137.

[6] N. Fontanals, R.M. Marcé, F. Borrull, Trends Anal. Chem. 24 (2005) 394.

[7] N. Masqué, R.M. Marcé, F. Borrull, Trends Anal. Chem. 17 (1998) 384.

[8] E. Turiel, A. Martin-Esteban, Anal. Bioanal. Chem. 378 (2004) 1876.

[9] E. Caro, R.M. Marcé, F. Borrull, P.A.G. Cormack, D.C. Sherrington, Trends Anal. Chem. (2005).

[10] C.W. Huck, G.K. Bonn, J. Chromatogr. A 885 (2000) 51.

[11] J.B. Quintana, I. Rodriguez, Anal. Bioanal. Chem. 384 (2006) 1447.

[12] C. Díez, J. Sanz, C. Camara, J. Chromatogr. A 1103 (2006) 183.

[13] V.A. Davankov, M.P. Tsyurupa, React. Polym. 13 (1990) 27.

[14] V.A. Davankov, M.P. Tsyurupa, M.M. Ilyin, L. Pavlova, J. Chromatogr. A 965 (2002) 65.

[15] J.-H. Ahn, J.-E. Jang, C.-G. Oh, S.-K. Ihm, J. Cortés, D.C. Sherrington, Macromolecules 39 (2006) 627.

[16] R. Wissiack, E. Rosenberg, M. Grasserbauer, J. Chromatogr. A 896 (2000) 159.

[17] J. Patsias, E. Papadopoulou-Morkidou, J. Chromatogr. A 904 (2000) 171.

[18] G.R. Aiken, E.M. Thurman, R.L. Malcom, H.F. Walton, Anal. Chem. 51 (1979) 1799.

[19] K.A. Georga, V.F. Samanidou, I.N. Papadoyannis, J. Chromatogr. B 759 (2001) 209.

[20] H. He, C. Sun, X.-R. Wang, C. Pham-Huy, N. Chikhi-Chorfi, H. Galons, M. Thevenin, J.-R. Claude, J.-M. Warnet, J. Chromatogr. B 814 (2005) 385.

[21] J. Giacometti, A. Milosevic, C. Milin, J. Chromatogr. A 976 (2002) 47.

[22] Z. Ma, Q. Wu, D.Y.W. Lee, M. Tracy, S.E. Lukas, J. Chromatogr. B 823 (2005) 108.

[23] V.F. Samanidou, K.I. Nikolaidou, I.N. Papadoyannis, J. Sep. Sci. 28 (2005) 2247.

[24] www.varianinc.com, (2006).

[25] A. Ziaková, E. Brandsteterová, J. Liq. Chrom. & Rel. Technol. 25 (2002) 3017.

[26] D.C. Delinsky, K. Srinivasan, H.M. Solomon, M.G. Bartlett, J. Liq. Chrom. & Rel. Technol. 25 (2002) 113.

[27] M. Rizzo, D. Ventrice, F. Monforte, S. Procopio, G. De Sarro, M. Anzini, A. Cappelli, F. Makovec, J. Pharm. Biomed. Anal. 35 (2004) 321.

[28] A. Covaci, S. Voorspoels, J. Chromatogr. B 827 (2005) 216.

[29] D.A. Azebedo, S. Lacorte, P. Viana, D. Barceló, Chromatographia 53 (2001) 113.

[30] D.A. Azebedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló, J. Chromatogr. A 879 (2000) 13.

[31] R. Bossi, K.V. Vejrup, B.B. Mogensen, W.A.H. Asman, J. Chromatogr. A 957 (2002) 27.

[32] L. Gomides, C.W. Götz, M. Ruff, H.P. Singer, S.R. Müller, J. Chromatogr. A 1028 (2004) 277.

[33] S. Öllers, H.P. Singer, P. Fässler, S.R. Müller, J. Chromatogr. A 911 (2001) 225.

[34] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Environ. Sci. Technol. 36 (2002) 1202.

[35] S. Abuin, R. Codony, R. Compaño, M. Granados, M.D. Prat, J. Chromatogr. A 1114 (2006) 73.

[36] K. Stoob, H.P. Singer, C.W. Goetz, M. Ruff, S.R. Mueller, J. Chromatogr. A 1097 (2005) 138.

[37] N.C. Dias, C.F. Poole, Chromatographia 56 (2002) 269.

[38] T.N. Decaestecker, E.M. Coopman, C.H. Van Peteghem, J.F. Van Bocxlaer, J. Chromatogr. A 789 (2003) 19.

[39] M. Farré, I. Ferrer, A. Ginebreda, M. Figueras, L. Olivella, L. Tirapu, M. Vilanova, D. Barceló, J. Chromatogr. A 938 (2001) 187.

[40] E. Ayano, H. Kanazawa, M. Ando, T. Nishimura, Anal. Chim. Acta 507 (2004) 211.

[41] R. Carabias-Martínez, E. Rodríguez-Gonzalo, E. Herrero-Hernández, F.J. Sánchez-San Román, M.G. Prado Flores, J. Chromatogr. A 950 (2002) 157.

[42] M.J. López de Alda, D. Barceló, J. Chromatogr. A 938 (2001) 145.

[43] R. Carabias-Martínez, E. Rodríguez-Gonzalo, E. Herrero-Hernández, J. Hernández-Méndez, Anal. Chim. Acta 517 (2004) 71.

[44] A. Asperger, J. Efer, T. Koal, W. Engewald, J. Chromatogr. A 960 (2002) 109.

[45] A. Asperger, J. Efer, T. Koal, W. Engewald, J. Chromatogr. A 937 (2001) 65.

[46] A.Y. Yang, L. Sun, D.G. Musson, J.J. Zhao, J. Pharm. Biomed. Anal. 1476 (2005) 521.

[47] R. Carabias-Martínez, E. Rodríguez-Gonzalo, P. Revilla-Ruiz, J. Chromatogr. A 1056 (2004) 131.

[48] M. Smith, G.E. Collins, J. Wang, J. Chromatogr. A 991 (2003) 159.

[49] R. Liu, J.L. Zhou, A. Wilding, J. Chromatogr. A 1022 (2004) 179.

[50] P. Kusch, G. Knupp, M. Hergarten, M. Kozupa, M. Majchrzak, J. Chromatogr. A 1113 (2006) 198.

[51] A.W. Trochimczuk, M. Streat, B. Korlarz, React. Funct. Polym. 46 (2001) 259.

[52] D. Drechny, A.W. Trochimczuk, React. Funct. Polym. 66 (2006) 323.

[53] H. Bagheri, M. Saraji, J. Chromatogr. A 910 (2001) 87.

[54] H. Bagheri, M. Saraji, D. Barceló, Chromatographia 59 (2004) 283.

[55] H. Bagheri, M. Saraji, J. Chromatogr. A 986 (2003) 111.

[56] H. Bagheri, A. Mohammadi, J. Chromatogr. A 1015 (2003) 23.

[57] H. Bagheri, A. Mohammadi, A. Salemi, Anal. Chim. Acta 513 (2004) 445.

[58] N. Fontanals, R.M. Marcé, M. Galià, F. Borrull, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 1927.

[59] N. Fontanals, P. Puig, M. Galià, R.M. Marcé, F. Borrull, J. Chromatogr. A 1035 (2004) 281.

[60] N. Fontanals, R.M. Marcé, M. Galià, F. Borrull, J. Polym. Sci. Part A: Polym. Chem. 42 (2004) 2019.

[61] N. Fontanals, M. Galià, R.M. Marcé, F. Borrull, J. Chromatogr. A 1030 (2004) 63.

[62] N. Fontanals, M. Galià, R.M. Marcé, F. Borrull, Chromatographia 60 (2004) 511.

[63] N. Fontanals, J. Cortés, M. Galià, P.A.G. Cormack, R.M. Marcé, F. Borrull, D.C. Sherrington, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 1718.

[64] N. Fontanals, M. Galià, P.A.G. Cormack, R.M. Marcé, D.C. Sherrington, F. Borrull, J. Chromatogr. A 1075 (2005) 51.

[65] J.S. Fritz, P.J. Dumont, L. Schimidt, J. Chromatogr. A 691 (1995) 133.

[66] P.J. Dumont, J.S. Fritz, J. Chromatogr. A 691 (1995) 123.

[67] J.J. Sun, J.S. Fritz, J. Chromatogr. 590 (1992) 197.

[68] J.J. Sun, J.S. Fritz, J. Chromatogr. 522 (1990) 95.

[69] N. Masqué, M. Galià, R.M. Marcé, F. Borrull, J. Chromatogr. A 771 (1997) 55.

[70] N. Masqué, M. Galià, R.M. Marcé, F. Borrull, The Analyst 122 (1997) 425.

[71] N. Masqué, M. Galià, R.M. Marcé, F. Borrull, J. Chromatogr. A 803 (1998) 147.

[72] N. Masqué, M. Galià, R.M. Marcé, F. Borrull, Chromatographia 50 (1999) 21.

[73] N. Masqué, E. Pocurull, R.M. Marcé, F. Borrull, Chromatographia 47 (1998) 176.

[74] N. Masqué, R.M. Marcé, F. Borrull, J. Chromatogr. A 793 (1998) 257.

[75] J.M.F. Nogueira, T. Sandra, P. Sandra, J. Chromatogr. A 996 (2003) 133.

[76] C.D. Sandau, A. Sjodin, M.D. Davis, J.R. Barr, V.L. Maggio, A.L. Watermann, K.E. Pretson, J.L. Preau, D.B. Barr, L.L. Neddham, D.G. Patterson, Anal. Chem. 75 (2003) 71.

[77] D.G. Watson, F.G. Araya, P.J. Galloway, T.J. Beattie, J. Pharm. Biomed. Anal. 35 (2004) 87.

[78] M.D. Marazuela, M.C. Moreno-Bondi, J. Chromatogr. A 1034 (2004) 25.

[79] P. Fidente, C. Di Giovanni, S. Seccia, P. Morrica, Biomed. Chromatogr. 19 (2005) 766.

[80] T. Kosjek, E. Heath, A. Krbavcic, Environ. Int. 31 (2005) 679.

[81] A. Posyniak, K. Mitrowska, J. Zmudzki, J. Niedzielska, J. Chromatogr. A 1088 (2005) 169.

[82] G. Sirvent, M. Hidalgo, V. Salvadó, J. Sep. Sci. 27 (2004) 1524.

[83] G. Sirvent, M. Hidalgo, V. Salvadó, J. Sep. Sci. 27 (2004) 613.

[84] K.F. Nielsen, P.W. Dalsgaard, J. Smedsgaard, T.O. Larsen, J. Agric. Food Chem. 53 (2005) 2908.

[85] A. Becalski, B.P.-Y. Lau, D. Lewis, S.W. Seaman, J. Agric. Food Chem. 51 (2003) 802.

[86] L. Ge, J.W.Y. Yong, N.K. Goh, L.S. Chia, S.N. Tan, E.S. Ong, J. Chromatogr. B 829 (2005) 26.

[87] N. Rosales-Conrado, M.E. León-González, L.V. Pérez-Arribas, L.M. Polo-Díez, J. Chromatogr. A 1076 (2005) 202.

[88] A. Salvador, D. Dubreuil, J. Denouel, L. Millerioux, J. Chromatogr. B 820 (2005) 237.

[89] D. Whittington, E.D. Kharasch, J. Chromatogr. B 796 (2003) 95.

[90] J. Yawney, S. Treacy, K.W. Hindmarsh, F.J. Burczynski, J. Anal. Toxicol. 26 (2002) 325.

[91] C.P.W.G.M.V.-V. Wissen, R.E. Aarnoutse, D.M. Burger, J. Chromatogr. B 816 (2005) 121.

[92] K. Inoue, T. Namiki, Y. Iwasaki, Y. Yoshimura, H. Nakazawa, J. Chromatogr. B 785 (2003) 57.

[93] K. Ishii, T. Furuta, Y. Kasuya, J. Chromatogr. B 759 (2001) 161.

[94] M.J. Rose, C. Fernandez-Metzler, B.A. Johns, G.R. Sitko, J.J. Cook, J. Yergey, J. Pharm. Biomed. Anal. 38 (2005) 695.

[95] E. Jiménez, D. Roy, D. Barrón, J. Barbosa, Electrophoresis 25 (2004) 65.

[96] D. Richard, B. Ling, N. Authier, T.W. Faict, A. Eschalier, F. Coudore, Anal. Chem. 77 (2005) 1354.

[97] E. Benito-Peña, A.I. Partal-Rodera, M.E. León-González, M.C. Moreno-Bondi, Anal. Chim. Acta 556 (2006) 415.

[98] T. Miyauchi, M. Mori, K. Ito, J. Chromatogr. A 1095 (2005) 74.

[99] T. Miyauchi, M. Mori, K. Ito, J. Chromatogr. A 1063 (2005) 137.

[100] H.-C. Chen, S.-P. Wang, W.-H. Ding, J. Chromatogr. A 1102 (2006) 135.

[101] D.N. Mallet, S. Dayal, G.J. Dear, A.J. Pateman, J. Pharm. Biomed. Anal. 41 (2006) 510.
[102] E. Bermudo, E. Moyano, L. Puignou, M.T. Galceran, Anal. Chim. Acta 559 (2006) 207.
[103] S. Huq, A. Dixon, K. Kelly, K.M.R. Kallury, J. Chromatogr. A 1073 (2005) 355.
[104] S. Weigel, R. Kallenborn, H. Hühnerfuss, J. Chromatogr. A 1023 (2004) 183.
[105] N. Fontanals, B.C. Trammell, M. Galià, R.M. Marcé, P.C. Iraneta, F. Borrull, U.D. Neue, J. Sep. Sci. 29 (2006) 1622.
[106] H. Zou, X. Huang, M. Ye, Q. Luo, J. Chromatogr. A 954 (2002) 5.
[107] F. Svec, C.G. Huber, Anal. Chem. 78 (2006) 2101.
[108] S. Xie, F. Svec, J.M. Fréchet, Chem. Mater. 10 (1998) 4072.
[109] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Anal. Chem. 75 (2003) 2517.
[110] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Anal. Chim. Acta 494 (2003) 149.
[111] C. Liu, N. Naismith, J. Economy, J. Chromatogr. A 1036 (2004) 113.
[112] A. Moral, M.D. Sicilia, S. Rubio, D. Pérez-Bendito, J. Chromatogr. A 1100 (2005) 8.
[113] M. Cantero, S. Rubio, D. Pérez-Bendito, J. Chromatogr. A 1067 (2005) 161.
[114] T. Saitoh, Y. Nakayama, M. Hiraide, J. Chromatogr. A 972 (2002) 205.
[115] F. Merino, S. Rubio, D. Pérez-Bendito, Anal. Chem. 76 (2004) 3878.
[116] F. Merino, S. Rubio, D. Pérez-Bendito, Anal. Chem. 75 (2003) 6799.
[117] H.-D. Liang, D.-M. Han, X.-P. Yan, J. Chromatogr. A 1103 (2006) 9.
[118] A. Penalver, E. Pocurull, F. Borrull, R.M. Marcé, Trends Anal. Chem. 18 (1999) 557.
[119] L. Cai, Y. Zhao, S. Gong, L. Dong, C. Wu, Chromatographia 58 (2003) 615.
[120] J. Yu, C. Wu, J. Xing, J. Chromatogr. A 1036 (2004) 101.
[121] Z. Zeng, W. Qiu, M. Yang, X. Wei, Z. Huang, F. Li, J. Chromatogr. A 934 (2001) 51.
[122] Z. Zeng, W. Qiu, Z. Huang, Anal. Chem. 73 (2001) 2429.
[123] D. Wang, J. Xing, J. Peng, C. Wu, J. Chromatogr. A 1005 (2003) 1.

[124] L. Yun, Anal. Chim. Acta 486 (2003) 63.
[125] X. Li, Z. Zeng, S. Gao, H. Li, J. Chromatogr. A 1023 (2004) 15.
[126] W. Wang, S. Gong, Q. Cao, Y. Chen, X. Li, Z. Zeng, Chromatographia 61 (2005) 75.
[127] H. Minjia, T. Chao, Z. Qunfang, J. Guibin, J. Chromatogr. A 1048 (2004) 257.
[128] D. Djozan, S. Bahar, Chromatographia 59 (2004) 95.
[129] A. Ghassempour, N.M. Najafi, A. Mehdinia, S.S.H. Davarani, M. Fallahi, M. Nakhshab, J. Chromatogr. A 1078 (2005) 120.
[130] M. Huang, G. Jiang, Y. Cai, J. Sep. Sci. 28 (2005) 2218.
[131] H. Bagheri, A. Mir, E. Babanezhad, Anal. Chim. Acta 532 (2005) 89.
[132] J. Wu, J. Pawliszyn, Anal. Chim. Acta 520 (2004) 257.
[133] J. Wu, J. Pawliszyn, J. Chromatogr. A 909 (2001) 37.
[134] J. Wu, H.L. Lord, J. Pawliszyn, H. Kataoka, J. Microcolumn Sep. 124 (2000) 255.
[135] J.-F. Huang, B. Lin, Q.-W. Yu, Y.-Q. Feng, Anal. Bioanal. Chem. 384 (2006) 1228.
[136] Y. Fan, Y.-Q. Feng, S.-L. Da, Z.-G. Shi, Anal. Chim. Acta 523 (2004) 251.
[137] Y. Fan, Y.-Q. Feng, S.-L. Da, X.-P. Gao, Analyst 129 (2004) 1065.
[138] Y. Wen, Y. Fan, M. Zhang, Y.-Q. Feng, Anal. Bioanal. Chem. 382 (2005) 204.
[139] Y. Fan, Y.-Q. Feng, J.-T. Zhang, S.-L. Da, M. Zhang, J. Chromatogr. A 1074 (2005) 9.
[140] J. Nie, Q. Zhao, J. Huang, B. Xiang, Y.-Q. Feng, J. Sep. Sci. 29 (2006) 650.
[141] M. Zhang, F. Wei, Y.-F. Zhang, J. Nie, Y.-Q. Feng, J. Chromatogr. A 1102 (2006) 294.
[142] H.-J. Zhang, J.-F. Huang, H. Wang, Y.-Q. Feng, Anal. Chim. Acta 565 (2006) 129.
[143] M. Kawaguchi, R. Ito, K. Saito, H. Nakazawa, J. Pharm. Biomed. Anal. 40 (2006) 500.
[144] C. Bicchi, C. Cordero, E. Liberto, P. Rubiolo, B. Sgorbini, F. David, P. Sandra, J. Chromatogr. A 1094 (2005) 9.

[145] W. Liu, H. Wang, Y. Guan, J. Chromatogr. A 1045 (2004) 15.
[146] C. Yu, M. Davey, F. Svec, J.M.J. Fréchet, Anal. Chem. 73 (2001) 5088.
[147] Y. Yang, C. Li, J. Kameoka, K.H. Lee, H.G. Craighead, Lab Chip 5 (2005) 869.
[148] Y. Yang, C. Li, K.H. Lee, H.G. Craighead, Electrophoresis 26 (2005) 3622.
[149] D.S. Peterson, T. Rohr, F. Svec, J.M.J. Fréchet, Anal. Chem. 75 (2003) 5328.
[150] J.C.C. Yu, E.P.C. Lai, Anal. Bioanal. Chem. 381 (2005) 948.
[151] Z. Altun, M. Abdel-Rehim, L.G. Blomberg, J. Chromatogr. B 813 (2004) 129.
[152] Z. Altun, L.G. Blomberg, E. Jagerdeo, M. Abdel-Rehim, J. Liq. Chrom. & Rel. Technol. 29 (2006) 829.
[153] M. Abdel-Rehim, P. Skansen, M. Vita, Z. Hassan, L. Blomberg, M. Hassan, Anal. Chim. Acta 539 (2005) 35.
[154] M. Vita, P. Skansen, M. Hassan, M. Abdel-Rehim, J. Chromatogr. B 817 (2005) 303.
[155] M. Abdel-Rehim, J. Chromatogr. B 801 (2004) 317.
[156] A. El-Beqqali, A. Kussak, M. Abdel-Rehim, J. Chromatogr. A 1114 (2006) 234.
[157] S. Lacorte, M.-C. Perrot, D. Fraise, D. Barceló, J. Chromatogr. A 833 (1999) 181.
[158] R. Kahlich, C.H. Gleiter, S. Laufer, B. Kammerer, Rapid Commun. Mass Spectrom. 20 (2006) 275.
[159] K.M. Peru, S.L. Kuchta, J.V. Headley, A.J. Cessna, J. Chromatogr. A 1107 (2006) 152.
[160] H.-C. Chen, W.-H. Ding, J. Chromatogr. A 1108 (2006) 202.
[161] Y. Fan, M. Zhang, Y.-Q. Feng, J. Chromatogr. A 1099 (2005) 84.

Figure captions

Figure 1. Recovery values after 100 ml (clear), 200 ml (dark), and 300 ml (striped) of standard solution spiked with phenol was percolated with HXLGp and HXLGmix (data not available for the other sorbents) through a precolumn packed with “in-house” hydrophilic sorbents (for details see Table 3) in SPE-LC-UV.

Figure 2. Electropherograms of spiked chicken sample tissues with different sorbents. (a) Bond Elut C18; (b) Oasis HLB; (c) SDB-RPS; (d) Oasis MAX. 50 mM phosphoric acid at pH 8.4; λ = 260 nm; 240 mg kg^{-1} of each substance. Peak designation: (1) danofloxacin; (2) ciprofloxacin; (3) marbofloxacin; (4) enrofloxacin; (5) difloxacin; (6) piromidic acid (IS); (7) oxolinic acid; (8) flumequine. Reproduced from [95] with permission from Wiley-VCH and the authors.

Figure 3. Comparison of quantities extracted from 1 µg mL^{-1} solutions of tetrafluorobenzoic acid N-hydroxysuccinimide ester derived amines: (1) methylamine, (2) dimethylamine, (3) ethylamine, (4) propylamine, (5) butylamine, (6) pentylamine, (7) hexylamine, with commercial 100 µm PDMS and 85 µm PA fibers and with the sol–gel crown-ether fibers: A. 4’-allyldibenzo-18-crown-6; B. 3’-allylbenzo-15-crown-5; C. allyloxyethoxymethyl-18-crown-6, whose structure is depicted in (b) and specified as 80 µm DB18C6, 84 µm B15C5, and 82 µm 18C6, respectively, in the legend of figure (a). Reproduced from [119] with permission from Vieweg and the authors.

Figure 4. LC chromatograms obtained by in-tube SPME of fluoroquinolones from the whole egg and albumin sample at 10 ng mL^{-1} in spiked whole egg sample (a) and control whole sample (b); spiked albumin sample (c) and control albumin sample (d). The extraction flow rate was 0.04 mL min−1; extraction time was 10 min. Peak designation: (1) ofloxacin, (2) norfloxacin, (3) ciprofloxacin, (4) enrofloxacin, (5) sarafloxacin. Reproduced from [135] with permission from Springer Berlin and the authors.

Figure 1

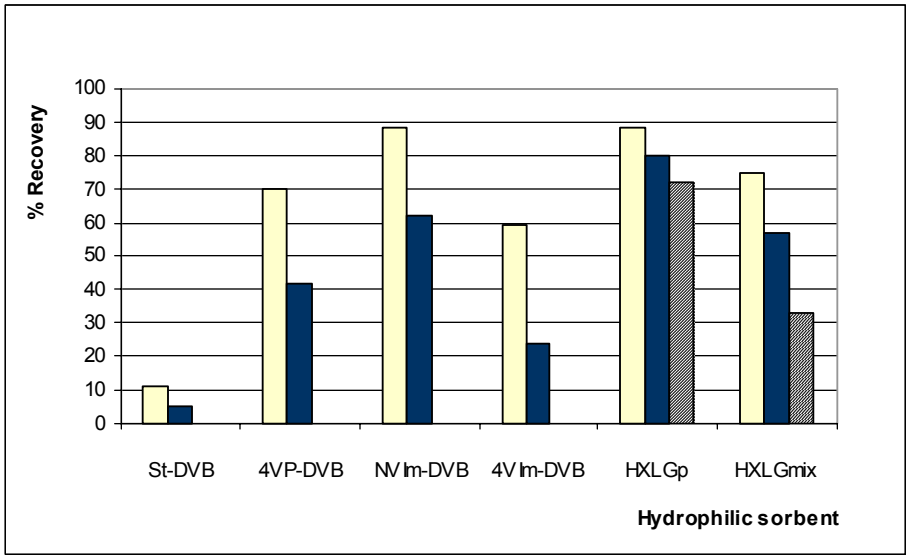


Figure 1

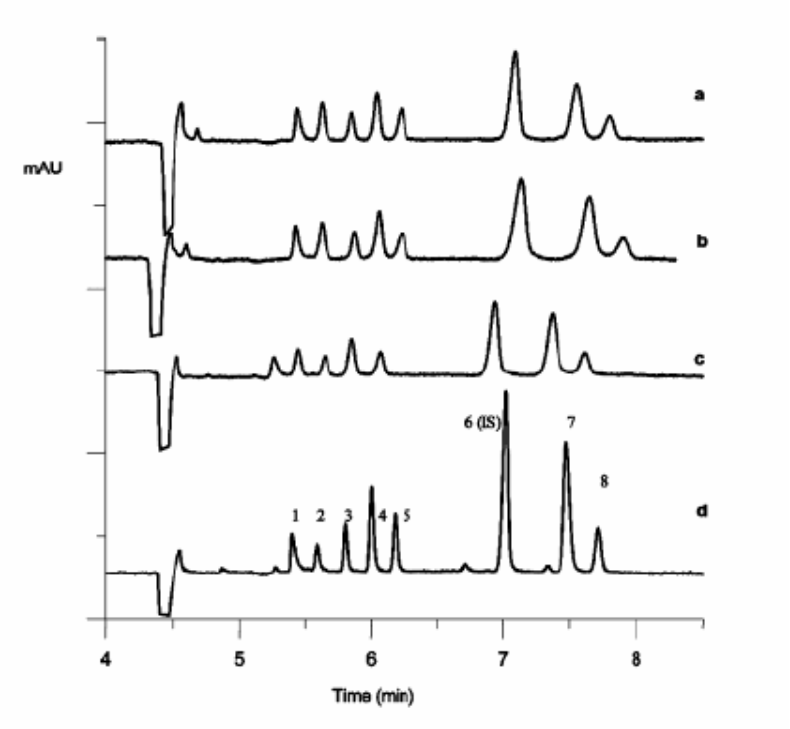
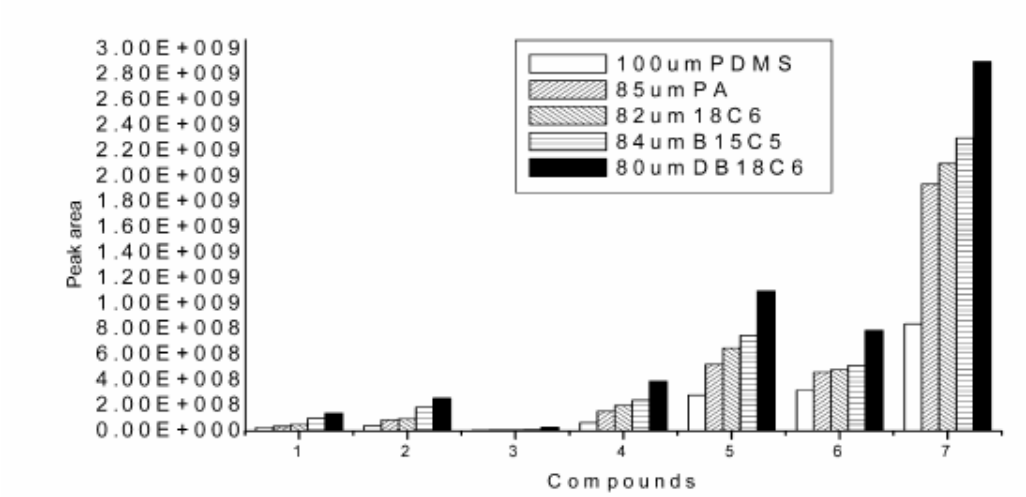
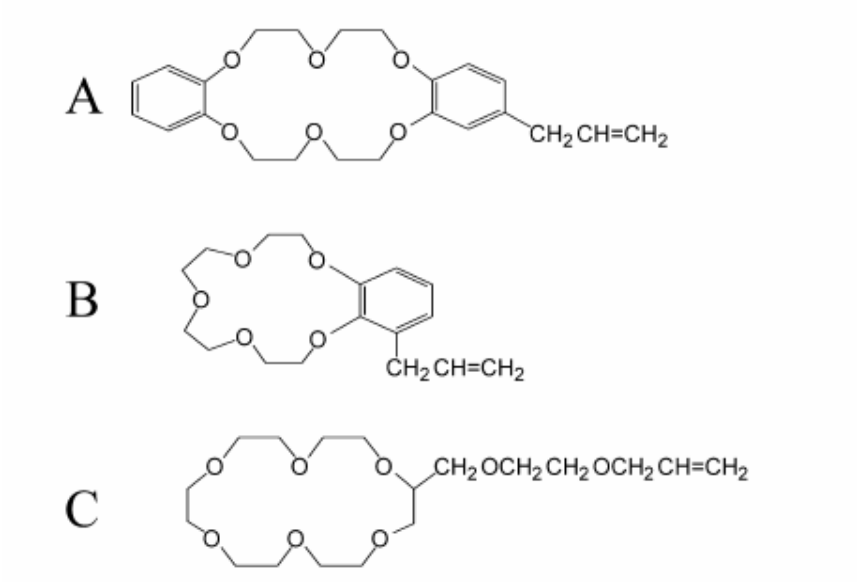


Figure 2


3.00E+009
2.80E+009
2.60E+009
2.40E+009
2.20E+009
2.00E+009
1.80E+009
1.60E+009
1.40E+009
1.20E+009
1.00E+009
8.00E+008
6.00E+008
4.00E+008
2.00E+008
0.00E+000
Peak area
100um PDMS
85um PA
82um 18C6
84um B15C5
80um DB18C6
1
2
3
4
5
6
7
Compounds

a)


A
CH2CH=CH2
B
CH2CH=CH2
C
CH2OCH2CH2OCH2CH=CH2

b)

Figure 3

Figure 4

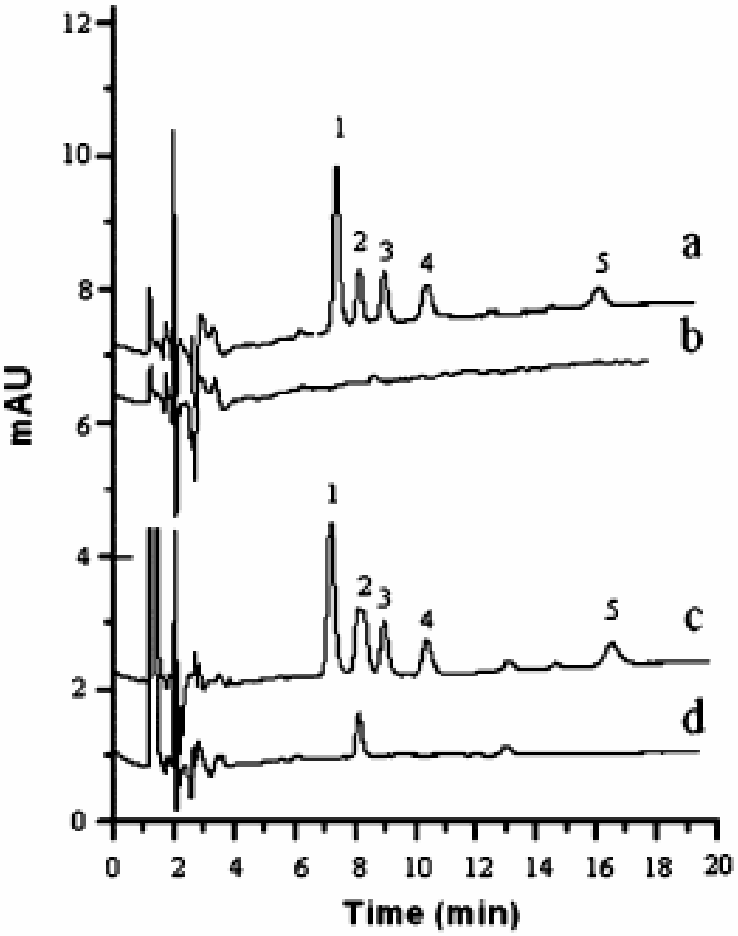


Figure 4

tables

Table 1. Structure and properties of some polymeric commercial sorbents

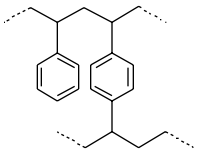
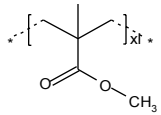
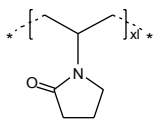
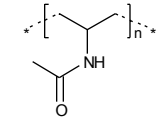
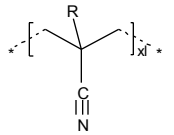
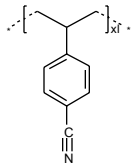
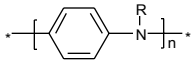
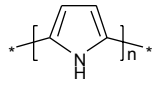
Copolymer structure	Sorbent	Area ($m^2 g^{-1}$)	Supplier
macroporous  St-DVB	XAD-1	100	Room & Haas
	XAD-2	300	Room & Haas
	XAD-4	≥750	Room & Haas
	XAD-16	800	Room & Haas
	PLRP-S-10	500	Polymer Lab.
	PLRP-S-30	375	Polymer Lab.
	Strata SBD-L	500	Phenomenex.
hypercrosslinked	Styrosorb 2m	910	Purolite Int.
	Styrosorb MT-43	1050	Purolite Int.
	Styrosorb MN-150	1070	Purolite Int.
	HySphere-SH	>1000	Spark Holland
	Amberchrom GC-161m	900	TosoHaas
	Envi-Chrom P	800-950	Supelco
	Bakerbond SDB-1	1060	J.T. Baker
	LiChrolut EN	1200	Merck
	Chromabond® HR-P	1200	Macherey-Nagel

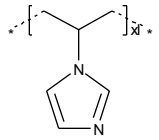
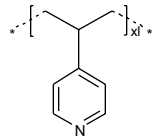
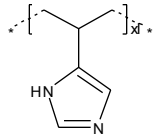
Table 2. Structure, properties and application of some commercial hydrophilic polymeric sorbents

Sorbent	Supplier	Copolymer structure	Surface area ($m^2 g^{-1}$)	Analyte	Matrix	Technique	Ref.
XAD-7	Room & Haas		450	fulvic acids	water	Batch-SPE-UV	[18]
XAD-8			310				
Abselut Nexus	Varian		575	isoflavones drugs tetracyclines fatty acids	plasma urine & serum animal tissue animal tissue	off-line-SPE-LC-MS off-line-SPE-LC-UV off-line-SPE-LC-DAD off-line-SPE-GC-FID	[22] [20] [23] [21]
		MA-DVB					
Focus		n.d.	n.d.	n.d.	n.d.	n.d.	
Oasis HLB	Waters		830	antibiotics pesticides herbicides EDCs biological comp.	water urine & plasma plasma	on-line-SPE-LC-MS/MS off-line-SPE-LC-MS/MS off-line-SPE-LC-MS off-line-SPE-LC-UV 96-well-SPE-LC-MS/MS	[36] [32] [47] [27] [46]
Porapak RDX		PVP-DVB	550	nitroaromatic anilines	water	off-line-SPE-LC-UV off-line-SPE-LC-ED/MS	[48] [157]
Discovery DPA 6S	Supelco		n.d.	EDCs alkyl amines	water	off-line-SPE-GC-MS	[49] [50]
		Polyamide					

xl: crosslinked with DVB; n: linear polymer ; n.d.: no data
Detectors: UV: ultraviolet; MS: mass spectrometry; DAD: diode array; FID: flame ionisation.

Table 3. Structure, properties and application of some "in-house" hydrophilic polymeric sorbents

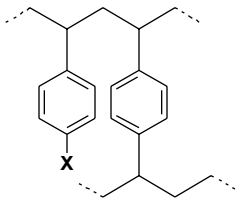
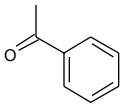
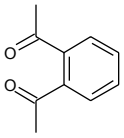
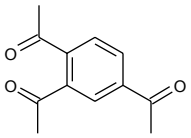
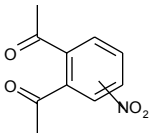
Sorbent	Copolymer structure	Surface area ($m^2 g^{-1}$)	%wt. polar content	Analyte[a]	Technique	Ref.
AN-DVB		460 [b]	5.9 %N [b]	phenols	Batch-SPE-UV	[51]
MAN-DVB	R = H; AN-DVB R = CH_3; MAN-DVB	560 [b]	4.8 %N [b]			
CMSt-DVB		308 [b]	2.6 %N [b]			[52]
PANI		48	n.d.	phenols	off-line SPE-GC-ECD	[53,55]
				polar pesticides	off-line-SPE-CE-DAD	[54]
PNMA	R = H; PANI	32	n.d.	phenols	off-line-SPE-GC-ECD/FID	[55]
PDMA	R = CH_3; PNMA R = phenyl; PDMA	38	n.d.			
PPy		40	n.d.	phenols pesticides PAHs	off-line-SPE-GC- FID/MS	[56]
				phenols	on-line-SPE-LC-UV	[57]

NVIm-DVB		626	6.3 N%	phenols polar pesticides	on-line-SPE-LC-UV off-line-SPE-LC-UV	[61]
4VP-DVB		710	2.1 N%		on-line-SPE-LC-UV	[59]
4VIm-DVB		504	8.1 N%			[62]
HXLGp		908	3.96 O%			[63,64]
HXLGmix		1889	2.95 O%			

[a] All in water sample; [b] Characterisation for 50:50 ratio resins; xl^2: hypercrosslinked

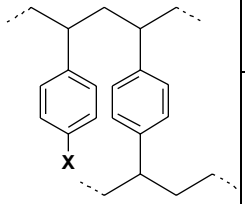
Detectors: ECD: electron capture.

Table 4. Structure, properties of some "in-house" chemically modified polymeric sorbents

Sorbent structure			Analytes[a]	Technique	Ref.
Polymer based	Chemically modified with (X):				
	sulfonic		organic solutes (phenols, hydroxy phenols, PAHs,…)	off-line-SPE-GC-FID	[65,66]
	hydroxy methyl				[65,67]
	acetyl				[65,67]
			phenols polar pesticides	on-line-SPE-LC-UV	[69]
	benzoyl				[70]
	o-carboxy benzoyl				[71]
	2,4-dicarboxy benzoyl				[72]
	2-carboxy-3/4-nitrobenzoyl				[72]

[a] All in water samples

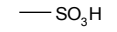
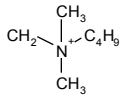
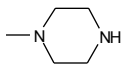
Table 5. Structure, properties and examples of applications of commercially available chemically modified polymeric sorbents

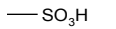
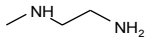
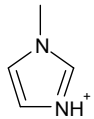
Sorbent	Supplier	Sorbent structure				Analytes	Matrix	Technique	Ref.
		Polymer based	Chemically modified with (X)		Area $m^2 g^{-1}$				
Bond Elut PPL	Varian		n.d.	n.d	700	phenols polar pesticides	water	on-line-SPE-LC-UV	[73,74]
Isolute ENV+	IST		hydroxyl		1100	carbamates PBDEs pesticides quinolones	water serum serum animal tissue	off-line-SPE-LC-MS off-line-SPE-GC-MS off-line-SPE-LC-MS off-line-SPE-CE-DAD	[75] [28] [76] [95]
Strata X	Phenomenex		pyrrolidone		800	quinolones pharmaceut. tetracyclines pesticides	milk water animal tissue water	off-line-SPE-LC-FLD/UV off-line-SPE-GC-MS off-line-SPE-LC-DAD on-line-SPE-LC-UV off-line-SPE-LC-UV	[78] [80] [81] [62] [79]
Speed-Advanta	Applied Separations		carboxyl[a]		n.d.	phenols	water	off-line-SPE-LC-UV off-line-SPE-GC-FID	[82,83] [83]

[a] Characterised in [82]. n.d.: no data

Detectors: FDL: fluorescence

Table 6. Structure, properties and some examples of applications of mixed-mode polymeric sorbents

Sorbent	Supplier	Sorbent structure			Analytes	Matrix	Technique	Ref.
		Polymer based	Ionic group	Ionic mode				
Oasis MCX	Waters	Oasis HLB (information in Table 2)		strong cation exchange	drugs	plasma	on/off-line-SPE-LC-MS/MS	[158]
							off-line-SPE-LC-MS	[88]
						food	96-well-SPE-LC-MS/MS	[94]
					herbicides	juice	off-line-SPE-LC-UV	[87]
					wood preservation.	wood	off-line-SPE-LC-UV	[98,99]
Oasis WCX				weak cation exchange	antibiotics	soil	off-line-SPE-LC-MS/MS	[159]
Oasis MAX				strong anion exchange	antibiotics	water	off-line-SPE-LC-DAD	[97]
					drugs	plasma	off-line-SPE-LC-UV	[91]
						saliva	off-line-SPE-LC-ED	[92]
					penicillin	food	off-line-SPE-LC-UV/MS	[84]
Oasis WAX				weak anion exchange	fluorescent whitening agent	water	off-line-SPE-LC-MS/MS	[100,160]
					pharmaceuticals		off-line-SPE-LC-UV	[105]

Strata-X-C	Phenomenex	Strata X (information in Table 5)		strong anion exchange	drugs acrylamide	urine plasma food	off-line-SPE-GC-MS off-line-SPE-LC-UV off-line-SPE-LC-MS off-line-SPE-LC-MS	[103] [103] [101] [102]
Strata-X-C-AW				weak anion exchange	n.d.	n.d.	n.d	
Strata-X-C-CW				strong cation exchange	n.d.	n.d.	n.d.	
Chromabond EASY	Macherel-Nagel	n.d.	n.d.	weak anion exchange	pharmaceuticals alkyl amines pesticides	water serum	off-line-SPE-GC-MS off-line-SPE-LC-MS	[104] [50] [76]
NVIm-DVB	prepared “in-house”	(information Table 3)		strong anion exchange	pharmaceuticals	waters	off-line-SPE-LC-UV	[105]

n.d.: no data

Table 7. Structure, properties and applications of other materials used as SPE sorbents

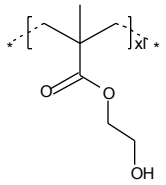
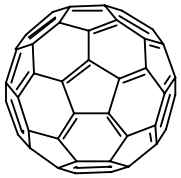
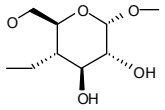
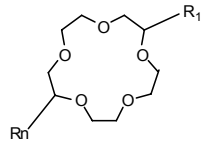
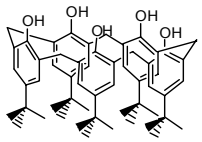
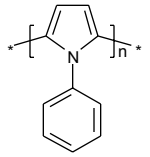
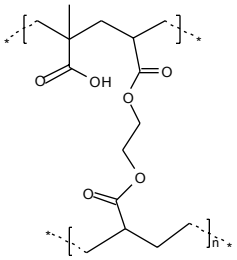
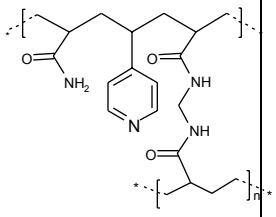
Sorbent			Analytes	Matrix	Technique	Ref.
Material	Chemical structure					
monolith	p(HEMA-DVB)		phenols	water	on-line-SPE-LC-UV	[108]
MWCNTs	fullerene		ECDs phthalates	water	off-line-SPE-LC-FLD off-line-SPE-LC-DAD	[109] [110]
Silica-based modif. with β-cyclodextrine	β-cyclodextrine		humic acids	water	Batch-SPE-UV	[111]

Table 8. Structure, properties and some applications of in-house prepared SPME coatings

Coating			Analytes	Matrix	Technique	Ref.
Name	Structure	Preparation				
Crown-ether		sol-gel technology	organophosporous aromatic amines phenols aliphatic amines	food water urine	fiber-SPME-GC-FPD fiber-SPME-GC-FID	[120] [121] [122,123] [119]
Calix[4]arene			aromatic amines PAHs	water	fiber-SPME-GC-FID	[125,126] [125]
PANI	See information in Table 3	electrodeposition	aliphatic alcohols phenols aromatic amines EDCs.	water	fiber-SPME-GC-FID fiber-SPME-LC-FLD	[128] [131] [127] [130]
PPY			BTEX & alcohols PAHs amines β-blockers	water water urine plasma	fiber-SPME-GC-FID in-tube-SPME-LC-UV	[132,133] [133] [133] [134]

PPPY			BTEX & alcohols	water	fiber-SPME-GC-FID	[133]
p(MMA-EGDMA)		monolith	pharmaceuticals fluoroquinones drugs biological comp.	urine plasma food animal tissue urine	in-tube-SPME-LC-UV in-tube-SPME-LC-UV/FLD PPME-CE-DAD	[137] [138] [135] [140] [141]
p(AA-VP-Bis)			pharmaceuticals phenols EDCs. biological comp. amphetamines	water urine	in-tube-SPME-LC-UV	[161] [139]

Detectors: FPD: flame photometric.