New cation-exchange resins with high reversed-phase character for solid-phase extraction of phenols

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Abstract

High capacity carboxylic acid functionalized resins, prepared by ring-opening metathesis polymerization, were used for solid-phase extraction (SPE) of phenols. Two resins, based on cross-linked poly-(*endo,endo*-norborn-2-ene-5,6-dicarboxylic acid) exhibited a capacity of 3.5 and 5.1 mequiv. COOH/g, respectively. Particle-loaded PTFE membranes were prepared from a 3.1 mequiv. COOH/g resin. The extraction behavior of the new materials versus two different EPA priority pollutant phenol standards was investigated. For most compounds, a quantitative recovery was observed. The extraction efficiency of the new resins was compared to those of other, commercially available materials such as silica C_{18} or carboxypropylsilica. The general advantages of the new materials, the mechanism of extraction, the influence of polarity and acidity of the compounds investigated as well as differences between membranes and columns containing the new particles are discussed. Finally, the extraction efficiency of the new resins for phenols from spiked soil samples using both standard SPE as well as batch-techniques was investigated. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phenolic compounds are released in many industrial processes. Depending on the substitutents, many of them are highly toxic and possibly mutagenic. Their removal from industrial waste waters as well as a rapid and reliable quantification are therefore to the fore. Different monitoring programs such as those of the US Environmental Protection Agency (EPA) included a variety of different phenols. As these compounds usually occur at low concentrations, sample preconcentration is necessary. In the last two decades, solid-phase extraction (SPE) has become an important technique for sample prepara-

tion in different fields, particularly for environmental and biological applications. The advantages over traditional liquid–liquid extraction are well known and have already been discussed extensively [1–3]. A vast variety of different sorbents has been developed so far, most of them based on carbon black [4–7], silica, polystyrene–divinyl benzene and certain acrylates [3,8–11]. Recently, Mayer and Fritz [12] as well as Buchmeiser and co-workers [13–17] described new types of sorbents for SPE of organic analytes as well as of metal ions. In this contribution, an in-depth investigation of the retention behavior of phenols on a new type of resin, consisting of a cross-linked poly-(*endo,endo*-[2.2.1]bicyclohept-2-ene-5,6-dicarboxylic acid), is presented. In order to elucidate the retention characteristics of this new

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type of resin towards phenols, it was compared with carboxypropylated- as well as with C_{18}-derivatized silica. The extraction efficiency of the new material proved to be better by any means compared to the other two standard SPE materials within the investigated range of concentration. Different modes of interaction of the corresponding analytes with each of the materials will be discussed in the following.

2. Experimental

2.1. Reagents and standards

Phenol, 3-cresol, 4-cresol, 4-chloro-3-cresol, 2,4,5-trichlorophenol, 2-methyl-4,6-dinitrophenol, pentachlorophenol and 2-chlorophenol were obtained from Fluka (Buchs, Switzerland), 2,4-dimethylphenol, 2,4,6-trichlorophenol from Merck (Darmstadt, Germany), 2,3,4,6-tetrachlorophenol from Riedel-de Haën (Germany) and 2-nitrophenol, 2,4-dinitrophenol, 2-*sec*-butyl-4,6-dinitrophenol (Dinoseb) and 2,4,-dichlorophenol from Sigma (St. Louis, MO, USA). All solvents, methanol, ethylacetate (both Merck), acetonitrile and acetone (both Fluka), were of gradient grade. Two different EPA method stock standard solutions were prepared by dissolving 1 mg/ml of each compound in methanol. All solutions were kept in dark at room temperature. The EPA 2 (method 8040 B-R) contained 3-cresol, 4-cresol, 2-chlorophenol, 2,4-dinitrophenol, 2,4-dimethylphenol, 2,6-dichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol and 2-*sec*-butyl-4,6-dinitrophenol. The PPS 3 (priority pollution standard) contained phenol, 4-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2-nitrophenol, 2,4-dimethylphenol, 4-chloro-3-cresol, 2,4-dichlorophenol, 2-methyl-4,6-dinitrophenol, 2,4,6-trichlorophenol and pentachlorophenol. For identification of the phenols by high-performance liquid chromatography (HPLC), 1 g/l standards of each phenol in methanol were prepared and stored in glass bottles in the dark at room temperature. Working solutions were prepared daily by dilution of the stock standards with HPLC grade water and subsequent acidification. Hydrochloric acid (37%) was used throughout. Water was purified in an E-Pure-system (Barnstead). 0.1% Trifluoroacetic acid (TFA) (99.7%, Fluka) was added to the eluents

(water and acetonitrile) for HPLC to suppress ionization of the phenols. Eluents were degassed using helium 5.0.

2.2. Equipment

HPLC analysis was carried out using a LC Modul 1 plus (Waters, Millford, MA, USA) with a programmable UV detector. Data were collected and processed using Millennium software Version 2.16 (Waters). Separations were performed using a 4×4 mm RP-18 pre-column connected to a 125×4 mm LiChrospher 100 RP-18 column.

2.3. Chromatographic conditions

Separations of the compounds by HPLC were achieved using a water–acetonitrile gradient. The eluents were acidified with 0.1% (v/v) TFA. Solvent A was a mixture of HPLC grade water containing 30% (v/v) acetonitrile, solvent B consisted of pure acetonitrile. The gradient was as follows: 0 to 24% solvent B within 11 min, 24 to 49% solvent B within 19 min, 100% solvent B within 3 min. The wavelength of the UV detector was set at $\lambda=280$ nm, except for pentachlorophenol, which was determined at $\lambda=302$ nm. The flow-rate was set to 1.0 ml/min. The sample volume was either 20 μl or 100 μl.

2.4. SPE materials

Silica C_{18} cartridges (22% carbon, 1000 mg, 6 ml void volume) were purchased from Spe-ed, Applied Separations (USA) and silica carboxypropylate columns (500 mg, 10 ml void volume) from ICT, Isolute (Austria). The preparation of carboxylic acid functionalized resins with a capacity of 3.5 mequiv. COOH/g and 5.1 mequiv. COOH/g, respectively, by ring-opening-metathesis polymerization (ROMP) is described elsewhere [14,15]. Sheets of experimental COOH resin-loaded membranes containing resin particles (3.1 mequiv. COOH/g, specific surface 24 m^2/g) were obtained from the 3M company (3M Co., St. Paul, MN, USA).

2.5. Procedures for SPE

SPE experiments using silica-based materials were

carried out at a pH>2 (see Tables). Silica SPE cartridges were activated with 8 ml of acetone and conditioned with 6 ml of water–acetone (50:50, v/v), water–acetone (20:80, v/v) and water. The sample was added to the reservoir and positive air pressure was adjusted to give a sample flow-rate of 1 ml/min. The sorbent was dried by passing air through the column. Finally, the sample was eluted using 3 ml acetonitrile. The collected eluate was diluted with water to a total volume of 5 ml.

A pH of 2 was chosen for SPE with the polymer resin. Precise values are given in the Tables. For these SPE experiments, 1.5 ml polypropylene SPE columns (Iso-Lute) were used. COOH resin particles were used as the SPE adsorbents and slurry packed using suspensions in acetone or acetone–water (20:80). The amount of polymer used is indicated in the Tables. The SPE column was finally treated with 6–15 ml acetone–water (20:80, v/v) and 6–10 ml water. Samples were prepared by adding a 100-μl aliquot of a methanol solution containing 1000 ppm of the analytes to the corresponding volume of deionized (DI) water. Aqueous solutions containing the analytes (pH<2) were passed over the columns filled with the corresponding material, using positive pressure to force liquids through the adsorbents. A flow-rate of 1–2 ml/min was maintained. For higher sample volumes, a 100 ml polypropylene (PP) syringe barrel fitted with a luer tip was connected to the SPE device and samples were sucked through the cartridges using a vacuum-box (Analytichem International) connected to a water jet pump. The vacuum was adjusted by a manometer in order to maintain a flow of 1 ml/min. For SPE experiments carried out with 100 mg of the resin, volumes of the solvents for activating and conditioning the sorbent were also doubled.

Particle-loaded membranes were treated as follows: six circles (5.5 mm in diameter, 0.9 mm thickness) were cut out from the membrane material and placed in a 1-ml SPE column. The membranes were then rinsed with 10 ml acetone and conditioned with 10 ml water. Aqueous samples (50 ml containing 11 priority pollutant phenols at a level of 300 ng/ml, acidified to pH<2) were passed through the membrane. Unless stated otherwise, the sample flow-rate was ca. 1 ml/min. Membranes were dried in an air stream and finally eluted with 2×1 ml of acetonitrile. The effluent was collected and analysed by HPLC.

Prior to analysis with HPLC, 10 to 20 ml air were blown through the sorbent. Elution of the retained phenols was carried out with 3 ml of acetonitrile which was allowed to soak into the packing for a few minutes. Finally, the collected eluate was diluted with water to a total volume of 5 ml. Unless stated otherwise, 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.

2.6. Breakthrough volumes and breakthrough curves

Two-ml PP SPE columns packed with COOH resin particles were used. COOH resin particles (50 mg, 5.1 mequiv. COOH/g) were added to 10 ml of methanol and sonicated to produce a slurry. Organic solutions containing 10 ppm of the phenols of interest were forced through the resin bed at a rate of 1.00 ml/min using positive pressure. The effluent was collected in 2-ml portions and checked for analytes by means of HPLC. Capacity factors were calculated for selected phenols according to Refs. [18,19].

2.7. Spiked samples

Blank soil samples were spiked with 11 priority pollutant phenols: soil samples were dried at 105°C overnight. The spiking solution was prepared by diluting 50 μl of the stock-standard PPS3 (in methanol) with 2 ml of acetone and water to 10 ml. The spiking solution was then added to 100 g of the dried soil under continuous stirring. Finally, the natural water content was reestablished by adding water. The soil was stored in the dark at room temperature for 2 h to allow diffusion processes to take place. Finally, the spiked sample was stored at +4°C in the dark. Spiked samples were subject to Soxhlet extraction for 12 h using 130 ml of acetone. The organic solvent was reduced to a total volume of 5 ml, and finally diluted with water to a total volume of 50 ml. The pH was adjusted to 1.5 using hydrochloric acid.

2.8. Batch method

A suspension of the polymer (100 mg COOH resin, 3.5 mequiv. COOH/g, 1 ml methanol–water 20:80, v/v) was prepared. The PPS-3 standard or the soil extract (pH 1.5) were extracted with 50 or 100 mg COOH resin, respectively, by shaking for 15 s. The mixture was filtered through a suction filter (porosity 4, 20 mm I.D.) and the resin was washed with 2–3 ml water. Elution was carried out with 1 ml of acetonitrile. The solvent was allowed to soak into the resin for several minutes prior to elution. Eluates were collected and quantified by means of HPLC.

3. Results and discussion

3.1. ROMP-based cation-exchange resins

ROMP was used for the preparation of the new COOH-functionalized resins [15]. The new resins were prepared from various amounts of norborn-2-ene-5,6-dicarboxylic acid anhydride and a cross-linker, 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-di-methanonaphtalene. A general description of the structure of the resulting resins exhibiting various capacities is given in 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, at the outside [15]. As a consequence, all functionalities are readily available for SPE. While the carboxylate groups provide sufficient hydrophilicity, the polyunsaturated character of the carrier chains as well as of the entire
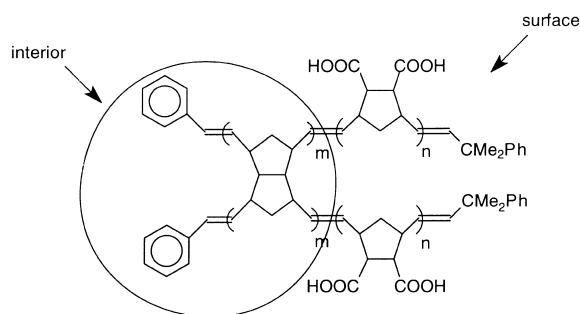

Fig. 1. Microstructure of COOH-functionalized resins prepared by ROMP.

backbone result in a significant reversed-phase character. The new resins were used in form of irregularly shaped 40 μm diameter particles. Investigations revealed, that a major part of the carboxylic acid groups (<97%) is located at the surface of the material, providing a high hydrophilicity and wetability [13]. As the new resins are entirely polymer-based, they are stable within the entire pH range and therefore allow a significantly lowered working pH. In no experiments, ''bleeding'' of the polymer was observed. Finally, all COOH resins have been recycled at least for 30 times without any loss of performance.

3.2. Chromatographic separation

Despite the large variety of separation systems for phenols [21,22,24,28–30,40,43–45], there are no reports on baseline separations of all 11 priority pollutant phenols which are defined as the PPS-3 standard within 30 min. This is due to the fact, that on the one hand, a mobile phase with a low solvent strength is required in order to separate the first nine components of the PPS-3 standard (with respect to their elution order), on the other hand only a mobile phase with a high solvent strength accomplishes elution of the least polar compounds, 2,4,6-trichlorophenol and pentachlorophenol. Several systems suffer from either long analysis times or incomplete separations. Especially the resolution of 2,4-dinitrophenol and o-nitrophenol as well as of 2-methyl-4,6-dinitrophenol and 2,4-dichlorophenol is usually only around 0.5. Separation of all 11 PPS-3 phenols with a resolution larger than 1.5 may be achieved in less than 24 min using the new gradient system described in Section 2.3 (Fig. 4). Also resulting from the baseline separations, relative standard deviations for each peak were in the range of 0.20–0.38% (determined from 5 independent injections). The use of a low solvent strength mobile phase employing methanol instead of acetonitrile resulted in significantly prolonged analysis times.

3.3. Extraction efficiency

Phenols may be adsorbed onto various materials from aqueous solutions using on-line and off-line preconcentration. Usually, a pH of approximately

1.5–2.0 is sufficient to suppress dissociation. Following this concept, the use of both polar and apolar sorbents for SPE of phenols has been reported earlier [20–36]. The high extraction efficiency of the new type of resins employed in the present work for various other organic compounds at concentrations of 10 mg/l has already been demonstrated [13]. The results obtained for 16 different EPA phenols at concentrations of 300 µg/l and 10 µg/l, respectively, are shown in Table 1. Experiments were performed under competitive conditions using mixtures of the corresponding compounds as defined for the EPA 2 and PPS3 standards. Except for phenol, which shows a recovery of 87% at a concentration of 10 µg/l, recoveries were almost quantitative. Incorporation of the polymer into a membrane is generally an efficient way to perform SPE [8,9,37,38]. In contrast to loose particles packed into a small column, a membrane represents a more dense packing. On the other hand, the amount of resin is significantly reduced as a major part of the membrane consists of PTFE fibrils into which the COOH resin particles are enmeshed to form a strong, porous sheet. A com-

parison of the results for SPE obtained with membranes with those of standard SPE experiments revealed acceptable, yet significantly reduced recoveries for most compounds. These are believed to result from irreversible adsorption of the corresponding analyte onto the teflon fibres. Due to the low specific surface area of teflon fibers, this adsorption is especially observed in the case of low analyte concentrations, while higher concentrations (e.g., 10 mg/l [13]) still give raise to high recoveries. Similar adsorption phenomena have already been observed for certain organochloropesticides [39].

In order to extend the extraction of phenols from aqueous matrices to more complex systems such as soil, extraction efficiencies of the new resins were finally investigated in batch-type experiments. A slurry of the resin was prepared and added to an aqueous standard solution. As expected, this type of experiment, which represents an extraction with only one equilibration step, gave raise to significantly lowered extraction efficiencies (8–96%). Nevertheless, this approach was pursued consequently, as it allows the enrichment of certain compounds from

Table 1
Recoveries for standard solutions

Compound	Recovery[a] $[\% \pm s_{(n-1)}]$	Recovery[b] $[\% \pm s_{(n-1)}]$	Recovery[c] $[\% \pm s_{(n-1)}]$	Recovery[d] $[\% \pm s_{(n-1)}]$
Phenol	87±16[e]	95±3	12±1	8±1
4-Nitrophenol	100±5[f]	98±1	66±6	30±1
2-Chlorophenol	99±5	94±0.4	60±5	29±2
2,4-Dinitrophenol	103±5	99±0.7	74±8	38±2
2-Nitrophenol	96±6	95±2	59±4	26±1
2,4-Dimethylphenol	98±3	96±1	75±8	37±2
4-Chloro-3-cresol	99±8	98±1	82±6	63±3
2,4-Dichlorophenol	101±5	96±0.4	82±5	68±2
2-Methyl-4,6-dinitrophenol	101±3	96±0.5	82±6	62±2
2,4,6-Trichlorophenol	96±11	97±0.8	83±2	77±3
Pentachlorophenol	97±18	86±4	80±5	75±3
3- and 4-Cresol	85±2[g]	104±3	41±5	79±4
2,6-Dichlorophenol	109±3[g]	101±2	88±9	96±6
2,4,5-Trichlorophenol	97±8[g]	100±2	94±3	84±5[g]
2,3,4,6-Tetrachlorophenol	105±6[g]	94±4	75±2	72±6[g]
2-*sec*-Butyl-4,6-dinitrophenol	87±3[g]	100±2	93±1	73±6[g]

[a] 100 ml of a standard (10 ng/ml of each analyte, $n=8$).
[b] 50 ml of a standard (300 ng/ml, $n=2$), [a]–[b] 50 mg COOH resin (5.1 mequi.v CO$_2$H/g).
[c] Membrane, 50 ml of a standard (300 ng/ml), [a]–[c] Flow-rate 1 ml/min.
[d] Batch experiment, 50 mg COOH resin (5.1 mequiv. COOH/g), 25 ml of a standard (300 ng/ml, pH 1.5, $n=3$).
[e] $n=6$.
[f] $n=7$.
[g] $n=4$.

heterogenous matrices which impede or even prevent standard SPE techniques.

3.4. Extraction mechanism

Usually, the mode of retention of phenols onto standard C_8 or C_{18} resins is explained by a reversed-phase (RP) mechanism. This explanation is definitely correct for sorbents, which are exclusively based on uncharged, apolar species, e.g., carbon black [40]. Nevertheless, in order to facilitate the interaction of the sorbent surface with water [10,41,42], many materials contain polar or protic functionalities such as acetyl, carboxyl, sulfonic acids, nitrilic or simply silanol groups. In these cases, the efficiency of the extraction strongly depends on the hydrophilicity of the surface combined with a sufficient RP character. In this contribution, the retention characteristics of mixtures of EPA phenols on three different resins were investigated. For that purpose, silica C_{18}, carboxypropyl silica and the new type of COOH-functionalized resin were used. As shown in Table 2, all phenols which are part of the EPA priority pollution standard (PPS3) are retained quantitatively by the new COOH-functionalized resin. Additional information about the high retention efficiency is given by breakthrough curves which were recorded for selected phenols under competitive conditions and are shown in Fig. 2. The high extraction efficiency is underlined by the fact, that only small
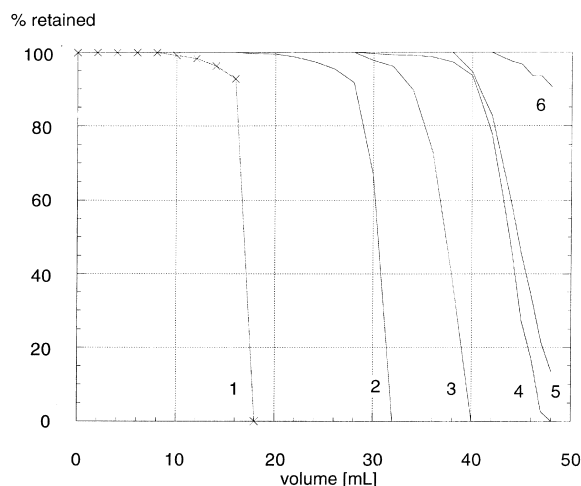

Fig. 2. Breakthrough curves for selected phenols. Phenol (1), 4-nitrophenol (2), 2-chlorophenol (3), 2,4-dinitrophenol (4), 2-nitrophenol (5), 2,4-dimethylphenol (6). Aqueous PPS-3 standard (10 µg/ml), pH 1.2, 50 mg resin (5.1 mequiv. COOH/g).

amounts (50 mg) of the new resin were used. Silica C_{18} shows acceptable recoveries (>90%) for six out of 11 phenols. Nevertheless, significant losses for phenol, 4-nitrophenol and pentachlorophenol were observed. While the low recovery for phenol (63.7%) may be explained by its high solubility in water (93 g/l), a more sophisticated argumentation applies to the latter two compounds. Their solubility in water is quite low but the pK_a value decreases from 10 (phenol) to 7.16 (4-nitrophenol) and 4.93 (penta-

Table 2
Comparison of recoveries (%) obtained with three different materials ($n=3$)

Compound	pK_a	Carboxypropyl silica[a] [recovery$\pm s_{(n-1)}$]	Silica C_{18}[b] [recovery$\pm s_{(n-1)}$]	COOH resin[b] [recovery$\pm s_{(n-1)}$]
Phenol	10.1	12	64	101
4-Nitrophenol	7.16	13	77	98
2-Chlorophenol	9.11	26	90	95
2,4-Dinitrophenol	4.09	16	95	99
2-Nitrophenol	7.21	29	89	93
2,4-Dimethylphenol	10.6	34	95	97
4-Chloro-3-cresol	9.55	49	95	98
2,4-Dichlorophenol	8.51	52	93	95
2-Methyl-4,6-dinitrophenol	4.34	36	93	99
2,4,6-Trichlorophenol	6.51	83	90	95
Pentachlorophenol	4.93	77	66	97

pH=2.0 (silica C_{18}, 1000 mg), 2.2 (carboxypropyl silica, 500 mg), 1.1 (COOH resin, 5.1 mequiv. COOH/g, 50 mg). Sample concentration 10 µg/ml of each compound, sample volume 10 ml. Flow-rate 1 ml/min, elution: 3 ml of acetonitrile.
[a] R.S.D.≤1%.
[b] R.S.D.≤3%.

chlorophenol). The enhanced acidity of these two compounds obviously leads to a pronounced dipole character which makes an extraction solely based on a RP mechanism less favorable. An entirely different effect was observed in the extraction of the same PPS3 phenols by a carboxypropyl silica-based sorbent. As a consequence of the short alkyl chain, no pronounced RP mechanism is present in this type of SPE material. Therefore, recoveries for most phenols were very poor (<50%). In terms of the efficiency of extraction, one might expect less acidic phenols to be retained more efficiently than the strongly acidic and polar ones. Interestingly, the chlorinated phenols are extracted more efficiently than the nitro-substituted or even alkyl-substituted ones. At a first glance, the pK_a value seems to play a minor role. A more careful investigation reveals that this assumption is not correct. Recoveries depend on the pK_a value in that the more acidic phenols are retained more strongly. This may be explained by additional hydrogen bonding between the carboxyl groups and the phenols. The more acidic the phenol, the more pronounced are the resulting hydrogen bridges. Nitro-substituted phenols misbehave in that they are capable of forming intra- and intermolecular hydrogen bonds. Consequently, hydrogen bonding with the carboxyl groups of the sorbent occurs less often which leads to a reduced adsorption. A description of the two different ways of hydrogen bonding is given in Fig. 3. This concept also explains the high recoveries of the new type of COOH-functionalized resins prepared by ROMP. As shown in Fig. 1, the backbone of the new material consists of a large amount of unsatur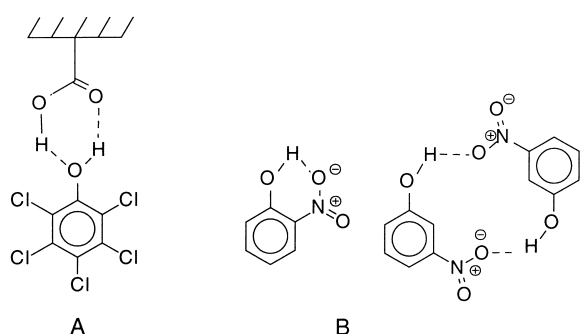ated double bonds as well as of a large amount of carboxylic acid groups. Depending on the analyte, the sorbent therefore provides sites for both RP as well as polar interactions. In order to be sure to provide a sufficient amount of carboxylic acid groups, two different COOH resins with a capacity of 3.5 and 5.1 mequiv. COOH/g, respectively, were chosen. No significant differences in extraction efficiency were observed.

Additionally, values for N were determined according to Gelenscér et al. [18,19]. A comparison of the data for phenols with those obtained for substituted anilines [15] reveals similar values for N/m within a range of 2000–7000. The loading capacity (prior to breakthrough) varied from 2–12 mg compound/g resin.

3.5. Spiked samples

In order to investigate extraction efficiencies of phenols from spiked soil samples, standard SPE as well as batch-type experiments were performed. In contrast to aqueous matrices, soil represents a rather challenging matrix, as the extraction and quantification of any compound therefore usually requires a multi-step procedure. Spiked samples were prepared as described above, extracted with acetone and acidified to a pH<2. This resulted in the precipitation of some insoluble organic material which mainly consisted of humic acids. This precipitate aggravated the use of standard SPE columns as it caused the clogging of the frits. Therefore solutions were filtered prior to SPE using resin-packed columns. Table 3 gives an overview of the results obtained. Acceptable recoveries for most of the compounds in a range of 60 to 95% were obtained. Fig. 4 shows a chromatogram of an extract of a spiked soil sample. Unfortunately, pentachlorophenol was basically lost during this procedure. This is attributed to adsorption of the compound onto the organic precipitate caused by hydrogen bonding. This assumption is backed-up by the finding, that pentachlorophenol is still retained in a batch-type experiment, were no removal of the humic acids is performed. Despite the significantly lowered recoveries, batch-type experiments may therefore still be regarded as useful complementary procedures for the enrichment of certain compounds, which are lost via standard SPE techniques.

Fig. 3. Hydrogen bonds formed between chlorophenols and COOH-derivatized resins (A), inter- and intramolecular hydrogen bonds of nitrophenols (B).

Table 3
Recoveries for spiked soil samples

Compound	Recovery[a] $[(\% \pm s_{(n-1)})]$	Recovery[b] $[(\% \pm s_{(n-1)})]$
Phenol	62±2	51±6
4-Nitrophenol	81±7	12±4
2-Chlorophenol	89±5	11±3
2,4-Dinitrophenol	72±4	25±4
2-Nitrophenol	95±5	41±6
2,4-Dimethylphenol	91±5	0
4-Chloro-3-cresol	89±5	51±6
2,4-Dichlorophenol	83±3	30±5
2-Methyl-4,6-dinitrophenol	62±5	37±8
2,4,6-Trichlorophenol	60±4	26±12
Pentachlorophenol	0.9±0.2	31±8

[a] SPE with 100 mg COOH resin (3.5 mequiv. COOH/g), pH 1.5.
[b] Batch experiment, 100 mg COOH resin (3.5 mequiv. CO_2H/g). Elution: 2×1 ml acetonitrile ($n=3$).
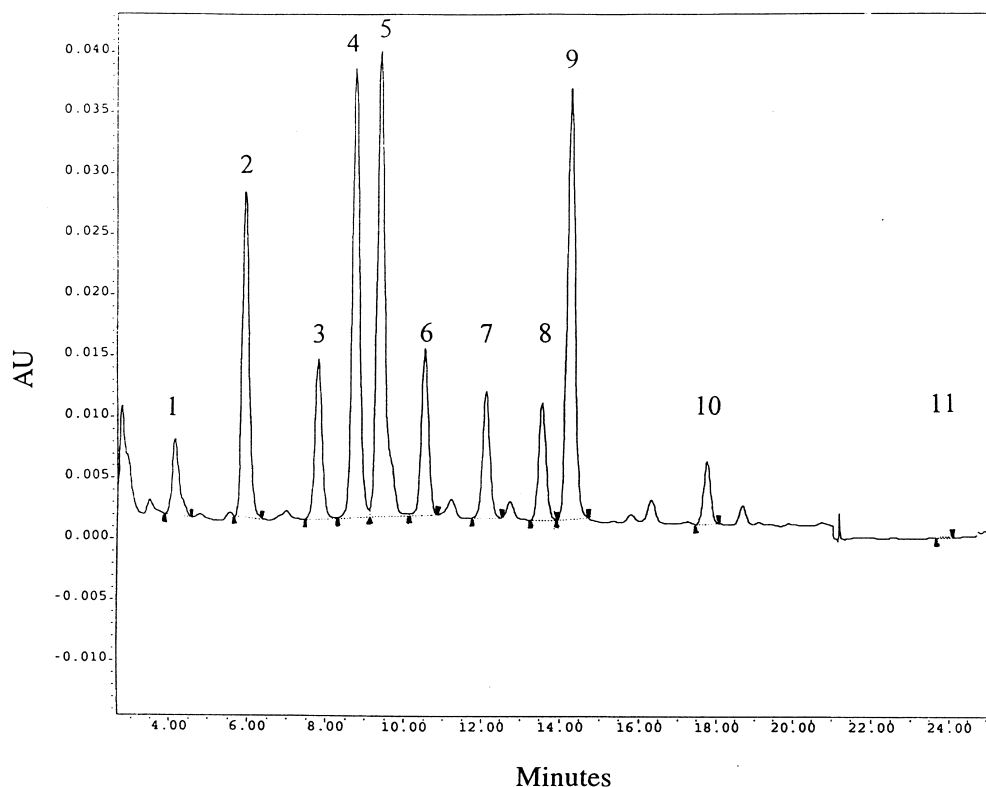

Fig. 4. Chromatogram of an extract of a spiked soil sample after SPE (100 mg COOH resin, 3.5 mequiv./g). For chromatographic conditions refer to Section 2.3. Order of elution: phenol, 4-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2-nitrophenol, 2,4-dimethylphenol, 4-chloro-3-cresol, 2,4-dichlorophenol, 2-methyl-4,6-dinitrophenol, 2,4,6-trichlorophenol, pentachlorophenol.

4. Conclusions

The new carboxylic acid-derivatized materials represent excellent sorbents for the extraction of a broad range of phenols at various concentrations. Sixteen phenols with significantly different solubilities as well as pK_a values have been investigated. The superiority of the new sorbents over other commercially available materials has been shown unambiguously. Acceptable recoveries are obtained after incorporation of the sorbents into a membrane. Nevertheless, besides a more simple handling, this incorporation does not lead to any significant advantages. The extraction mechanism of phenols with the new resins is believed to result both from RP interactions as well as from strong hydrogen bonding. The backbone structure of the new resins accounts for both mechanisms. These findings are backed-up by results obtained with standard silica-based materials. An additional advantage of the new resins is the fact, that they are entirely pH stable and therefore allow a significantly lowered working pH. Finally it should be emphasized, that all COOH resins may be recycled at least for 30 times without any loss of performance. Standard SPE as well as batch-type experiments have been performed in order to extract phenols from more complex matrices such as soil. Despite the fact, that batch extractions represent one-step equilibria, acceptable extraction efficiencies may be obtained for few compounds, which show low recoveries in standard SPE experiments.

Acknowledgements

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