

New, high-capacity carboxylic acid functionalized resins for solid-phase extraction of a broad range of organic compounds

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Abstract

New high capacity carboxylic acid-functionalized resins, prepared by ring-opening-metathesis suspension polymerization, were used for solid-phase extraction of organic compounds from water. Two resins, exhibiting a capacity range of 3.0 and 3.75 mequiv. COOH/g, respectively, have either been employed in their beaded form or in the form of particle-loaded membranes. A large variety of organic compounds such as phenols, alcohols, aldehydes and ketones, carboxylic acids, esters, chlorinated hydrocarbons, amines, nitrosamines as well as polycyclic aromatic hydrocarbons were successfully extracted by these materials. For most compounds, a quantitative recovery was observed. The extraction efficiency of the new resins was compared to those of other, commercially available high-performance materials such as Silicalite and Empore disks. The general advantages of the new materials, the mechanism of extraction, differences between membranes and columns containing the new particles as well as the extraction behavior versus the compounds investigated are discussed. © 1997 Elsevier Science B.V.

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1. Introduction

Identification and quantification of organic compounds in water or other matrices are necessary for solving various environmental, biological or clinical problems. For this purpose, solid-phase extraction (SPE) [1–4] is now a widely used method for sample concentration and clean-up. Although a number of solid sorbents are available, there is a need for new sorbents with a broader applicability for SPE. Despite the fact that standard silica-based materials

are widely accepted and available, they suffer from the disadvantage that they are not wettable by water alone and always need a conditioning step with a wetting solvent such as methanol. Additionally, these materials exhibit a significant pH-lability. Surface modified polystyrene–divinylbenzene (PS–DVB) materials [5,6] overcome both disadvantages. Usually, as a consequence of the ease of derivatization, sulfonic acid groups are introduced onto the surface of PS–DVB. These materials display enhanced surface hydrophilicity and improved extraction efficiencies [7]. However, these materials are unable to extract small, polar organics successfully. Recently,

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Mayer and Fritz [8] described a new type of zeolite, Silicalite, which exhibits good extraction properties, especially for small molecules. The selective adsorption is believed to be based on a molecular sieve-like interaction into the small, apolar cavities of the material. This type of zeolite represents a useful tool to close the gap for the extraction of water soluble, low-molecular-mass analytes. Unfortunately, Silicalite tends to degrade in very basic solutions and does not possess any ion-exchange capabilities.

In this contribution the use of a new organic polymeric material for SPE is described. The new material is a cross-linked poly(norbornene-5,6-dicarboxylic acid). A detailed description for the preparation of the resin using ring-opening-metathesis polymerization (ROMP) as well as of its mechanical and chemical properties is given elsewhere [9]. The striking features of the polymerization technique employed (ROMP), are the reproducibility in the synthesis, the use of functional monomers as well as the access to high capacity resins (3–4 mequiv. COOH/g). In addition to a high cation-exchange capability, the resin is characterized by a strong affinity for apolar compounds, a rather large particle diameter ($40 \pm 10 \mu\text{m}$), which results in a low back-pressure ($< 15 \text{ p.s.i.}$, $1 \text{ p.s.i.} = 6894.76 \text{ Pa}$) when used in SPE, and excellent chemical stability versus both acids and bases. The latter property allows the re-use of the material after careful clean-up using 2 M NaOH and HCl, respectively, for at least 30 times without any loss in performance. Additionally, the wettability of the resin is high, which makes a pretreatment with methanol prior to SPE no longer necessary. An in-depth investigation of its extraction properties in comparison to other high-performance materials, such as Silicalite (UOP, Des Plaines, IL, USA) and Empore extraction disks (3M Company, St. Paul, MN, USA) filled with sulfonated PS–DVB demonstrates the advantages of the new resin. Seventy-four different analytes with ten types of different functionalities such as phenols, alcohols, carboxylic acids, esters, aldehydes, ketones, amines, chlorinated hydrocarbons, N-nitrosoamines as well as polycyclic aromatic hydrocarbons (PAHs) have been chosen for the characterization of the new material. For all types of compounds, both the low- and high-molecular-mass homologues were investi-

gated. Most of these were extracted effectively by the COOH resin, even when the SPE bed dried out. Finally, for certain compounds, a comparison between two different forms of the new resin has been performed. For that purpose, the new resin was additionally used in form of a particle embedded membrane.

2. Experimental

2.1. Reagents and chemicals

Analytes studied were $>99\%$ pure and used as obtained from Fisher Scientific (Pittsburg, PA, USA), Fluka (Buchs, Switzerland) and Aldrich (Milwaukee, WI, USA). All solvents and reagents used (acetone, methanol, ethyl acetate, triethylamine, hydrochloric acid, trifluoroacetic acid) were of analytical-grade. Laboratory distilled water was further purified using a Barnstead Nanopure II system (Sybron Barnstead, Boston, MA, USA). Silicalite, was sieved to obtain 5–10 μm particles. Experimental membranes containing these particles were obtained from 3M. Experimental Empore-type membranes embedded with 8 μm PS–DVB sulfonated resin, 0.6 mequiv./g sulfonation capacity, were used as obtained from 3M and can be purchased commercially as SDB-RPS. Porous, COOH functionalized resins (3.0 and 3.75 mequiv. COOH/g, respectively, specific surface area 15–20 m^2/g) were prepared as described elsewhere [9]. Sheets of experimental COOH resin-loaded membranes containing these particles were obtained from 3M.

2.2. Procedure for SPE

For SPE experiments 1.5 ml polypropylene SPE columns (P.J. Corbert, St. Louis, MO, USA) were used. For larger amounts of analytes, a 30 ml glass syringe barrel fitted with a luer tip was connected to the SPE device. Silicalite and COOH resin particles as well as sulfonated PS–DVB resin and COOH resin loaded membranes were used as the SPE adsorbents. Silicalite and the COOH resin were slurry packed between two polypropylene frits (P.J. Corbert), using suspensions in methanol or methanol–water (20:80). The Silicalite particles were

additionally supported from the bottom with a piece of 2 μm filter paper. The bed heights measured for both sorbents approximately 0.5 cm. Prior to use, 3 ml of 0.1 *M* sulfuric acid was added to a stirred suspension of the polymer to ensure it was in the acidic form. A 0.5 ml volume of acetone and 1 ml deionized (DI) water were used to condition each column. For all experiments, the amount of polymer used was 50 mg. Samples were prepared by adding a 100- μl aliquot of a methanol solution containing 100 ppm of 2–3 analytes to 10 ml of DI water. The final concentration for all compounds was 1 ppm unless stated otherwise. Solutions containing the analytes were passed over the columns filled with the corresponding material. Except for the analysis of PAHs, positive pressure was used to force liquids through the adsorbents. Recoveries for all analytes were calculated as an average of at least three trials by comparing the relative peak areas with standards that were not subjected to SPE. Elution of all non-basic compounds from the columns was performed with either acetone or ethyl acetate. In the case of bases methylamine (2 *M* in acetone) was used.

For GC measurements (amines, nitrosoamines and PAHs), a GC 8030 (Fisons Instruments) with MD 800 mass spectrometer (Fisons Instruments) was used. The stationary phase consisted of a SE 54 capillary column [poly(5%-diphenyl–95%-dimethylsiloxane), 0.25 mm I.D., 0.1–0.15 μm film thickness, Mega]. Other analytes were quantified by GC using a Shimadzu (Kyoto, Japan) GC 14 A, equipped with an AOAC-14 autoinjector, flame ionization detector and a C-R4A Chromatopac data analysis system. The CG column was a Supelco SPB-5 column, 15 m \times 0.32 mm with a phase thickness of 1 μm .

2.3. Breakthrough volumes and breakthrough curves

The high-performance liquid chromatography (HPLC) column used was a 10 cm \times 4.6 mm I. D. stainless-steel column packed with 500 mg of COOH resin particles. The particles were added to 10 ml of methanol and sonicated to produce a slurry. A Shandon HPLC packing pump (Shandon Southern, Sewichely, PA, USA) was used at a pressure of 2000 p.s.i. to pack the slurry into the column. The HPLC

system consisted of a Gilson (Middleton, WI, USA) Model 302B HPLC pump equipped with a Model 802 Gilson manometric module. A Scientific Systems (State College, PA, USA) Model LP-21 pulse dampener was used for feed solution delivery. Aqueous feed solutions containing 150 ppm of the organic compounds of interest were pumped through at a rate of 1.00 ml/min. The effluent was monitored on-line with a Kratos 783 UV–Vis detector (Applied Biosystems, Ramsey, NJ, USA) or an Erma 7510 refractive index detector (Chrom Tech, Apple Valley, MN, USA). Breakthrough curves were recorded by a Hitachi D-200 Chromato-Integrator (EM Science, Cherry Hill, NJ, USA). The amount and type of resin indicated in the tables was treated with 2 ml portions of the standards and the effluent was checked for analytes by means of GC–MS.

3. Results and discussion

ROMP was used for the preparation of the new COOH functionalized resins [9]. 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*-dimethanonaphtalene to form particles (Fig. 1).

The new polymers were found to consist of an inert, cross-linked interior and a molecular fur, bearing the linear chains formed by the functional monomers, on the outside [9]. As a consequence, all functionalities are readily available for SPE. Fig. 1 shows the synthetic pathway as well as the backbone and interior structure of the polymer. While the carboxylate groups provide sufficient hydrophilicity, the polyunsaturated character of the carrier chains as well as of the entire backbone result in a significant reversed-phase character. Electron-microscope investigations (Fig. 2) revealed, that the material formed consists of irregularly shaped, agglomerated particles with a mean particle diameter of ca. 40 μm which accounts for the low backpressure applied (5–10 p.s.i.). The specific surface of the 3.75 mequiv. COOH/g resin was 15 m²/g, indicating a non-porous or microporous structure. Nevertheless, a significant non-permanent porosity must be assumed,

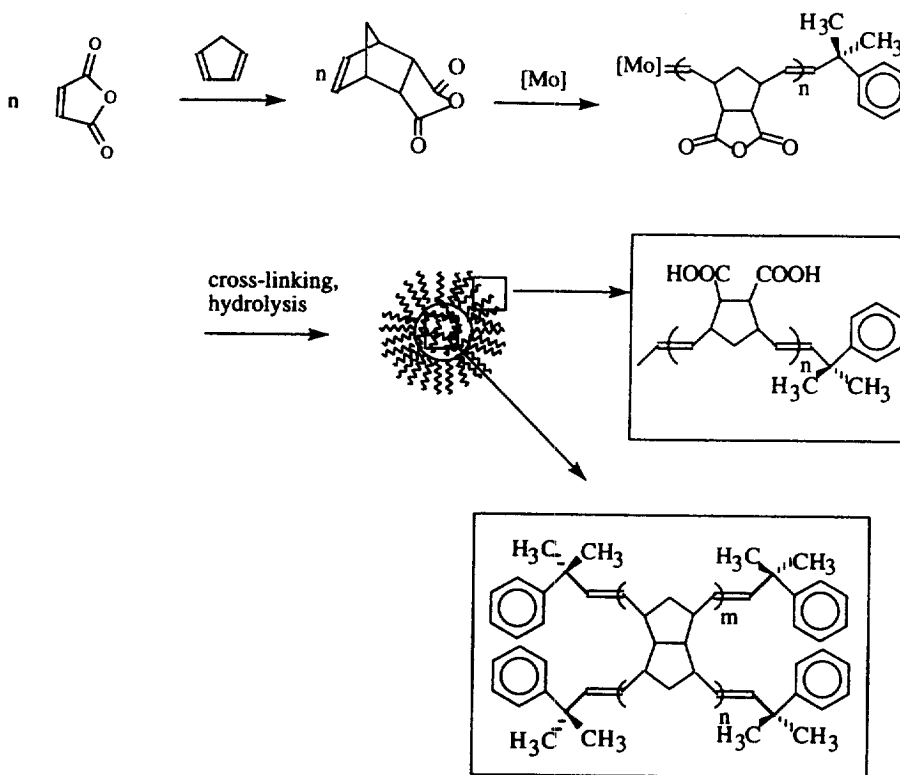


Fig. 1. Preparation of the COOH resin. For experimental details refer to Ref. [9].

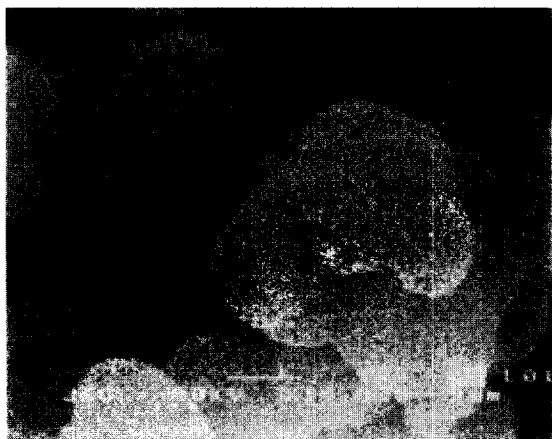


Fig. 2. REM picture of COOH resin ($C=3.75$ mequiv./g). Specific surface area $15 \text{ m}^2/\text{g}$.

as considerable swelling (+60%) takes place upon treatment with any polar solvent such as methanol or water, leading to a particle with ca. $400 \mu\text{l}$ pore volume/g resin.

Porous PS–DVB-based resins have proved to be very effective for SPE of a wide variety of organic compounds from predominately aqueous samples. Their effectiveness is enhanced by chemical introduction of polar groups, such as acetyl or sulfonic acid moieties on the resin surface. However, these modified PS–DVB-based resins do not or very poorly extract small, polar organic compounds such as lower alcohols, aldehydes, ketones and carboxylic acids. Silicalite is able to successfully extract these compounds. Molecules small enough to enter the 6 \AA diameter channels are retained by interaction of the hydrophobic parts of the analyte with the hydrophobic interior of the Silicalite. Molecules that do not fit the channels are extracted poorly or not at all [8].

The new COOH functionalized resin was expected to possess characteristics of both the polystyrene resins and Silicalite. Hydrophobic analytes would be extracted through interactions with the hydrophobic part of the polymer, which is represented both by the cross-linked interior as well as by the unsaturated backbone bearing the carboxyl groups. More hydrophilic analytes would be retained by the carboxyl groups located at the outside of the particles, which generally increase the hydrophilicity of the entire resin. A comparison of the extraction behavior versus different types of analytes between Silicalite, PS–DVB membranes and the COOH resin, both in its beaded as well as membrane embedded form is discussed in the following sections.

3.1. Phenols

Despite the fact that phenols are acidic, they may be concentrated on a weak cation exchanger by adjusting pH below 2. In this case, the mode of retention is exclusively based on a reversed-phase mechanism [10–23]. Following this concept, the use of polar sorbents or weak cation exchangers has been reported earlier [24,25]. Nevertheless, the efficiency of extraction strongly depends on the hydrophilicity of the surface combined with a sufficient RP character. Percentage recoveries of nine phenols using Silicalite particles, a sulfonated PS–DVB resin-loaded membrane and the COOH resin are listed in Table 1. The average recovery of the phenols using the COOH polymer was 99% with a relative standard deviation of 2% which is higher than the recoveries using the other two sorbents (88 and 92%, respectively). Silicalite is believed to give lower recoveries of many of the phenols because of their quite bulky structures. The slightly enhanced recoveries obtained with the COOH resin in comparison to the PS–DVB-based membranes are believed to result from a better hydrophilicity and a higher contents on RP-active sites of the COOH resin, which are provided by both its high capacity (3.0 mequiv. COOH/g) as well as its unique fur-type structure.

3.2. Extraction of various alkyl compounds

Organic compounds, which are neither acidic or basic are usually extracted by alkyl-derivatized sil-

ica, PS–DVB or activated carbon [26,27]. Percentage recoveries of thirteen different alcohols using the three different materials are compared in Table 1. The most striking difference is in the C₃–C₄ alcohols, which are retained strongly by Silicalite. From a maximum around C₆ the silicalite recoveries decrease gradually with increasing chain length. This results from the fact that the high-molecular-mass homologues fit less into the 6 Å cavities of Silicalite. Recoveries on the PS–DVB resin-loaded membrane remain almost constant between C₅ and C₁₄. The COOH polymer gave recoveries similar to the sulfonated PS–DVB resin-loaded membrane, showing higher recoveries for propanol, butanol and pentanol than the Empore disc. In addition, the average recovery of the other alcohols was 92% for the other two sorbents, which is higher than the 74% recovery using Silicalite. Carboxylic acids, which are soluble in water are extracted by Silicalite with significantly higher recoveries. Those with more than 4 carbons show better recoveries with either the PS–DVB resin-loaded membrane or the COOH polymer.

Data for the extraction of aldehydes, ketones, esters as well as chlorinated alkanes are given in Table 1. In several instances the lower-molecular-mass compounds of a homologous series are retained more strongly by Silicalite and the COOH polymer than by PS–DVB resin-loaded membrane. Examples include 2-butanone, the C₂ to C₅ esters, as well as the chlorinated alkanes. Additionally, recoveries for chlorinated alkanes and some carbonyl compounds shown in Table 1 are higher for the COOH-based resin than for Silicalite. It is worth noting, that the efficiency of extraction seems to be constant in the case of the COOH-based resin, while Silicalite tends to show lower recoveries for larger, bulky molecules. The fact, that the COOH resin extracts even smaller molecules as efficiently as Silicalite, which has a high affinity towards small, polar compounds, suggests a micropore structure similar to that of Silicalite in the conditioned state of the COOH resin, resulting in some molecular sieve-like extraction properties. These may be explained by the fact, that the entire resin is synthesized in a chlorinated solvent and thus is processed in a highly solvent swollen state. In the course of work-up, this solvent is removed. Template-like cavities may result, which exactly fit small molecules like CHCl₃,

Table 1
Recoveries (%) for compounds 1–48

Class	No.	Compound	Silicalite	Empore disc	COOH resin ^a	COOH membrane ^b
Phenols	1	Phenol	66	84	101	96
	2	2-Chlorophenol	33	89	101	100
	3	4-Chlorophenol	90	95	101	–
	4	3-Nitrophenol	56	105	92	93
	5	2,5-Dimethylphenol	54	92	97	–
	6	4-Ethylphenol	98	96	105	–
	7	4-Propylphenol	98	98	103	–
	8	4- <i>tert.</i> -Butylphenol	27	87	97	–
	9	<i>m</i> -Cresol	97	93	100	95
Alcohols	10	1-Propanol	84	0	2	3
	11	1-Butanol	95	10	13	10
	12	2-Butanol	94	6	20	16
	13	1-Pentanol	92	99	82	–
	14	1-Hexanol	99	91	99	–
	15	1-Octanol	89	94	95	100
	16	2-Octanol	–	–	101	–
	17	1-Decanol	82	89	100	93
	18	1-Dodecanol	75	89	83	75
	19	1-Tetradecanol	58	87	84	–
	20	3-Phenyl-1-propanol	73	99	95	–
	21	2-Ethyl-1-propanol	92	90	94	–
Carboxylic acids	23	Acetic acid	2	0	0.5	–
	24	Propionic acid	62	0	2	2
	25	Butyric acid	78	13	20	14
	26	Valeric acid	95	104	106	93
Aldehydes	27	<i>trans</i> -Crotonaldehyde	91	24	8	5
	28	Benzaldehyde	89	94	84	78
	29	Salicylaldehyde	54	96	92	–
	30	<i>n</i> -Valeraldehyde	100	74	89	–
	31	Hexanal	107	94	84	–
	32	Nonylaldehyde	84	96	92	–
Ketones	33	2-Butanone	92	0	72	71
	35	2-Pentanone	90	88	94	96
	36	4-Methyl-2-pentanone	104	88	85	92
	37	2-Hexanone	93	89	96	–
	38	3-Hexanone	81	89	93	–
	39	2-Heptanone	–	–	98	–
Esters	40	Ethyl acetate	91	55	90	95
	41	Ethyl propionate	88	61	98	96
	42	Ethyl butyrate	90	75	108	98
	43	Pentyl benzoate	82	70	72	–
	44	Methyl benzoate	68	94	100	–
Chloroalkanes	45	Chloroform	82	81	89	87
	46	1,2-Dichloroethane	83	77	85	78
	47	1,1-Dichloroethane	80	77	92	91
	48	1,2-Dichloropropane	85	85	92	90

pH was 2.0 for phenols and acids. Sample volumes, 10 ml; concentration, 1 ppm each analyte; sampling rate, 1 ml/min; elution with 0.5 ml acetone.

^a 3.0 mequiv. COOH/g.

^b 3.0 mequiv. COOH/g resin embedded in a PTFE membrane.

Standard deviations for all compounds were $\leq 2.0\%$.

Table 2
Loading capacities for COOH resin (3.0 mequiv. COOH/g) for various test compounds

Compound	Capacity (mg compd/g)
Phenol	2
4-Chlorophenol	40
2-Chlorophenol	5
<i>m/p</i> -Cresol	8
Ethyl acetate	20
Propylamine	42
Pyridine	10
Pentamethyldiethylenetriamine	45 ^a
Dizabicyclooctane (DABCO)	46 ^a
Di- <i>N</i> -morpholinodiethyl ether	24 ^a
4-Methylmorpholine	17 ^a
4-Ethylmorpholine	17 ^a
<i>N,N</i> -Dimethylethanolamine	43 ^a
1,4-Dimethylpiperazine	3 ^a
<i>N,N</i> -Dimethylaniline	25
2,6-Diisopropylaniline	40
1-Naphtylamine	17

^a Solutions in ethyl acetate.

$\text{ClCH}_2\text{CH}_2\text{Cl}$, Cl_2CHCH_3 , $\text{ClCH}_2\text{CHClCH}_3$ as well as certain short chain esters. As a consequence, the COOH resin possesses the characteristics of both Silicalite and the sulfonated PS–DVB resin loaded membrane. The COOH resin contains molecular sites

which are responsible for the ability to retain hydrophobic compounds. The presence of COOH groups imparts an increased surface hydrophilicity as well as ion-exchange capabilities.

3.3. Amines and *N*-nitrosoamines

Amines are usually extracted by weak cation exchangers [25,28–30]. Strong cation exchangers often suffer from the fact, that strongly basic amines may not be eluted quantitatively. As expected, the COOH resin shows a high extraction capability as well as high recoveries for amines [9]. These findings agree with the fact, that the COOH resin possesses a significantly higher capacity (3.0 mequiv./g) than the sulfonated PS–DVB material (0.6 mequiv./g). Additionally, elution is achieved more easily because the ion pairing is weaker ($\text{p}K_1 = 4.5$, $\text{p}K_2 = 8$) than in the case of sulfonic acids ($\text{p}K \approx -1$). Both water soluble (e.g., pyridine) as well as water insoluble amines are extracted very well. Table 2 shows the high loading capacities for a large variety of amines. By contrast, the neutral *N*-nitrosoamines are extracted only by hydrophobic sorption; thus only the water insoluble, higher-molecular-mass homologues such as *N*-nitrosobutylamine are extracted quantitatively (Table 3).

Table 3
Recoveries (%) for compounds 49–58

Class	No.	Compound	Silicalite	Empore disc	COOH resin
Amines ^a	49	Propylamine	63	0	96
	50	<i>n</i> -Butylamine	72	52	90
	51	Pentylamine	78	93	90
	52	Pyridine	77	35	90
<i>N</i> -Nitrosoamines ^b	53	<i>N</i> -Nitrosoethylmethylamine	–	–	0
	54	<i>N</i> -Nitrosodiethylamine	–	–	47
	55	<i>N</i> -Nitrosopyrrolidine	–	–	7
	56	<i>N</i> -Nitrosomorpholine	–	–	6
	57	<i>N</i> -Nitrosopiperidine	–	–	40
	58	<i>N</i> -Nitrosobutylamine	–	–	101

Sampling rate: 1 ml/min; elution was performed with 0.5 ml methylamine (2 *M* in acetone) for bases and 1 ml ethyl acetate–triethylamine (1:1) for *N*-nitrosoamines, respectively.

COOH resin: ^a 3.0 mequiv. COOH/g, ^b 3.75 mequiv. COOH/g.

COOH membrane: 3.0 mequiv. COOH/g resin embedded in a PTFE membrane.

Standard deviations for all compounds were $\leq 2.0\%$.

3.4. Incorporation of the COOH polymer into a membrane

Incorporation of a polymer into a membrane is generally a more efficient way to perform SPE [31–34]. In contrast to loose particles packed into a small column, a membrane represents a more dense packing. For that purpose, the COOH resin particles were enmeshed in a network of PTFE fibrils to form a strong, porous sheet. Several circles were cut from the membrane sheet and packed into a small column to the same height as that previously packed with loose COOH resin particles. Results of SPE with the loose particles and the membrane column shown in Table 1 reveal, that the PTFE fibrils, which themselves possess a high extraction capacity for apolar compounds, did not affect recoveries of the various compounds.

3.5. Breakthrough curves

Load capacity is another good indication of the extraction ability of a resin. 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. Breakthrough curves were determined by passing an aqueous solution of the analyte of interest through a column packed with the COOH resin particles until breakthrough occurred. The curves were plotted as the ratio of effluent concentration, C , to influent concentration, C_0 , versus the volume of effluent. The total number of moles of analyte adsorbed was calculated by multiplying the retention volume, V_R , by the concentration of the influent. For this study, V_R was defined as the extrapolated volume from the curve at the point $C/C_0=0.5$. Capacities for several analytes were calculated from breakthrough curves and are given in Table 2. The highest capacities by weight were 4.0% for 4-chlorophenol, 4.2% for propylamine, 4.5% for pentamethyldiethylentriamine, and similar capacities for several other amines. Effective extraction behavior versus basic, compounds was also observed in the

sampling of volatile amines from air and will be reported elsewhere [35].

3.6. Extraction of PAHs

PAHs are usually extracted onto an alkyl-derivatized silica or onto PS–DVB [36,37]. These apolar compounds may be used to characterize the reversed-phase properties of a resin. In this contribution, sixteen EPA priority PAHs have been studied. Some 2-propanol was added to the aqueous sample to increase the solubility of the PAH compounds. The positive influence of 2-propanol on the stabilization of PAH solutions in water at the low ppb level has been reported earlier [38]. Table 4 shows the recoveries obtained using different amounts of 2-propanol. While addition of 2-propanol favors high recoveries for the high-molecular-mass homologues, high recoveries for the low-molecular-mass homologues are obtained in pure water. These findings are in accordance with the results reported by El Harrak et al. [38] Generally, PAHs are extracted very well by the new resin at the level of $1 \mu\text{g}/\text{l}$. The average range of recovery for all three solvent systems, including the membrane, was found to be 82.6–85.6%.

4. Conclusions

A new polymeric resin has been developed, that contains a high concentration of carboxyl groups. These groups provide good water wetting of the surface and thereby circumvent the need for pretreatment with an organic solvent prior to SPE. The carboxyl groups also enable analytes to be taken up by an ion-exchange mechanism as well as by sorption due to hydrophobic attraction. It has been found previously that resins with approximately 0.6 to 1.0 mequiv./g of sulfonic acid groups retain analytes well both by hydrophobic sorption and by ion exchange but that hydrophobic retention becomes very poor at sulfonate concentrations of ≈ 2.0 mequiv./g or more [7]. By contrast, the new COOH resins with ion-exchange capacities of 3.0 to 3.75 mequiv./g retain analytes by both hydrophobic sorption and ion exchange.

The new resin retains an unusually wide variety of

Table 4
Recoveries (%) for compounds 59–74

Class	No.	Compound	COOH resin ^a	COOH resin ^b	COOH membrane ^c
PAHs	59	Naphtalene	31	18.3±1.5	99±10.2
	60	Acenaphtalene	82	55.6±5.0	92±5.2
	61	Acenaphthene	97	77.7±4.0	92±6.7
	62	Fluorene	103	94.0±4.0	91±6.2
	63	Phenanthrene	103	98.7±4.0	94±4.2
	64	Anthracene	97	88.0±3.5	76±5.0
	65	Fluoranthene	97	94.0±1.7	85±4.1
	66	Pyrene	100	93.7±2.1	84±3.9
	67	Benzo[a]anthracene	99	95.0±8.7	74±4.5
	68	Chrysene	87	91.3±6.1	76±3.2
	69	Benzo[b]fluoranthene	94	93.0±6.6	67±3.2
	70	Benzo[k]fluoranthene	94	90.7±4.9	70±5.7
	71	Benzo[a]pyrene	89	89.0±2.0	61±3.5
	72	Dibenzo[a,h]anthracene	82	97.3±10.4	77±14.2
	73	Benzo[ghi]perylene	36	82.7±17.2	98±26.6
	74	Indeno[1,2,3-cd]pyrene	79	100.3±11.0	86±14.4

^a 1000 ml of compounds 59–74 (1 µg/l each) in water–isopropanol (90:10).

^b 1000 ml of compounds 59–74 (1 µg/l each) in water–isopropanol (85:15).

^c 500 ml of compounds 59–74 (1 µg/l each) in water.

Sampling rate: ^a and ^b 7 ml/min, ^c 3.5 ml/min. Elution: ethylacetate (^a and ^b 2 ml, ^c 1 ml). COOH resin: 3.0 mequiv. COOH/g, COOH membrane: 3.0 mequiv. COOH/g resin embedded in a PTFE membrane.

organic analytes efficiently. The high COOH capacity favours high loadings of basic compounds but apolar or acidic compounds such as phenols are also extracted efficiently. As a consequence, the new resin is widely applicable for SPE and it may be used for the full screening of contaminated aqueous solutions. Restrictions in applications are presented only by a few non basic, water-soluble analytes, which are extracted poorly or not at all. The physical nature of the resin allows its incorporation into a membrane without changing its extraction properties. As a consequence to its physical nature and relatively large particle size, the backpressure in packed SPE columns is unusually low, which is an advantage over many sorbents used in SPE.

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