

Sorbents for Preconcentration of Phenols from Polluted Waters. Supramolecular Assistance

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Abstract

New sorbents capable of forming hydrogen and it-jt bonds with phenols were prepared. These sorbents possess aromatic Ti-acceptor residues and hydrogen donor and acceptor sites. The surroundings of the sites are of different polarities. Sorption efficiency of these materials was studied by reversed-phase high performance liquid chromatography. The testing mixtures consisted of three phenols of different polarity and acidity.

Keywords: phenols, preconcentration, bounded phases, SPE, HPLC

Introduction

Analytical control of environmental pollution includes determining limited numbers of substances; e.g., inorganic compounds, volatile organic compounds, polyaromatic hydrocarbons, biphenyls, and some special pollutants like dioxines, pesticides or phenols.

The presence of phenol and its derivatives in the environment results from their wide use in many areas of industry; they are also formed by the degradation of some pesticides (e.g. 2-chlorophenol is a degradation product of 2,4-D herbicide) and during biodegradation processes in the environment. Although for many years all phenols have been known to be bacteriostatic, their harmful effects with respect to living organisms differ from one compound to the another. Some chlorophenols, e.g. 2,4,6-trichlorophenol and pentachlorophenol, are suspected carcinogens [1]. Harmfulness measured by LD₅₀ of priority pollutant phenols is similar to that of pesticides belonging to 1-3 group, according to the classification of Cremlyn [2].

As mentioned above, phenols are harmful to living organisms; there is a great interest in methods allowing the detection and determination of very low concentrations of these compounds. A widely used and recommended approach to determining total phenols in water and wastewater is a spectrophotometric method based on the formation of a color complex with 4-aminoantipirine. The detection limit of the method is 1 µg/dm³. The detection limit achieved in LC with UV detection is in the

range of 1 - 10 mg/dm³ of phenols, which is too low for environmental analyses as the concentration of these compounds in water and wastes (apart from particular cases) are at the ng/dm³ level.

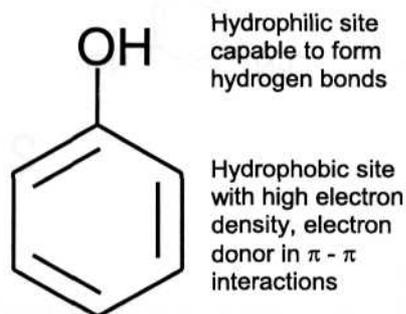
In order to improve the sensitivity of these methods it is necessary to preconcentrate phenols *prior* to analytical determination. This can be achieved by using liquid-liquid extraction (LLE) or solid-phase extraction (SPE), or by the application of membranes [3, 4].

Preconcentration of phenols by LLE is accompanied by common inconveniences and the final result of analysis depends on numerous parameters related to the extraction efficiency varying from 37 to over 90% for phenol and from 36 to 93% for 2-chlorophenol [5-7]. Similarly, serious differences in extraction efficiency were observed with other phenols.

Preconcentration on solid sorbents allows some of these problems to be eliminated, but considerable differences in efficiency are observed even with the same type of sorbent. Many sorbents have been used to concentrate phenol and its derivatives [7-20] but based on published data it is impossible to unambiguously conclude which of the applied sorbent is the most useful, because different authors have obtained very different results. This can be illustrated considering phenol as an example: the sorption found for C₁₈ sorbent were in the limits from 3 to 96% [14, 19]. In general practice, for preconcentration of non-polar phenols octadecylsilicas were applied. For species of medium polarity copolymer based adsorbents were applied, whereas highly polar

phenols are efficiently sorbed on porous graphitic carbon [14, 20]. Large differences of phenol preconcentration are observed.

Preconcentration of phenols is troublesome because of their unique properties. Phenols are polar, relatively soluble in water and they are volatile with steam. This makes preconcentration by solvent evaporation or by extraction very difficult. Extraction requires a huge amount of solvent. Using extraction, analysts introduce into the environment more and more pollutants exceeding their "natural" abundance. This is the reason why the newest analytical procedures do not require solvents and other reagents.



Phenol is a weak acid:

- well soluble in water and in organic solvents
- volatile
- volatile with steam

Fig. 1. Specific features of phenols.

The present paper explores the results of preconcentration of some phenols on new sorbents based on chemically modified silica gel.

To design a valuable sorbent for phenols, their properties were considered first (Figure 1). The OH group is capable of forming hydrogen bonds as a donor or as a proton acceptor. The lipophilic aromatic system is electron rich and could also interact as a π -donor. Attempts were made to elaborate appropriate sorbents utilizing specific structural features of phenols. The sorbents should be able to form hydrogen bonds and $\pi - \pi$ bond with electron rich aromatic residues. Assuming the above statements to be true, new sorbents based on silica gel were prepared. Silica gel was glycidoxypropylsilylated and the product was reacted with acids containing an electron deficient aromatic system capable of playing the role of an p-acceptor. The remaining OH groups are hydrogen donors, whereas the C-O-C and C=O residues are proton acceptors enabling the formation of hydrogen bonds with phenols. The scheme of the synthesis and structures of the surface modified materials are shown in Figure 2.

Materials and Methods

Apparatus

A Merck-Hitachi liquid chromatograph was used, equipped with a 4250 UV-VIS type detector, an L6200

pump, a D-2500 integrator and Rheodyne Model 7125 injection valve with a 20 μ l loop. The column (250 x 4.6 mm i.d.) was packed with LiChrospher RP-18 c, $dp = 5 \mu$ m

SPE - unit Merck.

Reagents

For analytical purposes analytical-reagent grade chemicals were used; in other cases reagent-grade chemicals were applied. Methanol (Lichrosolv) was from Merck. Pure water was from Millipore (Austria). Phosphoric acid was from POCH, Gliwice, Poland. Phenols (stock solutions) standards were: phenol ($c = 4.7 \text{ mg/cm}^3$), 2-chlorophenol ($c = 4.8 \text{ mg/cm}^3$) and pentachlorophenol ($c = 2.2 \text{ mg/cm}^3$) received from the Institute of Industrial Chemistry (Warsaw, Poland).

Preparation of Sorbents

a) Glycidoxypropylsilylated silica gel.

To a suspension of silica gel (50 g; dried at 180° for 5 hours [21], MN-Kieselgel 60) in 100 cm^3 , dry toluene glycidoxypropyltriethoxysilane (6 cm^3) was added. The mixture was heated for 6 h at 100°, then cooled and the solid material was collected by filtration. The product was washed with water, methanol and finally with acetone and dried under reduced pressure. The yield of glycidoxypropylsilylated material [22] was 54 g.

b) 8-Hydroxy-7-(2,4,6-trinitrophenoxy)propoxypropylsilylated silica gel (Sorbent 1)

A mixture of the above described glycidoxypropylsilylated material (5 g), ethyl ether (15 cm^3) and picric acid (1 g) was shaken overnight at room temperature. The solid material was removed by filtration and the solid material was washed with water, methanol and acetone and dried in *vacuum*. The yield of sorbent 1 was 5.2 g.

c) 8-Hydroxy-7-(3,5-dinitrobenzoyloxy)propoxypropylsilylated silica gel (Sorbent 2)

This compound was obtained as above from glycidoxypropylsilylated material (20 g) and 3,5-dinitrobenzoic acid (1 g) in 30 cm^3 ethyl ether. The product was collected, washed with water, saturated sodium hydrogen-carbonate solution, water, methanol and acetone and dried. The yield of sorbent 2 was 21 g.

d) 8-Acetoxy-7-(3,5-dinitrobenzoyloxy)propoxypropylsilylated silica gel (Sorbent 3)

5 g of sorbent 2 was suspended in 10 cm^3 of acetic anhydride and left to stand overnight at room temperature. The solid material was washed with water, methanol and acetone and dried as above. The yield of sorbent 3 was 5.1 g.

e) 8-Decanoyloxy-7-(3,5-dinitrobenzoyloxy)propoxypropylsilylated silica gel (Sorbent 4)

This material was prepared by acylation of glycidoxypropylsilylated silica gel (5 g) in a mixture of 15 cm^3 methylene chloride, 5 cm^3 dry pyridine and 2 g of decanoyl chloride for 1 day at room temperature. The solid material was collected, washed with water, methanol, and acetone and dried. The yield of sorbent 4 was 5.3 g.

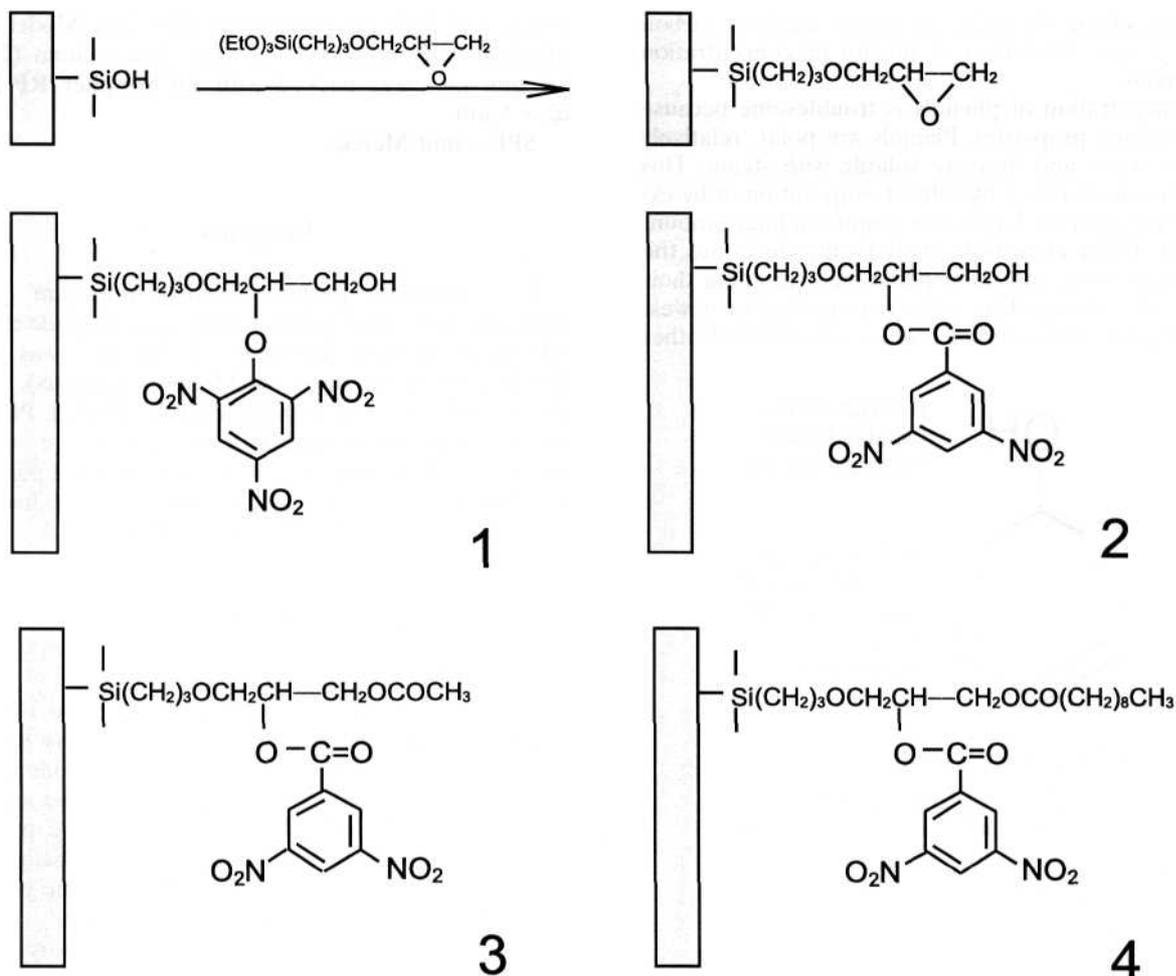


Fig. 2. Scheme of synthesis and surface structures of new sorbents.

Preconcentration Procedure

1000 mg samples of sorbents, prepared as described above, were placed in polyethylene tubes and washed with 10 cm^3 acetonitrile and 10 cm^3 of water. Water samples spiked with phenols were filtered through a wet sorbent bed under reduced pressure. Velocity of flow of water samples was fixed at $1.5 \text{ cm}^3/\text{min}$. The sorption was investigated by change pH of water samples (pH 3 and 7) and by change of phenol concentration. The adsorbed phenols were eluted from the sorbent with four 1 cm^3 portions of acetonitrile and the eluates were collected separately. In each fraction the amount of phenol was determined by LC under conditions described below. The mobile phases were:

- methanol/water (45:55 v/v) for phenol and 2-chlorophenol, and

- methanol/water (85:15 v/v) for pentachlorophenol.

Both phases were acidified to pH 3 with phosphoric acid. The wavelength of the UV detector was set at 280 nm, except for pentachlorophenol. The last was determined at 305 nm. The content of each component was determined on the basis of a calibration curve.

The mass of adsorbed phenol and phenol remaining

in solution was balanced for each experiment. The total amount of phenol was in the 95-97% limit.

Results and Discussion

The synthesis of sorbents was performed obeying guidelines [21] ensuring the formation of monomeric coverage of silica gel surface. All materials were prepared using standard procedures.

All the above sorbents possess residues of electron deficient aromatic groups and many proton acceptor sites like carbonyl, NO_2 and OH on surface anchored compounds. Sorbent 1 is unstable; continuous leaching of picric acid is observed in water. Hence, it was not used for further experiments. Sorbent 2 only slightly sorbs phenol, o-chlorophenol and pentachlorophenol (Figure 3). More efficient is sorbent 3 in which the electron deficient dinitrobenzoyl and NO_2 , $\text{C}=\text{O}$ and $-\text{O}-$ residues remain, but the CH_2OH group is acetylated to decrease the polarity of the binding site surrounding. In sorbent 4 the CH_2OH was esterified with decanoyl chloride. The long aliphatic residue is much more lipophilic and shields better the binding site from aqueous medium than does

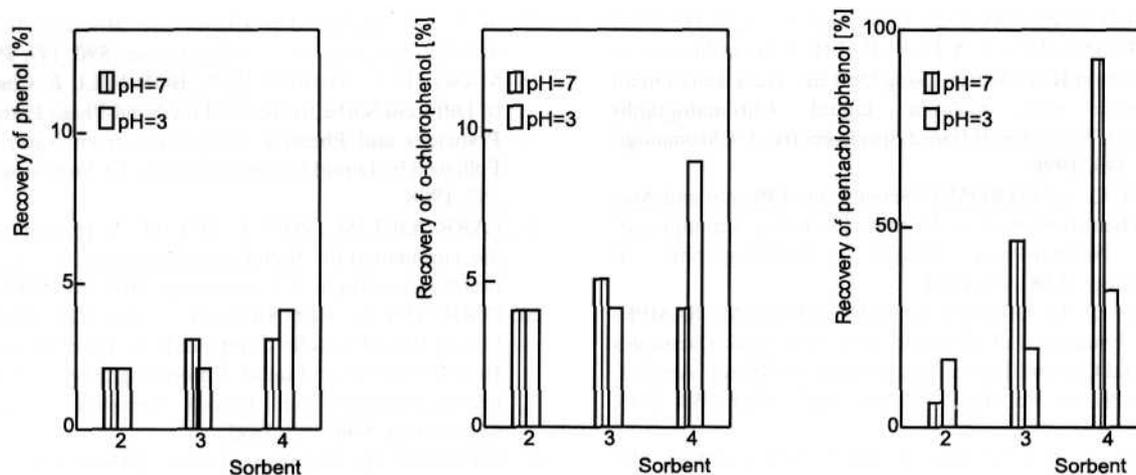


Fig. 3. Recovery of phenols with the use of sorbents 2-4.

the acetyl group in sorbent 3. The sorption of phenols increases from sorbent 2 to 4. This expresses the importance of lipophilic shielding of the binding sites. The lipophilic "layer" slows down the release of adsorbed phenols; it is in general agreement with higher relative stability of hydrogen bonds and increased π - π interactions in non-polar media.

Sorption of phenols from aqueous solutions at different pH revealed another effect of interactions. At neutral conditions, sorbent 4 entrapped 4% phenol, 9% o-chlorophenol and 92% pentachlorophenol from water. The higher the pH the larger the concentration of phenolate anion. The last anion, due to higher electron density, is a better p-donor. o-Chlorophenol and pentachlorophenol are more acidic than the mother compound. Hence, the effect of pH is expressed best for chlorophenols. Moreover, sorbents 3 and 4 possess no hydrogen donors in binding sites and the best sorption of pentachlorophenol was found with more lipophilic sorbent 4. This indicates a preferential role of π - π and "hydrophobic" interaction on phenol sorption. By all respects sorbent 4 is the best among studied modified silica gels.

Conclusions

Preconcentration of phenols with the use of sorbents is generally possible. Design of effective sorbents should take into consideration their specific interactions with phenols. These compounds interact with binding sites of sorbent by typical supramolecular interactions like hydrogen bonds and π - π interactions which are favorable for effective sorption. Sorption efficiency increases when the binding sites possess lipophilic surroundings. Simple "hydrophobic" interactions of phenols with C_{18} phases are not sufficient for effective sorption.

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References

1. AFGAN B.K., CHAN S.Y., (eds.) Analysis of Trace Organics in the Aquatic Environment C.R.C. Press Inc. Boca Raton, Florida **1989**.
2. CREMLYN R. Pesticides, Preparation and Mode of Action, J. Wiley & Sons, Chichester **1978**.
3. MELCHER R.G., BAKKE D.W., HUGHES G.H. On-line membrane/liquid chromatographic analyzer for pentachlorophenol and other trace phenols in wastewater. *Anal. Chem.*, **64**, 2259, **1992**.
4. SCHMIDT L., SUN J.J., FRITZ J.S., HAGEN D.F., MARKELL C.G., WISTED E.E. Solid-phase Extraction of Phenols Using Membranes Loaded with Modified Polymeric Resins. *J. Chromatogr.* **641**, 57, **1993**.
5. AFGAN B.K., BELLIVEAU P.E., LAROSE R.H., RYAN J.F. An Improved Method for determination of Trace Quantities of Phenols in Natural Waters. *Anal. Chim. Acta.* **71**, 355, **1974**.
6. REALINI P.A. Determination of Priority Pollutant Phenols in Water by HPLC. *J. Chromatogr. Sci.* **19**, 124, **1981**.
7. MAKUCH B., GAZDA K., KAMINSKI M. Determination of Phenol and Monochlorophenols in Water by Reversed-Phase Liquid Chromatography. *Anal. Chim. Acta* **284**, 53, **1993**.
8. GAWDZIK B., GAWDZIK J., CZERWINSKA-BILL U. Use of Polymeric Sorbents for the Off-Line Preconcentration of Priority Pollutant Phenols from Water for High-Performance Liquid Chromatographic Analysis. *J. Chromatogr.* **509**, 135, **1990**.
9. LAMPRECHT G., HUBER J.F.K. Ultra-Trace Analysis of Phenols in Water Using High-Performance Liquid Chromatography with On-Line Reaction Detection. *J. Chromatogr. A* **667**, 47, **1994**.
10. EDER K., BUCHMEISTER M.R., BONN G.K. New-Cation Exchange Resins with Reversed-Phase Character for Solid-Phase Extraction of Phenols. *J. Chromatogr. A* **810**, 43, **1998**.
11. MASQUE N., GALIA M., MARCE R.M., BORRULL F. Chemically Modified Polymeric Resin Used as a Sorbent in Solid-Extraction Process to Determine Phenolic Compounds in Water. *J. Chromatogr. A* **771**, 55, **1997**.

12. SOMSEN G.W., JAGD J., GOOIJER C., VELTHORST N.H., BRINKMAN U.A.Th., VISSER T. Identification of Herbicides in River Water Using On-Line Trace Enrichment Combined with Column Liquid Chromatography - Fourier-Transform Infrared Spectrometry. *J. Chromatogr. A* **756**, 145, **1996**.
13. BRAGE C., SJOSTROM K. Separation of Phenol and Aromatic Hydrocarbons from Biomass Tar Using Aminopropylsilane Normal-Phase Liquid Chromatography. *J. Chromatogr.* **538**, 303, **1991**.
14. BORRO C., Di CORCIA A., MARCHETTI M., SAMPERII R. Evaluation of Graphitized Carbon Black Cartridges for Rapid Organic Traces Enrichment from Water: Application to Priority Pollutants Phenols. *Anal. Chem.* **58**, 2048, **1986**.
15. MONDE T., KAMIUSUKI T., KURODA T., MIKUMO K., OHKAWA T., FUKUBE H. High-Performance Liquid-Chromatographic Separation of Phenols on a Fluorocarbon-Bonded Silica Gel Column. *J. Chromatogr. A* **722**, 273, **1996**.
16. LASKORTE S., FRAISSE D., BARCELO D. Efficient Solid-Phase Extraction Procedure for Trace Enrichment of Priority Phenols from Industrial Effluents with High Total Organic Carbon Content. *J. Chromatogr. A* **857**, 97, **1999**.
17. SUN J.J., FRITZ J.S. Chemically Modified Resins for Solid-Phase Extraction. *J. Chromatogr.* **590**, 197, **1992**.
18. MASQUE N., MARCE R.M., BORRULL F. Comparison of Different Sorbents for On-Line Solid-Phase Extraction of Pesticides and Phenolic Compounds from Natural Water Followed by Liquid Chromatography. *J. Chromatogr. A* **793**, 257, **1998**.
19. LARROQUE M., VIEN L., BLEISE A. Dosage du phénol par chromatographie liquide haute performance avec détection fluorimétrique. *J. Chromatogr.* **407**, 384, **1987**.
20. COQUART V., HENNION M.C. Trace-Level Determination of Polar Phenolic Compounds in Aqueous Samples by High-Performance Liquid Chromatography and On-Line Preconcentration on Porous Graphitic Carbon. *J. Chromatogr.* **600**, 195, **1992**.
21. BIERNAT J.F., KONIECZKA P., TARBET B.J., BRADSHAW J.S., IZATT R.M. Complexing and Chelating Agents Immobilized on Silica Gel and Related Materials and their Application for Sorption of Inorganic Species. *Separation and Purification Methods.* **23**, 77, **1994.a**
22. LITTLE C.J., DALE A.D., EVANS M.B. Screen for the Evaluation of Chemically Bonded Supports used in Reversed-Phase High-Performance Liquid Chromatography. *J. Chromatogr.* **153**, 381, **1978**.