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Journal of Chromatography A, 885 (2000) 51–72

JOURNAL OF  
CHROMATOGRAPHY A

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Review

## Recent developments in polymer-based sorbents for solid-phase extraction

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### Abstract

A review with 136 references on the principles and recent developments in the solid-phase extraction based on polymer sorbents is presented. New polymer-based materials, chromatographic modes, experimental configurations are described and their advantages for a rapid sample preparation of certain classes of compounds with different functional groups are discussed and compared to silica-based sorbents. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Reviews; Solid-phase extraction; Sorbents; Polymer-based sorbents

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## 1. Introduction

The development of a complete analytical method includes a number of steps from sample collection to the final report of the results. Intermediate stages involve sample storage, sample preparation, isolation of analytes, their identification and finally, quantification. However, sample preparation is the most tedious and time-consuming step and a possible source of the imprecision and inaccuracy of the overall analysis. The principal objective of sample preparation for chromatographic analysis are dissolution of the analytes in a suitable solvent and removal from the solution of as many interfering compounds as possible. Therefore, solid-phase extraction (SPE) is widely used for the preconcentration and clean-up of analytical samples, for the purification of various chemicals and for applications such as the removal of toxic or valuable substances from a variety of predominantly aqueous solutions. Typical applications include methods for the determination of trace amounts of pesticides [1,2], determination of trace organic contaminants in water [3,4], analysis of industrial waste waters [5], determination of azaarenes [6], evaluation of porous polymers [7], isolation of organic compounds from ground water [8], sampling of priority pollutants in waste water [9], collection and concentration of environmental samples in general [10] and pretreatment of biological samples, e.g., such as urine [11,12]. SPE was introduced in the early 1970s and avoids or minimizes the disadvantages of liquid–liquid extraction (LLE). Compared to LLE, SPE reduces the time required especially if automated methods are used; it can handle small samples (50–100  $\mu\text{l}$ ) and it requires small volumes of solvent. Before the mid-1970s the term solid-phase extraction did not appear and did not start to be commonly used until 1985. In the last 15 years a great increase in the use of SPE as a preparation step in the overall analytical process has occurred.

For analytical purposes, SPE is usually performed using a small column or cartridge containing an appropriate packing. Also membranes loaded with appropriate resins and solid-phase microextraction (SPME), e.g., for gas chromatographic analysis have been used for SPE [13]. In common practice the adsorbed materials are eluted from the resin with a small amount of organic solvent. The most common-

ly used material for SPE is chemically bonded silica, usually with a  $\text{C}_8$  or  $\text{C}_{18}$  organic group. On the other side the most commonly used polymeric resin in SPE is porous polystyrene. Chemically bonded silica and porous polystyrene have several shortcomings for their use in SPE: (1) while silica itself is hydrophilic and alkaline instable, the hydrocarbon chains make the surface hydrophobic. The consequence is poor surface contact with predominantly aqueous solutions. (2) Porous polystyrene resins also have a hydrophobic surface. (3) 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 [14]. The activating solvent can be leached out of the resin, thereby causing the extraction to become ineffective. This is especially true if the SPE column becomes dry because air is sucked into the column. The results are reduced capacity and reproducibility. (4) Many types of organic compounds are incompletely extracted from predominantly aqueous solutions. This problem especially occurs with bonded silica packings [3,7,9]. The target of creating new types of chemically bonded resins is to overcome these drawbacks.

For an improvement it has been shown that introduction of polar groups into a polystyrene–divinylbenzene (PS–DVB) resin greatly increases the retention of polar organic compounds. As one of the first in 1992, Sun and Fritz [15] modified PS–DVB with alcohol and acetyl functional groups. The modified resins exhibited excellent hydrophilicity and a reduced dependence on wetting prior to extraction. They also yielded higher recoveries compared to their unmodified homologues. According to the chemical character of the functional group chemically bonded to the copolymer the resulting phases are classified as non-polar, polar, or ion exchangers. The polarity depends on the nature of the solid phase, giving rise to different chromatographic modes as in liquid chromatography. Furthermore Schmidt and Fritz [16] showed that also derivatization with other functionalities can be carried out. They used a sulfonated PS–DVB resin for the simultaneous extraction of bases and neutrals. The modified polymeric resins can be used for SPE in either of two modes: resin packed into mini columns or disks of resin-loaded membranes.

During the last few years a series of different

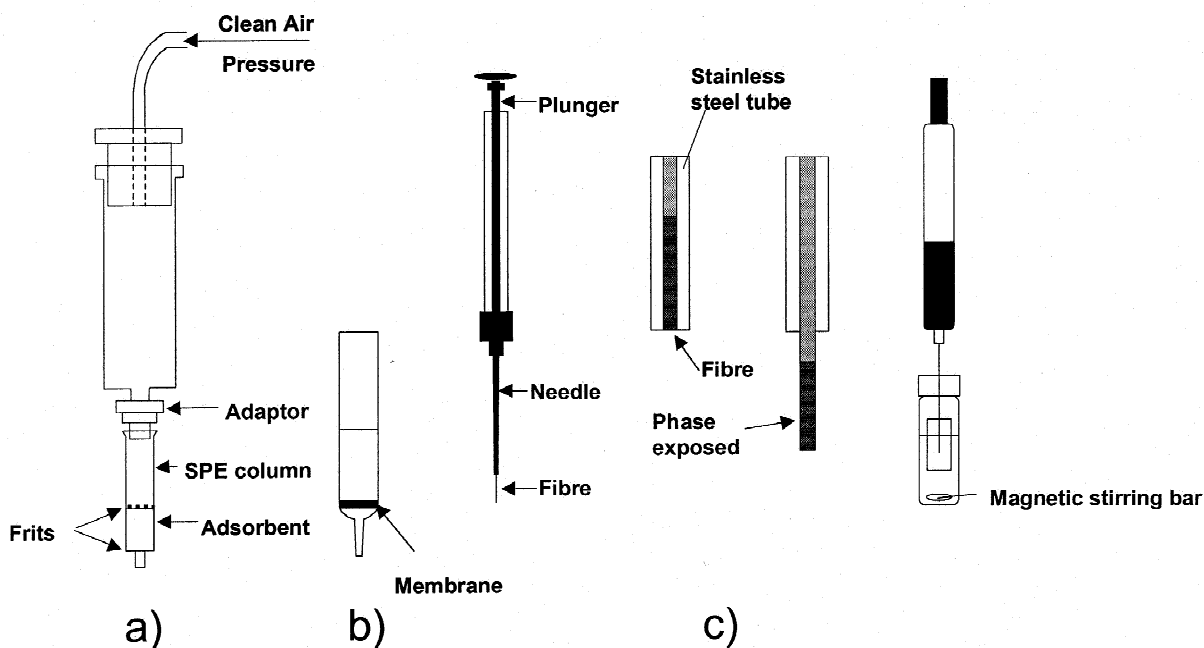


Fig. 1. (a) Solid-phase extraction apparatus; (b) membrane technology for solid-phase extraction; (c) solid-phase microextraction device.

polymer-based materials for the SPE of either acidic, neutral and basic compounds out of different sample matrices have been developed. In general polymer phases have the advantage over bonded silicas that they can be used over the entire pH range and the disadvantage that the conditioning of the cartridge is more time consuming. In this review the synthesis, chromatographic modes, applications, advantages and disadvantages and experimental configurations of polymer-based materials for SPE are discussed and compared to other sorbents.

## 2. Basis of solid-phase extraction

### 2.1. Column technology for solid-phase extraction

The principle of SPE is similar to that of LLE, involving a partitioning of compounds between two phases. It is also similar to liquid–solid extraction (LSE), where the extraction procedure consists in putting into a vessel the analytes with a suitable adsorbent material (solid phase) and shaking for a controlled time [17,18]. In SPE the analytes to be extracted are partitioned between a solid and a liquid – rather than between two immiscible liquids as in

LLE – and these analytes must have a greater affinity for the solid phase than for the sample matrix (retention or adsorption step). Compounds retained on the solid phase can be removed at a later step by eluting with a solvent with a greater affinity for the analytes (elution or desorption step). The different mechanisms of retention or elution are due to intermolecular forces between the analyte, the active sites on the surface of the adsorbent and the liquid phase or matrix. In modern SPE the adsorbent is packed between two fritted disks in a polypropylene cartridge and liquid phases are passed through the cartridge either by suction or by positive pressure (gravity, gas pressure from a syringe or by centrifugation). The experimental procedure consists of the following steps:

1. Activation of the sorbent by passing through an appropriate solvent.
2. Removal of the activation solvent.
3. Application of sample; the analytes will be retained by the sorbent (sorption or retention step).
4. Removal of interfering compounds.
5. Elution of the analytes.

An apparatus that can be used for SPE is shown in Fig. 1a [15]. Modern SPE is, therefore, a technique placed between the classical LSE and column liquid

chromatography and is in full accord with the IUPAC definition of chromatography [19,20].

Possible objectives on SPE are:

- Removal of interfering compounds.
- Pre-concentration of the sample.
- Fractionation of the sample into different compounds or groups of compounds as in classical column chromatography [21–30].
- Storage of analytes that are unstable in a liquid medium or with relatively high volatility [31–33].
- To carry out derivatization reactions between the reactive groups of the analyte(s) and those on the adsorbent surface [33–42].

Therefore the SPE process can be carried out either on-line or off-line. The experimental procedure using the SPE cartridges above is known as off-line SPE. One important parameter to control the development of an SPE method is the breakthrough volume which is the sample volume where the analyte starts to be eluted from the exit of the cartridge. The value of breakthrough volume is a function of the chromatographic retention of analyte on the particular sorbent in the SPE cartridge and can only be altered by a change of sorbent [43,44].

## 2.2. Membrane technology for solid-phase extraction

Membranes or disks consist of a 0.5 mm thick membrane (Fig. 1b) whereas the adsorbent is immobilised in a web of microfibrils, which allows higher flow-rates than SPE cartridges [45–50]. There are two distinct types of membranes available commercially, whereas the most used one is Empore from 3M (St. Paul, MN, USA). Normally membranes are used when the sample volume is very large and the concentration of the analytes is low, e.g., in the trace analysis of organic pollutants in water. Extraction disks can also be coupled on-line with liquid chromatographic systems using specifically designed disk holders [51–54]. Furthermore it was shown, that it is also possible to couple extraction disks on-line with a gas chromatographic system for the determination of organophosphorous pesticides in water [55]. The extraction process can be performed in three different ways:

(i) The sample is passed through the disk with the aid of a vacuum source. The analytes are retained

and then removed with a small volume of a suitable eluent.

(ii) The membrane is suspended in the liquid sample for a controlled period of time, then allowed to dry briefly in air and finally the analytes are directly detected by means of a solid state spectroscopic technique.

(iii) Similar to the second point, but the analytes are desorbed by suspending the disk in a solvent and then detected in the extract.

## 2.3. Solid-phase microextraction

Solid-phase microextraction (SPME) has gained widespread acceptance in many areas in recent years. It has been applied for the determination of a wide spectrum of analytes in a variety of matrices. The most widespread seems to be the analysis of volatile and semi-volatile compounds in water. Examples in this area include the determination of substituted benzene compounds [56,57], volatile organic compounds [58–60], polycyclic aromatic hydrocarbons and polychlorinated biphenyls [61], pesticides [62–67], phenols [68,69], fatty acids [70], as well as lead [71]. In SPME the solid phase is a fiber of various materials [72–76]. Possible solid phases that have been investigated include, e.g., polyimide, fused-silica, liquid crystal polyacrylate, Carbowax, cross-linked Langmuir–Blodgett layers, Carbowax and graphite. There are two distinct types of SPME coatings available commercially: poly(dimethylsiloxane) (PDMS) and poly(acrylate) (PA). The remaining coatings, including PDMS–DVB, Carbowax–DVB, Carbowax–TR (template resin–DVB with uniform pore sizes) and Carboxen, are mixed coatings in which the primary extracting phase is a porous solid. For protection the fiber is housed in the needle of a microsyringe (Fig. 1c). In use the plunger is depressed a measured amount thus lowering the fiber into the liquid sample for a controlled period of time. Analytes are adsorbed aided by agitation to the sample with a spin bar. Adsorption is complete after about 10 min. Then the fiber is withdrawn into the needle. Analytes are thermally desorbed by introducing the needle into the heated injector of a gas chromatograph. This procedure can be applied to the vapor phase in equilibrium with a liquid or a solid to effect headspace sampling of volatiles.

### 3. Polystyrene–divinylbenzene-based sorbents

#### 3.1. Polystyrene–divinylbenzene-based polymers

PS–DVB resins are finding increasing use because of their efficiency, ruggedness and wide pH stability.

##### 3.1.1. Acetyl and hydroxymethyl derivatized polystyrene–divinylbenzene materials

Various hydrophilic functional groups were chemically attached to the benzene rings of porous, cross-linked polystyrene resins [77] as stationary phase for high-performance liquid chromatography (HPLC). Furthermore it was found that the efficiency of porous resins used in SPE varies with the porosity, those with the largest surface area giving the greatest retention [78]. Sun and Fritz [15] inserted an acetyl- or hydroxymethyl group into a porous PS–DVB Amberchrome 161 (Supelco, Bellefonte, PA, USA, spherical, 50  $\mu\text{m}$ , 720  $\text{m}^2/\text{g}$ ) resin that provides a more hydrophilic surface and is easily wetted by water alone. The acetyl derivative was prepared by reaction with acetyl chloride. Small columns of these chemically modified resins were found to be very efficient for the SPE of many types of organic solutes from aqueous samples. Comparative recovery studies showed that especially the acetyl resin and even the hydroxymethyl modified surface are superior to both silica packings and unmodified organic resins for the SPE of organic compounds, and especially for polar organics such as phenols, aliphatic and pyridinic compounds (Table 1). For aliphatic and pyridinic compounds the average of the recoveries was 95% for Amberchrome 161–COCH<sub>3</sub>, 81% for Amberchrome 161 and 65% for C<sub>18</sub> Si. The organic compounds eluted from SPE column with ethyl acetate were collected and analyzed using gas chromatography (GC) with flame ionization detection (FID) [15].

##### 3.1.2. Acetylated polystyrene–divinylbenzene materials used in membrane technology

In order to allow the use of large sample volume membranes derivatized with an acetyl group can be used, which shows excellent hydrophilicity and a lesser dependence on wetting prior to extraction. These membranes also yielded higher recoveries compared to the unmodified analogue. This is attributed to an increase in surface polarity allowing the aqueous sample to make better contact with the resin surface. Fritz et al. [79] also investigated membranes impregnated with PS–DVB or acetyl-PS–DVB resin beads for SPE of ppm (w/w) concentrations of phenols from aqueous samples. Spherical highly cross-linked 5–8  $\mu\text{m}$  PS–DVB resins with a specific surface area of 400  $\text{m}^2/\text{g}$  (Sarasep, Santa Clara, CA, USA) were investigated. In a macro procedure 47 $\times$  0.5 mm disks with 200–500 ml sample volumes at approximately 200 ml/min flow-rates and in a smaller-scale procedure a thicker disk (3 mm) packed into a conventional SPE column (7 mm I.D.) were used. It was shown that samples of 500 ml can be passed through a 47 mm membrane disk using conventional filtration under reduced pressure very rapidly (ca. 2.5 min). For subsequent elution of the analytes a total of three 3-ml portions of tetrahydrofuran (THF) is recommended. Recoveries for 16 different phenols, including those included in the US Environmental Protection Agency (EPA) list of priority pollutants, averaged 98% with a standard deviation of  $\pm 2\%$  [80].

##### 3.1.3. Polystyrene–divinylbenzene sulfonated resins

It could be clearly demonstrated that lightly sulfonated PS–DVB resins (5–8  $\mu\text{m}$ , 400  $\text{m}^2/\text{g}$ , Sarasep, Santa Clara, CA, USA) display excellent hydrophilicity and improved extraction efficiencies of polar organic compounds over underivatized resins [79]. The degree of sulfonation has a major

Table 1  
Recoveries (%) of phenols, aromatic compounds and polyhydroxy aromatic compounds by SPE under wet loading conditions [15]

Compound	Recovery (%)			
	C <sub>18</sub> Si	Amberchrome PS–DVB	Amberchrome PS–DVB–CH <sub>2</sub> OH	Amberchrome PS–DVB–COCH <sub>3</sub>
Phenol	6	91	94	100
<i>p</i> -Cresol	16	91	98	101
Anisole	78	91	94	98
Nitrobenzene	54	92	96	100

effect on retention of such compounds [80]. The best performance for SPE was found to be with resins with about 0.6 mequiv./g of sulfonate groups. Sulfonated resins can also be used for group separation of neutral and basic organic compounds. The effect of sulfonate capacity of the resin on SPE was studied by measuring the capacity factor ( $k$ ) of several solutes using a very small column packed with a sulfonated resin. A plot of the capacity factor  $k$  for phenol as a function of resin sulfonate capacity is given in Fig. 2. Curves of very similar shape were obtained for catechol, ethyl pyruvate and 2,3-butanedione, although the capacity factors of these are lower than for phenol. Fritz et al. found that the following points are significant for the solutes tested:

(1) For all tested compounds the plot has a maximum at approximately 0.6 mmol sulfonate/g resin. This value correlates with the onset of wetting of the dry resin by water without any pretreatment.

(2) Increasing degrees of sulfonation cause a marked decrease in  $k$ .

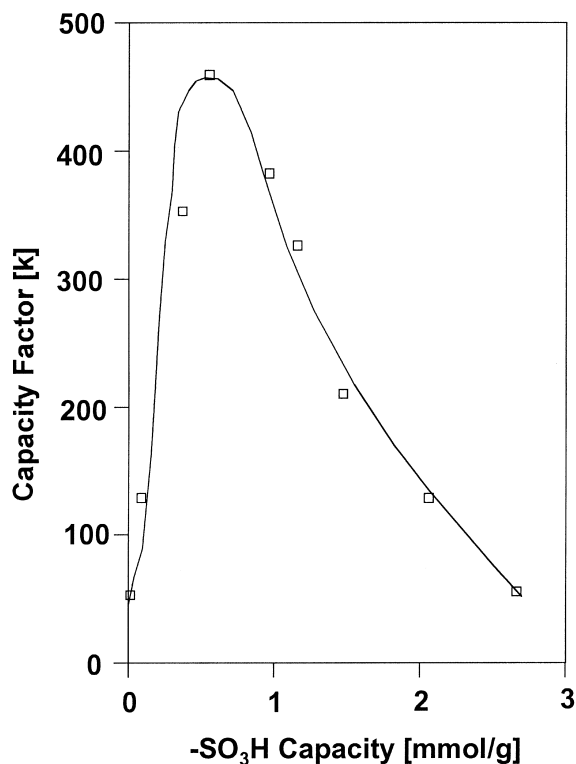


Fig. 2. Capacity factors of phenol on sulfonated resins (aqueous solution) [79].

(3) For an average capacity of 0.6 mmol/g unsulfonated resin and sulfonated resin 2.17 mmol/g were mixed. It was shown that the  $k$  for this mixture was low (ca. 50), indicating that the actual degree of sulfonation, rather than the average degree of sulfonation, is the critical factor.

Table 2 compares the recoveries of several analytes on sulfonated and unsulfonated SPE resin columns. The data indicate that it is not necessary to pretreat the column, e.g., with methanol when a sulfonated resin is used. With samples containing different organic compounds it is often desirable to simplify the analysis by a preliminary separation into neutral, basic and acidic groups. Sulfonation of a polymeric resin converts it into a cation exchanger. If the sulfonation is performed quickly under very mild conditions, the resulting resin contains solutes by two different mechanisms. Neutral compounds are retained by simple adsorption, while protonated bases are retained by an anion-exchange mechanism. This means, that simultaneous concentration of organic compounds thus becomes possible from aqueous samples, followed by selective elution of neutral and basic compounds. The scheme for separating neutral and basic organic solutes into groups is as follows:

- The organic solutes are retained by passing an aqueous sample (adjusted to pH 2.0) through a column packed with a porous resin with a sulfonate capacity of approximately 1.0 mmol/g.
- Neutral compounds are eluted with methylene chloride and the compounds are determined by GC.
- Basic compounds are eluted by 2 M methylamine in methanol and the individual solutes separated and determined by GC.
- A solution of 2 M HCl in methanol is passed through to generate the resin.

Schmidt and Fritz [16] applied this scheme for the extraction of five neutral and six basic compounds out of an aqueous matrix. After preconcentration the compounds were separated into groups. Fig. 3a shows the gas chromatogram obtained for the neutral group. Fig. 3b shows the gas chromatogram of the compounds in the basic group.

Fritz et al. describe furthermore that for optimum efficiencies a SPE column should be very short (a few millimeters) and be packed with resins of

Table 2  
Comparison between sulfonated (0.4 mequiv./g) and unsulfonated PS–DVB resins<sup>a</sup> [79]

Compound	Recovery (%)			
	PS–DVB sulfonated		PS–DVB unsulfonated	
	Not wetted	Wetted	Not wetted	Wetted
Anisole	94	96	83	89
Benzaldehyde	90	89	87	96
Nitrobenzene	96	95	88	96
Hexylacetate	94	94	84	82
Benzylalcohol	90	98	78	81
Phenol	98	95	77	89
Catechol	59	34	ND	ND
<i>m</i> -Nitrophenol	98	99	89	95
Mesityl oxide	98	97	93	99
<i>tert</i> -2-Hexenyl acetate	93	90	79	89
Average±RSD (%)	95±3.2	94±3.4	84±5.5	91±6.3

<sup>a</sup> Wetting solvent is methanol. Average of three runs. ND=Not detected.

particle size in the range of 5–10  $\mu\text{m}$ . Smaller particles require a higher pressure to force the sample through the column. Incomplete retention of samples can occur because of channeling through very short columns. These difficulties can be largely avoided by using sulfonated resin-loaded membranes, which again show decreased channeling and

improved mass transfer [80]. These sulfonated membranes can be used much like a piece of filter paper in a Büchner funnel. An extensive survey was made of 44 different analytes (1 ppm each) using sulfonated resin (0.6 mmol/g). The analytes included several compounds containing each of the following functional groups: alcohol, phenol, aldehyde, ketone,

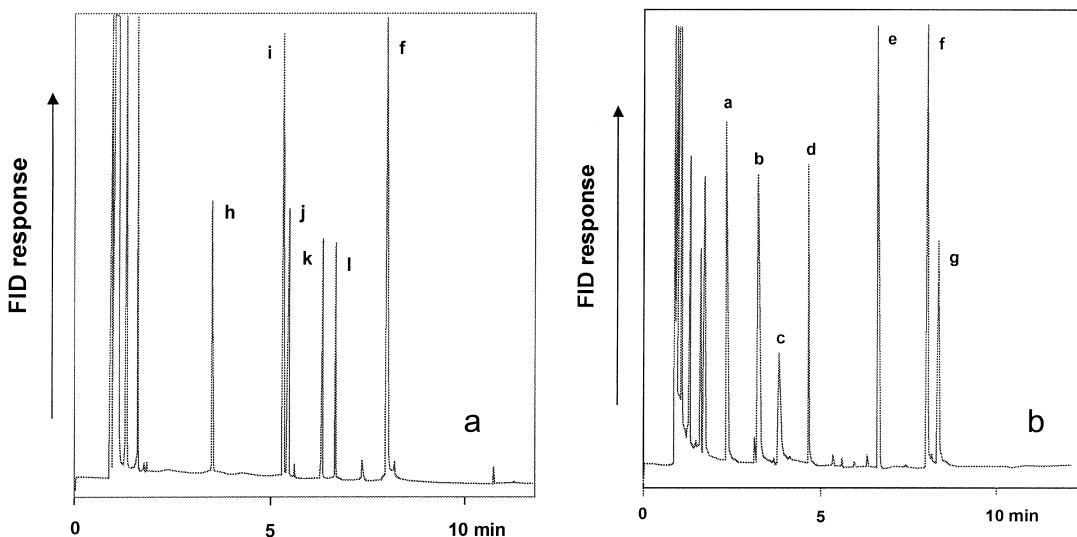


Fig. 3. (a) Gas chromatogram of neutral compounds concentrated from aqueous solution with ion-exchange resin and eluted with methylene-chloride. Peaks: h=ethyl crotonate; i=propyl benzene; j=1-octanol; k=benzonitrile; l=nitrobenzene; and f=quinoxaline (internal standard). (b) Gas chromatogram of basic compounds concentrated from aqueous solution with ion-exchange resin from aqueous solution and eluted with methylamine in methanol. Peaks: a=pyridine; b=hexyl amine; c=cyclohexyl amine; d=2,4-lutidine; e=*N,N'*-dimethyl aniline; f=quinoxaline (internal standard); and g=quinoline [16].

ether, ester, haloalkane, nitrile and nitro. The average recovery was 96% with a relative standard deviation (RSD) of ca. 3%. Breakthrough curves for *p*-cresol, ethyl acetoacetate, isophorone and nitrobenzene were used to compare membranes with sulfonated and unsulfonated resin (Fig. 4). The sulfonated membrane yielded sharper and more efficient breakthrough for all compounds tested [81]. Since breakthrough is closely related to  $k$  [82], the breakthrough volume ( $V_B$ ) or retention volume ( $V_R$ ) for a particular analyte is a good indication of the extraction ability of the resin.  $V_B$  is defined as the volume after extrapolating the middle portion of the curve to the  $x$ -axis, and  $V_R$  as the volume at  $C/C_0=0.5$ .  $C/C_0$  is the ratio of analyte effluent concentration to influent concentration. The resin load capacity may also be determined from a breakthrough curve. This is the total number of moles of analytes adsorbed by a resin, and is calculated by multiplying  $V_R$  by the influent concentration [83]. Dumont et al. compared the breakthrough curves for two membranes – one embedded with underivatized PS–DVB and the other with sulfonated PS–DVB (0.6 mequiv./g capacity). In this study the sulfonated resin membrane, being more hydrophilic, produced a much sharper breakthrough than the underivatized membrane which allows breakthrough almost immediately. Further-

more, extraction efficiency of the more polar compounds like *p*-cresol and ethyl acetoacetate is dramatically increased with the sulfonated membrane. It may be expected that less polar compounds would be more easily extracted with an underivatized resin, but this is not necessarily the case. The less polar compounds, such as nitrobenzene and isophorone, have slightly higher load capacities and  $V_R$  on the underivatized membrane, whereas  $V_B$  is much lower. This is caused by the poor curve shape and early breakthrough on the underivatized membrane. It shows that  $V_B$  is the parameter of most concern for SPE because dilute samples are usually used and the load capacity of a resin is seldom approached. A sulfonated membrane would therefore be the better adsorbent to use for SPE of these types of compounds.

#### 3.1.4. Comparison of silica-based sorbents with polystyrene–divinylbenzene SPE-based materials

A solvent effect as the origin of the porous-polymer sorbent's favorable retention of hydrogen-bond substances compared to octadecylsiloxane-bonded, silica-based material especially for membranes and furthermore in general was described by Mayer et al. [84]. Because of the fact that the most important factor in determining breakthrough vol-

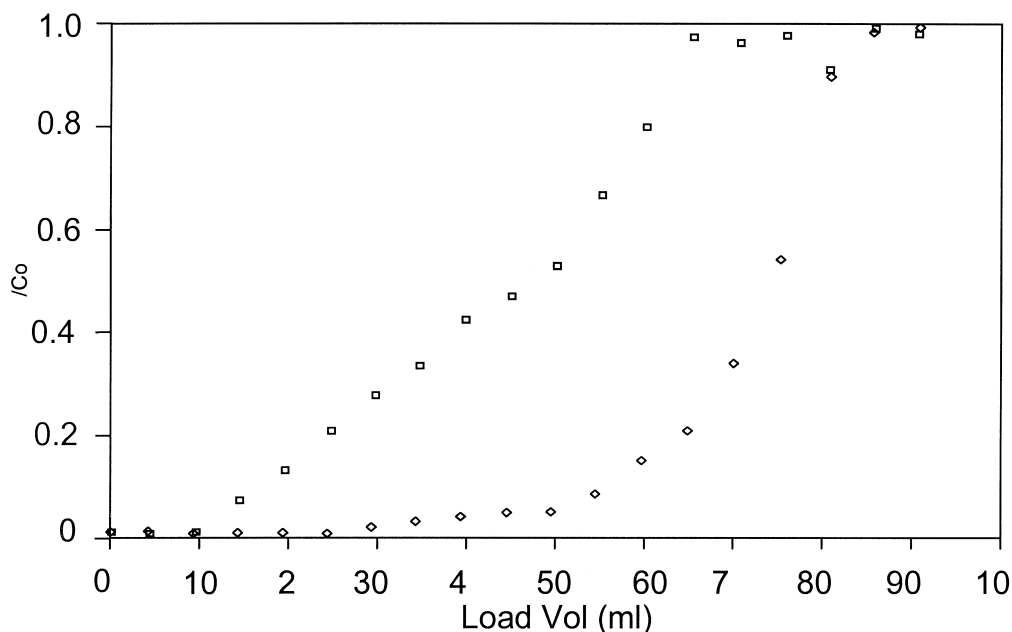


Fig. 4. Breakthrough curves for *p*-cresol on a PS–DVB sulfonated (◇) and PS–DVB unsulfonated (□) membrane [80].



umes was retention a solvation parameter model to characterize retention in terms of solute and sorbent characteristics based on Eq. (1) was established for the better understanding of the extraction mechanism using particle-loaded membranes:

$$\log V_B = c + mV_x/100 + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H \quad (1)$$

where  $V_B$  is the breakthrough volume,  $V_x$  the solute's characteristic volume,  $R_2$  the solute's excess molar refraction,  $\pi_2^H$  is a measure of the solute's ability to stabilize a neighboring dipole by virtue of its capacity for orientation and induction interactions, and  $\alpha_2^H$  and  $\beta_2^H$  are parameters characterizing the solute's hydrogen-bond acidity and basicity, respectively. The system coefficients  $m$ ,  $r$ ,  $s$ ,  $a$ ,  $b$  and  $c$  are characteristic of the sampling system (sorbent and sample solvent). The parameters are evaluated by multiple linear regression analysis by determining the breakthrough volume for a series of solutes with known explanatory variables. This model allows to estimate for any solute in the sampling system for which the solute explanatory variables are known or can be reasonably estimated from empirical combining rules [85–88].

Cavity formation is significantly easier for the solvated octadecylsiloxane-bonded silica sorbent than is the case for the solvated porous polymer. All polar interactions favor solubility in the sample solvent and result in a general decrease in the breakthrough volume. The reason that silica-based material can more effectively compete with water as a hydrogen-bond base than can the porous polymer is that most likely due to the lone pair electrons on the oxygen of the siloxane and silanol groups. Water is a moderate hydrogen-bond acid and methanol should be able to effectively compete with it. The porous polymer is effectively hydrophobic and should take up methanol in preference to water in a more selective manner than the structurally heterogeneous silica-based sorbent with its significant proportion of polar groups. The silanol groups of the silica-based material must be effectively involved in internal hydrogen bonding and hydrogen bonding to sorbed components of the sample solvent, and are unavailable to solutes entering the sorption layer. The difference in relative concentration of methanol, and possibly the thickness of the sorption layer, is

responsible for the greater apparent hydrogen-bond acidity of the porous-polymer sorbent compared to the silica-based material. Differences in extraction properties of the two materials can be highlighted by considering the contribution of individual intermolecular interactions to the breakthrough volume. For non-polar compounds and weakly polar compounds like *n*-butylbenzene the octadecylsiloxane-bonded silica sorbent is preferred. Most dipolar compounds are hydrogen-bond bases and for these compounds retention on the porous polymer is more favorable because of the higher cavity term. In general for the retention of low-molecular-mass polar solutes the porous polymer sorbent provides larger breakthrough volumes because it more effectively competes with water in dipolar and solute hydrogen-bond base interactions. On the other side the octadecylsiloxane-bonded sorbent has a more favorable cavity term and competes more effectively with water for solutes that are hydrogen-bond acids but, in general, for polar solutes the balance of all interactions still favors retention by the porous polymer. Furthermore it has to be mentioned that the addition of a small amount of organic solvent to the sample is not a completely necessary step [89]. The discussed results suggest that the selectivity of the sorbent is significantly influenced by the choice of organic solvent employed. In most cases methanol is used but sorbents with a contra selectivity may be capable of significant changes in breakthrough volumes. The experimental protocol in combination with the solvation parameter model provides an experimental framework to study these effects quantitatively.

### 3.2. Polystyrene–divinylbenzene monolithic derived materials [90]

In order to get cheap SPE materials the synthesis of this stationary phase was carried out with styrene, divinylbenzene and dodecanol or other porogenic solvents and polymerized within 16 h at 75°C initiated by azoisobutyronitrile (AIBN) [91]. This very rapid synthesis yields a polymeric block, which can easily be crunched, e.g., by a vibration ball mill to a macroparticulate polymeric material. Depending on the solvent applied during the polymerization procedure, materials of different porosity and surface areas can be obtained. Small, macroporous 3–5 μm particles are forming larger conglomerates in the

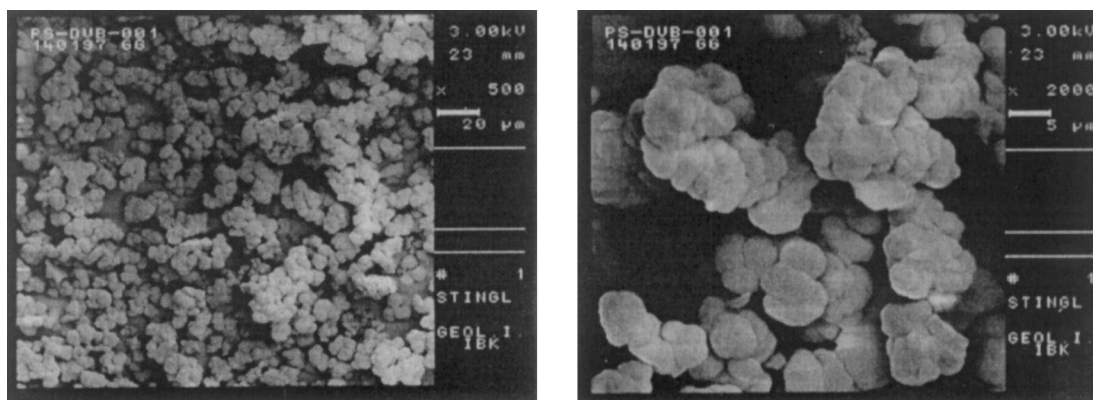


Fig. 5. Scanning electron micrographs of the crushed units of PS-DVB-*n*-dodecanol, magnified 500 and 2000 times [90].

range of 50–70  $\mu\text{m}$  (Fig. 5). The porous properties of the resin are affected by the concentration of the free-radical initiator, the degree of crosslinking and the type and amount of porogen [92]. Using these resins for SPE in environmental analysis, e.g., pesticides, it shows the advantage of high recoveries and easy handling properties during all SPE steps. The developed resins yield excellent recoveries of 13 investigated organochlorine and organophosphorous pesticides. The PS-DVB-*n*-octanol sorbent yields better recoveries than a commercially available reversed-phase sorbent on the basis of silica gel which is normally used in standard procedures (Table 3). The average recovery using the crushed

material was 77% compared to 69% using silica-based sorbents.

Tsyurupa et al. [93] describe the on-line pre-concentration of phenols and chlorophenols in a sorption cartridge packed with microporous hyper-crosslinked polystyrene for the determination by HPLC. Biporous hyper-crosslinked polystyrene-type sorbents were shown to effectively purify about 100 bed volumes of water from phenol under neutral or acidic conditions and linear flow-rates up to 4 cm/min, which is of big practical importance. Rapid and quantitative elution of sorbates from the hyper-crosslinked polystyrene materials is facilitated by the unique ability of the latter to additionally swell with

Table 3

Comparison of recoveries (%) for pesticides using a PS-DVB sorbent and a reversed-phase sorbent on silica basis [90]

Pesticide	Symbol	Recovery (%)	
		PS-DVB- <i>n</i> -octanol monolithic derived materials	Speed C <sub>18</sub> /18%
$\alpha$ -Hexachlorocyclohexane	$\alpha$ -HCH	100	90
$\beta$ -Hexachlorocyclohexane	$\beta$ -HCH	99	95
Lindane	Lin	99	93
Quintozine	Quin	75	74
$\delta$ -Hexachlorocyclohexane	$\delta$ -HCH	98	92
Heptachloroepoxide	HCE	82	67
<i>o,p</i> -Dichlorophenyl-dichloroethane	<i>o,p</i> -DDE	53	51
$\alpha$ -Endosulfane	AEN	86	72
<i>p,p</i> -Dichlorodiphenyl-dichloroethene	<i>p,p</i> -DDE	50	46
<i>o,p</i> -Dichlorodiphenyl-dichloroethane	<i>o,p</i> -DDE	72	56
<i>p,p</i> -Dichlorodiphenyl-dichloroethane	<i>p,p</i> -DDD	67	62
<i>o,p</i> -Dichlorodiphenyl-trichloroethane	<i>o,p</i> -DDT	57	51
<i>p,p</i> -Dichlorodiphenyl-trichloroethane	<i>p,p</i> -DDT	57	49
Average recovery (%)		77	69

organic or aqueous–organic eluents applied. Hypercrosslinked polystyrene sorbents are neutral hydrophobic polymers containing no polar groups. Nevertheless, they definitely swell with water. This unusual property is caused by the high inner strains which exist in the network of the dry material. When, after the synthesis, the reaction solvent is evaporated from the final gel, inner strains appear and grow, because many rigid bridges which were introduced in the swollen state prevent and finally stop the shrinkage of the polymeric network. The dry material obtained has low density, which makes it accessible to small molecules. Moreover, because of the strains, the network tends to return into the swollen unstrained state by incorporating any organic molecules or, to a smaller extent, water. This relaxation of inner strains and expansion is an important driving force for adsorption of all organic compounds from aqueous and gaseous media. On the other hand, an additional increase in the volume of the polymeric phase on replacing water for an organic or aqueous–organic eluent strongly facilitates a rapid and quantitative desorption of compounds extracted from water and air.

### 3.3. Possibility of storing compounds on polymeric solid-phase extraction cartridges

Ferrer and Barceló [94] describe the use of PS–DVB copolymer-based stationary phases for the storage of pesticides. They investigated the stability of four pesticides (desethylatrazine, fenamiphos, fenitrothion and fonofos) under different storage conditions after preconcentration in disposable SPE cartridges containing new polymer sorbent materials (Hysphere and LiChrolut). They found that complete recovery for all the compounds in a ground water sample was observed for 1 month when the temperature was kept at  $-20^{\circ}\text{C}$ . Degradation of fenamiphos and fenitrothion occurred in pre-columns stored at  $4^{\circ}\text{C}$  and at room temperature after 1 month. Fonofos was stable when compared to the storage in  $\text{C}_{18}$  pre-columns. The influence of the pH of the water sample on the concentration and the chemical structure of the pesticides was investigated which resulted in significant losses of fenamiphos and fenitrothion. A comparison of the breakthrough volumes for the two kinds of sorbent material showed that they are comparable with the exception of desethylatrazine.

The breakthrough volumes obtained with Hysphere-1 cartridges for desethylatrazine is higher than 300 ml while in  $\text{C}_{18}$  cartridges the breakthrough is around 20 ml. As expected, the polymeric phase retains polar analytes in a larger extension than the conventional  $\text{C}_{18}$  ones. Other studies from the group of Ferrer and Barceló [94] in off-line [95] and on-line [96] for organophosphorus and phenolic compounds indicated that LiChrolut offers high recoveries due to a large surface area and the type of interaction with polar analytes.

## 4. Ring-opening metathesis polymerization-based polymers

A high-capacity carboxylic acid-functionalized resin prepared by ring-opening metathesis polymerization (ROMP)-based on cross-linked *endo,endo*-poly(norborn-2-ene-5,6-dicarboxylic acid) for the sampling of volatile, airborne amines from polyurethane (PU) foams was described [97–99]. Six tertiary amines namely pentamethyldiethylenetriamine (PMDTA), diazabicyclooctane (DABCO), *N*-methylmorpholine (NMM), *N*-ethylmorpholine (NEM), 1,4-dimethylpiperazine (DMP) and *N,N*-dimethylethanolamine (DMEA) (Fig. 6) which represent commonly used promoters for the formation of PUs from diisocyanates and polyols were investigated. The COOH-functionalized resin consists of an inert, crosslinked interior and a molecular fur, bearing the linear chains formed by the functional monomers at the outside [99,100]. The preparation of the carboxylic acid-functionalized resin is given in Fig. 7. The synthesis was performed by reacting molybdenum-based Schrock-carbenes with the functional monomer norborn-2-ene-5,6-dicarboxylic acid anhydride. The resulting prepolymer was cross-linked using 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene to form particles. All functionalities are readily available for ion pairing and additionally the carboxylate groups provide sufficient hydrophobicity [98]. Electron microscope investigations revealed that the material consists of irregularly shaped, agglomerated particles with a non-porous structure. The material is entirely pH stable and reusable for at least 30–40 times without any loss of performance. Recoveries were determined by passing known amounts of the amines over

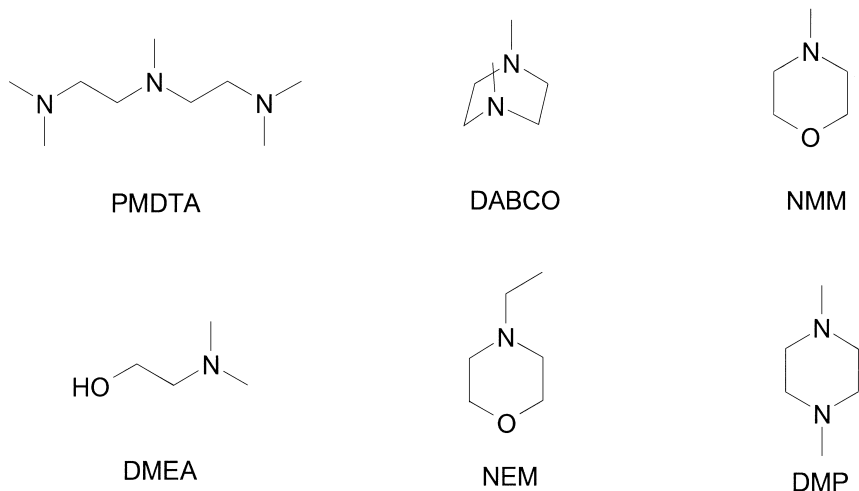


Fig. 6. Structures of tertiary amines [97].

the resin using single compound standards (Table 4). Finally, the new carboxylic and derivatized resin provided excellent properties for the sampling of airborne aliphatic mono-, di- and triamines. The resin allows the sampling of non UV-absorbing, non-derivatizable, polar amines with high extraction efficiencies and recoveries. The high recoveries which

were obtained over a broad range of concentration in SPE experiments using solutions of the amines were also observed in the sampling of the same compounds from the gas phase. It was shown, that the combination of GC–mass spectrometry (MS) with Fourier transform infrared spectroscopy (FT-IR) additionally allowed the fast recording of concen-

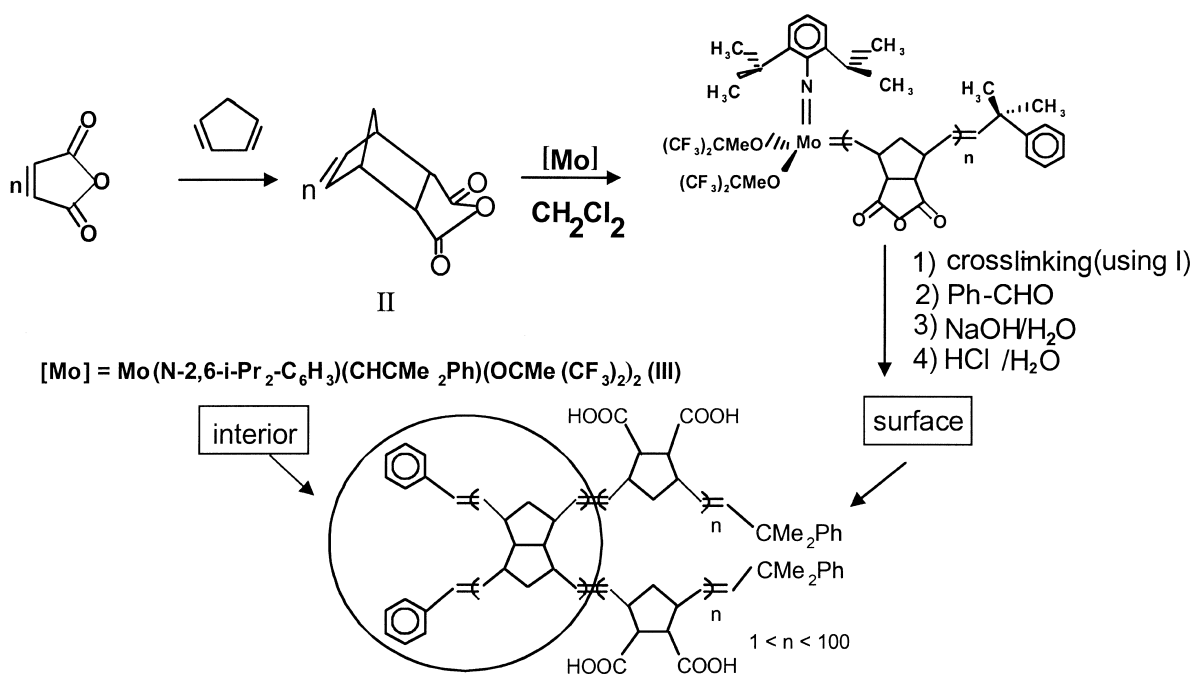


Fig. 7. Preparation of the ROMP-COOH-functionalized resin [101].

Table 4  
Recoveries of amines using single compound standards in methanol (50 mg resin) [97]

Amine	Concentration (ppm)	Recovery (%)	Loading (% of capacity)
PMDTA <sup>a</sup>	300	117.9	10.8
	100	98.0	1.8
	5	102.7	0.9
DABCO <sup>a</sup>	275	103.3	12.1
	100	101.2	1.9
	5	100.6	1.0
MMM <sup>b</sup>	100	95.7	1.1
	66	93.4	1.4
	5	92.7	0.5
MEM <sup>b</sup>	100	96.7	0.9
	70	91.5	1.3
	5	89.7	0.5
DMP <sup>b</sup>	100	95.4	1.9
	65	93.3	3.6
	5	95.3	0.9
DMEA <sup>b</sup>	100	101.2	1.2
	75 <sup>c</sup>	90.0	3.6
	5	95.1	0.6

<sup>a</sup> Elution with 3 ml Et<sub>3</sub>N–MeOH (50:50).

<sup>b</sup> Elution with 2 ml Et<sub>2</sub>NH–MeOH (50:50).

<sup>c</sup> One hundred mg resin.

tration profiles. In general the entire set-up allows the fast routine analysis of volatile, basic compounds. Additionally, the high stability of the resin as well as the high loading capacities make the ROMP-material highly attractive as filter materials for air clean-up. Compared to the porous PS–DVB crunched material and the octadecylsilica-based sorbent the ROMP-material showed in average the same recovery (77%) as the crunched material and a higher average recovery than the silica-based material for the extraction of the pesticides listed in Table 3.

Following the new concept for the preparation of carboxylic acid-functionalized resins for SPE with significantly enhanced capacity using ROMP, dipyriddy amide-functionalized resins have been prepared by Sinner et al. [101]. Calculation of crystal data showed that the angle between the nitrogen atom of the carboxylic acid amide allows the extraction of only “soft” metal ions such as Pd<sup>2+</sup> and

Hg<sup>2+</sup>. Detailed investigations on the extraction selectivity and efficiency for both metal ions were performed by variation of pH and concentration. To obtain some insight into kinetics, experiments were carried out using both standard SPE techniques as well as batch experiments. Selectivity was found to be dependent on the presence of certain inorganic ions. While unbuffered or acetate-buffered systems lead to a decrease in affinity of the corresponding metal ions toward the solid phase in the order Pd > Hg > Cu > Os > Ir ~ Rh, the presence of phosphate seems to favor the extraction of mercury. Selectivity is changed to the following order: Hg > Cu > Pd > Os > Ir ~ Rh. The high affinity of the new resins toward these two metal ions is underlined by the fact that these metals may be extracted quantitatively over a broad range of concentrations. Another interesting property for this new type of resin for large-scale industrial applications is the fact, that high metal loadings may be achieved. Table 5 gives an overview of the maximum loading prior to breakthrough for different concentrations of the analytes. Additionally, data for batch experiments showed, that high loadings up to 60% and more may be achieved for both metal ions in this type of extraction. This corresponds to an amount of 65 mg of palladium and 120 mg of mercury per gram of resin. While both metal ions are extracted with about the same efficiency in a batch experiment, considerable lower loadings of mercury compared to palladium are obtained in a flow through experiment using packed columns. This indicates a higher rate constant for the formation of the palladium complex in comparison with the one for mercury. Once bound to

Table 5  
Maximum loadings for mercury and palladium using dipyriddy amide-functionalized polymers prepared by ring opening metathesis polymerization (ROMP) [101]

Metal ion (concentration)	Loading (% of theoretical capacity)
Pd (1%)	57
Pd (1000 ppm)	50
Pd (100 ppm)	42.3
Pd (20 ppm)	14.1
Hg (1%)	52.6
Hg (25 ppm)	2.47
Hg (18 ppm)	2.31
Hg (225 ppb)	1.35

the resin, the metals may again be removed therefrom by recomplexation. Thus, elution of a palladium-loaded column with a few milliliters of a solution of thiourea (0.5 M) in 1.5 M HCl or in THF–water (10:90) allows a quantitative recovery (99%) of the metal. The same high recoveries are obtained for a mercury-loaded column using solutions of dimercaptosuccinic acid (DMSA) in THF–methanol (20:80).

Buchmeiser et al. also described a high-capacity carboxylic acid-functionalized resin prepared by ROMP containing *cis*-1,4-butanedioic acid (succinic acid) units for the extraction of rare-earth elements (REEs) from rock digests [102]. The large amount of polar groups ensures a high wettability of the resin by water. A small amount of the material (usually 0.3 g) allows the quick, simple, and quantitative extraction of lanthanides from standards over a broad range of concentrations (Table 6). At a suitable pH, all other metal ions, such as group 2 metals are not retained. The quantitative removal of large amounts of interfering metal ions, especially Fe(III) and Al(III), was supported by adding a suitable masking agent. The high-performance of this resin is underlined by the fact that all REEs are also extracted with high recoveries and low rsd from complex matrices from the digest of rocks using lithium metaborate (LiBO<sub>2</sub>). Finally, the elaborated extraction conditions were applied to the extraction of the REEs from three GSR-rocks (rock standard reference material). Twenty-one samples each of granite and andesite, as well as 19 samples of basaltic rock, were treated according to the procedure described above and passed over SPE columns. There are two major differences between the investigated types of rocks. While the silicate contents increases in the order basalt (44.64%) > andesite (60.62%) > granite

(72.38%), the iron and group II metal content decreases in the same order. As a consequence of the addition of methanol to the rock digests, the presence of even large amounts of silicate did not significantly aggravate handling. Nevertheless, granite samples required a quick extraction procedure in order to maintain the pH within the desired range (5.3–5.5). Upon addition of the masking solution and adjustment to the correct pH, no more spectral interferences by any of the metal ions were detected. This indicated a sufficient masking efficiency of the applied reagents as well as high selectivity of the resin (Fig. 8).

## 5. Other copolymers for solid-phase extraction

### 5.1. Divinylbenzene-*n*-vinylpyrrolidone copolymer

Oasis HLB is a macroporous copolymer consisting of two monomer components, the lipophilic divinylbenzene and the hydrophilic *n*-vinylpyrrolidone. These two monomers construct a hydrophilic–lipophilic balance [103]. The transfer of a method from the silica-based reversed-phase to the Oasis products needs less sorbents because of the up to five times higher capacity. In the opposite to silica-based RP-resins the macro porous and wettable resin shows a less complicated adsorption mechanism, that is not influenced by the metallic impurities or the changing concentration of silanol groups. The material can be used for the determination of polar and apolar organic compounds from aqueous solutions. Acidic, neutral and basic components can be isolated with a very simple method that shows high recoveries (Fig. 9). Because of the high pH-stability (pH 1–14) and the high compatibility to organic solvents clean

Table 6

Average recoveries (%) and relative standard deviations ( $\sigma_m$ , %) for La through Lu (without Pm) on succinic acid-derivatized resin (3.1 mequiv. of COOH/g, 300 mg)<sup>a</sup> [102]

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
5 ppb	90.0	93.0	101.3	97.5	101.6	98.8	97.9	96.1	97.3	98.3	100.2	99.7	92.2	96.9
$\sigma_n$ ( $n=3$ )	0.7	3.3	2.5	3.5	3.2	1.3	4.1	0.6	2.1	0.8	2.1	1.0	4.6	1.9
500 ppb	92.3	94.7	102.1	94.9	100.1	100.3	92.4	96.8	97.1	95.0	97.8	101.8	91.5	98.1
$\sigma_n$ ( $n=4$ )	3.2	6.6	3.1	2.4	6.0	5.2	3.0	6.6	2.9	1.7	2.6	6.0	3.4	5.0

<sup>a</sup> Mixed standard containing 500 and 5 ppb La through Lu (without Pm), respectively, in 1 M HNO<sub>3</sub>, pH was adjusted to 5.5 using an acetate buffer.

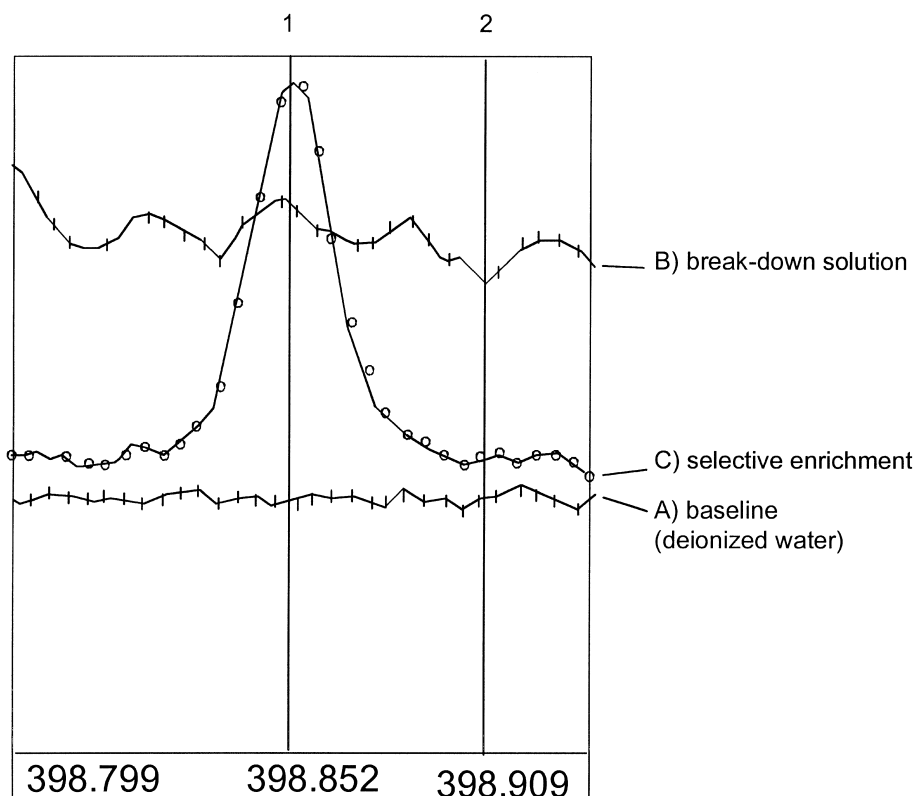


Fig. 8. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) signal for lanthanum. (1) On-peak quantification ( $\lambda=398.852$  nm), (2) background position ( $\lambda=398.887$  nm). (A) Deionized water, (B) rock digest, (C) La signal after sample clean-up and preconcentration step [102].

extracts can be achieved by simple pH-modifications or modifications in the concentration during the elution step. In this way analytes are retained in non-ionic and strong lipophilic form. Interferences can be separated with higher concentrated organic solvents. Because of the wetting ability the retention and the high recoveries are kept constant for a wide spectrum of analytes even if air is flushed through the SPE cartridge<sup>1</sup>.

### 5.2. Sulfonated divinylbenzene-*n*-vinylpyrrolidone copolymer

Beside of the classical Oasis HLB there also exists the Oasis MCX that combines the properties of the HLB sorbents with the characteristics of a strong cation exchanger. The additionally introduced sul-

fonic acid groups ( $-\text{SO}_3\text{H}$ ) cause an improved selectivity and sensitivity for basic additives in plasma, urine or whole blood. Experiments with human urine have shown that equilibration is no

Table 7  
Recoveries for basic additives without any pretreatment of the Oasis MCX SPE cartridge [104]

Basic additive	Content ( $\mu\text{g}/\text{ml}$ )	Recovery (%)	RSD (%)
Methadone	0.01	100	2.7
Methadone-metabolite (EDDP)	0.04	99	1.0
Estazolame	0.20	98	1.5
Propranolol	0.08	100	2.7
Oxprenolole	0.08	90	3.2
Metoprolole	0.08	100	3.4
Verapamile	4.5	100	1.2
Nor-Verapamil	3.4	98	0.5
Methoxy-verapamile	6.7	100	3.3
Codeine	0.12	99	1.2
Codeine-6-glucuronide	0.12	100	1.5
Ranitidine	0.24	92.5	2.6

<sup>1</sup>Oasis is a registered tradename (Waters, Milford, MA, USA).

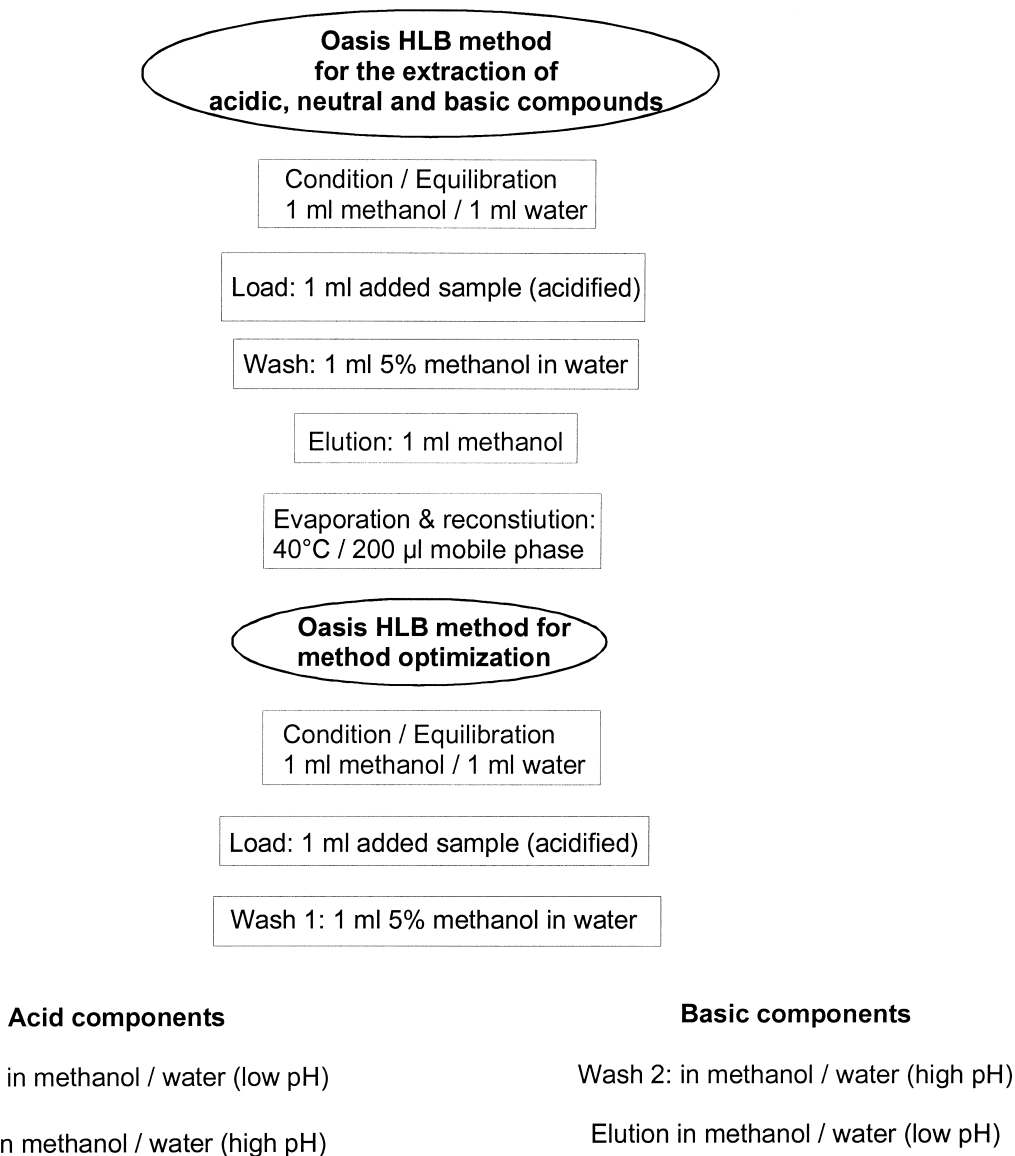


Fig. 9. One simple SPE method can be used for sample preparation of a large number of acidic, neutral and basic compounds with high recoveries (>85%) and low standard deviation (RSD<5%,  $n=6$ ). If necessary the general procedure can be optimized for improved selectivity and sensitivity [103].

longer necessary [104]. Recoveries for basic additives are much higher than compared to silica-based sorbents (Table 7 and Fig. 10). The combined reversed-phase and cation exchanger properties of the Oasis MCX material allows one to separate samples into an acidic–neutral fraction (elution with

methanol) and into a basic fraction (elution with ammonium hydroxide–methanol) (Figs. 11 and 12). In this way a screening for additives is based on investigation of the methanolic fraction for acidic and neutral components and the ammonium hydroxide–methanol fraction for basic compounds.





## 6. Solid-phase microextraction based on new polymeric coatings

Górecki et al. [105] described that the extraction of analytes by the new porous polymer SPME fibers is rather based on adsorption than on absorption. The paper includes theoretical description of the extraction process for adsorption fibers, including PDMS–DVB (polydimethylsiloxane–divinylbenzene), Carbowax–DVB and Carbowax–TR (template resin) [106]. The most widely used is PDMS, which is a liquid coating. Even though it looks like a solid, it is in fact a high viscosity rubbery liquid. PA is a solid crystalline coating that turns into liquid at desorption temperatures. Fig. 13 illustrates the initial and equilibrium/steady-state stages of the extraction process for absorption- and adsorption-type SPME

coatings. Independently of the nature of a coating, analyte molecules initially get attached to its surface. Whether they migrate to the bulk of the coating or remain at its surface depends on the magnitude of the diffusion coefficient of an analyte in the coating. Diffusion coefficients of organic molecules in PDMS are close to those in organic solvents, therefore diffusion into PDMS is relatively fast and this coating extracts via absorption. Diffusion coefficients in poly(acrylate) are lower by about an order of magnitude, but still large enough for absorption to be the primary extraction mechanism. On the other hand, diffusion coefficients of organic molecules in the bulk of divinylbenzene and Carboxen are so small that within the time frame of SPME analysis, essentially all the molecules remain on the surface of a coating. Should the organic molecules remain there

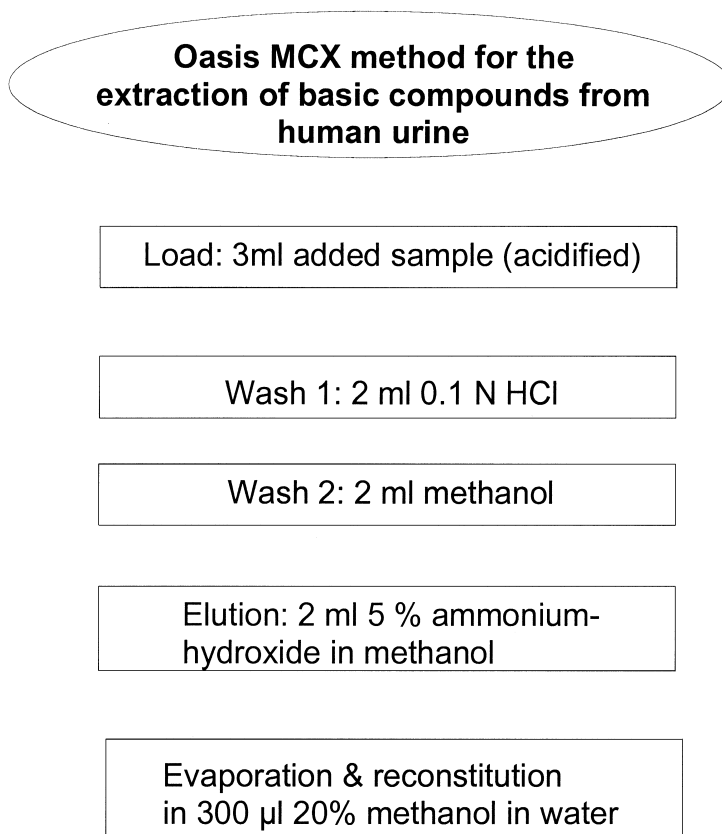


Fig. 11. General instruction for the extraction of acidic, neutral and basic additives with Oasis MCX. Acidic and neutral components are in eluate 1, basic compounds are in eluate 2 [104].

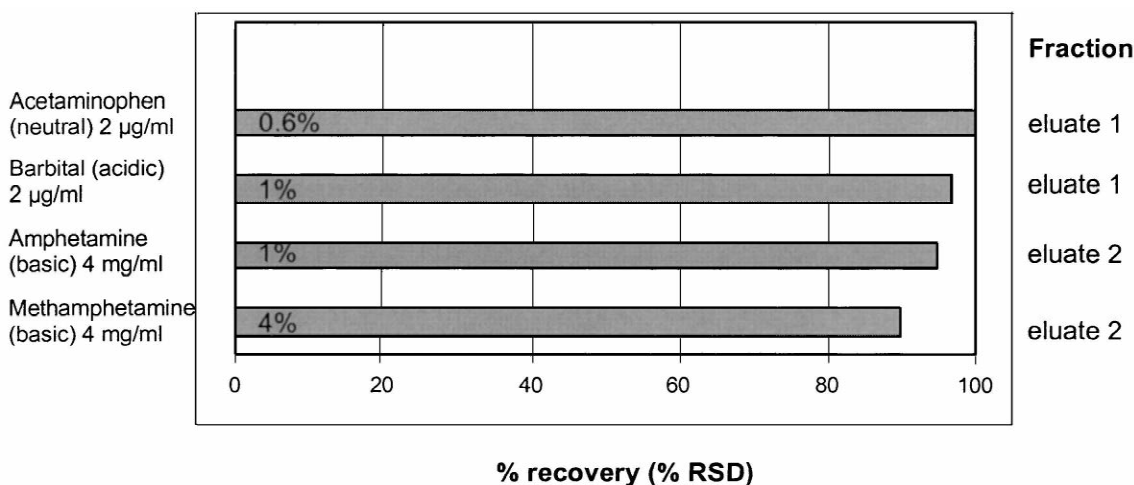


Fig. 12. Oasis MCX products allow the efficient fractionation of additives with high recoveries for acidic, neutral and basic additives in two separated fractions [103].

for a very long time (days or weeks), they still might diffuse into the bulk of the coating (over very short distances). This would manifest itself during analysis as persistent carryover, difficult to eliminate even after repeated desorptions. For all practical purposes, however, adsorption is the only extraction mechanism for those coatings [107–111].

## 7. Conclusions and future prospects

Nowadays, SPE is a well-established technique and, due to its advantages over other sample preparation techniques, has been used for the analysis of numerous different classes of compounds in a variety of matrices. The introduction of new polymeric solid phases and more selective chromatographic modes with high and different affinities, the development of new experimental configurations in order to adapt SPE to specific situations and the improvement of automatic devices will undoubtedly lead to their application in different fields of chemical analysis. New polymeric stationary phases for SPE incorporate a hydrophilic group into a polymeric resin which enables excellent surface contact to be made with an aqueous sample without resorting to any pretreatment of the resin with an organic solvent. However,

perhaps the most exciting areas for further science on this topic involve the development of new polymeric resins for fast, selective and quantitative analysis of ingredients from complex matrices like human serum. Especially the direct injection approach for drugs and bioorganics in samples of virtually all types of biofluids is a truly general approach that should be immediately applicable to the study of in vivo metabolisms, pharmacokinetics and for drug screening. The ability to eliminate almost all sample preparation and pretreatment steps, other than simple filtration and perhaps pH adjustment, which were also automatable, represents a significant step forward in the ability to determine trace levels of different kinds of components. Applications of these automated approaches to the analysis of natural occurring compounds in even very complex matrices should be suitable areas for future/current studies. Nowadays there are many off-line SPE instruments on the market. Some of them perform all the SPE processes automatically but the transfer of the eluates from the SPE to the HPLC is manual (semi-automated systems). However, others are able to automatically transfer the eluates to the HPLC injector and perform the chromatographic analysis so that unattended sample preparation and analysis can be carried out in fully automated systems [112–136].

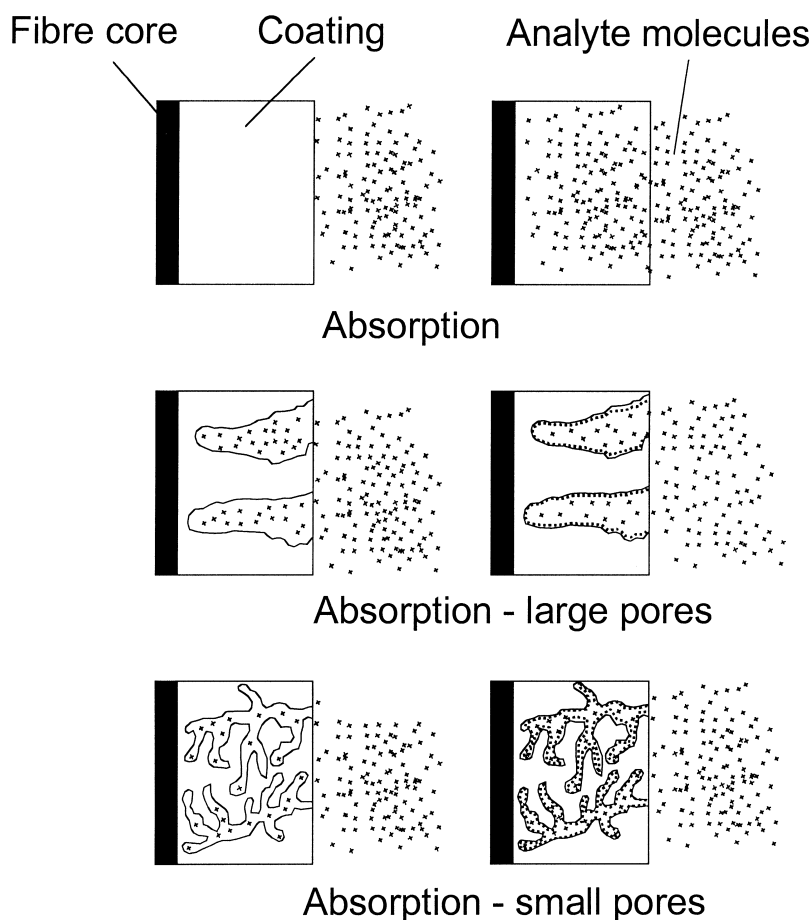


Fig. 13. Comparison of absorption and adsorption extraction mechanisms (cross-sections of the coated fibers). Diagrams on the left illustrate the initial stages of the processes. Diagrams on the right illustrate the steady-state condition [105].

## 8. Nomenclature

AIBN	Azobisisobutyronitrile
DVB	Divinylbenzene
FID	Flame ionization detection
GC	Gas chromatography
$k$	Capacity factor
LLE	Liquid–liquid extraction
LSE	Liquid–solid extraction
PA	Poly(acrylate)
PDMS	Polydimethylsiloxane
ppm	Parts per million
PS–DVB	Polystyrene–divinylbenzene
PU	Polyurethane
ROMP	Ring opening metathesis polymerization

SP	Solid phase
TR	Template resin
$V_B$	Breakthrough Volume
$V_R$	Retention volume

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