New materials with hydrophilic character for solid-phase extraction

N. Fontanals, R. M. Marcé*, F. Borrull
Departament de Química Analítica i Química Orgànica
Universitat Rovira i Virgili
Imperial Tàrraco, 1
43005 Tarragona
Spain
Phone +34 977 55 81 70
Fax +34 977 55 95 63
*e-mail: marce@quimica.urv.es

Keywords: hydrophilic polymeric sorbents; solid-phase extraction; polar pollutants

Summary

Solid-phase extraction is increasingly being used as a sample pretreatment technique to cover a wide range of analytes, including the most polar ones. This involves the development of new sorbents that are able to trap the most polar analytes. Here we provide an overview of the new sorbents, both commercially available ones and ones synthesized in-house, that improve the extraction of the most polar compounds in solid-phase extraction. We include mainly polymeric sorbents with a large specific surface area and a hydrophilic character obtained either by copolymerizing polar monomers or by introducing polar functional groups. Other novel material technology, such as monoliths, is also described.

We describe the morphological and chemical properties of these new sorbents and relate them to their retention capabilities towards polar compounds. We discuss the recoveries of polar compounds when these sorbents are used in SPE and compare them with recoveries when other sorbents are used.

1. Introduction

Solid-phase extraction (SPE) has gradually replaced the classic liquid-liquid extraction (LLE) and become the most common sample-preparation technique in areas such as environmental, biological and food analyses [1-3]. In SPE the analytes to be extracted are partionated between a solid phase and a liquid phase, and these analytes must have greater affinity for the solid phase than for the sample matrix. The choice of sorbent is therefore a key point in SPE because it can control parameters such as selectivity, affinity and capacity [4,5]. This choice depends strongly on the analytes of interest and its interactions through the functional groups of the analytes. However, it also depends on the kind of sample matrix and its interactions with both the sorbent and the analytes [2,4,5].

The classic SPE materials range from the chemically bonded silica, with C_8 or C_{18} organic group among others, the carbon or ion-exchange to the polymeric materials based on styrene-divinylbenzene (St-DVB). Other sorbents, which enhance selectivity, are immunosorbents (ISs), molecularly imprinted sorbents (MIPs) and restricted access materials (RAM) [1,5,6].

New materials have been developed in the last few years, since the above materials present low recoveries for the polar compounds or are too specific for a particular analyte. These new materials are mainly polymeric sorbents that improve their retention towards polar compounds by increasing surface contact either by introducing functional moieties or by increasing the specific surface area itself.

In this article, we review these new materials used as packing in SPE. We also review other materials that have been synthesized for their sorption

properties and tested in batch experiments. We focus both on new commercially available sorbents and on sorbents synthesized by research groups to overcome specific problems.

2. Classic sorbents

Before detailing the new materials for SPE, we revise the most important preceding sorbents used in SPE.

Silica-phase chemically bonded with various groups has been the most common material for SPE. These sorbents can be classified as reversed-phase sorbents with octadecyl (C_{18}), octacyl (C_8), ethyl (C_2), phenyl (Ph), cyclohexyl (CH) or as normal-phase sorbents with cyanopropyl (CN), aminopropyl (NH_2) or diol functional groups [2]. Their interaction mechanisms are mainly based on hydrophobic interactions (Van der Waals forces) between the analytes and the stationary phase [1]. However, silica sorbents have several disadvantages, such as low recovery in extracting polar compounds, instability at extreme pH and the presence of some residual silanol groups [3].

Other SPE sorbents are the existing forms of carbon, such as graphitized carbon blacks (GCBs) and porous graphitic carbon (PGC). These materials have a low specific surface area (~ 100 m^2 g^{-1}) and are characterized by their great adsorption capacity and their chemical, thermal and mechanical (only PGC) resistance. The disadvantage of these sorbents, however, is that some compounds show excessive retention, or even irreversible retention [5,7].

Porous polymers overcome some of the problems of silica- and carbon-based sorbents since, in the case of silica-based sorbents, polymeric sorbents

are stable throughout the pH range and, in the case of carbon-based sorbents, the compounds adsorbed are easily eluted [1].

The most widely used polymeric sorbent is macoporous styrene-divinylbenzene (St-DVB), which presents a hydrophobic structure with specific surface area up to 500 m^2 g^{-1}. Their interactions with the analytes (due to the hydrophobic character of the sorbent) are basically by the π-π sites of the aromatic rings that form 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 [5].

3. Highly and hyper-crosslinked polymeric sorbents

One way to improve the retention of the analytes in St-DVB sorbents is by increasing the specific surface area. More π-π sites in the aromatic rings will then be accessible to interact with the analytes. St-DVB sorbents with high specific surface areas can be prepared using high levels (typically > 50% vol.) of crosslinker (DVB). However, at very high levels of crosslinker the efficiency of the crosslinking process diminishes significantly because, as steric impediment does not allow some pedant aromatic groups to get involved in the crosslinking, there is no improvement in the specific surface area [8].

Another way to improve the degree of crosslinking was developed in the early 1970s by Tsyurupa and Davankov [9]. This involves the extensive post-crosslinking of linear polystyrene or slightly crosslinked polystyrene in the presence of solvent and Friedel-Crafts catalyst to obtain what is now generally regarded as hypercrosslinked material. Due to the highly crosslinked and

biporous structure, these materials have an extremely high specific surface area (1000-2000 m^2 g^{-1}) and a special kind of porosity whose properties benefit with an excellent sorption properties [9-11].

There are many commercially available polymeric sorbents with high specific surface areas: Styrosorb MN-150 (1070 m^2 g^{-1}, Purolite Int.), Lichrolut EN (1200 m^2 g^{-1}, Merck), HySphere (>1000 m^2 g^{-1}, Spark Holland) or Envi-Chrom P (800-950 m^2 g^{-1}, Supelco) (Table 1). These materials are patented, so their structure is unknown, but, because of their high specific surface area and excellent sorption properties, they are presumed to be hypercrosslinked.

Some studies [5,12] where these polymeric resins were compared to silica or carbon sorbents to extract polar compounds from aqueous samples obtained better results with the polymeric resins. However, the main disadvantage of using highly crosslinked sorbents is their hydrophobicity, which, in the extraction of the most polar compounds, leads to poor retention. To overcome the hydrophobicity of the resins, part of the research into new SPE materials has recently focused on the development of new hydrophilic polymeric materials. In the next section we discuss several ways of obtaining hydrophilic sorbents and describe how they can be applied in SPE.

4. Hydrophilic polymeric sorbents

Sorbents that combine the polymer skeleton (reversed-phase mechanism and π-π interactions) with the occurrence of functional groups (which improve the wetting characteristics, provide better mass transfer and increase possibilities for interaction with functional groups of the analytes) increase the retention of polar compounds. The hydrophilic sorbent can be obtained by

copolymerizing monomers containing suitable functional groups or by introducing a functional group to the existing hydrophobic polymers. These two ways of obtaining hydrophilic sorbents are discussed in this section.

4.1 Copolymers with a hydrophilic monomer

These sorbents described in this section are macroporous copolymers that are mainly made from a balanced ratio of a hydrophilic monomer (which contributes in the polarity of the resin) and a crosslinked agent, which is generally DVB (which contributes to the increase in the specific surface area), though some of the resins described just have the hydrophilic part. Table 1 shows the properties and characterization of some commercial polymeric sorbents and Table 2 shows the structure of the monomers that make up the sorbents.

Commercially available sorbents

One hydrophilic sorbent recognized world-wide is Oasis® HLB (Waters), which is a macroporous poly(N-vinylpyrrolidone-divinylbenzene) (PVP-DVB) copolymer and has a specific surface area of ~800 m^2 g^{-1} (see Tables 1 and 2). As a wide range of applications using the Oasis® HLB material has been reported, in this review we include only studies in which Oasis® HLB is compared to other SPE materials in the extraction of compounds from aqueous matrix.

A good example is an extensive theoretical study [13] which concluded that a conventional polymeric sorbent (PLRP-S-10) is more suitable for extracting moderate polar compounds, whereas Oasis® HLB is better for extracting more

polar compounds. Several other papers also report that Oasis® HLB is better able to analyse some of the most polar compounds such as aniline, caffeine and phenol than the silica-based [14-16], carbon-based [15] or hydrophobic polymeric sorbents such as PS2 (Sep-Pak, Waters) [17], HySphere (Spark Holland) (>1000 $m^2 g^{-1}$) [18] and Lichrolut EN (Merck) (1200 $m^2 g^{-1}$) [19].

On the other hand, in the extraction of a group of estrogens by on-line SPE [20], HySphere (Spark Holland) (Table 1) —which is a hydrophobic polymeric sorbent based on (St-DVB), >1000 $m^2 g^{-1}$— was preferred because, due to its higher retention, Oasis® HLB caused band broadening. This band broadening might have been prevented if the particle size of Oasis® HLB (30-60 μm) had been as narrow as the particle size of HySphere (5-15 μm).

Sorbent particle size can also affect the efficiency of the extraction (recovery) since it can change the number of theoretical plates. However, large differences in the results with sorbent of different particle sizes may also be attributed to charge-to-charge variability. For example, when ibuprofen at 20 ng l^{-1} was extracted from 1 liter of tap water with 200 mg of Oasis® HLB with particles of 30 μm or 60 μm, its recoveries varied from 98% to 74%, respectively [21]. These differences could therefore be attributed to something other than just particle size.

The Waters Corporation also commercializes Porapak RDX, which is also a copolymer based on PVP-DVB, though its specific surface area remains unknown (Table 1). Lacorte *et al.* [22] compared the recoveries in the off-line SPE with different sorbents and different quantities of them -Porapak RDX (500 mg) (PVP-DVB), Oasis® HLB (30, 60, 200 mg) (PVP-DVB, 830 $m^2 g^{-1}$) and Envi-Chrom P (500 mg) (St-DVB, 800-950 $m^2 g^{-1}$)- after percolating 200 ml of

sample spiked with a group of chlorobenzidines. In all cases the results were better for Oasis® HLB even though less of the sorbent was used.

More recently, Abselut Nexus (Varian) which is a hydrophilic commercial sorbent based on the copolymer of methacrylate-divinylbenzene (MA-DVB) (575 m^2 g^{-1}) (see Tables 1 and 2), has been commercialized. The main application of Abselut Nexus is in the clean-up of complex matrices i.e. biological matrices with the subsequent extraction of compounds [23-25]. In one of these applications [23], Abselut Nexus was compared to Oasis® HLB in the extraction of caffeine metabolite products from biological samples. The recovery rates of these two resins were not significantly different. However, Abselut Nexus was selected for further studies because it had a smaller bed volume and therefore provided higher flushing rates.

Other resins based on polymethacrylate are Amberlite XAD-7 and Amberlite XAD-8 (Supelco). XAD resins have been used for several years. A recent study [26] compared the sorption properties of phenol, o-cresol and 2-nitrophenol with XAD-8 (polymethacrylate, 310 m^2 g^{-1}) and XAD-4 (St-DVB, 880 m^2 g^{-1}) (see Table 1). It was demonstrated that the polarity of Amberlite XAD-8 dominated the larger specific surface area of Amberlite XAD-4 in the retention of these phenolic compounds.

The polymer based on polyamide (Table 2) and commercialized under the trademark of Discovery DPA-6S (Supelco) (Table 1) is another polymeric hydrophilic sorbent with few square meters per gram of specific surface area (because it is a linear polymer). To our knowledge, only one application as SPE sorbent has been reported [27]. For the purposes of comparison, this application is discussed in the next section.

In-house synthesized sorbents

As well as the commercial hydrophilic sorbents, some authors have described the synthesis of polar sorbents, whose retention properties have been tested in SPE of polar compounds. Other authors have tested the properties of the newly synthesized materials by batch equilibration, which can be considered as preliminary studies of SPE. Although batch experiments do not consider factors such as morphological properties (particle size, porous diameter, etc.) or compatibility between sorbents, the retention capacity of the materials can be predicted. We have therefore included several examples in which the materials were evaluated by batch experiments since they may be useful for comparison purposes.

Bagheri and co-workers synthesized several conductive polymers: polyaniline (PANI) [28,29] (the hydrophilic monomer structure and characterization of all the in-house synthesized sorbents in this section are also given in Table 2), poly-N-methylaniline (PNMA) [28], polydiphenylamine (PDPA) [28] and polypyrrole (PPy) [30]. All these polymers have specific areas lower than 40 m^2 g^{-1} since they are lineal polymers and have no crosslinked agent. However, the presence of nitrogen atoms in their structures improves polarity and retention towards polar compounds. Results with these conductive polymers were evaluated and compared to other commercial sorbents for the enrichment of polar pollutants from water samples [28-30]. The results for PANI, PNMA, PDPA and PPy were similar to the polymeric Lichrolut EN (St-DVB, 1200 m^2 g^{-1}, Merck) and Oasis® HLB (PVP-DVB, ~800 m^2 g^{-1}, Waters) for extracting a group of chlorophenols by off-line SPE-GC-ECD but the results for

phenol were better with the commercial sorbents. The authors attributed the low recovery of phenol with the conductive polymers to the fact that these polymers suffer from a lack of specific surface area and do not trap phenols as efficiently as Oasis® HLB or Lichrolut EN.

These results clearly show that, as well as the polarity of the sorbent, the specific surface area also affects the retention of polar compounds. The following studies tested how both specific surface area and polarity of the resin contributed to the retention of polar compounds. To verify which parameter had the greatest effect, different sets of resins were synthesized with hydrophobic character (styrene-divinylbenzene (St-DVB)) and with hydrophilic character (4-vinylpyridine-divinylbenzene (4VP-DVB) [31], N-vinylimidazole-divinylbenzene (NVIm-DVB) [32] and 4-vinylimidazole-divinylbenzene (4VIm-DVB) [33]) (see Table 2), all with a range of specific surface area from a few square meters per gram to about 700 m^2 g^{-1} and different hydrophilic monomer contents. When these resins were tested as a sorbent for SPE for extracting polar compounds, it was confirmed that both polarity and specific surface area contribute to the retention of the most polar compounds. Figure 1 shows the influence of specific surface area combined with the hydrophilicity of the four above sorbents (St-DVB, 4VP-DVB, NVIm-DVB and 4VIm-DVB) in the extraction of oxamyl – $C_6H_{10}N_3O_3$- (a) and phenol - C_6H_6O- (b). In both cases, the NVIm-DVB sorbent, which provides the best balance between specific surface area and hydrophilicity, presented the best recoveries. If we compare the retention behavior of 4VP-DVB and 4VIm-DVB, particularly in the case of phenol (fig1b), we can see that, since the higher recoveries were achieved with 4VP-DVB, specific surface area (728 m^2g^{-1} of 4VP-DVB towards 504 m^2g^{-1} of 4VIm-DVB)

may have a greater effect than nitrogen content (2.14%wt.N of 4VP-DVB towards 8.1%wt.N of 4VIm-DVB).

The recoveries for 4VP-DVB and NVIm-DVB sorbents obtained in the on-line SPE of several sample volumes of a mixture of pesticides and phenolic compounds were compared to the recoveries for hypercrosslinked materials based on St-DVB, such as Amberchrom GC-161m (900 m^2 g^{-1}), Envi-Chrom P (800-950 m^2 g^{-1}) and Lichrolut EN (1200 m^2 g^{-1}) [34] (Table 1), and Amberchrom GC-161m chemically modified with acetyl [35], benzoyl [36], o-carboxibenzoyl [37], 2,4-dicarboxibenzoyl [38] and 2-carboxi-3/4-nitrobenzoyl [38] (the chemical structures of the functional groups that modified the polymers are shown in Figure 2). The results were better with sorbents containing hydrophilic monomer. Moreover, under the same conditions as before, the NVIm-DVB sorbent had similar recoveries to those of Oasis® HLB [33,39], since both combine a high specific surface area (627 m^2 g^{-1} and ~800 m^2 g^{-1}, respectively) and hydrophilic monomer content (6.3 %wt.N and 2.3 %wt.N). On the other hand, the recoveries with 4VIm-DVB sorbent were lower than for Oasis® HLB [33]. These low recoveries may be attributed to the lack of specific surface area (504 m^2 g^{-1}), since 4VIm-DVB has the highest nitrogen content (8.1 %wt.N).

The prevalence of the hydrophilicity was also confirmed when two hypercrosslinked resins with different oxygen contents and specific surface areas -HXLGp (908 m^2 g^{-1}, 3.96 %wt.O) and HXLGmix (1889 m^2 g^{-1}, 2.95 %wt.O)- were tested in SPE for three phenolic compounds (resorcinol, phenol and 4-nitrophenol) [40]. For example, the recovery for 300 ml of extracted

phenol when HXLGp was used as sorbent was 72%, whereas when HXLGmix was used, the recovery was down to 33%.

When hypercrosslinked resins are evaluated, three factors must be considered: specific surface area, porous distribution and hydrophilicity. Hypercrosslinked sorbents have a favorable porous distribution, which is partly responsible for the high specific surface area. An example of these better retention properties for hypecrosslinked resins is shown in Table 3. Taking into account that the three resins –HXLGp (908 m^2 g^{-1}, 3.96 %wt.O), Oasis® HLB (~800 m^2 g^{-1}, 2.3 %wt.N and somewhat %wt.O) and NVIm-DVB (627m^2 g^{-1}, 6.3 %wt.N)- have similar specific surface areas and hydrophilicities and that the better recoveries are achieved for the hypercrosslinked sorbent, we may conclude that the porous morphology in hypercrosslinked resin positively affects the retention of the analytes [41].

Figure 3 shows the recoveries of phenol (which can be considered a relevant polar compound in SPE sorbent tests) after percolating 100 ml of phenol under the same conditions by on-line SPE (40mg)-HPLC-UV for all the above sorbents and also for Strata X and Bond Elut PPL, which are commercial, chemically modified sorbents (for more details see the next section).

Throchimczuk *et al.* [42,43] also investigated the effect of specific surface area and hydrophilicity of the synthesized polymers by comparing the efficiency of the resins for extracting some phenolic compounds in batch mode. In a first set of resins [42] based on acrylonitrile (AN) or methacrylonitrile (MAN) (Table 2) with different percentages of (50%, 60% or 70%) DVB, the best sorption properties were for the resins with a fifty-fifty ratio (50%AN-50%DVB or 50%MAN-50%DVB). On the other hand, when the synthesized resin was based

on vinylnaphtalene-divinylnaphthalene (VN-DVN) (Table 2) and had a hydrophobic character, a higher specific surface area was favorable in the retention of phenolic compounds [43].

4.2 Functionalised sorbents

Chemically modifying existing polymers is another method for obtaining polar sorbents. This option has been adopted either by the research groups to improve the available sorbents or by the manufacturers.

In-house synthesized sorbents

Fritz developed the first modified resins with the introduction of acetyl [44,45], hydroxymethyl [44,45] or sulfonic [45] groups. Masqué et al. also modified the commercial resin Amberchrom GC-161m with such moieties as acetyl [35], benzoyl [36], o-carboxybenzoyl [37], 2-carboxy-3/4-nitrobenzoyl and 2,4-dicarboxybenzoyl [38] (see structure in Fig. 2). When these resins were tested by on-line SPE, the recoveries were higher than their unmodified analogues (see the recovery chart for phenol (Fig. 3)).

Some research groups have modified the hypercrosslinked resins with an amine [11] and carbonyl [11,46] groups. The effect of the occurrence of the functional groups was verified by an increase in the retention capacities when these sorbents were compared in batch experiments.

Commercially available sorbents

Concerning the commercial chemically modified resins, the first available was supplied by Varian as Bond Elut PPL (Table 1), whose functional group, due to

patent pending, is unknown. In an earlier study [47], the results obtained with Bond Elut PPL for the SPE of the eleven priority EPA phenolic pollutants from water were comparable to those obtained with a chemically modified sorbent with an o-carboxybenzoyl moiety [37].

Although in initial studies [16,48], Isolute ENV+ (International Sorbent Technology) (Table 1) was considered as just a hydrophobic highly crosslinked St-DVB, it is actually a hydroxylated highly crosslinked St-DVB with a specific surface area of approximately 1000 m^2 g^{-1}. Some studies have compared Isolute ENV+ to Lichrolut EN [21], Oasis® HLB [49,50] or Abselut Nexus [50], with similar or slightly worse results for Isolute ENV+.

More recently, other modified styrenic resins have become available. Strata™ X (Phenomenex) (~800 m^2 g^{-1}) (Table 1) is a surface-modified St-DVB polymer whose retention mechanisms are hydrophobic, hydrogen-bonding and aromatic.

Like other new hydrophilic sorbents (i. e. Abselut Nexus), Strata™ X was also used to clean-up biological samples such as plasma [51] and milk [52].

Strata™ X sorbent has been compared [53] to other commercially available sorbents for the retention of polar compounds in SPE. Strata™ X (200 mg) was selected from several sorbents—Isolute ENV+, Isolute C18, Oasis® HLB, Oasis MCX, Bond Elut C18 and Strata™ X—as the best phase for extracting a group of pharmaceutical compounds from surface water by off-line SPE. However, after percolating 100 ml of sample, recoveries were no higher than 60% with most compounds (i. e. acetyl-sulfamethoxazole, lofepramine, propanolol and tamoxifen).

On the other hand, when Strata™ X (1.3%wt. N, ~800 m^2 g^{-1}) was compared to the hydrophilic sorbents based on NVIm-DVB (6.3%wt.N, 627 m^2 g^{-1}) [39]

and 4VIm-DVB (8.1%wt.N, 504 m^2 g^{-1}) [33] and the commercial Oasis® HLB (2.3%wt.N, ~800 m^2 g^{-1}) for the extraction of polar pollutants from water samples, the results for Strata™ X were similar to those for 4VIm-DVB and worse than those for the other two hydrophilic sorbents [33]. Figure 3 shows the results for phenol. These results again confirm that a suitable sorbent for extracting polar compounds should have a proper balance between specific surface area and polar group content.

Another modified St-DVB copolymer is Chromabond® EASY (Macherey-Nagel) (650–700 m^2 g^{-1}) (Table 1), though some authors have claimed that this copolymer is an St-DVB carrying a “weak anion exchanger” [21].

Spe-ed Advanta (Applied Separations) is another commercially available chemically modified sorbent, whose properties are unknown. In a recent study [54] Spe-ed Advanta sorbent presented better recoveries than Isolute ENV+ in the extraction of a group of phenolic compounds.

4.3 Comparison between sorbents

This section reports some studies that have compared these new hydrophilic commercial sorbents. In one study [50], for instance, many hydrophilic sorbents (Abselut Nexus, Isolute ENV+, Oasis® HLB, Strata™ X and Chromabond® EASY) were tested for the extraction efficiency of persistent organic pollutants (POPs) from human serum. All the hydrophilic sorbents performed well, with high recoveries of all analytes of interest. However, at the maximum bed height used (32 mm) some sorbents caused leaking and back pressure problems; another problem encountered with some bulk supplies of sorbent was lot-to-lot variability in particle size, so there were differences in extraction efficiencies.

Strata™ X and Chromabond® EASY were ruled out because they presented these complications. Overall, Oasis® HLB provided the highest recoveries.

Liu *et al.* [27] compared several sorbents for the extraction efficiency of a group of endocrine-disrupting phenolic compounds. Among these sorbents, Strata™ X (Phenomenex), Discovery DPA-6S (Supelco) and Oasis® HLB (Waters) were tested as polymeric sorbents. Good recoveries for most of the compounds were achieved on Strata™ X (200 mg) and Discovery DPA-6S (500 mg), but Oasis® HLB (200 mg) showed the best recoveries overall.

Chromabond® EASY, Abselut Nexus, Isolute ENV+ and Oasis® HLB were also compared [21] in the extraction of a group of acidic, neutral and basic pharmaceuticals from water samples. These four sorbents presented similar recoveries for neutral compounds, whereas both acidic and basic pharmaceuticals showed higher retentions with Oasis® HLB. Table 4 shows the results obtained with these four sorbents and other commercial St-DVB-based sorbents [21].

Another feature of hydrophilic sorbents such as Abselut Nexus, Oasis® HLB and Chromabond® EASY, one that is emphasized by the manufacturers, is that the cartridge does not need conditioning before the sample is applied. With the new hydrophilic sorbents, therefore, the traditional SPE process with four steps can be minimized to three steps by eliminating the conditioning part and developing the so-called non-conditioned SPE (NC-SPE) technique.

The NC-SPE method was positively applied [25] when Abselut Nexus was used to extract diclofenac from human plasma. The authors stated that the method saved time and money and was easier to perform than the previously published methods. Weigel *et al.* [21] checked the feasibility of Abselut Nexus

and Chromabond® EASY without the conditioning step by running an extraction with conditioned and non-conditioned cartridge in parallel for the extraction of a group of pharmaceuticals from water. For Chromabond® EASY, most recoveries were the same under both conditions except for acidic compounds, whose recoveries fell to 0%. Moreover, Chromabond® EASY presented co-elution of matrix compounds that prevented the proper quantification of some compounds. For Abselut Nexus, almost all recoveries decreased without the conditioning step. According to these authors, another consequence of avoiding the conditioning step before extraction is the higher flow resistance caused by the frits of the cartridge. The non-conditioned step may therefore be advisable, depending on what the conditions and matrix to be extracted are.

5. Other sorbent improvements

5.1 Monoliths

So far the shape of the polymers for SPE described in this review has been that of a spherical beads. A new shape to prepare macroporous polymers is by direct polymerization in situ in a mold, producing monoliths. Monoliths are rigid structures with a proper balance between small pores (specific surface area for the required interactions) and large pores (which allow liquid flow at low back pressures).

Monolithic columns have been widely used because they are easy to prepare (which facilitates reproducibility), a wide variety of starting material can be used to prepare them and the results achieved are satisfactory. They have been applied to liquid chromatography (HPLC), electrochromatography (CEC) of small molecules, chiral compounds, proteins and peptides, among others

[55,56]. With regard to SPE, the research group of Fréchet and Svec (who has been deeply investigating monolith technology) studied using a monolith column as the material for SPE [57]. They prepared two monoliths with similar specific surface areas (~ 400 m^2 g^{-1})—one based on St-DVB and one based on p(2-hydroxyethylmethacrylate-ethylstyrene-divinylbenzene). After checking the suitability of the porous structure, they also tested the retention towards a group of phenolic compounds. Again the results showed that the retentions were higher with the more polar sorbent.

The same research group also applied some hydrophillic monoliths in microscale preparation, developing the on-chip SPE [58] or micro SPE (μSPE) in the needle of the electrospray [59]. So far, however, they have not been used in the extraction of polar compounds.

Using monoliths in SPE to extract polar compounds is therefore simple and straightforward. On the other hand, the need for the monoliths to have a balanced pore structure leads to materials with a lack of specific surface area and therefore with less possible retention of the analytes than those obtained with conventional materials. For this last reason, monolith technology in SPE for polar analytes has not been used as much as in other techniques (e.g. HPLC or CEC) or other compounds (e.g. proteins).

5. 2 Sorbent without polymer skeleton

Though the main interest in improving the sorbents for SPE is in the field of polymers, other materials have also been evaluated as SPE materials for polar compounds. These materials are discussed in this section.

Silica modifications

Silica gel was chemically modified with such groups as poly(methyloctadecylsiloxane (PMODS) [60], aminopropyl (NH_2) [60], aniline, 3-phenylchloropropylamine and benylamine [61]. The PMODS and NH_2 modified materials were compared to analogous commercial sorbents with improved recoveries in the analysis of a group of pesticides in off-line SPE followed by HPLC-UV [60]. When the aniline, 3-phenylchloropropylamine and benylamine [61] sorbents were compared to the silica C_{18} commercial sorbent, the recoveries provided by the modified sorbents were lower than those for C_{18} in the preconcentration of phenolic compounds, but similar or slightly higher for a group of organochloride compounds.

Silica was also modified with β-ciclodextrines (βCD). One application of this sorbent is removing humic acids from water, since βCD combines a hydrophilic exterior and a hydrophobic interior and can trap a wide range of compounds such as humic acids [62].

Multi-walled carbon nanotubes

Carbon nanotubes (CNT) are fullerene (carbon atoms clustering in spherical structures) related structures consisting of graphene cylinders closed at either end with caps containing pentagonal rings. Multi-walled carbon nanotubes (MWNTs) arise when there are many carbon atoms layers in the wall of the nanotubes. Because of their unique electronic, mechanical and chemical properties, MWNTs have great potential in many fields [63,64]. Among the varied application fields, Cai and co-workers used MWNTs as a sorbent in SPE for extracting a group of endocrine disruptors [63] and a group of phthalates [64]

from aqueous samples. In these studies MWNTs were more efficient for extracting pollutants than previously tested fullerene C_{60} sorbents, [65]. In comparative studies, MWNTs were more effective than or as effective as C_{18} or St-DVB based sorbents [63,64].

Although the above studies claimed that MWNTs were promising materials in SPE fields, further work should be done with a wider range of polar compounds to confirm that MWNTs are suitable sorbents for extracting polar pollutants in SPE.

8. Conclusions

The development of new sorbents in order to better trap the polar analytes is a growth research field in SPE, as is demonstrated by the wide availability of synthesized and commercial sorbents.

Polymer-based sorbents are the most versatile ones, both for extracting a wide range of analytes or for performing analysis under different matrix conditions. To further improve the retention of polar analytes, a part from the enlargement of the specific surface area, a possibility is the introduction of hydrophilicity. Hydrophilicity in the sorbents can be achieved by copolymerizing a polar monomer or by chemically modifying a hydrophobic structure with a proper functional group.

The polarity of the sorbent surface and a large surface area allow a greater number of two types of interactions (π-π and polar) with the analytes, thus leading to higher recoveries.

A suitable sorbent for extracting the most polar compounds should therefore combine a large specific surface area and hydrophilicity. Generally, this balance depends on the analyte to be extracted and the experimental conditions.

Acknowledgements

The authors gratefully acknowledge the *Departament d'Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya* for financial support (2001SGR 00319) and for N. Fontanals' predoctoral (2001FI 00641) grant.

References

[1] J.S. Fritz, Analytical Solid-Phase Extraction, Wiley-VCH, New York, 1999.

[2] E.M. Thurman, M.S. Mills, Solid Phase Extraction - Principles and Practice, Jonh Wiley & Sons, New York, 1998.

[3] C.F. Poole, Trends Anal. Chem. 22 (2003) 362.

[4] J.R. Dean, Extraction methods for environmental analysis, John Wiley & Sons cop., New York, 1998.

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

[6] N. Masqué, R.M. Marcé, F. Borrull, Trends Anal. Chem. 20 (2001) 477.

[7] M.-C. Hennion, P. Scribe, in D. Barceló (Editor), Enviromental Analysis: Techniques, Applications and Quality Assurance, Elveiser Science, Amsterdam, 1993, p. 23.

[8] R. Law, D.C. Sherrington, C. Snape, I. Ando, H. Kurosu, Macromolecules 29 (1996) 6284.

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

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

[11] Z.C. Zhai, J.L. Chen, Z.H. Fei, H.L. Wang, A.M. Li, Q.X. Zhang, React. Funct. Polym. 57 (2003) 93.

[12] I. Rodríguez, M.P. Llompart, R. Cela, J. Chromatogr. A 885 (2000) 291.
[13] N.C. Dias, C.F. Poole, Chromatographia 56 (2002) 269.
[14] T.N. Decaestecker, E.M. Coopman, C.H. Van Peteghem, J.F. Van Bocxlaer, J. Chromatogr. A 789 (2003) 19.
[15] A. Asperger, J. Efer, T. Koal, W. Engewald, J. Chromatogr. A 960 (2002) 109.
[16] M. Peruzzi, G. Bartolucci, F. Cioni, J. Chromatogr. A 867 (2000) 169.
[17] E. Ayano, H. Kanazawa, M. Ando, T. Nishimura, Anal. Chim. Acta 507 (2004) 211.
[18] R. Wissiack, E. Rosenberg, M. Grasserbauer, J. Chromatogr. A 896 (2000) 159.
[19] R. Carabias-Martínez, E. Rodríguez-Gonzalo, E. Herrero-Hernández, F.J. Sánchez-San Román, M.G. Prado Flores, J. Chromatogr. A 950 (2002) 157.
[20] M.J. López de Alda, D. Barceló, J. Chromatogr. A 938 (2001) 145.
[21] S. Weigel, R. Kallenborn, H. Hühnerfuss, J. Chromatogr. A 1023 (2004) 183.
[22] S. Lacorte, M.-C. Perrot, D. Fraise, D. Barceló, J. Chromatogr. A 833 (1999) 181.
[23] K.A. Georga, V.F. Samanidou, I.N. Papadoyannis, J. Chromatogr. B 759 (2001) 209.
[24] V.F. Samanidou, C.V. Antoniou, I.N. Papadoyannis, J. Liq. Chrom. & Rel. Technol. 24 (2001) 2161.
[25] C. Arcelloni, R. Lanzi, S. Pedercini, G. Molteni, I. Fermo, A. Pontiroli, R. Paroni, J. Chromatogr. B 763 (2001) 195.
[26] Y.H. Wang, S.H. Lin, Adsorpt. Sci. Technol. 21 (2003) 849.
[27] R. Liu, J.L. Zhou, A. Wilding, J. Chromatogr. A 1022 (2004) 179.
[28] H. Bagheri, M. Saraji, J. Chromatogr. A 986 (2003) 111.
[29] H. Bagheri, M. Saraji, D. Barceló, Chromatographia 59 (2004) 283.
[30] H. Bagheri, A. Mohammadi, A. Salemi, Anal. Chim. Acta 513 (2004) 445.
[31] N. Fontanals, R.M. Marcé, M. Galià, F. Borrull, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 1927.
[32] N. Fontanals, R.M. Marcé, M. Galià, F. Borrull, J. Polym. Sci. Part A: Polym. Chem. 42 (2004) 2019.

[33] N. Fontanals, M. Galià, R.M. Marcé, F. Borrull, Chromatographia (2004) (in press).

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

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

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

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

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

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

[40] N. Fontanals, M. Galià, P.A.G. Cormack, R.M. Marcé, F. Borrull, D.C. Sherrington, J. Polym. Sci. Part A: Polym. Chem. (2004) (in press).

[41] N. Fontanals, M. Galià, P.A.G. Cormack, R.M. Marcé, D.C. Sherrington, F. Borrull, J. Chromatogr. A (2004) (to be published).

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

[43] A.W. Trochimczuk, S. Aoki, K. Yamabe, A. Jyo, Eur. Polym. J. 38 (2002) 941.

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

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

[46] A. Li, Q. Zhang, G. Zhang, J. Chen, Z. Fei, F. Liu, Chemosphere 47 (2002) 981.

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

[48] M. Castillo, D. Puig, D. Barceló, J. Chromatogr. A 778 (1997) 301.

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

[50] 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.

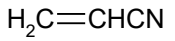
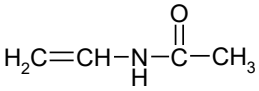
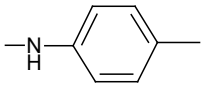
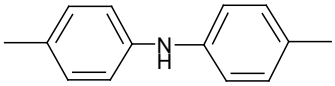
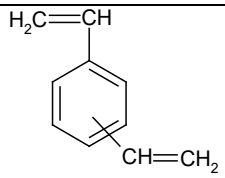
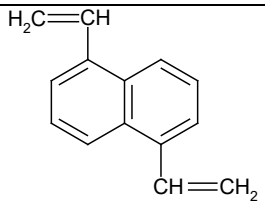
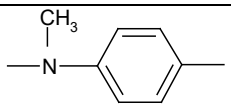
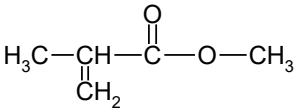
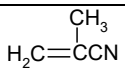
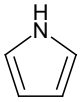
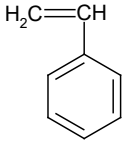
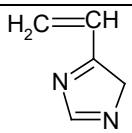
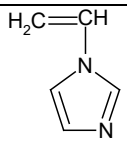
[51] D.G. Watson, F.G. Araya, P.J. Galloway, T.J. Beattie, J. Pharm. Biomed. Anal. 35 (2004) 87.
[52] M.D. Marazuela, M.C. Moreno-Bondi, J. Chromatogr. A 1034 (2004) 25.
[53] M.J. Hilton, K.V. Thomas, J. Chromatogr. A 1015 (2003) 129.
[54] G. Sirvent, M. Hidalgo, V. Salvadó, J. Sep. Sci. 27 (2004) 613.
[55] H. Zou, X. Huang, M. Ye, Q. Luo, J. Chromatogr. A 954 (2002) 5.
[56] F. Svec, J.M.J. Fréchet, Ind. Eng. Chem. Res. 38 (1999) 34.
[57] S. Xie, F. Svec, J.M. Fréchet, Chem. Mater. 10 (1998) 4072.
[58] C. Yu, M. Davey, F. Svec, J.M.J. Fréchet, Anal. Chem. 73 (2001) 5088.
[59] D.S. Peterson, T. Rohr, F. Svec, J.M.J. Fréchet, Anal. Chem. 75 (2003) 5328.
[60] L.F.C. Melo, C.H. Collins, I.C.S.F. Jardin, J. Chromatogr. A 1032 (2004) 51.
[61] T.M. Pizzolato, J.L. Foschiera, F. Gomes, A.M. Geller, A. Lopes, M.C. Ruaro, J.H.Z. dos Santos, J. Sep. Sci. 26 (2003) 1180.
[62] C. Liu, N. Naismith, J. Economy, J. Chromatogr. A 1036 (2004) 113.
[63] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Anal. Chem. 75 (2003) 2517.
[64] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Anal. Chim. Acta 494 (2003) 149.
[65] E. Ballesteros, M. Gallego, M. Valcárcel, J. Chromatogr. A 869 (2000) 101.

Table 1. Properties of some polymeric commercial sorbents.

	Sorbent	Material	Supplier	Surface area (m^2 g^{-1})
Macroporous	XAD-1	St-DVB	Supelco	100
	XAD-2	St-DVB	Supelco	300
	XAD-4	St-DVB	Supelco	880
	PLRP-S-10	St-DVB	Polymer Lab.	500
	PLRP-S-30	St-DVB	Polymer Lab.	375
Hypercrosslinked	Envi-Chrom P	St-DVB hc	Supelco	800-950
	Bakerbond SDB-1	St-DVB hc.	J.T. Baker	1060
	LiChrolut EN	St-DVB hc.	Merck	1200
	Styrosorb 2m	St-DVB hc.	Purolite Int.	910
	Styrosorb MT-43	St-DVB hc.	Purolite Int.	1050
	Styrosorb MN-150	St-DVB hc.	Purolite Int.	1070
	Chromabond® HR-P	St-DVB hc	Macherey-Nagel	1200
	HySphere	St-DVB hc.	Spark Holland	>1000
	Amberchrom GC-161m	St-DVB hc.	TosoHaas	900
Hydrophilic monomer	XAD-7	pMA	Supelco	450
	XAD-8	pMA	Supelco	310
	Oasis® HLB	PVP-DVB	Waters	830
	Porapak RDX	PVP-DVB	Waters	n.d.
	Abselut Nexus	MA-DVB	Varian	575
	Discovery DPA-6S	Poliamida	Supelco	n.d
Chemically modified	Bond Elut PPL	St-DVB c.m.	Varian	700
	Isolute ENV+	St-DVB-OH.	IST	1000-1100
	Strata™ X	St-DVB c.m.	Phenomenex	800
	Chromabond® EASY	St-DVB c.m.	Macherey-Nagel	650-700
	Spe-ed Advanta	St-DVB c.m.	Applied Separations	n.d.

hc: hypercrosslinked; MA: methacrylate; PVP: polyvinylpyrrolidone; c.m.: chemically modified; n.d.: no data

Table 2. Monomer structure of the cited polymers.

Monomer	Structure	Polymer	Source/reference
Acrylonitrile (AN)		AN-DVB	[42]
Amide (AM)		PAM	Discovery DPA-6S, Supelco
Aniline (ANI)		PANI	[28,29]
Diphenylaniline (DPA)		PDPA	[28]
Divinylbenzene (DVB)		St-DVB	See hydrophobic monomers in Table 1, [31] and others
Divinylnaphthalene (DVN)		VN-DVN	[43]
N-methylaniline (NMA)		PNMA	[28]
Methacrylate (MA)		MA-DVB PMA	Nexus, Varian; XAD-7 & XAD-8, Supelco
Methacrylonitrile (MAN)		MAN-DVB	[42]
Pyrrol (Py)		PPy	[30]
Styrene (St)		St-DVB	See hydrophobic monomers in Table 1, [31] and others
4-vinylimidazole (4VIm)		4VIm-DVB	[33]
N-vinylimidazole (NVIm)		NVIm-DVB	[32]

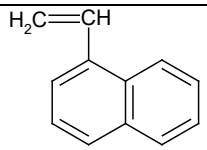
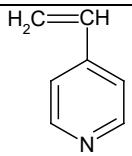
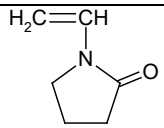
Vinylnaphthalene (VN)		VN-DVN	[43]
4-vinylpyridine (4VP)		4VP-DVB	[31
Vinylpyrrolidone(VP)		PVP-DVB	Oasis® HLB & Porapack RDX, Waters

Table 3. Recoveries obtained with hypercrosslinked HXLGp and the macroporous OASIS® HLB and NVIm-DVB sorbents in on-line SPE for different sample volumes spiked with the group analyte mixture in Milli-Q water. For all conditions see text.

	HXLGp		OASIS® HLB		NVIm-DVB
	200 ml	300 ml	200 ml	300 ml	200 ml
Oxamyl	89	86	62	53	55
Methomyl	94	90	46	41	37
DIA	85	84	69	63	n.d
Ph	80	72	60	52	62
DEA	89	88	96	91	n.d
4-NP	97	85	91	90	83
MCPA	80	81	83	86	84

% Relative standard deviations (R.S.D.) (n =3) were lower than 7.

Table 4. Recovery rates (RR) and realtive standard deviations (R.S.D.) of the three replicates extractions (n=3) with some SPE sorbents. Reproduced from reference [21] by permission of Science Publishers and the authors

Sorbent		Bakerbond SDB-1		Lichrolut EN		Isolute Env+		Chromabond HR-P		Chromabond EASY		Abselut Nexus		Oasis HLB	
Polymer type		PS-DVB		PS-DVB-EVB		PS-DVB-OH		PS-DVB		PS-DVB-AX		PS-MA		PS-DVB-NVP	
Surface area (m^2g^{-1})		1060		1200		1000		1200		650-700		500-650		810	
Particle size (μm)		40-120		40-120		90		50-100		40/80		65-80		30	
Amount (mg)		200		200		200		500		500		200		200	
Recoveries (%)	log Kow	RR[a]	R.S.D.[b]	RR	R.S.D.	RR	R.S.D.	RR	R.S.D.	RR	R.S.D.	RR	R.S.D.	RR	R.S.D.
Paracetamol	0.3	60	4	37	4	39	22	72	4	50	25	0	0	14	2
Caffeine	-0.1	99	4	91	2	99	9	94	3	99	3	25	2	97	3
DEET	2.0	96	3	100	3	94	6	91	2	100	3	91	3	100	3
Carbamazepine	2.7	100	3	97	2	104	3	95	5	99	3	95	1	101	2
Oxazepam	2.3	65	3	74	2	81	4	27	5	80	4	91	4	98	1
Fluoxetine	-	69	4	80	5	86	7	53	5	86	4	94	4	88	2
Metoprolol	0.6	81	6	79	13	50	14	52	4	79	3	97	2	96	7
Propranolol	1.9	68	4	65	8	36	22	50	6	70	1	90	2	98	4
Estrone	3.7	92	2	75	0	80	3	54	5	71	3	92	1	96	3
17β-Estradiol	4.1	96	2	89	3	101	5	85	5	95	0	95	1	98	2
Clofibric acid	-1.3	54	3	29	1	48	10	25	4	27	3	23	3	83	6
Bezafibrate	-0.4	55	9	55	5	43	9	23	5	18	110	87	2	95	2
Ibuprofen	0.3	46	2	61	4	55	9	6	10	10	25	68	1	98	1
Diclofenac	-0.4	42	6	62	3	38	7	19	4	1	92	90	3	102	2

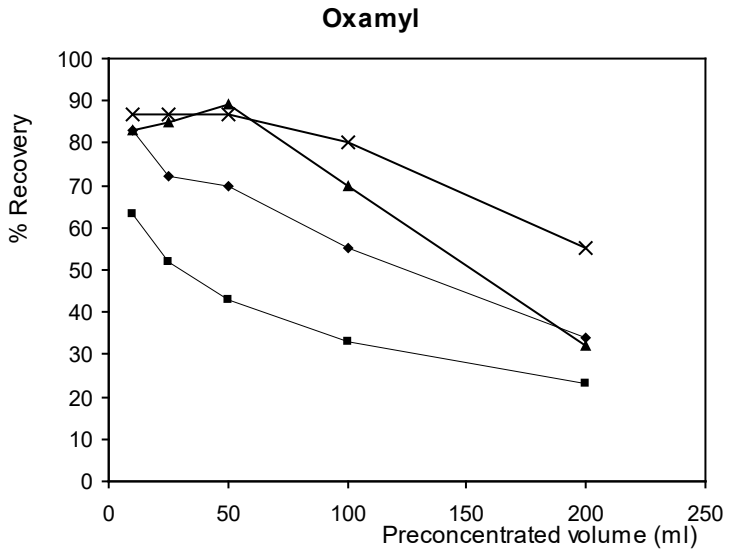
Conditions: 1 l tap water samples (pH 7.8) spiked at a concnetration of 2-5 μg l^{-1}. log Kow: calculated values for pH 8. PS: polystyrene, DVB: divinylbenzene, EVB: ethylvinylbenzene, OH: hydroxy, AX: weak anion exchange, MA: methacrylate, NVP: N-vinylpyrrolidone. [a] n=1; [b] R.S.D. determined from an earlier series (elution volume 70 ml, n=3)

Figure captions

Figure 1. Effect of polarity and specific surface area of the polymer on the recovery values of oxamyl and phenol at volumes of 10-200 ml: (■) St-DVB 710 m^2 g^{-1}; (♦) 4VP-DVB 728 m^2 g^{-1}; %N=2.14; (✕) NVIm-DVB 627 m^2 g^{-1}; %N=6.26; (▲) 4VIm-DVB 504 m^2 g^{-1}; %N=8.1. For the polymer structure, see Table 2.

Figure 2. Scheme of the chemically modified polymers.

Figure 3. Recoveries of phenol with different polymeric sorbents after the percolation of 100 ml of Milli Q samples under the same conditions by on-line (40 mg) SPE-HPLC-UV. For the polymer characterization see Tables 1 and 2 and Figure 2. * cm: chemically modified.


Oxamyl
% Recovery
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
Preconcentrated volume (ml)

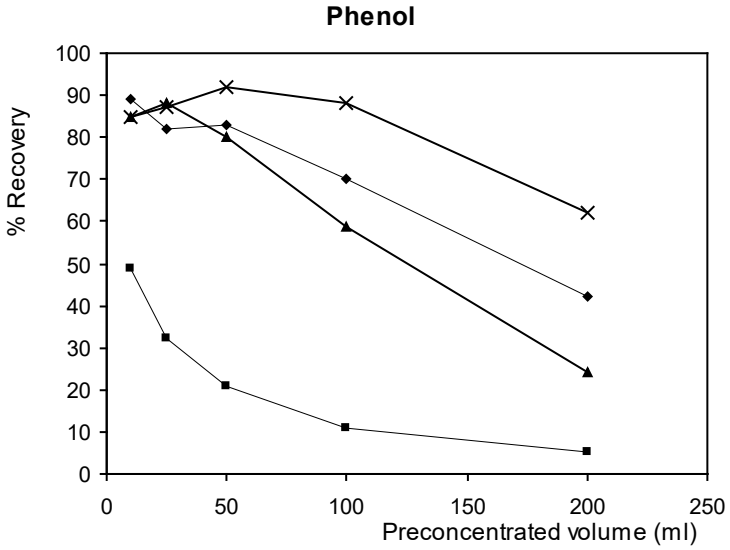

Phenol
% Recovery
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
Preconcentrated volume (ml)

Figure 1

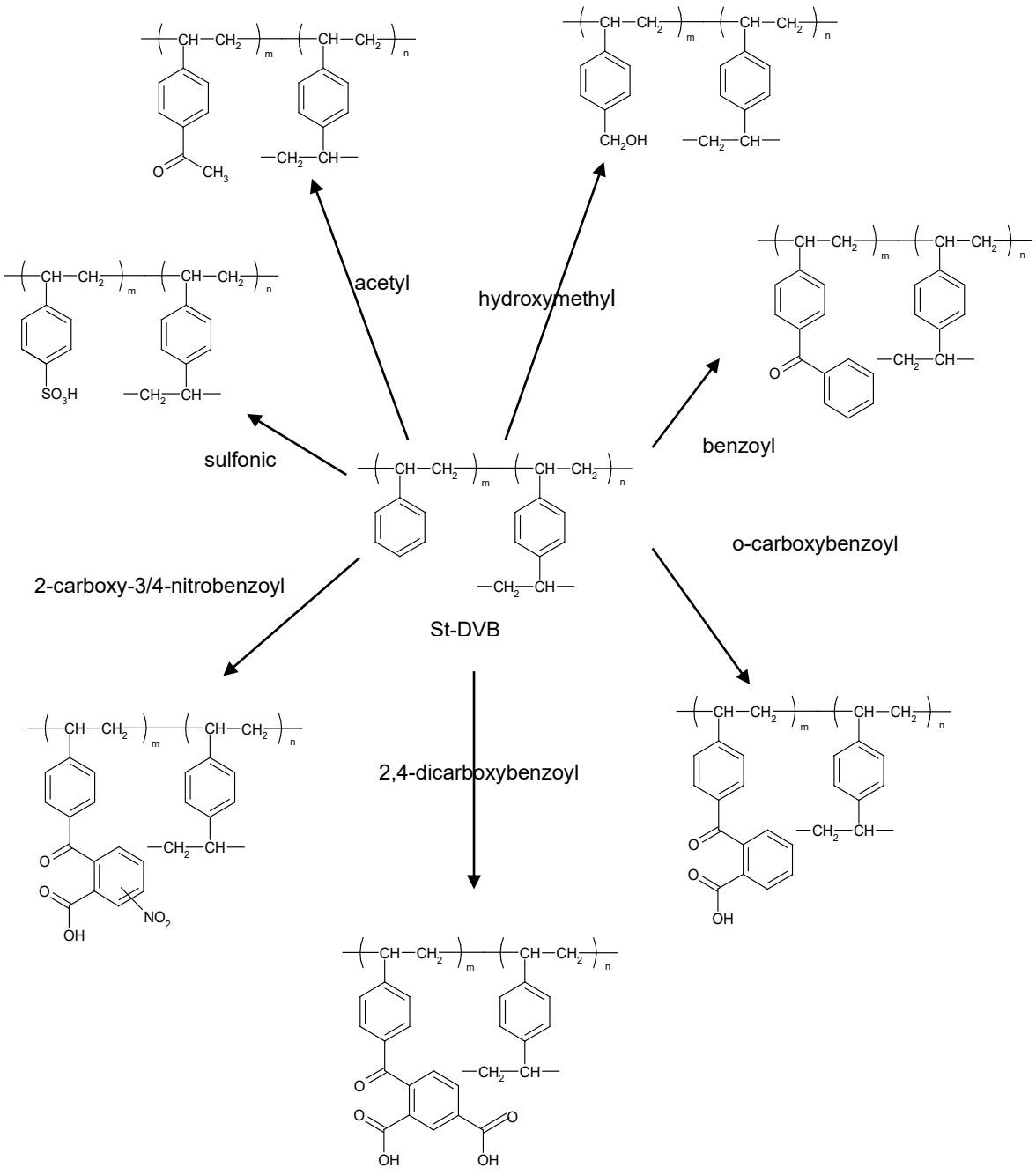

acetyl
hydroxymethyl
sulfonic
benzoyl
o-carboxybenzoyl
2-carboxy-3/4-nitrobenzoyl
St-DVB
2,4-dicarboxybenzoyl

Figure 2

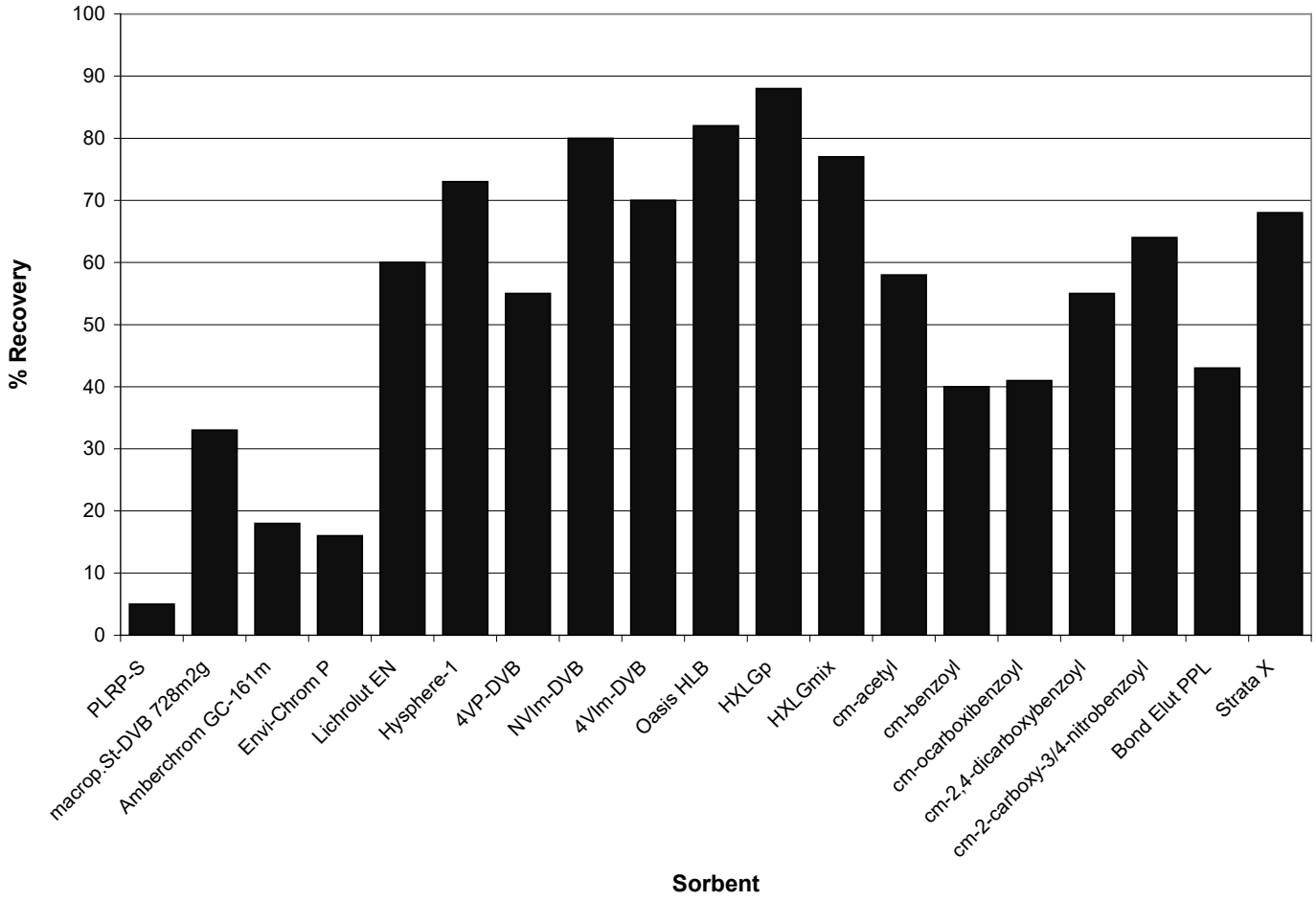

% Recovery
100
90
80
70
60
50
40
30
20
10
0
PLRP-S
macrop.St-DVB 728m2g
Amberchrom GC-161m
Envi-Chrom P
Lichrolut EN
Hysphere-1
4VP-DVB
NVIm-DVB
4VIm-DVB
Oasis HLB
HXLGp
HXLGmix
cm-acetyl
cm-benzoyl
cm-ocarboxibenzoyl
cm-2,4-dicarboxybenzoyl
cm-2-carboxy-3/4-nitrobenzoyl
Bond Elut PPL
Strata X
Sorbent

Figure 3