Review

Chemically modified polymeric sorbents for sample preconcentration

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Abstract

Solid-phase extraction is an attractive alternative in sample preparation because it overcomes many drawbacks of liquid–liquid extraction and makes on-line determination possible by hyphenation with chromatographic techniques. Driven by the need for more effective and more selective sorbents, advances in solid-phase extraction include the development of new materials. This paper describes different types of chemically modified sorbents for the solid-phase extraction of compounds from aqueous samples. Chemical introduction of different functional groups into a polymeric resin improves the efficiency of solid-phase extraction by providing better surface contact with the aqueous samples; also, these sorbents have a greater capacity than the typical solid-phase materials for polar compounds have. The most important new sorbents are the chemically modified resins based on styrene–divinylbenzene copolymers. Preparation of these new sorbents is described, and advantages and drawbacks of off-line procedures and on-line procedures are also discussed. Applications for off-line and on-line chromatographic determinations of polar compounds are presented. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Sorbents; Solid-phase extraction; Poly(styrene–divinylbenzene) resins

Contents

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1. Introduction

Solid-phase extraction (SPE) is a cost-effective and recognised alternative to liquid–liquid extraction (LLE) for sample preparation that overcomes many drawbacks of the traditional extraction by using two immiscible liquids. There is no emulsion formation, and cleaner extracts result in longer column lives for gas chromatography (GC) and high-performance liquid chromatography (HPLC). SPE procedures are used not only to extract traces of organic compounds from samples, but also to remove the interfering components of the complex matrices. In the last few years, several reviews and books have been written dealing with sample preparation, and more specifically with different aspects of the SPE [1–6]. One important parameter to be taken into account in SPE is the selectivity of the stationary phases, especially when compounds are to be extracted from complex matrices, since the main objective is to remove interferences prior to the analysis. To date, typical SPE materials are based on silica with functional C_{18}, C_8, CN and other groups bonded. Other materials as carbon black or polystyrene–divinylbenzene (PS–DVB) copolymers are also frequently used, but all these stationary phases are generally non-selective and can lead to difficulties with interferences co-extracted. The SPE sorbents can be classified into non-polar phases, polar phases and iso-exchange phases [3]. The non-polar sorbents are those that contain methyl, octyl or octadecyl functional groups bonded to the surface of silica to alter their retentive properties. Polar sorbents are unmodified silica or silica with cyano, amino and diol bonded groups. The ion-exchange phases have either cationic or anionic functional groups.

Modified silica with C_{18} reversed-phase sorbent is one of the most widely used packing materials for SPE because of its greater capacity compared to other bonded silicas, such as the C_8 and CN types [7]. The mechanism of retention is based on hydrophobic interactions between the solutes and the stationary phase (Van der Waals forces), and on secondary interactions such as hydrogen bonding and dipole–dipole forces (hydrophilic or polar interactions). Nevertheless, the main drawback of such sorbents is their narrow pH stability range. Consequently, when SPE has to be carried out in extremely acidic or basic media, reversed-phase polymeric sorbents (generally based on PS–DVB) are used. In addition to their broader pH-stability range that increases the flexibility of the method, these kind of sorbents have a greater surface area per gram and they show relatively selective for analytes with aromatic rings because of the specific π–π interactions. Included in this group of sorbents are the commercially available XAD-2 and XAD-4 resins, that show good capability to retain triazines, phenols and other aromatic polar compounds [8–10], and PRP-1 and PLRP-S, widely used for the extraction or organic pollutants [11–14]. Another group of sorbents, also useful for extraction of polar compounds from water samples, are the so-called highly cross-linked polymers. These sorbents allow greater π–π interactions between aromatic analytes and the sorbent, as a consequence of their higher degree of cross-linking and their higher specific surface area, up to 1000 m^2 g^{-1} [12]. Some of these sorbents, tested by Barceló and co-workers [13,15], are commercially available under the names of Podapack RDX, Isolute ENV and LiChrolut EN, the latter yielding better recoveries and higher breakthrough volumes than polymeric resins like PLRP-S, especially for polar compounds like phenols.

Chemically bonded silica and porous polystyrene resins have several shortcomings for use in SPE. While silica itself is hydrophilic, the hydrocarbon chains make the surface hydrophobic. The consequence is poor surface contact with predominantly aqueous solutions. Porous polystyrene resins also have a hydrophobic surface, and because of this, pretreatment of the SPE materials with an activating solvent; such as methanol, acetone or acetonitrile, must be used to obtain better surface contact with the

aqueous solution being extracted. However, the activating solvent can be gradually leached out of the resin, thereby causing the extraction to be ineffective. A better strategy is to make the surface of the extractant solid-phase permanently hydrophilic through a chemical reaction.

In the last decade, chemically modified resins have been developed and applied to the trace enrichment of polar substances. These sorbents have excellent hydrophobicity and yield higher recoveries than unmodified ones [1]. In this article, these modified polymeric sorbents, their application to SPE and comparison with their analogues are reviewed.

2. Chemically modified resins based on polystyrene–divinylbenzene

The most widely used polymeric sorbents are the PS–DVB copolymers, which have a hydrophobic surface and overcome many of the limitations of bonded silicas, especially those related to the limited pH stability or the presence of the silanol groups. In general, PS–DVB resins have greater analyte retention, mainly for polar compounds, than bonded silicas, because their hydrophobic surface contains a relatively large number of active aromatic sites that allow π–π interactions. Nevertheless, sorbents based on PS–DVB have some drawbacks, such as their lack of selectivity and low breakthrough volumes for highly polar compounds, which leads to their incomplete extraction from predominantly aqueous samples. These drawbacks can be largely overcome by using modified resins obtained by attaching polar groups to the aromatic ring on the PS–DVB. In recent years, the performance and suitability for SPE of several polar functional groups modifying PS–DVB have been studied. These groups are listed in Table 1, being mainly acyl derivatives which sometimes have one or more carboxylic acid groups. PS–DVB copolymers with partially substituted quaternary ammonium groups or slightly sulfonated have also been used for SPE of organic solutes, because they have excellent hydrophilicity, thus extracting polar organic compounds more efficiently than underivatized resins do. In general, all these derivatized PS–DVB resins are not commercially available, except those with sulfonic or quaternary

ammonium groups, which are also ion exchangers. Therefore, when they are needed, they have to be prepared in the laboratory by modifying a commercially available resin.
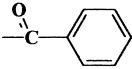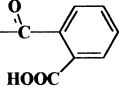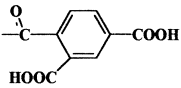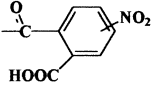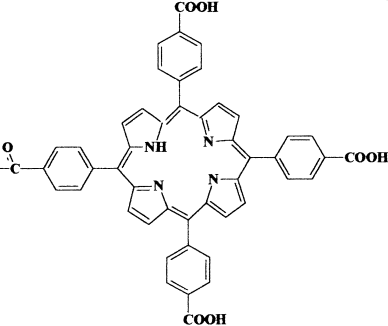
2.1. Chemical modification of polystyrene–divinylbenzene

A considerable body of literature has been generated on the functionalization of cross-linked polystyrene resins, and this subject was already reviewed by Frechet and Farral in 1977 [16] and by Sherrington in 1980 [17]. Acylation allows a variety of functionalization to be achieved; these transformations are normally carried out easily from an acylating agent by means of the Friedel–Crafts reaction, using carbon disulfide or nitrobenzene as the solvent and aluminium chloride as the catalyst. Sulfonation is carried out by reaction of the resin with sulfuric acid. The use of organic swelling agents results in faster and milder conditions, which yield clean and more uniform products. Regarding quaternary ammonium substitutes, these are obtained by the amination of chloromethylated resins, using tertiary amines like trimethylamine. Fig. 1 shows a scheme of the PS–DVB modification cases reviewed in this paper. Next, more details are given about each of the functionalization procedures followed by different authors.

2.1.1. Acetyl derivative

Acetylation can be carried out by using acetyl chloride added dropwise over a mixture containing the PS–DVB to be modified and the aluminium chloride. Sun and Fritz [18,19] use carbon sulfide as the solvent and need to keep the reaction at 50°C for 24 h, stirring with a magnetic bar from time to time through the whole reaction. Masqué et al. [20] use nitrobenzene as the solvent, which requires less time and temperature to complete the reaction: 3 h at 0°C. Once the reaction has been finished, the final product is filtered, washed and dried and the presence of the carbonyl group can be proved by means of the strong band at 1870 cm^{-1} on the IR spectrum or by nuclear magnetic resonance (NMR) spectroscopy. The extent of the modification can be estimated by oxygen elemental analysis.

Table 1
Modifiers of the polystyrene–divinylbenzene

Group		Refs.
Acetyl		[18–20,32–34]
Hydroxymethyl		[19,33,34]
Benzoyl		[21]
o-Carboxybenzoyl		[22,24,35,36]
2,4-Dicarboxybenzoyl		[23]
2-Carboxy-3/4-nitrobenzoyl		[23]
Sulfonate		[27,29,33,37]
Trimethylammonium		[38,39]
Tetrakis(*p*-carboxyphenyl) porphyrin (H$_2$TCPP)		[26]

2.1.2. Hydroxymethyl derivative

The synthesis of this derivative can be made by a Friedel–Crafts reaction using paraformaldehyde as a reagent. The reaction is carried out in acetic acid–acetic anhydride medium using anhydrous zinc chloride as the catalyst, at 60°C overnight [18,19]. Once the reaction has finished, the resin is filtered, rinsed with methanol and heated with a mixture of metha-nol–concentrated hydrochloric acid (90:10) for 1 h. The concentration of –CH$_2$OH groups on the resin can be determined by a standard acetylation procedure using acetic anhydride in pyridine as the reagent or by oxygen elemental analysis.

2.1.3. Benzoyl derivative

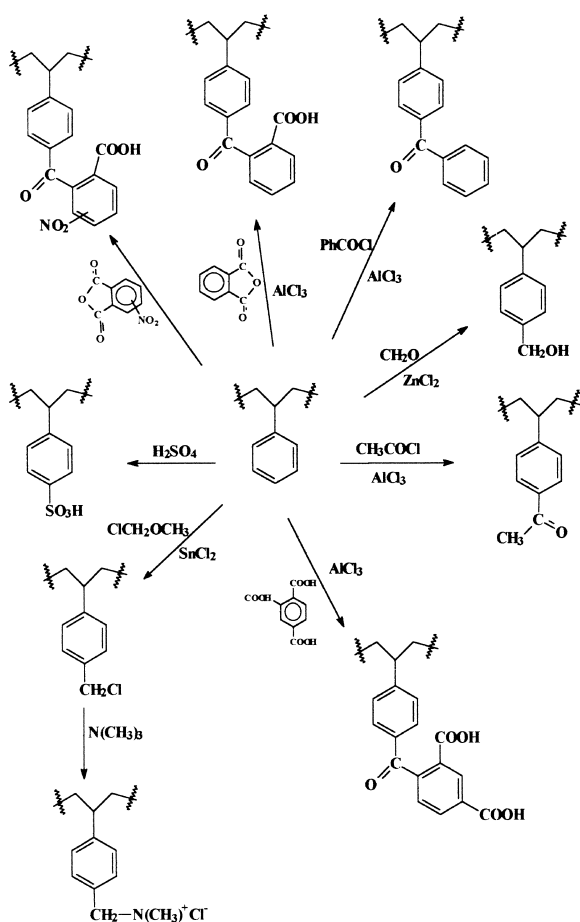Masqué et al. [21] prepare this derivative of the

Fig. 1. Scheme of chemical modification of PS–DVB resin.

PS–DVB by stirring commercial cross-linked PS–DVB in nitrobenzene at room temperature for 12 h. Afterwards, aluminium chloride is added slowly and the mixture is cooled to 0°C before adding the benzoyl chloride dropwise. The reaction mixture is stirred at this temperature for 3 h before being quenched with acetone containing 1% hydrochloric acid. These authors characterize the product by IR spectrometry and establish the extent of the modification by means of the elemental analysis.

2.1.4. o-Carboxybenzoyl derivative

The synthesis of the *o*-carboxybenzoyl derivative of PS–DVB can by carried out by using phthalic anhydride as acylating agent. Masqué et al. [22] perform the reaction at room temperature by stirring

the divinylbenzene–cross-linked polystyrene with nitrobenzene for 8 h and then adding the aluminium chloride under mechanical stirring and, subsequently, the phthalic anhydride. After 15 h stirring, these authors quench the reaction by adding acetone with 1% of hydrochloric acid.

2.1.5. 2,4-Dicarboxybenzoyl derivative

This derivative of the PS–DVB has been prepared and its performance as a sorbent for SPE studied by Masqué et al. [23]. In this case, the acylating agent was the trimellytic acid (1,2,4-benzenetricarboxylic acid). First, before adding this acid, the PS–DVB copolymer was swollen in nitrobenzene at room temperature under mechanical stirring for 8 h. Afterwards, the $AlCl_3$ was added slowly, and then the trimellytic acid previously dissolved in nitrobenzene. As in other reports by the same author, the modified polymer was characterized by IR spectroscopy and the extent of the modification was checked by elemental analysis. This, in the present case, was 6%, which is lower that the values obtained with other modifications, maybe due, according to the author, to restricted accessibility to reactive sites or to the fact that the anhydrides are not as reactive as other reagents [24].

2.1.6. 2-Carboxy-3/4-nitrobenzoyl derivative

The notation -3/4- is used by Masqué et al. [23] to indicate a mixture with the nitro group in position 3 or 4. The authors prepare the nitrophthalic anhydride used for the acylation from the previous dehydration of the 3-nitrophthalic acid. Once the anhydride has been prepared, washed with diethyl ether and dried, a commercially available PS–DVB was modified like the 2,4-dicarboxybenzoyl derivative.

2.1.7. Tetrakis(p-carboxyphenyl)porphyrin (H₂TCPP) derivative

To obtain this derivative, H_2TCPP has to be synthesized in a first step following a procedure described by Alder et al. for tetraphenylporphyrins [25]. Then, the chemically modified sorbent is prepared by ketone linkage, adding thionyl chloride ($SOCl_2$) to the H_2TCPP and heating after adding the resin and 1,1,2,2-tetrachloroethane. $AlCl_3$ is added after cooling to room temperature and the resulting mixture is kept at 10°C for 16 h [26]. In this case, the

amount of porphyrin bonded to the PS–DVB resin was determined indirectly by the Mn–porphyrine complex formation, extraction of the retained Mn in concentrated acid media and subsequent atomic absorption spectrometry.

2.1.8. Sulfonate and trimethylammonium derivatives

Since these derivatives are frequently used as ion exchangers in chromatography and preparative analysis, they are easily commercially available under different names and characteristics. Typical commercial phases are Hamilton PRP-X200, Amberlite IRA-200, Dowex DR-2030, Sep IC-H (Lida) or Novo-Clean IC-H (Alltech) for sulfonate cation-exchange resins, and Hamilton PRP-X100, Amberlite IRA-900, Dowex 11 or Sep IC-OH (Lida) for trimethylammonium anion-exchange resins. Nevertheless, depending on the kind of work to be done, it may still be necessary to modify the resin. Thus, Dumont and Fritz [27] have studied the effect of the resin sulfonation on the retention of polar organic compounds in SPE, preparing several sulfonated resins by adding concentrated sulfuric acid to a slurry formed by a mixture of PS–DVB and glacial acetic acid. After a given reaction time and temperature, the reaction was quenched and the degree of sulfonation was calculated by measuring the cation-exchange capacity.

2.2. Characteristics of polystyrene–divinylbenzene resins

In order to be useful for SPE, a resin must fulfill certain requirements: in addition to a suitable particle size, a selective interaction with the analyte, often achieved by combining reversed-phase and ion-exchange mechanisms, plays an important role. Shown in Table 2 are the commercial resins used for modification by the authors reviewed here, along with some of their physical characteristics.

3. Other modified polymers

As has been stated in the previous sections, the use of surface-modified PS–DVB copolymers with different polar substituents overcomes the disadvantages suffered by standard silica-based material used for SPE, as are their lack of pH stability under acidic or basic conditions, the low breakthrough for polar analytes, and the fact that they are not wettable by water alone and always need a conditioning step with a wetting solvent, such as methanol.

Other modified polymers have been studied, trying to achieve higher capacities or a broader and controllable functional variety. Thus, Buchmeiser and co-workers [28,29] describe the synthesis of new materials for SPE applying the technique of ring-opening-metathesis polymerisation (ROMP) of 1,4,4a,5,8,8a - hexahydro - 1,4,5,8 - *exo,endo* - dimethanophthalene and its copolymerization with the functional monomer *endo,endo*[2.2.1]bicyclohept-2-ene-5,6-dicarboxylic anhydride, using the well-defined Schrock catalyst $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)\text{-}CHCMe_2Ph[OCMe(CF_3)_2]_2$ as initiator. This new concept entails the polymerisation of well-defined, prefunctionalized monomers by a rigid and selective mechanism, leading to stationary phases of entirely predeterminable, predictable and reproducible prop-

Table 2
Physical characteristics of the polymeric resins

Resin	Particle size (μm)	Surface area (m^2 g^{-1})	Pore size (nm)	Refs.
Amberchrom 161	40–50	720		[19,33]
Amberchrom GC-161m	50–100	900	11–17	[20–24]
Sarasep	8–10	415		[19,27,32]
PLRP-S 10	10–15	500	10	[24]
PLRP-S 30	10–15	375	30	[24]
XAD-2	100–150[a]			[26]
XAD-4	100–150[a]			[26]

[a] Obtained after ground in a mortar and sieved.

erties with regard to particle size, porosity, function-
ality and capacity. The resulting cross-linked poly-
mers have been investigated by the authors in terms
of the influence of the polymerisation sequence, as
well as of the stoichiometries on swelling behavior,
surface area, capacity, accessibility of the functional
groups and the use in SPE. Electron microscopic
investigations made by the authors show that the
materials formed consist of irregularly-shaped, ag-
glomerated particles with different mean diameter
and specific surface, depending on the polymeri-
sation sequence and the stoichiometries. These poly-
mers, whose general structure is shown in Fig. 2,
have an excellent hydrophilicity as a consequence of
the carboxylic groups; but, moreover, the polyun-
saturation of the carrier chain, as well as the entire
backbone, provide a significant reversed-phase
character. Consequently, it is expected that they have
adsorbent characteristics of both the polystyrene
resins and the silica sorbents; hydrophobic analytes
would be extracted though interactions with the
hydrophobic part of the polymer, while hydrophilic
analytes would be retained by the carboxyl groups.
Thus, the authors study and compare the extraction
efficiency of some resins prepared by the described
ROMP procedure versus other commercially avail-
able sorbent materials, for a large variety of organic
compounds like phenols, alcohols, aldehydes and
ketones, carboxylic acids, esters, chlorinated hydro-
carbons, amines, nitrosamines and polycyclic aro-
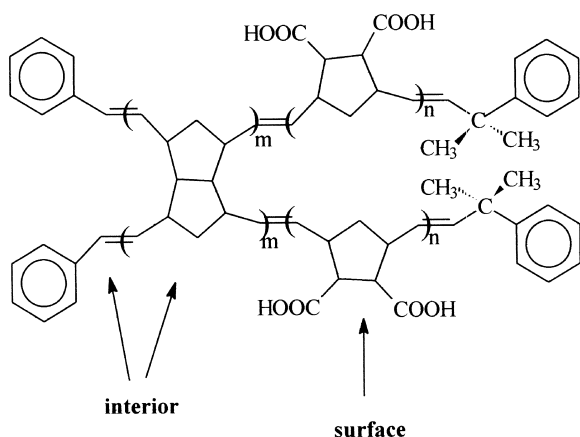matic hydrocarbons. In general, these resins retain

Table 3
Retention values obtained for different sample amounts[a]

	Recovery (%)		
	400 µg	600 µg	1000 µg
2,4-D	87	95	102
2,4-DP	98	88	101
2,4,5-T	92	93	98
2,4,5-TP	93	94	101
MCPA	96	99	103
Dicamba	97	90	89

[a] 2,4-D=(2,4-Dichlorophenoxy)acetic acid; 2,4-DP=2-(2,4-di-
chlorophenoxy)propanoic acid; 2,4,5-T=(2,4,5-trichlorophenoxy)-
acetic acid; 2,4,5-TP=2-(2,4,5-trichlorophenoxy)propanoic acid;
MCPA=(2-methyl-4-chlorophenoxy)acetic acid; Dicamba=(3,6-
dichloro-2-methoxy)benzoic acid.

the studied analytes efficiently. The large number of
carboxylic groups favors high loadings of basic
compounds, but non-polar or acidic compounds such
phenols are also extracted efficiently.

Another modified polymer also used for SPE of
highly polar compounds is an anion exchanger based
on the commercial MFE-Polymer, which is a poly-
mer of the hydroxyethylmethacrylate (HEMA) con-
taining quaternary ammonium functional groups
[30,31]. This sorbent, with a particle size of 50 µm,
has been packed in a 150×4.5 mm conventional LC
chromatographic column, and its efficiency to pre-
concentrate phenoxy acid herbicide residues has been
studied. It has been found that this sorbent has a high
capacity to retain these herbicides efficiently, being
capable of retaining up to 1000 µg when the
preconcentration step is carried out in aqueous acidic
medium at pH below 1 (Table 3). At this pH, all the
phenoxy acid herbicides are neutral molecules; there-
fore, this fact suggests that the mode of retention is
exclusively based on a reversed-phase mechanism,
and the high retention capacity is, probably, a
consequence of the high polarizing power of the
quaternary ammonium groups, capable to induce
strong dipoles in the neutral phenoxy acid.

4. Solid-phase extraction procedures

The most frequent design in SPE is a column
which usually is prepared in the laboratory. Many
different types and amounts of sorbents are contained

Fig. 2. Scheme of the polymer obtained by ring-opening-
metathesis polymerisation (adapted from Ref. [28]).

Table 4
Description of SPE systems with columns

Sorbent	Column (height×I.D., mm)	Conditioning/ washing solvent	Activating solvent	Elution solvent	Refs.
Acetyl-PS–DVB, hydroxymethyl-PS–DVB	8–10×6	Methanol, ethyl acetate, acetonitrile	Methanol	Ethyl acetate	[19]
PRP X-100	125×4	60 mM Nitric acid in 99% methanol	Water at acidic pH	Acetonitrile	[38,39]
PRP X-100	20×2	Acetonitrile–NaOH, pH 10	Aqueous NaOH solution	Water	[41]
Benzoyl-PS–DVB	10×3	Methanol	Water at pH 2.5	Methanol	[21]
Acetyl-PS–DVB	10×3	Methanol	Water at pH 2.5	Methanol	[20]
o-Carboxybenzoyl-PS–DVB	10×3	Methanol	Water at pH 2.5	Methanol	[22]
Bond Elut PPL	10×3	Acetonitrile	Water at pH 2.5	Acetonitrile	[40]
o-Carboxybenzoyl-PS–DVB	10×3	Acetonitrile	Water at pH 2.5	Acetonitrile	[24,36]
o-Carboxybenzoyl-PS–DVB or Bond Elut PPL	10×3	Acetonitrile	Water at pH 2.5	Acetonitrile or acetonitrile–water	[35]
2-Carboxy-3/4-nitrobenzoyl-PS–DVB or 2,4-dicarboxybenzoyl-PS–DVB	10×3	Acetonitrile	Water at pH 2.5	Acetonitrile or acetonitrile–water	[23]
H$_2$TCPP-PS–DVB	50×2		Water at pH 3		[26]
Acetyl-PS–DVB, hydroxymethyl-PS–DVB		Methanol–water		Dichloromethane	[34]
MFE-Polymer with quaternary ammonium groups	150×4.6	60 mM Nitric acid in 99% methanol and water	Not necessary	Methanol–nitric acid solution	[30]
MFE-Polymer with quaternary ammonium groups	150×4.6	60 mM nitric acid in 99% methanol and water	Not necessary	Acetonitrile–60 mM hydrochloric acid solution	[31]

M.E. León-González, L.V. Pérez-Arribas / J. Chromatogr. A 902 (2000) 3–16

11

between two polyethylene or stainless steel frits in glass, polypropylene or steel cartridges which have different column volumes. Prior to their use, columns must be cleaned by passing a solvent through them; sometimes a drying step is also necessary; and finally the sorbent is activated with an organic solvent. Once the analytes are retained, elution is carried out with an organic solvent, whose nature often depends on the detection system used. Some of these variables are summarized in Table 4.

For a maximum efficiency, a SPE column should be very short and should be packed with resin of small particle size. However, smaller particles require higher pressure to force the sample through the column, and incomplete retention of sample solutes can occur because of channeling through short columns. Another design which has become available is the disk. Two different kinds of disks have been used: membranes impregnated with acetyl-PS–DVB resin beads [32] and Empore type membranes embedded with sulfonated resins [27–29,33].

SPE with chemically modified sorbents has been carried out in the off-line and on-line modes. On-line procedures use an extraction sorbent in a pre-column. The methods which combine SPE with HPLC are the most frequently used, mainly to determine polar compounds in water [20–24,35,36,40]. In the on-line procedures there is no sample manipulation between preconcentration and analysis, so loss and contamination risks are avoided, and detection limits and reproducibility values can be better. But the off-line SPE approach will remain useful for analyzing complex samples, because of its greater flexibility and whenever elution solvent is not compatible with the method of analysis or must be reduced before the analysis [19,29,31–34,37,39].

In on-line SPE procedures, sorbents are chosen not only for their efficiency at trapping analytes, but also for their compatibility with the sorbent in the analytical column, which should have the same or higher retention properties as the pre-column material. The pre-column should be as small as possible in order to prevent band broadening [33]. This effect can be minimized using the ''back-flush mode'', in which analytes are desorbed only by the organic solvent of the mobile phase [21–23,35,36,40]. In this mode, the equipment design has been modified and

the mixer chamber has been replaced with a T junction with zero dead volume [1].

5. Efficiency of chemically modified resins

The efficiency of resins used for SPE is most commonly determined by measuring the percentage recovery of test solutes. Several authors [27,33] claim that this process depends on the efficiency of elution of the analytes from the SPE sorbent as well as on the efficiency of the initial extraction step, and they propose another way to compare the behavior of different resins, using the measurement of the capacity factor of the extraction step. Following this procedure, Dumont and Fritz [27] have studied the effect of resin sulfonation on the retention of polar organic compounds and have evaluated the use of sulfonated resins for the separation of groups of neutral and basic organic compounds [33].

Load capacity is another good indication of the extraction ability of the resins. It is defined as the total number of moles or mass of analyte extracted by a given amount of resin. In the case where an ion-exchange mechanism is present, it also gives a rough idea of the accessibility of the functional groups. In the case where the extraction is based only on hydrophobic sorption, it is often related to the specific surface area of the resin in the conditioned state [29]. A critical factor in the enrichment step is the breakthrough volume of the analyte. It corresponds to the aqueous sample volume that can be percolated through the pre-column without any loss of the analyte, i.e., the whole amount of analyte percolated is trapped by the sorbent. The breakthrough volume can be estimated from the capacity factor of the analyte in pure water and the void volume of the column or disk, and taking into account the analytical retention volume of the solute in water [42]. The breakthrough volume can also be determined experimentally though the breakthrough curves, which are determined by passing an aqueous solution of the analyte of interest through the modified sorbent until breakthrough occurs. There are several ways to represent these curves. In one of them [27,29], the ratio of effluent concentration, c, to influent concentration, c_0, is plotted versus the

volume of effluent; the total number of moles of analyte adsorbed is calculated by multiplying the retention volume by the concentration of the influent, where retention volume is defined as the extrapolated volume from the curve at the point $c/c_0 = 0.5$. Volumes between 34 ml for *p*-cresol and 76 ml for nitrobenzene were obtained with an Empore membrane embedded with sulfonated PS–DVB [27]. Other authors have studied the breakthrough volumes by determining the decrease in the recovery of a fixed amount of triazines [39] or phenols [38] in volumes between 250 and 2000 ml. Recoveries higher than 97% were obtained for phenols [38], and between 74 and 101% for triazines [39], when 1000 ml of water was preconcentrated on PS–DVB copolymer containing quaternary ammonium groups. For on-line enrichment, a different procedure has been used to obtain breakthrough curves: a standard solution of the target analyte was directly introduced into the detector, by-passing a valve with the pre-column; when a stable response was obtained, the valve was moved so that the sample was passed through the pre-column at a fixed flow-rate. The breakthrough volume is considered as the volume at which the detector signal reaches 10% of the total signal [21]. Volumes of 14 ml for phenol were obtained with benzoyl-PS–DVB resin [21], *o*-carboxylbenzoyl-PS–DVB [22] and acetyl-PS–DVB [20] using this procedure.

6. Applications

Chemically-modified resins have been developed and used in the SPE of polar compounds mainly from aqueous samples. Several authors have demonstrated that these resins have excellent hydrophilicity and also give higher recoveries than their unmodified analogues [19,27,29,32,33]. This has been attributed to an increase in surface polarity which enables the aqueous sample to make better contact with the resin surface. Table 5 shows some applications as well as the sorbents used.

Of the polar compounds which are of environmental interest, phenolics are a most significant group. They are usually determined by HPLC with UV, fluorescence or electrochemical detection, but none of these techniques allow to reach the detection limits established by the legislation. Several commercial sorbents, such as PLRP-S, Amberchrom, Envi-Chrom P and LiChrolut EN, have been used to preconcentrate phenols by coupling an on-line SPE system to a modified liquid chromatograph, where compounds were eluted only by the organic solvent of the mobile phase [20]. These commercial sorbents have been compared to a chemically modified polymeric resin (PS–DVB) with an acetyl group. The best breakthrough volumes were obtained for the acetyl sorbent and for LiChrolut EN. The acetyl sorbent was more suitable for the determination of phenolic compounds in water than were PLRP-S, Amberchrom or Envi-Chrom P, but gives worse results than LiChrolut EN (a more highly cross-linked and porous polymer with high specific area).

Attempts to improve recoveries of phenols and pesticides in water by SPE coupled to LC–UV have been made, using a chemically modified polymeric sorbent with a benzoyl group [21]. Highly cross-linked copolymers have very different characteristics from those of the stationary phase in the LC analytical column, which may lead to significant peak broadening. To solve this problem, the compounds retained on the SPE column must be eluted with only the organic solvent of the mobile phase. Masqué et al. [21] have followed this procedure when comparing the performance of a benzoyl-PS–DVB sorbent versus that of PLRP-S and Envi-Chrom P. The synthesized sorbent gives better recoveries for oxamyl, methomyl and phenol, and similar results for the less polar compounds, like atrazine, simazine or bentazone. On the other hand, the matrix effect in the Ebro river water was similar for the three sorbents.

In order to increase the polarity of PS–DVB, *o*-carboxybenzoyl has been attached to PS–DVB. The resulting *o*-carboxybenzoyl-PS–DVB sorbent has been tested for the SPE of some pesticides and phenolic compounds in environmental waters [22]. The authors claim that the introduction of a hydrophilic moiety like the *o*-carboxybenzoyl group into the PS–DVB resin increases surface polarity and allows a better contact between the resin surface and aqueous samples. This synthesized sorbent yielded a better breakthrough volume for phenol and better recoveries for the phenolic compounds and pesticides studied than did the commercial sorbents studied. When on-line SPE–HPLC is used to analyze surface

Table 5
Applications using SPE with chemically-modified resins

Analytes	Matrix	SPE phase	Analysis	Ref.
Phenols and pesticides	River water	Benzoyl-PS–DVB	On-line LC–UV	[21]
Polar pesticides and phenols	River water	2-Carboxy 3/4-nitrobenzoyl-PS–DVB or 2,4-dicarboxybenzoyl-PS–DVB	On-line LC–UV	[23]
Carbamates and phenols	Tap and river water	o-Carboxybenzoyl-PS–DVB	On-line LC–UV	[36]
Phenols	Tap and river water	o-Carboxybenzoyl-PS–DVB	On-line LC–UV or LC–electrochemical detection	[35]
Phenols, carbamates and triazines	River water	o-Carboxybenzoyl-PS–DVB	On-line LC–UV	[24]
Phenolic compounds, triazines, carbamates, chlorophenoxy acid and diazines	Tap and river water	Bond Elut PPL	On-line LC–UV	[40]
Phenolic compounds, triazines, carbamates and chlorophenoxy acids	Tap and river water	o-Carboxybenzoyl-PS–DVB	On-line LC–UV	[22]
Phenolic compounds	River water	Acetyl-PS–DVB	On-line LC–UV On-line LC–fluorescence	[20]
Chlorophenoxy acid herbicides	Tap and river water	PRP X-100	On-line LC–UV	[41]
Organic pollutants	Water	Acetyl-PS–DVB or hydroxymethyl-PS–DVB	GC–MS	[34]
Phenol and chlorophenols	Tap water	H$_2$TCPP-PS–DVB	LC–UV	[26]
Triazine herbicides	Surface water	PRP X-100	GC–MS	[39]
Phenols	River water	PRP X-100	LC–UV	[38]
Phenols, aromatic compounds and polyhydroxy aromatic compounds	Water	Acetyl-PS–DVB or hydroxymethyl-PS–DVB	GC–flame ionization detection (FID)	[19]
Phenolic and aromatic compounds	Water	Acetyl-PS–DVB or hydroxymethyl-PS–DVB	GC–FID LC–UV	[33]
Phenols, Alcohols, carboxylic acids, aldehydes, ketones, esters, chloroalkanes, amines and nitrosamines	Pure water	Sulfonated PS–DVB	GC–MS GC–FID	[29]
Polar organic compounds	Pure water	Sulfonated PS–DVB	GC–FID	[27]
Phenols	Water	Acetyl-PS–DVB	GC–FID LC–UV	[32]
Alcohols, esters, ketones, phenols and aldehydes	Urine, bovine serum, albumin and human serum	Sulfonated PS–DVB	GC–FID	[37]
Phenoxy acid herbicide residues	Tomato	MFE-Polymer containing quaternary ammonium groups	LC–UV	[30]
Phenoxy acid herbicide residues	Green bean	MFE-Polymer containing quaternary ammonium groups	Capillary LC–UV	[31]

M.E. León-González, L.V. Pérez-Arribas / J. Chromatogr. A 902 (2000) 3–16

13

water samples containing high levels of humic substances, a matrix interference hampers the determination of the early eluting peaks for the more polar analytes [22,35,36]. This matrix interference increases when a SPE sorbent with high sorptive power is used. Masqué and co-workers [22,35,36] have used different chemical reagents to reduce the initial chromatographic band, which can prevent the analysis of polar organic pollutants in humic-containing water samples.

Other chemical modifications of the PS–DVB with 2-carboxy-3/4-nitrobenzoyl or with 2,4-dicarboxybenzoyl have been made to improve the efficiency of the SPE process by increasing polar interactions with the analytes [23]. Recoveries obtained for oxamyl, methomyl, 2,4-dichlorophenoxyacetic acid, atrazine, phenol, dimethoate and desisopropylatrazine show that the best adsorbent is the one that contains the nitro group in the moiety introduced. The presence of a carboxyl group in the moiety also produces better recoveries.

On-line SPE preconcentration and clean-up has also been used for HPLC determination of chlorophenoxy acid herbicides in water [41]. The extraction and preconcentration of analytes was carried out in a polymeric reversed-phase pre-column, and on-line clean-up was performed by a selective transfer of the ionized compounds to a second pre-column packed with PRP X-100. This method allows the determination of chlorophenoxy acids at low μg l^{-1} concentrations in water. Commercially available columns based on PS–DVB copolymers containing quaternary ammonium groups (PRP X-100) have also been used to preconcentrate triazine herbicides and their degradation products below μg l^{-1} levels from agricultural run-off waters and ground water samples [39]. Breakthrough volumes were larger than 2000 ml, except for cyanazine, whose breakthrough volume was 1000 ml. Triazines were eluted with 10 ml of pure methanol and the collected sample was evaporated under reduced pressure to a final volume of 0.5 ml. Triazines were analyzed by GC–MS, and recoveries between 67 and 105% were found. PRP-X 100 has also been used to preconcentrate priority pollutant phenols from river water [38]. The breakthrough volume was higher than 1000 ml for all phenols studied. After preconcentration, phenols were determined in river water, and the

other organic substances retained in the preconcentration step do not prevent the chromatographic analysis. Recoveries between 92 and 105% were obtained for nitro and chlorophenols added to Manzanares river water.

Sun and Fritz [19] propose the insertion of an acetyl or hydroxymethyl group into porous PS–DVB to provide a more hydrophilic surface, that can be easily wetted by water alone. These authors showed that the modified resins were superior to both silica packings and unmodified organic resins for the SPE of polar organic compounds such as phenols. Schmidt et al. explored the result obtained when acetyl-PS–DVB resins are incorporated into SPE membranes, using them to extract phenols from water [32]. In their study, these authors conclude that phenols in the low ppm concentration range can be concentrated from aqueous samples; recoveries obtained were between 73 and 96% when derivatization was used.

Powell [34] has studied hydroxymethyl- or acetyl-PS–DVB for preconcentration of pollutant compounds. He found that acetyl resin retains triazines such as atrazine better than the hydroxymethyl modified material; but recovery of phenol was very poor. The best recoveries for the 11 test compounds were obtained when acetyl resin and an amino-bonded silica are used together.

Empore membranes embedded with sulfonated resins were used for SPE of compounds such as *p*-cresol, ethyl acetoacetate, isophorone and nitrobenzene [27,33]. These membranes yielded sharper and more efficient breakthrough volumes than those embedded with unsulfonated resins. A thin membrane disk containing lightly sulfonated polystyrene has been used to perform SPE on a semi-micro scale [37]. Semi-micro SPE needs a reduction of the sample size, and the volume of the eluting solvent must be around 20–50 μl.

Different PS–DVB resins have been used for modification with an *o*-carboxybenzoyl moiety for on-line SPE of some polar phenolic compounds, pesticides and metabolites, which were subsequently determined by HPLC–UV [24]. In this study, chemically modified Amberchrom was selected as the best sorbent for trace enrichment of polar compounds. The polarity of its surface and its larger surface area allowed a greater number of two types of interactions

(π–π and polar) with the analytes, and consequently higher recoveries.

In an attempt to improve the efficiency of SPE procedures, materials based on polymers other than PS–DVB have been tested. HEMA containing ammonium functional groups has been used to pre-concentrate phenoxy acid herbicide residues [30,31]. Retention of these herbicides on the referred material is possible in an aqueous acidic medium, probably because of the high polarizing power of the quaternary ammonium groups over the herbicides studied.

A new material based on a cross-linked poly(norbornene-5,6-dicarboxylic acid) has been used to preconcentrate seventy four different analytes with ten types of different functionalities, such as phenols, alcohols, carboxylic acids, esters, aldehydes, ketones, amines, chlorinated hydrocarbons, *N*-nitrosamines and polycyclic aromatic hydrocarbons [29]. Slightly enhanced recoveries were obtained for phenols with this new material, in comparison with the PS–DVB-based membranes. This new resin contains molecular sites which are responsible for the ability to retain hydrophobic compounds like alkyl substances. It also shows a high extraction capability and high recoveries for amines; by contrast, the neutral *N*-nitrosamines are not retained and only *N*-nitrosobutylamine is extracted quantitatively.

7. Conclusions

The chemically modified resins retain a wide variety of organic analytes efficiently. They have a higher sorption capacity for the most polar compounds than their unmodified analogues do. The development of other functionalized polymers and miniaturization would appear to be the next goals for research on SPE.

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